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I

INTRODUCTION

The formation of silicon–silicon bonds through the transition metal promoted dehydrocoupling of hydrosilanes was reported approximately 30 years ago.[1] This first brief report concerned the condensation and the accompanying disproportionation of the secondary silanes, $PhMeSiH_2$, Ph_2SiH_2, and Et_2SiH_2, in the presence of Wilkinson's catalyst, $(Ph_3P)_3RhCl$, and also contained a brief comment on the corresponding reactions of the primary silane, $PhSiH_3$. The observations lay dormant for about a dozen years before the next publication appeared that reported the polymerization of primary silanes ($PhSiH_3$ and $HexSiH_3$) to linear polysilanes as promoted by titanocene complexes, Cp_2TiR_2 ($R = CH_3$, $CH_2C_6H_5$).[2] However, with the titanium catalyst precursors, no

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disproportionation products were observed. Thus, the major activity in transition metal promoted oligomerization or polymerization of hydrosilanes dates from the mid-1980s onward.

There are several types of reactions of hydrosilanes that are promoted by transition metal complexes. In addition to homodehydrocoupling, Eq. (1) and heterodehydrocoupling, Eq. (2) (this process is sometimes referred to as dehydrogenative coupling), and disproportionation, Eq. (3) (only one possibility is depicted), an additional process and one of the most popularly employed is the *addition* of a Si–H bond to a substrate that contains a multiple bond. The addition reaction is referred to as hydrosilylation and a generalized example is shown in Eq. (4).

$$\equiv \mathrm{SiH} + \mathrm{HSi}\equiv \rightarrow \equiv \mathrm{SiSi}\equiv + \mathrm{H_2} \qquad \text{Homodehydrocoupling} \tag{1}$$

$$\equiv \mathrm{SiH} + \mathrm{HEl} \rightarrow \equiv \mathrm{SiEl} + \mathrm{H_2} \qquad \text{Heterodehydrocoupling} \tag{2}$$

$$2\mathrm{RR'_2SiH} \rightarrow \mathrm{R'_2SiR_2} + \mathrm{R'_2SiH_2} \qquad \text{Disproportionation} \tag{3}$$

$$\equiv \mathrm{SiH} + \mathrm{El{=}C{<}} \rightarrow \equiv \mathrm{SiElCH} \qquad \text{Hydrosilylation} \tag{4}$$

Since transition metal complexes can promote several different reactions of SiH bonds, the selection of a particular complex to promote a desired reaction is not obvious and generally the choice relies on a prior model. In some cases a balance in rates of the different processes generalized in Eqs. (1–4) is required and this type of problem will be discussed at various points in later sections. In fact, there are occasionally coupling products reported in studies whose principal aim was hydrosilylation (particularly by electron-rich elements) and some examples will be included later in Table V. In general, this overview will deal only with studies aimed at homodehydrocoupling [Eq. (1)] and will principally focus on systems where silicon–silicon bond formation dominates over other processes. Several reviews and/or commentaries that include aspects of homodehydrocoupling have previously been published.[3] It is the purpose of the current review to summarize the status of homodehydrocoupling in terms of both the successes and the failures. There are several areas that will be addressed. Section II will be concerned with the types of transition metal complexes of Group 4 metals that are precursors to catalysts that promote homodehydrocoupling (as opposed to other processes involving SiH bonds). Section III will briefly cover the mechanisms that have been proposed for homodehydrocoupling. Section IV addresses the types of hydrosilane substrates that can be coupled successfully by metallocene catalysts. Section V describes some of the properties of the polysilanes produced from dehydrocoupling and Section VI discusses the role that other metals, particularly electron-rich metals, have played in dehydrocoupling of hydrosilanes. In the conclusion, the limits of this approach as a synthetic route to polysilanes will be assessed.

II

PROMOTION OF DEHYDROCOUPLING WITH METALLOCENE COMPLEXES OF GROUP 4

By far the most studied transition metals for promotion of silicon–silicon bond formation are the metallocene derivatives of Group 4 and these are summarized in Table I. The complexes have been divided into classes that depend somewhat loosely on the non-Cp substituents on the metal (Classes 1–10). Classes 1–3 include the sequence Cp_2MR_2, Cp_2MRX, Cp_2MX_2 ($R =$ organic or silyl group; $X =$ inorganic group), Class 4 contains the metallocene dichlorides that are activated by anionic reagents and Classes 5 and 6 contain extensions of anion activation. Metallocene derivatives activated by Lewis acids (LA), ammonium borate salts, or the combination of metallocene/^{n}BuLi/LA designed to provide cationic metallocene species are included in Classes 7 and 8. Systems where the precursor complex may loosely be viewed as M(II) are summarized in Class 9. Within each class the examples are ordered in terms of metallocenes with no substituted Cp-rings followed by those with substituted rings. Table I ends with the few non-Cp Group 4 complexes that have been reported to dehydrocouple hydrosilanes. Metal precursors from other groups that have been utilized for dehydrocoupling are summarized later in Section VI.

Within the metallocene systems, there are basically three catalyst variations that have been developed. The first to be introduced was Cp_2MMe_2 ($M = Ti$, Zr: Harrod[4]), closely followed by $CpCp^*M(SiR_3)X$ ($M = Zr$, Hf; $R = Me$, Ph, $SiMe_3$; $X = Cl$, alkyl; Tilley[43]) and the combination catalyst, $Cp_2MCl_2/^n$BuLi ($M = Ti$, Zr, Hf; Corey[45]).

The reaction of hydrosilanes with Cp_2TiMe_2 are characterized by an induction period that ends with the initiation of a deep blue color characteristic of the presence of Ti(III) species. Identified in solutions where dehydrocoupling was occurring were the complexes $(Cp_2TiSiH_2Ph)_2$ (which dimerizes through Ti–H–Si bridges), as well as $[Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2]$.[5] Both complexes could be isolated when reactions of Cp_2TiMe_2 and $PhSiH_3$ were conducted on a stoichiometric scale (excess of $PhSiH_3$ for the former case) and both were crystallographically characterized. A related complex, $Cp_2Zr(SiMePhH)(\mu\text{-}H)_2(PhH_2Si)ZrCp_2$,

TABLE I

CATALYST PRECURSORS OF GROUP 4 EXAMINED FOR DEHYDROCOUPLING OF HYDROSILANES

Class	General formula	R or X: M^{Ref}
1. Cp$_2$MR$_2$ R = organic, hydride	Cp$_2$MR$_2$	Me: **Ti**[4,5,6a,7–14,18] **Zr**[7a,8–11,14–22] **Hf**[6b][a] CH$_2$Ph: **Ti**[4] CH$_2$SiMe$_3$: **Ti**;[23] **Zr**[24] Bu: **Ti**;[10,18] **Zr**[10,18] Ph: **Ti**[25,26] H: **Zr**[15]
	Cp$_2$MR$_2$ + L	Me: **Ti**,[27] L = PMe$_n$Ph$_{3-n}$; **Zr**,[28] L = c-C$_6$H$_{10}$.
R = silyl, organic	Cp$_2$M(Si)R	Me: **Zr**[14] (Si = Si$_6$Me$_{11}$,); **Zr**[29] [Si = Si(SiMe$_3$)$_3$] SiMe$_3$: **Zr**[30] [Si = Si(SiMe$_3$)$_3$]
Cp$'_2$MR$_2$ or Cp^{1}Cp^{2}MR$_2$	CpCp*MR$_2$	Me: **Ti**;[6b] **Zr**[6b,21] H: **Zr**[21,31] (dimer)
R = organic, hydride	Cp$^*_2$MR$_2$	Me: **Ti**;[6b] **Zr**[6b][b] H: **Hf**[30,32]
	(Cp^{Me})$_2$MMe$_2$	Me: **Ti**;[6b] **Zr**[6b]
	(Cp^{Si})Cp*MR$_2$	Me: **Zr**[21] H: **Zr**[21]
	(Cp^{Si})$_2$MR$_2$	Me: **Zr**[21]
	(Cp^{N})(Cp^{Si})MR$_2$	Me: **Ti**[33]
	(Cp^{N})$_2$MR$_2$	Me: **Ti**,[34] **Zr**[34] Bz: **Ti**[34]
	(Ind)$_2$MR$_2$	Me: **Ti**;[11,35] **Zr**[11,36]
	[(1,2-bisindenyl)ethane]MR$_2$	Me: **Ti**,[11,23,37] **Zr**[11,36,37]
	[(1,2-BTHIE)]MR$_2$	Me: **Ti**,[11,37] **Zr**[11,37,38]

R = silyl, organic	$CpCp^*M[Si(SiMe_3)_3]R$	Me: **Zr**;[32,39,40] **Hf**[30,40]
	$Cp^*(Cp^{Me})M[Si(SiMe_3)_3]R$	Me: **Zr**[21]
	$[Me_2Si(C_5H_4)_2]M[Si(SiMe_3)_3]R$	Me: **Zr**[21]
	$[Me_2Si(C_5H_4)(C_5Me_4)]Zr[Si(SiMe_3)_3]R$	Me: **Zr**[21]
2. Cp_2MRX and Cp^1Cp^2MRX	Cp_2MRCl	$Si(SiMe_3)_3$: **Zr**;[21,41] **Hf**[41] $SiMe_3$: **Zr**;[41] **Ti**[40] Si_6Me_{11}: **Zr**;[14] **Hf**[14] H: **Zr**[17]
	$CpCp^*MRCl$	$Si(SiMe_3)_3$: **Zr**;[21,30,40,41,42] **Hf**[30,32,39,40,41] SiH_2Ph: **Hf**[30,43] $(SiHPh)_3H$: **Hf**[30]
	$(Cp^{Si})_2MRCl$	$Si(SiMe_3)_3$: **Zr**;[44] **Hf**[39,41]
3. Cp_2MX_2 and $Cp^1Cp^2MX_2$	Cp_2MX_2	F: **Ti**;[45,46] **Zr**;[45,46] **Hf**[45] OPh: **Ti**;[45] **Zr**;[45] **Hf**[45] OAr: **Ti**;[47] **Zr**[47] NMe_2: **Ti**;[45] **Zr**;[45] **Hf**[45]
	$(Cp^N)_2MX_2$	OPh: **Ti**[34]
	$(Cp^N)(Cp^{Si})MX_2$	OPh: **Ti**[33]
4. Cp_2MCl_2 (activated by anions)	$Cp_2MCl_2/2^nBuLi$	**Ti**[13,48–53,56,64a] **Zr**[17,48–50,52,53,55,57–62] **Hf**[48–53,57,63,64a]
	$Cp_2MCl_2/2^nBuLi$/olefin	**Ti**;[64a] **Zr**;[64a] **Hf**[64a]
	$Cp_2MCl_2/2MeLi$	**Ti**;[38,59] **Zr**;[38] **Hf**[38]
	Cp_2MCl_2/Red-Al	**Ti**;[51,52,65,69] **Zr**;[52,65–69] **Hf**[51,52,65–69]
	$Cp_2ZrCl_2/LiAlH_4$	**Zr**[70a]
	$Cp_2MCl_2/Naph^-$	**Zr**[70b]

(*Continued*)

TABLE I
Continued

Class	General formula	R or X: M^{Ref}
Cp'_2MCl_2 or $Cp^1Cp^2MCl_2$ (activated by anions)	$(Cp^{Me})_2MCl_2/2^nBuLi$	**Zr**[58]
	$(Cp^{Si})_2MCl_2/2^nBuLi$	**Hf**[63]
	$(Cp^{Si*})_2MCl_2/2^nBuLi$	**Zr**;[55] **Hf**[55]
	$(Cp^{Si*})CpMCl_2/2^nBuLi$	**Ti**;[55] **Zr**[55]
	$(Cp^{R})_2MCl_2/2^nBuLi$	**Ti**;[71,72] **Zr**;[71,72] **Hf**[71,72]
	$Cp^{R}CpMCl_2/2^nBuLi$	**Ti**;[71,72] **Zr**[71,72]
	$(Cp^{N})_2MCl_2/2^nBuLi$	**Ti**;[73] **Zr**[73]
	$Cp^*_2MCl_2/2^nBuLi$	**Zr**[57]
	$Cp^*CpMCl_2/2^nBuLi$	**Zr**[58]
	$Cp^*Cp^{N2}MCl_2/2^nBuLi$	**Zr**[74] ($n = 2, 3$)
	$Cp^*Cp^{R2}MCl_2/2^nBuLi$	**Zr**[74] ($n = 1, 2$)
	$[\mu\text{-}\{C_5H_4SiMe_2CH_2SiMe_2C_5H_4\}]\text{-}[CpMCl_2]_2/4^nBuLi$	**Ti**;[75] **Zr**[75]
	$[\mu\text{-}\{C_5H_4SiMe_2(CH_2)_2SiMe_2C_5H_4\}][CpMCl_2]_2/4^nBuLi$	**Ti**;[75] **Zr**[75]
	$Me_2Si[C_5H_4MCl_2]_2/2^nBuLi$	**Zr**;[63] **Hf**[63]
	$[Me_2C(C_5H_3SiMe_3)_2]MCl_2/2^nBuLi$	**Ti**;[76,77] **Zr**;[76,77] **Hf**[63,76,77] (El = C, Si; rac and meso forms)
	[(1,2-tetrahydroindenyl)ethane]-$MCl_2/2MeLi$	**Ti**;[38] **Zr**[38]
	Rac-(EBI)$MCl_2/2^nBuLi$	**Zr**[17]
	$K[(Cp^{Et})_2MH_3]$	**Zr**[78a]
5. $Cp'_2M(OAr)Cl$ or $Cp'_2M(OAr)_2$ + RLi	$Cp_2M(OAr)Cl/^nBuLi$	**Zr**[62] [Ar = 2,6-$^tBu_2$-4-Me; 2,6-$^iPr_2$, 2,4,6-F_3, 2,6-$(MeO)_2$]
	(S,S)-[BTHIE]Ti(binaphtholate)/^nBuLi	**Ti**[79]
	$Cp_2M(OMe)_2/(Me_3Si)_3SiLi \cdot 3THF$	**Zr**[80] (patent)
6. $Cp'MMe_3$, $Cp'MCl_3/3^nBuLi$,	$CpMMe_3$	**Ti**;[6b] **Zr**[6b] [b]

$CpMXCl_2/2^nBuLi$ (mono-Cp systems)	Cp^*MMe_3	**Ti**;[6b] **Zr**[6b] [b]
	$Cp[C_6H_5C(NSiMe_3)_2]ZrCl_2/^nBuLi$	**Zr**[78b]
	$CpMCl_3/3^nBuLi$	**Ti**;[57] **Zr**;[57]
	$Cp^*MCl_3/3^nBuLi$	**Zr**[57]
7. $Cp'_2MR_2 + B(Ar_F)_3$ or $[NR_4]$ [anion] (cationic species)	$Cp_2MMe_2/B(C_6F_5)_3$	**Zr**[60,58]
	$Cp_2MMe_2/Ph_3C^+[B(C_6F_5)_4]$	**Zr**[60]
	$Cp_2MMe_2/[NH^nBu_3][B(3,5\text{-}Me_2C_6H_3)_4]$	**Zr**[21]
	$[Cp_2M(\mu\text{-}SiH_2Ph)]_2^{2+}\,2[BBu_n(C_6F_5)_{4-n}]$	**Zr**[81]
	$Cp_2M(CH_2SiMe_3)_2/B(C_6F_5)_3$ or $B(C_6F_4\text{–}C_6F_5)_3$	**Ti**[23]
R = organic or hydride	$(IndCH_2CH_2Ind)MMe_2/B(C_6F_5)_3$ or tris(perfluoronaphthenyl)borane or tris(perfluorobiphenyl)borane	**Ti**[23]
	$CpCp^*MMe_2/B(C_6F_5)_3$	**Hf**[82]
	$CpCp^*MMe_2/[NH^nBu_3][B(3,5\text{-}Me_2C_6H_3)_4]$	**Hf**[21]
	$CpCp^*MMe_2/[NHMe_2Ph][B(C_6F_5)_4]$	**Zr**[21]
	$CpCp^*MMe_2/[NHEt_3][BPh_4]$	**Zr**[21]
	$Cp^{Si}Cp^*MMe_2/[NH^nBu_3][B(3,5\text{-}Me_2C_6H_3)_4]$	**Zr**[21]
	$Cp^{Me}Cp^*M[Si(SiMe_3)_3]Me/[NH^nBu_3][B(C_6F_5)_4]$	**Zr**[21]
	$Me_2Si(C_5H_4)(C_5Me_4)ZrMe_2 + [NH^nBu_3][B(3,5\text{-}Me_2C_6H_3)_4]$	**Zr**[21]
	$[CpCp^*MH_2]_2/[NH^nBu_3][B(C_6F_5)_4]$	**Zr**[21]
	$(Cp^{Me})_2MH_2/B(C_6F_5)_3$	**Zr**[60]
	$(Cp^{Me})_2MH_2/Ph_3C[B(C_6F_5)_4]$	**Zr**[60]
8. $Cp'_2MCl_2/^nBuLi + B(C_6F_5)_3$	$Cp_2MCl_2/2^nBuLi/B(C_6F_5)_3$	**Zr**;[58,60,83] **Hf**[60,79]
	$(Cp^{Me})_2MCl_2/2^nBuLi/B(C_6F_5)_3$	**Zr**[58,60]

(*Continued*)

TABLE I

Continued

Class	General formula	R or X: $\mathrm{M}^{\mathrm{Ref}}$
	$(\mathrm{Cp^{Si}})_2\mathrm{MCl_2/2^{\mathit{n}}BuLi/B(C_6F_5)_3}$	**Zr**[58]
	$\mathrm{CpCp^*MCl_2/2^{\mathit{n}}BuLi/B(C_6F_5)_3}$	**Zr**;[58,60,79,83] **Hf**[60]
	$\mathrm{(Ind)_2MCl_2/2^{\mathit{n}}BuLi/B(C_6F_5)_3}$	**Zr**[60]
	$\mathrm{(EBI)MCl_2/2^{\mathit{n}}BuLi/B(C_6F_5)_3}$	**Zr**[60]
	$\mathrm{(THI)_2MCl_2/2^{\mathit{n}}BuLi/B(C_6F_5)_3}$	**Zr**[60]
9. M(0) **$\mathrm{Cp_2M(RC{\equiv}CR)}$** **or** **$\mathrm{Cp_2M(PMe_3)_2}$**	$\mathrm{Cp_2M(Me_3SiC{\equiv}CSiMe_3)}$	**Ti**[84]
	$\mathrm{Cp_2M(Me_3SiC{\equiv}CSiMe_3)L}$	**Zr**[84] (L = THF, py)
	$\mathrm{[Me_2SiCp_2]M(Me_3SiC{\equiv}CSiMe_3)(py)}$	**Zr**[84b]
	$\mathrm{[IndCH_2CH_2Ind]M(Me_3SiC{\equiv}CSiMe_3)}$	**Ti**;[84] **Zr**[84]
	$\mathrm{[Ind]_2M(Me_3SiC{\equiv}CSiMe_3)(THF)}$	**Ti**;[84b] **Zr**[84b]
	$\mathrm{O[SiMe_2Cp]_2M(Me_3SiC{\equiv}CSiMe_3)(py)}$	**Ti**;[84b] **Zr**[84b]
	$\mathrm{Cp_2M(\eta^2\text{-}H\text{–}SiPh_2H)(PMe_3)}$/norbornene	**Ti**[85]
10. Non-Cp systems	$\mathrm{(Me_3Si)_3SiMCl_3\cdot tmeda}$	**Hf**[86]
	$\mathrm{M(O^{\mathit{i}}Pr)_4}$	**Ti**[87,88]
	$\mathrm{[M]_{\mathit{s}}\text{–}H}$	**Zr**[89]
	$\mathrm{(^{\mathit{t}}BuO)_3M[Si(SiMe_3)_3]}$	**Zr**[40]
	$\mathrm{MCl_4/M'Cl_3/Li}$	**Zr/Ti**[90]

Cp = $\mathrm{C_5H_5}$; Cp* = $\mathrm{C_5Me_5}$; $\mathrm{Cp^{Me}}$ = $\mathrm{C_5H_4Me}$; $\mathrm{Cp^{Si}}$ = $\mathrm{C_5H_4SiMe_3}$; $\mathrm{Cp^{R}}$ = $\mathrm{C_5H_4CMe_2CHMe_2}$; $\mathrm{Cp^{N}}$ = $\mathrm{C_5H_5CH_2CH_2N^{\mathit{i}}Pr_2}$; Ind = indenyl; $\mathrm{Cp^{Si*}}$ = $\mathrm{C_5H_4SiMe_2}$(**1**R)-*endo*(+)-$\mathrm{OC_{10}H_{17}}$; $\mathrm{Cp^{N2}}$ = $\mathrm{(CH_2)_{\mathit{n}}NMe_2}$; $\mathrm{Cp^{R2}}$ = $\mathrm{C_5H_4(CH_2)_{\mathit{n}}CHMe_2}$; $\mathrm{Cp^{Et}}$ = $\mathrm{C_5Et_5}$; BTHIE = (1,2-bis(3-tetrahydroindenyl)-ethane); py = pyridine.

[a] No coupling observed.

[b] Only traces of oligomers reported.

was formed from Cp_2ZrMe_2 and excess $PhSiH_3$ and was the only NMR observable zirconium species in catalytic reactions.[15] Related dimers were also observed in reactions of Cp_2ZrMe_2 with $PhMeSiH_2$, Ph_2SiH_2, $^{n}BuMeSiH_2$, and $H_2PhSiSiPhH_2$[19] and analogs of the titanium dimers were reported from the same monosilanes.[12] Replacement of the Me group in Cp_2MMe_2 with other organic groups as well as silyl substituents was developed as an extension of this basic catalyst precursor (see examples in Class 1 in Table I). Other variations involved incorporation of substituents on the Cp-rings but retaining either the Me group or a hydride, i.e., $CpCp'MMe_2$ or $Cp^1Cp^2MMe_2$ (see later entries in Class 1, Table I).

A second catalyst system, $CpCp^*M[SiR_3]X$ (primarily $R = SiMe_3$) was introduced and developed by Tilley and co-workers.[43] In general, X may be either Cl or Me. Most of the early publications from the Tilley group on this topic involved establishing the mechanism for the metallocene promoted dehydrocoupling reaction.[3h,3o,30,40,42,43] The silyl substituent of $CpCp^*Zr[Si(SiMe_3)_3]Me$, was removed instantaneously on addition of $PhSiH_3$ but more slowly in the chloro-substituted system, $CpCp^*M[Si(SiMe_3)_3]Cl$.[40] Under fluorescent room light (within 5 min for $M = Zr$ and 1 h for $M = Hf$) quantitative (or nearly so) yields of $CpCp^*M(SiH_2Ph)Cl$ and $HSi(SiMe_3)_3$ were obtained.[42] The zirconium complex decomposes to give polymeric material but the Hf analog is stable as a solid. From a study of the slower reacting Hf complexes with $PhSiH_3$, Tilley and co-workers were able to establish the experimental support for the polymerization mechanism[3o,3h,30] that will be described in Section III.

The remaining catalyst system, a combination of the commercially available metallocenes, Cp_2MCl_2 ($M = Ti$, Zr, Hf) with $^{n}BuLi$ was introduced by Corey and co-workers.[3m,48,49] With this system there is no induction period when used for the condensation of $PhSiH_3$, and secondary silanes can be coupled at reasonable rates at higher temperatures.

Each of these catalyst systems had strengths and weaknesses. The basic metallocenes, Cp_2MMe_2, employed by Harrod, must be synthesized from commercial reagents and are not thermally stable. Generally, use of Cp_2MMe_2 ($M = Ti$, Zr) precursors in silane polymerizations provided relatively low molecular weight polysilane from $PhSiH_3$ and the products contained relatively large quantities of cyclic polysilanes. The $CpCp^*M[Si(SiMe_3)_3]X$ system also has the disadvantage of requiring the synthesis of both the precursor to the silyl ligand ($Si(SiMe_3)_3$) as well as the complexes $CpCp^*M[Si(SiMe_3)_3]X$ ($X = Cl$, $M = Zr$,[91] Hf[41]; $X = Me$, Zr,[92] Hf[30]) themselves. The silyl group is removed more easily than the organic groups utilized in Harrod's catalyst and the combination of the Cp and the Cp* ligands on the metal center seems to provide for higher molecular weight polysilane and a lower percentage of cyclics. The added advantage of the facile removal of the silyl substituent (relative to an organic group) provides more rapid entry to the actual catalytic species. The use of Cp* in place of one of the Cp ligands also may improve the lifetime of the catalyst preventing conversion to an inactive species such as a dimer. The third catalyst system which combines commercial reagents and thus provides direct access to a catalyst system has the disadvantage that is inherent in the use of non-substituted Cp ligands on the metal. As will be described later, the reaction of Cp_2ZrCl_2 with ^nBuLi has been studied by two groups who have demonstrated how complex the system is in actuality although these studies were performed in the *absence* of hydrosilane.[93,94]

A novel feature of both Cp_2TiMe_2 and $Cp_2TiCl_2/2^nBuLi$ dehydrocoupling mixtures was observed in the condensation of the silane, $H_2MeSi(CH_2)_2SiH_3$. The fastest condensation obviously involves the primary silane center but there are residual secondary silane centers on the pendant groups in the product. When reacting solutions were deactivated by admitting oxygen the usual blue color disappeared producing an inactive yellow solution (presumed to contain Ti(IV)). However, an active catalyst was regenerated when the solutions were warmed gently and turned green. This regeneration was believed to be the result of the residual Si–H functional groups in either the oligomers or polymers that were produced by the original catalyst mixture.[13,47] The "revived" catalyst promoted cross-linking of the polysilane.

The M_n values of the polysilanes produced from $PhSiH_3$ with these first catalyst systems generally fell between about 1000 and 3500 amu. Tilley's studies demonstrated the effect of solvent on molecular weight values and showed that reactions run neat provided the longer chains with a lower percentage of cyclic materials. The percentage of cyclics could also be reduced by lowering the temperature.[3h] Under conditions where a dynamic vacuum was applied and small amounts of toluene added to keep the system mobile, a maximum M_n value of about 5300 was obtained for $H(PhSiH)_nH$ with the catalyst precursor $CpCp^*Zr[Si(SiMe_3)_3]Me$. The chain length for this M_n value is estimated to be about 70 silicon atoms.[21,95]

The three systems described in earlier paragraphs can be considered first generation catalyst precursors. In the next phase of development of catalyst systems for dehydrocoupling, modifications of the basic structures were attempted with the aim of improving the molecular weights and minimizing the percent of cyclic byproducts. At least some of the structural modifications were modeled after metallocenes that were utilized for the polymerization of olefins. These structural changes involved the synthesis of substituted Cp^X-rings ($X = Me$,[6b] Me_3Si,[21] $(CH_2)_nNR_2$;[33,34] either one or both rings of the metallocene), ansa-metallocenes (an atom or atoms bridge the two Cp-rings), and bimetallic complexes. Entries in Table I under Classes

1 and 4 demonstrate these modifications. These types of structural changes did not produce a significant improvement in the M_n values of the polysilanes produced over the values obtained with the first generation catalysts. However, the cumulative results did ultimately demonstrate indirectly that the substituents on the ring could be important in producing the highest M_n values observed with the "second generation" pre-catalysts.

Another approach utilized in metallocene promoted olefin polymerizations involved the generation of cationic species, generally by the addition of a Lewis acid to remove an organic group from [TM–R] to give $[TM]^+$ $[R–LA]^-$ or by a protonic reagent (typically an ammonium salt) that converted [TM–R] to RH and $[TM^+]$[anion]. This tactic has been employed by both Harrod[58,60,79,81,83] and Tilley[21] as outlined in Class 7 in Table I. A similar approach has been utilized for Cp'_2MH_2 precursors as well (see final entries in Class 7). Harrod has also used the combination catalyst system, $Cp^1Cp^2MCl_2/^nBuLi$ with added $B(C_6F_5)_3$,[58,60,79,83] as shown in the examples in Class 8 in Table I. The overall result of the polymerizations using cationic metallocenes is not clear and appears to depend on the metallocene substituents (both on the Cp-ring and on the metal) and the reagent added to the metallocene to produce the cationic species. In the best case, the M_w of $H(PhSiH)_xH$ (linear fraction only) increased about 50% in the change from $CpCp^*ZrMe_2$ to $CpCp^*ZrMe_2/[NHEt_3][BPh_4]$ (although the time periods studied are not comparable).[21] The M_w for the polysilane (fractionated polymer) increased >400% when $B(C_6F_5)_3$ was added to the combination of $CpCp^*ZrCl_2/2^nBuLi$ and the percent cyclics reduced from 20 to 10%.[60] However, Marks and co-workers used $Cp_2Ti(CH_2TMS)_2$ to polymerize $PhSiH_3$, but when $B(C_6F_5)_3$ was added the M_w of the polysilane was *reduced* to 40% of the value observed in the absence of the Lewis acid. The combination of $(EBI)TiMe_2/B(C_6F_5)_3$ produced only dimers and trimers.[23] The related reactions that start with $CpCp^*HfMe_2$ takes yet a third course. When $CpCp^*HfMe_2$ is treated with $B(C_6F_5)_3$, the solid cation-like complex, $CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3$ could be isolated. Subsequent reaction of the hafnium Lewis acid "adduct" with $PhSiH_3$ provided a quantitative yield of $[CpCp^*HfH][\mu\text{-}HB(C_6F_5)_3]$ (and $PhMe_2SiH$).[82] Use of the hydride "adduct" provided polysilane (from $PhSiH_3$) of about the same molecular weight as that obtained from $CpCp^*HfHCl$. However the polymer produced was of a decidedly different nature as a consequence of the fact that the cation-like complex actually initiates two reaction pathways, the one being dehydrocoupling (~25%) and the other a redistribution (75%) of $PhSiH_3$ to Ph_2SiH_2 and SiH_4. The SiH_4 generated was incorporated into the polysilane chain and ultimately resulted in cross-linking. The presence of cross-linking was determined by ^{29}Si NMR spectroscopy.[82] One of the few other examples of cross-linking in the dehydrocoupling of a primary silane comes in the condensation of $MeSiH_3$ in the presence of Cp_2MMe_2 (M = Ti, Zr). In this case the observation of cross-linking (through a tertiary SiH in the backbone of the polysilane polymer) was attributed to the small size of the methyl substituent.[8]

Other modifications of the basic systems have come primarily in the replacement of butyllithium with other anionic reagents in combination with the metallocene dichloride. The use of hydride reagents such as Red-Al ($Na[H_2Al(OCH_2CH_2OCH_3)_2]$) and N-Selectride ($Na[HB(^sBu)_3]$ with Cp_2MCl_2 has been utilized by Woo and co-workers to promote dehydrocoupling.[51,52,65–69] Addition of reducing agents such as $LiAlH_4$[70a] and $Naph^-$[70b] to Cp_2ZrCl_2 have been specified in patents. These cases are found in Class 4 in Table I. There were no significant improvements in the molecular weight of the polysilane produced from condensation of $RSiH_3$ with these alterations in the ‘‘combination catalyst’’ system.

Thus far the discussion has focused on the three metallocene precursors: Cp_2MR_2 (R = organic or silyl), Cp_2MRCl (especially R = silyl), in both of which R is removed or replaced when the hydrosilane is added, and Cp_2MCl_2 which must be activated by organolithium reagents or hydride reducing agents. Metallocene dichlorides do not react with hydrosilanes in the absence of an activating agent. However, it can be demonstrated that Cp_2MX_2 (X = F, M = Ti,[45,46] Zr,[45,46] Hf;[45] OPh, M = Ti,[45,47] Zr,[45,47] Hf;[45] NMe_2, Ti,[45] Zr,[45] Hf[45]) will react directly with silanes to transfer X to the silicon center[45] (see Class 3 in Table I) although the phenoxide derivative must be heated before dehydrocoupling is observed. Presumably metallocene hydrides were formed in an exchange reaction with the hydrosilane but such species could only be identified in reactions of the titanocene complexes.[45] The M_n values for $H(PhSiH)_xH$ produced from such Cp_2MX_2 systems range from about 1400 to 2600 and are similar to those produced by other metallocenes with unsubstituted Cp-rings. The highest molecular weight polysilane was obtained when X = NMe_2 for all three metals. Additional studies by the Corriu/Moreau group demonstrated that $Cp_2M(OAr)_2$ complexes were stable and tunable precursors for dehydrocoupling of primary silanes but were less effective for secondary silanes.[47] Although $Cp_2Ti(OPh)_2$ required thermal activation, $Cp_2Ti(OC_6H_4R\text{-}p)_2$ (R = Cl, Me, CN, OMe) reacted with $PhSiH_3$ at room temperature but with an induction period whose length was determined by the substituent on the aryloxide. The approach was also extended to the use of $Cp_2Zr(OPh)_2$. The resulting polymers from both the Zr and the Ti complexes were similar to those obtained from Cp_2MMe_2 or $Cp_2MCl_2/2^nBuLi$.

The metallocene alkoxides have also been utilized as partners in the combination catalyst approach as shown in Table I, Class 5. Only two examples were tested but one of these was the chiral pre-catalyst (*S*,*S*)-[1,2-bis(η^5-tetrahydroindenyl)ethane]titanium binaphtholate activated by ^{n}BuLi.[79] With the chiral pre-catalyst, slow stepwise oligomerization of $PhSiH_3$ occured but disappointingly, there was no influence on the stereochemical outcome of the coupling reaction. This point will be addressed in the section that deals with the properties of the polysilanes produced in dehydrocoupling. In the second example (a patent[80]), $(Me_3Si)_3SiLi \cdot 3THF$ was added to $Cp_2Zr(OMe)_2$ and is the only case that attempts to mimic Tilley's type of catalyst system from a combination catalyst approach. Another variation on the metallocene aryloxide theme is the system $Cp_2M(OAr)Cl/^nBuLi$ ($Ar = C_6H_5$, C_6F_5, and 3 cases where Ar has *ortho*-substituents: ^{t}Bu, ^{i}Pr, MeO) studied by Tanaka and Obora.[62] Aryloxides with bulky substituents ortho to the oxide linkage produced the highest M_n values and smallest amounts of cyclic byproducts although the polydispersities were about 5 (higher than usually observed for the "first" generation catalysts). The M_n values are in the same range that is usually found for metallocenes without substituents on the Cp-rings.[62]

Three other variations are included in Table I each of which contains a limited number of examples. Removal of one of the Cp-rings to give $CpMX_3$ has been examined (Class 6, Table I). Only traces of oligomers were produced on reaction of $CpMMe_3$ (M = Ti, Zr) with $PhSiH_3$[6b] but more than 50% conversion of $PhSiH_3$ to dimers through tetramers was realized with $Cp'MCl_3/3^nBuLi$.[57] Lower oxidation state M(II) systems (Class 9, Table I) in the form of Cp'_2M(alkyne) complexes also promoted dehydrocoupling. Of the series of alkyne complexes, the use of $Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)py$ with $PhSiH_3$ produced the highest M_n value (>3000) for $H(PhSiH)_xH$ but the M_w/M_n value was ~ 6 in contrast to values < 2 for most other catalyst systems (see Section IV.A). Finally, only a few non-Cp containing Group 4 complexes have been studied for dehydrocoupling of $PhSiH_3$ and these are given in Class 10, Table I. There was no inherent improvement attained with these modifications.

III

MECHANISTIC PROPOSALS

The question of how the polysilane is produced in a dehydrocoupling process has fascinated all those who have studied the reaction. There have been several mechanistic suggestions starting with the earliest proposal by Harrod that silylenes (which presumably inserted into SiH) bonds were involved (Fig. 1)[5] or that the sequence may involve the

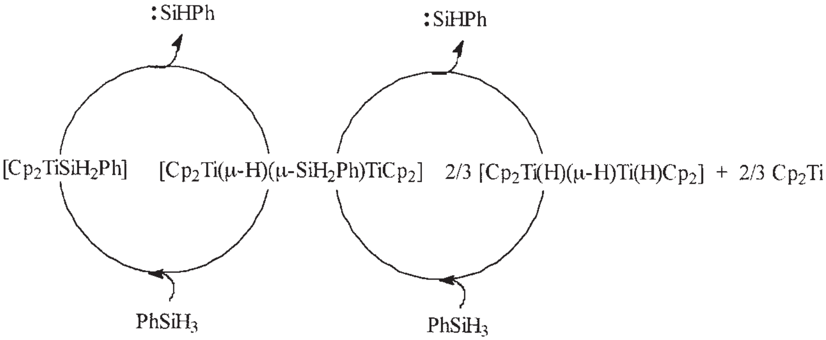

FIG. 1. Early silylene mechanism proposed by Harrod.[5]

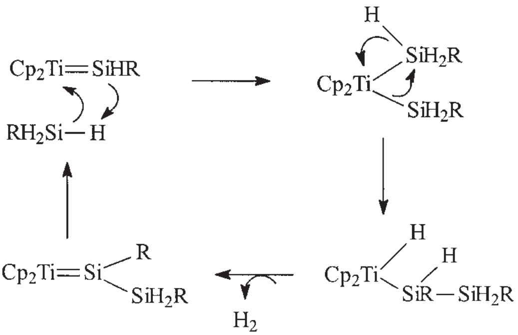

FIG. 2. Metal silylene mechanism proposed by Harrod.[6a]

generation/reaction of a metal silylene complex (Fig. 2).[6a] The intervention of silylenes was also favored by Hengge and co-workers on the basis of the product distributions produced in reactions of hydrogen terminated oligomers with Cp_2MMe_2.[9]

The most widely accepted mechanism for Group 4 metallocene promoted dehydrocoupling reactions is the σ-bond metathesis mechanism proposed by Tilley as shown in Fig. 3.[3h,3o,30,40,96] The reaction of the metallocene precursor is believed to produce a metallocene hydride (unknown oxidation state) which then enters the catalytic cycle. The first of two σ-bond metathesis steps results in formation of a metal silyl and the second results in Si–Si coupling. As discussed by Tilley,[3h] the step involving Si–Si bond formation is the most crowded of the σ-bond metathesis transition states and accounts for the observation that primary silanes are usually more reactive toward dehydrocoupling than are secondary silanes. Tilley also

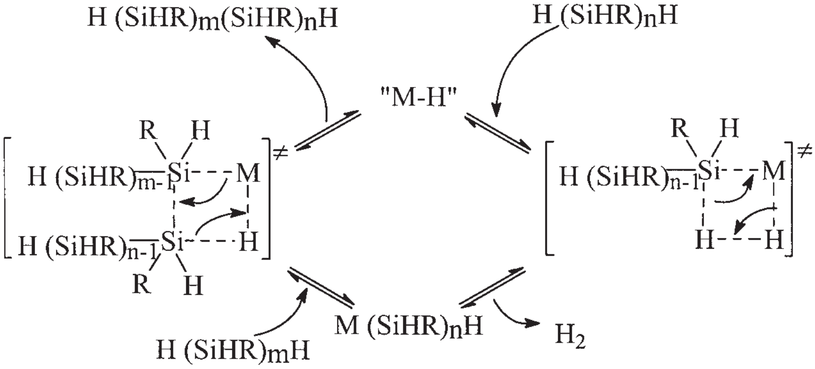

FIG. 3. σ-Bond metathesis mechanism proposed by Tilley.[3h,3o,30,40]

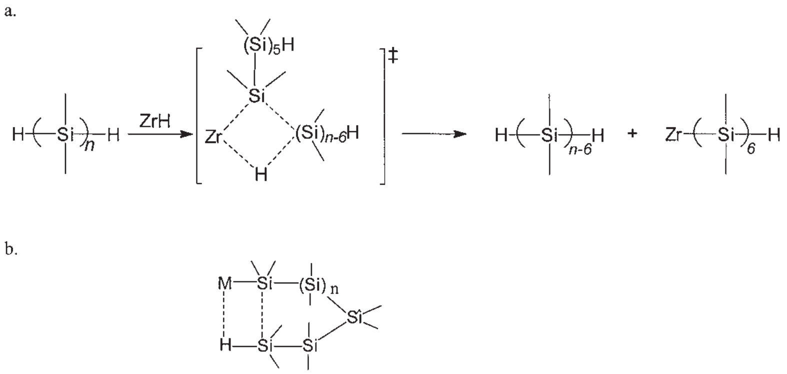

FIG. 4. Formation of cyclics by σ-bond metathesis ($n = 1, 2\ldots$).[3h,49]

proposed that in the polymerization, the fastest Si–Si bond forming step would add one silicon at a time to the end of a chain. This process would involve the least crowded transtion state as the bulkier group (the growing chain) which is actually a secondary silyl center would be in a position β to the metal center when coupling to the Si group on the metal. The overall result would be linear chain growth as long as monomer is present.

As shown in Fig. 3, the σ-bond metathesis steps are reversible. Thus, reaction of the "MH" species with an internal Si–Si bond of a chain could result in chain degradation as shown in Fig. 4.[49] If small oligomers are formed (or remain at the metal center) after attack of an MH at an internal Si–Si bond, such oligomers could cyclize through a

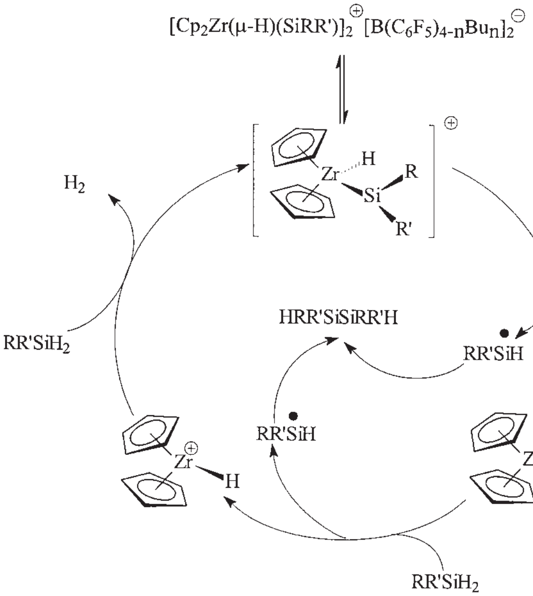

FIG. 5. Redox cycle for dehydrocoupling by silicon radicals. One of three variations proposed by Harrod.[3d,60,81,83]

transition state as in Fig. 4b.[3h] If this mechanism is operative then the rate of intramolecular metathesis vs. intermolecular metathesis will determine whether chain growth occurs or cyclization to short chains becomes competitive.

Harrod's most recent mechanistic proposal for "cation-like" silylzirconocenes is the redox mechanism, one variation of which is shown in Fig. 5.[3d,60,81,83] In cases where Zr(IV) is *not* reduced to Zr(III), σ-bond metathesis is likely. However, if Zr(III) is produced, Harrod favored generation of silyl radicals through a Zr(III)/Zr(IV) redox cycle and subsequent coupling of silyl radicals produced the silicon oligomer or polymer. Additional arguments for possible radical processes will be provided in a later section.

A last consideration in this section is the catalytic species generated from the combination of Cp_2MCl_2 and $^{n}BuLi$. Although there is no general agreement as to the mechanistic details of homocoupling, a metal hydride is in all likelihood involved. Corey's proposal for a sequence of reactions leading to a catalytic cycle is shown in Fig. 6.[48,50,63]

The coupling of Cp_2ZrCl_2 with $^{n}BuLi$ to form Cp_2ZrBu_2 at low temperaure was demonstrated by Negishi.[97] Buchwald has shown that warming of Cp_2ZrBu_2 in the presence of phosphine provided

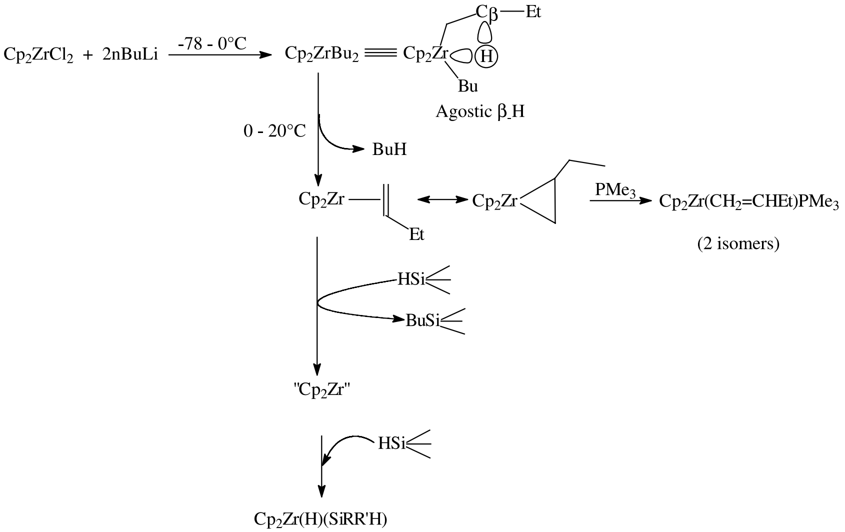

FIG. 6. Reaction pathway for conversion of Cp_2ZrCl_2 and ^{n}BuLi to a complex that could enter into a σ-bond metathesis cycle for dehydrocoupling as proposed by Corey.[50,63]

Cp_2Zr(butene)L[98] probably formed from elimination of butene (β-hydride elimination) from Cp_2ZrBu_2 to form Cp_2Zr(butene). In the presence of a hydrosilane, Cp_2Zr(butene) reacts to form H(Bu)SiRR′ (observed in the reaction of $PhMeSiH_2$) or possibly "Cp_2Zr" which would then react rapidly with a hydrosilane to form $Cp_2Zr(H)(Si\equiv)$.[99] The hydrosilylzirconocene could then enter a σ-bond metathesis cycle as shown in Fig. 3. The nature of the species generated from the combination of Cp_2ZrCl_2 and 2 equiv. of ^{n}BuLi has been studied by both Harrod[93] and Choukroun.[94] Both reported that Zr(III) species were formed and observed by ESR. Addition of 2^{n}BuLi to Cp_2ZrCl_2 gave a species identified as $Cp_2Zr(\eta^3$-Me–allyl) which decomposes to "Cp_2ZrH" at higher temperature.[94] The allyl complex was estimated to be formed in ~40 to 50% yield. Addition of $PhMe_2P$ as a trapping agent led to the formation of a paramagnetic σ-allyl complex assigned the structure, Cp_2Zr(σ-Me-allyl)($PPhMe_2$). Harrod and Dioumaev showed that the solution is more complex by using a combination of EPR and multidimensional, multinuclear NMR spectroscopy. A number of species were identified including Cp_2ZrR (R = H, Bu), $[Cp_2Zr(CH{=}CHCH_2CH_3)H]_2$, crotylzirconocene(IV) hydride, a zirconacyclopropane, and a zirconacyclopentane(IV).[93] However, it should be noted that these species were generated in the absence of a silane or of another trapping agent. For instance, when two equivalents of Ph_2SiH_2 were added to a solution containing Cp_2Zr(butene), the dimer, $[Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2(Ph_2SiH)ZrCp_2]$ was isolated in 85% yield and crystallographically characterized.[99] Similar dimers have been reported by Harrod.[19]

IV

SILANES INVOLVED IN DEHYDROCOUPLING

The types of silanes that have been studied in dehydrocoupling reactions promoted by Group 4 metallocene derivatives include primary silanes $RSiH_3$, secondary silanes $RR'SiH_2$, tertiary silanes $RR'R''SiH$ (attempted), disilanes (or other oligomers), and bis-silanes such as $HRR'Si–X–SiRR'H$ where X is generally an organic linker. Each of these groups will be discussed separately.

A. *Primary Arylsilanes*

The benchmark used in almost all investigations has involved the condensation of phenylsilane as can be seen in the listing of primary silanes in Table II. Table II also includes the class of complex used to promote the dehydrocoupling. There is no standard set of conditions used by the various investigators for the dehydrocoupling of hydrosilanes, therefore it is problematic to compare results from one investigator to another. Results will vary as a function of time, silane/metal complex ratio, presence or absence of solvent, temperature, and whether the polymer has been fractionated during the workup procedure. Most catalyst systems produce a bimodal distribution for the polysilane product. Fractionation of the polymer product will remove the majority of the low molecular weight cyclic polysilanes. Thus, the M_w and M_n values of fractionated polymers will be higher than that of the entire product mixture. There are two reports that have compared a number of complexes for the condensation of $PhSiH_3$,[21,60] so that within each of these reports, some conclusions may be drawn. Table III summarizes selected results from sets of experiments that were performed by the same investigators. There are several conclusions that can be drawn from the data. Comparison of entries in 1, 2, 3, and 4 show the increase in M_w and M_n between a CpCp*Zr-precursor and the unsubstituted zirconocene precursor. The effect of the remaining non-Cp substituents can be seen in entry 2 in the change from Me to the Cl derivative which is a much slower catalyst. The formation of a cationic species from $CpCp^*ZrMe_2$ results in an increase in the M_w of the polysilane (compare data from entries 3 and 1). The utility of a metallocene hydride is

TABLE II

CONDENSATION OF PRIMARY SILANES BY METALLOCENE CATALYSTS

Primary silane	Catalyst class[a] (Ref)
$PhSiH_3$	**1**[9,11,12,21–23,25–30,33–35,39,93,95,97,104,106,111,116–119] **2**[64,69,81–83,95,97,104,113,114] **3**[6,25,42,46,58] **4**[3,7,17–19,29,31,50,53,54,66,76,90,91,104] **5**[13,20] **6**[15,97,111] **7**[5,26,50,66,69] **8**[20,66] **9**[33] **10**[2,14b,49,63,97]
$ArSiH_3$	
o-$CH_3C_6H_4$	**1**[29]
m-$CH_3C_6H_4$	**1**[29]
p-$CH_3C_6H_4$	**1**;[6b,29] **2**;[41,42] **4**[54]
p-$MeOC_6H_4$	**1**;[22,25] **2**;[41] **4**;[62] **5**[62]
p-FC_6H_4	**1**;[22] **2**[41]
p-$Me_2NC_6H_4$	**1**;[22] **4**;[62] **5**[62]
o-$F_3CC_6H_4$	**1**[29]
m-$F_3CC_6H_4$	**1**[29]
p-$F_3CC_6H_4$	**1**[22,29]
p-$MeSC_6H_4$	**4**;[62] **5**[62]
3,5-$Me_2C_6H_3$	**1**[22]
3,5-$(F_3C)_2C_6H_3$	**1**[22]
2,4,6-$Me_3C_6H_2$	**2**[41,42]
C_6F_5	**1**[22]
$PhCH_2SiH_3$	**1**;[6a,7,27] **2**;[41,42] **4**;[66] **7**[81]
$ArCH(Me)CH_2SiH_3$[b]	**4**[67]
$ArCH(Me)CH_2SiH_3$[c]	**4**[69]
$RSiH_3$	
Me	**1**[7,8,12]
$Et_3Si(CH_2)_2$	**4**[56]
^{n}Bu	**1**;[16] **4**[49]
^{n}Hex	**1**;[4,6a] **4**[49]
Cy	**1**;[102] **2**[41,42]
$(Si_6Me_{11})SiH_3$	**1**[14]

[a] See Table I for structures of each Class.

[b] Ar = C_6H_5, 3-$H_3CC_6H_4$, 2,5-$Me_2C_6H_3$, 3-ClC_6H_4, 3-Cl-4-MeC_6H_3, 4-$PhOC_6H_4$, naphthyl.

[c] Ar = p-XC_6H_4 (X = Cl, Me, PhO).

TABLE III

SELECTED EXAMPLES OF DEHYDROCOUPLING OF $PhSiH_3$ BY METALLOCENES OF GROUP 4

	Catalyst (Class[a])	Time	M_n[b]	M_w[b]	c = cyclic l = linear	Ref.
1.	Cp_2ZrMe_2 (1)	24 h	560	1200	c + l	21
	$CpCp^*ZrMe_2$ (1)	24 h	2900	6940	l	21
	$[CpCp^*ZrH_2]_2$ (1)	15 h	5660	13,880	l	21
2.	$Cp_2Zr[Si(SiMe_3)_3]Me$ (1)	15 min	990	1690	c + l	21
	$Cp_2Zr[Si(SiMe_3)_3]Cl$ (2)	7 h	1240	2540	c + l	21
	$CpCp^*Zr[Si(SiMe_3)_3]Me$ (1)	2 days	5260	11,670	l	21
3.	$Cp_2ZrMe_2 + [NH^{n}Bu_3][BAr_4]$[c] (7)	15 min	1390	2930	l	21
	$CpCp^*ZrMe_2 + [NHMe_2Ph][(C_6F_5)_4]$ (7)	10 h	4070	9150	l	21
4.	$Me_2Si(C_5H_4)_2Zr[Si(SiMe_3)_3]Me$ (1)	24 h	1020	1990	c + l	21
	$Me_2Si(C_5H_4)(C_5Me_4)Zr[Si(SiMe_3)_3]Me$ (1)	24 h	3060	5570	l	21
5.	$Cp^*(Cp^{Si})ZrMe_2$[d] (1)	24 h	190	210	c + l	21
	$Cp^*(Cp^{Si})ZrH_2$ (1)	14 h	4730	10,250	l	21
6.	$Cp_2Ti(NMe_2)_2$ (3)	2 days	1285	1909	c + l	45
	$Cp_2Zr(NMe_2)_2$ (3)	2 days	2024	3135	c + l	45
	$Cp_2Hf(NMe_2)_2$ (3)	2 days	2608	4366	c + l	45
7.	$Cp_2ZrCl_2/2^{n}BuLi$ (4)	1 day	1860	3000	l	60
	$Cp_2ZrCl_2/2^{n}BuLi/B(C_6F_5)_3$ (8)	1 day[e]	7270	13,790	l	60
		7 days[f]	5550	10,700	l	60
		17 days[g]	1640	2710	l	60
	$CpCp^*ZrCl_2/2^{n}BuLi/B(C_6F_5)_3$ (8)	[h]	9920	20,400	l	79
	$CpCp^*HfCl_2/2^{n}BuLi/B(C_6F_5)_3$ (8)	[h]	7400	12,700	l	79
8.	$Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)\cdot py$ (9)	72 h	3253	19,460	c + l	84b
	$Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)\cdot py/toluene$ (9)	72 h	958	4840	c + l	84b
9.	$Cp_2ZrCl_2/2^{n}BuLi$ (4)	120 h	1600	3200	l	62
	$Cp_2Zr(O\text{-}2,6\text{-}^{t}Bu\text{-}4\text{-}MeC_6H_2)Cl/^{n}BuLi$	120 h	5700	11,900	l	62
	$Cp_2Zr[O\text{-}2,6\text{-}(MeO)_2C_6H_3]Cl/^{n}BuLi$	120 h	1700	3400	l	62

[a] Class for the metal complex is defined in Table I.

[b] Measurements of M_n and M_w are determined by GPC relative to polystyrene. Only data for reactions that are run neat are included unless specified otherwise.

[c] $BAr_4^- = [B(3,5\text{-}Me_2C_6H_3)_4]^-$.

[d] $Cp^{3i} = C_5H_4SiMe_3$.

[e] 5 mol% catalyst.

[f] 1 mol% catalyst.

[g] 0.25 mol% catalyst.

[h] Time period was not specified.

demonstrated in the comparison of $CpCp^*ZrMe_2$ and $[CpCp^*ZrH_2]_2$ in entry 1 and the related set of compounds in 5. Entry 6 illustrates the effect of changing metal while keeping the other structural features the same. In general, for simple systems, the M_w of the polysilane produced increases in the sequence Ti < Zr < Hf and the % cyclics are in the order Hf < Zr < Ti. The addition of a Lewis acid to the $Cp_2ZrCl_2/2^{n}BuLi$ system is shown in Entry 7 and also illustrates the decrease in M_w with decreasing mol% of catalyst. The last two sets of entries provide unusually high molecular weights for metallocene systems that contain unsubstituted Cp-rings. It is possible that in the mixed alkoxychlorometallocene (Entry 9) if a hydride is produced on reaction of the dichloride with ^{n}BuLi, the presence of the bulky alkoxy group may prevent dimerization of the metal unit to a catalytically inactive form. The results for the polysilane molecular weight (M_w) produced from the alkyne complex in Entry 8 seems higher than what would be expected on the basis of other unsubstituted metallocene systems since it is one of the highest values recorded for any system, however, the M_n value is low (~3300).[84b] The only other H(PhSiH)$_x$H with a M_w near 20,000 was produced from CpCp*ZrCl$_2$/2^{n}BuLi/B(C$_6$F$_5$)$_3$ and the polymer has a M_n value near 10,000.[77] On the other extreme there are metallocenes that react with PhSiH$_3$ to provide oligomers (usually disilane through tetrasilane or pentasilane). These metallocenes include (*S*,*S*)-[1,2-bis(η^5-tetrahydroindenyl)ethane]titanium binaphtholate/2^{n}BuLi,[79] both *rac*- and *meso*-[Me$_2$C(C$_5$H$_3$SiMe$_3$)$_2$]HfCl$_2$/2^{n}BuLi,[63] [Me$_2$C(C$_5$H$_4$)$_2$]HfCl$_2$/2^{n}BuLi,[63] CpCp*Hf–(SiHPhSiHPhSiH$_2$Ph)Cl[40] Ind$_2$ZrMe$_2$, and [1,2-bis(indenyl)ethane]dimethylzirconocene.[36,37] Therefore all three of the basic catalyst systems can be rendered ineffective for polymerization but probably not all for the same reason although steric bulk in the metallocene or for the silyl substituent initially bound to the metal center most likely plays a significant role.

The dehydrocoupling of arylsilanes, ArSiH$_3$, has also been studied and reveals some interesting features about the condensation reaction. One of the earliest reports was that of Waymouth who studied the condensation of RC$_6$H$_4$SiH$_3$ (R = CH$_3$, CF$_3$) with Cp$_2$Zr[Si(SiMe$_3$)$_3$]Me and observed the following relative rates of polymerization relative to the position of R: *p*-CF$_3$ ~ *m*-CF$_3$ > H > *p*-CH$_3$ > *m*-CH$_3$ >> *o*-CH$_3$ ~ *o*-CF$_3$.[29] Actually the *o*-substituted phenylsilanes did not give homopolymer under the conditions similar to those used for the condensation of the *m*- and *p*-systems. From this limited subset one could conclude that electron-withdrawing substituents accelerate the dehydrocoupling of arylsilanes and electron-donating groups cause a reduction in the rate of the coupling reaction. More recently, Kira and co-workers studied the condensation of a series of substituted arylsilanes with Cp$_2$ZrMe$_2$.[22] The M_w of the polysilane polymers seemed to be a function of whether there were electron-withdrawing groups vs. electron-releasing groups. Although the times for the condensation reaction varied from about 0.5 to 2 days, the M_w values for the polysilane produced from RC$_6$H$_4$SiH$_3$ followed the order (R, M_w value): *m*-CF$_3$ (17,200) > *p*-CF$_3$(9900) > *p*-F(7000) > H(3600) > *p*-MeO (3500) > *p*-^{i}PrO (2800) > *p*-Me (2300) > 3,5-Me$_2$C$_6$H$_3$ (2200) > C$_6$F$_5$ (1100) > 3,5-(F$_3$C)$_2$

(1000).[22] The condensation of p-$Me_2NC_6H_4SiH_3$ was also studied but since the starting material is a solid, it was necessary to use a solvent for the coupling reaction, thus the results cannot be compared directly to the other systems. It is noteworthy, however, that the products were oligomers.[22] The authors concluded that the degree of polymerization was affected by both electronic and steric effects in agreement with the conclusion in the Waymouth study. Although it was a limited subset of arylsilanes, Tanaka and co-worker also observed lower M_w values in the condensation of $ArSiH_3$ with $Cp_2Zr(O\text{-}2,6\text{-}({}^tBuO)_2\text{-}4\text{-}MeC_6H_2)Cl/{}^nBuLi$ when an electron-donating substituent was present (results are compared for the same time period): $PhSiH_3$ (13,300) > p-$MeOC_6H_4SiH_3$ (2800).[62] If an olefin is added to a Cp_2TiMe_2/silane mixture, H_2 evolution is suppressed and the olefin is hydrogenated. The dependence of cyclohexene co-hydrogenation rate in the presence of primary silanes with Cp_2TiMe_2 followed the order: $C_6H_5SiH_3$ (13.2) > p-$MeC_6H_4SiH_3$ (9.8) > $PhSiD_3$ (3.6) > ${}^nC_6H_{13}SiH_3$ (1.0) ~ $C_6H_5CH_2SiH_3$ (1.0) > c-$C_6H_{11}SiH_3$ (0.5) relative to $C_6H_5SiH_3$ in the absence of cyclohexene (3.0).[100] The observed order of reaction also reflected the order of homocoupling in the absence of olefin. It should be noted that the homocoupling of $PhSiH_3$ is faster in the presence of olefin than in the absence of olefin.[100] Other interesting features are the isotope effect operating in the condensation of $PhSiD_3$ and the lower reactivity of the primary alkylsilanes.[100]

The reaction of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ with primary silanes has been studied in detail at the stoichiometric level. Normally, the primary silane (including p-$FC_6H_4SiH_3$) displaces the $Si(SiMe_3)_3$ ligand [as $HSi(SiMe_3)_3$] and produces $CpCp^*Hf(SiH_2R)Cl$. However, the σ-bond metathesis of p-$XC_6H_4SiH_3$ ($X = Cl$, Br) does not occur.[41] This result suggests that a limitation on the use of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ to initiate the dehydrocoupling of silanes with substituents that containing Cl or Br will probably occur.

B. *Other Primary Silanes*

When the phenyl(aryl) group is moved to a position one unit away from the silicon center producing $PhCH_2SiH_3$, the rate of dehydrocoupling decreases dramatically. Condensation of $PhCH_2SiH_3$ in the presence of Cp_2TiMe_2 produced a mixture of cyclic oligosilanes (Si_6 and Si_7). Prolonged contact with the catalyst converted the mixture of oligomers into another mixture of cyclics that contained the *all trans*-$(PhCH_2SiH)_6$.[7a] When the reaction was run in toluene for 6 weeks at r.t., the all trans isomer was isolated in ~35% yield.[7b] The conversion is thermodynamically favored by the low solubility of the *all trans* cyclohexamer. The isomerization must involve the breaking of Si–Si bonds and demonstrates the reversibility of the dehydrocoupling process. Condensation of $PhCH_2SiH_3$ with Cp_2ZrMe_2 produced only cyclic material.[19] The condensation of $PhCH_2SiH_3$ with Cp_2ZrCl_2/Red-Al has also been studied. The M_w value observed for the polysilane products was only 890 compared to a $M_w = 3910$ observed for the polymer from $PhSiH_3$ produced under the same conditions.[66] Harrod and Dioumaev also used the reaction of $PhCH_2SiH_3$ with $[Cp_2Zr(\mu\text{-}SiH_2Ph)]_2{}^{2+}2[BBu_n(C_6F_5)_{4-n}]^-$ to demonstrate the presence of a paramagnetic intermediate, $[Cp_2Zr^{III}]^+[BBu_n(C_6F_5)_{4-n}]$ in support of the Zr(IV)/Zr(III) redox mechanism discussed in Section III.[81]

One of the characteristics of the condensation of primary alkylsilanes is a slower rate of reaction than that observed for phenylsilane. For instance, the relative rate of polymerization of $PhSiH_3$ to that of $HexSiH_3$ is 13 to 1 for Cp_2TiMe_2 and 20 to 1 for Cp_2ZrMe_2.[19] The condensation rate of $HexSiH_3$ is also affected by the metal in Cp_2MMe_2 as the relative rate of condensation for M = Zr is 5 times that of M = Ti.[19] It is not surprising that the rate of condensation of $(c\text{-}C_6H_{11})SiH_3$ ($c\text{-}C_6H_{11}$ may be viewed as a "secondary" alkyl group) was approximately half that of $^nHexSiH_3$ (as reflected by initial cyclohexene co-hydrogenation rates[100]). Hilty and co-workers monitored the course of the condensation of $^nBuSiH_3$ by GC and GC-MS, and observed oligomers and cyclics up to Si_7 and dominated by cyclics for DP values ≥ 5.[16] The absence of an IR band (GC/FT-IR) at 930 cm^{-1} demonstrated the absence of SiH_2 end groups in materials assigned a cyclic structure. Reactions were conducted in toluene and ~56% mass recovery of a mixture of oligomers was obtained after 24 h. The condensation of both $^nBuSiH_3$ and $^nHexSiH_3$ with $Cp_2MCl_2/2^nBuLi$ (M = Ti, Zr, Hf) in toluene has also been monitored by gas chromatography and the oligomers characterized by GC-MS.[49] Oligomers up to Si_{11} could be observed for $^nBuSiH_3$ but only up to Si_7 for $^nHexSiH_3$. Linear oligomers were produced in the initial stages of the condensation but as the reaction continued, cyclic polysilanes formed with increasing numbers of isomers as the number of silicon atoms increased. In the condensation of $^nBuSiH_3$, the two possible diastereomers of the tetrasilane, $H(^nBuSiH)_4H$ were formed in equal proportions with the titanium catalyst but only one diastereomer was observed with the hafnium system. With zirconium, one of the diastereomers is formed more rapidly at room temperature with both $^nBuSiH_3$ and $^nHexSiH_3$ although this differential disappears at 50 °C.[49] The origin of the rate difference in the production of the diastereomers of Si_4 is unknown. The condensation of $Et_3SiCH_2CH_2SiH_3$ with $Cp_2TiCl_2/>2^nBuLi$ at 70 °C gave 43% of fractionated polymer with a DP range between 12 and 15 after 48 h.[56] There was no evidence for cross-linking in the products produced at this higher temperature.

One of the most interesting results for an alkylsilane came from the study of the dehydrocoupling of the primary silane with the smallest alkyl group, CH_3SiH_3. The dehydrocoupling with Cp_2MMe_2 (M = Ti, Zr) occurs at reasonable rates to provide quantitative yields of a polymer. The polymer produced from $MeSiH_3$ in toluene after 1 day at 65 °C (M = Ti) had a M_w of $\sim 13{,}000$ but a P_D of 10.[8] Prolonged contact with the catalyst or increasing the temperature appeared to produce cross-linked polymer which became insoluble as indicated in the intensity ratio for the ν_{CH}/ν_{SiH} bands which increases with cross-linking. The ^{29}Si NMR spectra of soluble polymer exhibited only SiH and SiH_2 units and no quaternary silicon centers (produced if cross-linking occurs). The cross-linking requires that an internal tertiary SiH center react although tertiary silanes do not normally exhibit dehydrocoupling. The authors suggested that the cross-linking occurs in the methylsilane case because of the smaller steric effect of the CH_3 group relative to other organic substituents. The high values for the polydispersity observed for the methylsilane polymers was attributed to branching/cross-linking that occurs after the monomer concentration becomes small.[8]

As a last example, the condensation of the silylsilane, $(Si_6Me_{11})SiH_3$ in toluene gave dimer after 24 h in the presence of Cp_2MMe_2 (M = Zr, 95%; Ti, 30%) and a cleavage byproduct $Si_6Me_{11}H$ (M = Zr, 5%; Ti, 10%).[14] Thus, the condensation of $MeSiH_3$ and of $(Si_6Me_{11})SiH_3$ represent the two extremes in dehydrocoupling of primary silanes with Cp_2TiMe_2.

C. *Secondary Silanes*

There seems to be some myth that secondary silanes do not couple well in the presence of catalysts from Group 4. The examples discussed in this section should dispel that myth although there will be limitations that would be expected on the basis of trends observed for primary silanes. When changing from a primary silane to a secondary silane, a SiH bond is replaced with an organic group which would be larger than the hydride substitutent and thus the problem of steric hindrance to homocoupling of the secondary silane becomes a more serious problem. A tactic that can be used to surmount the slower coupling of secondary silanes can be the addition of a carefully selected hydrogen acceptor to the reaction mixture although this can introduce by-products associated with hydrosilylation of the olefin that acts as the hydrogen acceptor. The secondary silanes that have been subjected to homocoupling and the catalyst

TABLE IV

CONDENSATION OF SECONDARY SILANES BY METALLOCENE CATALYSTS

Secondary silane	Catalyst by Class(Ref)
$PhMeSiH_2$	**1**[4,12,19,25–27]
	2[41,42]
	3[45]
	4[14b,48,64,76]
	9[85]
$PhMeSiD_2$	**4**[50]
$PhCD_3SiH_2$	**4**[50]
$PhEtSiD_2$	**4**[50]
(m-$CH_3C_6H_5$)$MeSiH_2$	**4**[48]
Ph_2SiH_2	**1**[12,15,25,27,19,112a,116b]
	2[41,42]
	3[47]
	4[48]
	9[84b,85]
	10[78]
Ph_2SiD_2	**1**[27] [a]
Ar_2SiH_2	
Ar = p-$MeOC_6H_4$	**1**[25]
Ar = p-ClC_6H_4	**1**[25]
Silaheterocycles [b]	**1**[48]
R_2SiH_2	
R = Bu	**3**[47]
R = Pr	**4**[64] [c]
$BuMeSiH_2$	**1**[12]
(Si_6Me_{11})$MeSiH_2$	**1**[14]

[a] In the presence of phosphines.

[b] Sila-heterocycles: 3,7-di-^{t}Bu-9,9-dihydrosilafluorene, 9,10-dihydro-9-silaanthracene and 10,11-dihydro-*5H*-dibenzo[b,f]silepin.

[c] In the presence of olefin.

precursors used to promote this process are listed in Table IV. It is clear that, paralleling the observations in the condensation of primary silanes, it is the phenyl-substituted secondary silanes that are the most successfully coupled to oligomers and that dialkylsilanes require either forcing conditions or the presence of a hydrogen acceptor. There are no conditions yet reported for the metallocene promoted dehydrocoupling of secondary silanes to polysilanes.

In his first publication[4] reporting the use of Cp_2TiMe_2 to polymerize primary silanes, Harrod also described the condensation of $PhMeSiH_2$ in toluene and the coupling of this secondary silane occurred much more slowly than the coupling of primary silanes. After 2 weeks at r.t., 50% of the initial silane remained unreacted and the oligomers were reported to have an average degree of polymerization of four.[4] In a later report, only disilane and trisilane (up to 70%) were observed over long reaction periods (neat $PhMeSiH_2$ and Cp_2MMe_2 ($M = Ti$, Zr) at 80 °C).[19] The coupling of $PhMeSiH_2$ with $Cp_2MCl_2/^nBuLi$ requires heating and at 90 °C ($M = Zr$), after 96 h about 80% of the starting silane has been converted to $H(PhSiMe)_xH$.[48] From a combination of GC and HPLC, disilane through octasilane could be identified but only disilane through tetrasilane were isolated as individual oligomers. After 24 h at 90 °C, the predominant products were the disilane and trisilane [M(% conversion) = Ti (39%); Zr (50%); Hf (44%)].[48] Results from $CpMCl_3/^nBuLi$[57] and $Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)py$[84b] are similar. In the case of Cp_2TiPh_2, higher temperatures were utilized and 68% conversion of $PhMeSiH_2$ to a 2.3/1 mixture of trisilane/disilane was attained after 24 h at 110 °C.[26] In the presence of a hydrogen acceptor, the yields and average molecular weight of the oligomer mixture generally increase although the approach works most successfully with $Cp_2TiCl_2/^nBuLi$ where in the presence of cyclooctene, 98% conversion of $PhMeSiH_2$ to oligomers was achieved (90 °C, 24 h).[64a] With these same conditions, $Cp_2MCl_2/^nBuLi$/cyclooctene both $M = Zr$ and Hf precursors gave SiH/HC coupling products as the major product in addition to minor hydrosilylation byproducts. In the presence of suitable olefins, $Cp_2TiCl_2/^nBuLi$ will give dehydrocoupling products even at room temperature.[64b] The choice of olefin is critical with the $Cp_2MCl_2/2^nBuLi$ combination as there are four processes that are promoted by this system: hydrosilylation, the equivalent of SiH/HC dehydrocoupling, SiH, HSi dehydrocoupling, and olefin isomerization followed by hydrosilylation.[64a] Cyclooctene also improved the dehydrocoupling of $PhMeSiH_2$ to oligomers with Cp_2TiPh_2.[26] After 24 h at 110 °C and with a silane/cyclooctene mole ratio of 3/1, 80% conversion of the monosilane to trisilane (88%) and disilane (7%) was achieved.

There are no published studies of the electronic effect of *p*-substituted aryl substituents in $ArMeSiH_2$ that parallel those described for $ArSiH_3$.[22,29] However, in unpublished work, we examined the initial rate of condensation of $ArMeSiH_2$ ($Ar = p\text{-}XC_6H_4$, $X = NMe_2$, OMe, CF_3, F, and Me) with $Cp_2ZrCl_2/2^nBuLi$.[101] For reaction times under 7 h, the rate of condensation followed the order: $NMe_2 < OMe < CF_3 \sim F < Me < H$. However, this is somewhat deceptive as in the case of $(p\text{-}F_3CC_6H_4)MeSiH_2$ and $(p\text{-}FC_6H_4)MeSiH_2$, solutions decolorized within 1–4 h of reaction and no further oligomerization was observed. This is in contrast to the results observed for the primary silanes where both $(p\text{-}F_3CC_6H_4)SiH_3$ and $(p\text{-}FC_6H_4)SiH_3$ were successfully converted to polysilanes and, indeed, produced higher M_w values than the parent $PhSiH_3$.[22] Therefore, electron-donating substituents in the secondary silanes, $ArMeSiH_2$, result in slower coupling reactions than in $PhMeSiH_2$ but electron-withdrawing substituents appear to deactivate the catalyst system (at least the one produced in $Cp_2ZrCl_2/^nBuLi$). We also observed no dehydrocoupling of $ClCH_2(Ph)SiH_2$ paralleling the results described at the end of Section IV.A[102a] and $(C_2Cl_5)_xSiH_{4-x}$ ($x = 1, 2$) also does not undergo dehydrogenative coupling.[102b]

That dehydrocoupling with metallocene catalysts exhibits some serious steric problems is indicated by the higher temperatures required for the successful coupling of secondary silanes (at least at reasonable rates). Increasing the "bulk" of the secondary silane would be expected to either shut down the dehydrocoupling reaction or to prevent formation of oligomers higher than the disilane. Replacement of the Me-substituent in $PhMeSiH_2$ with a Ph group to give Ph_2SiH_2 essentially results in the latter. Reaction of Ph_2SiH_2 at 90 °C for 72 h with $Cp_2ZrCl_2/2^nBuLi$ converted 91% of the starting monosilane to a mixture of $HPh_2SiSiPh_2$ (82%), Ph_2BuSiH, and unreacted Ph_2SiH_2 (18%).[4] Somewhat similar results were reported for the reaction of Ph_2SiH_2 with Cp_2TiPh_2 at 110 °C/24 h although in this case Ph_3SiH (3%) was also observed.[26] The addition of cyclooctene to the reaction mixture appeared to make no difference in the course of the coupling of Ph_2SiH_2 with Cp_2TiPh_2.[26] However, when Ph_2SiH_2 is heated for 1 h at 45 °C with norbornene and $Cp_2Ti(\eta^2\text{-}H\text{–}SiPh_2H)PMe_3$, a quantitative yield of the disilane was obtained.[85] The choice of olefin as hydrogen acceptor will probably depend on the silane that undergoes dehydrocoupling. When norbornene is present in the condensation of $PhMeSiH_2$ with $Cp_2TiCl_2/2^nBuLi$, 89% conversion occurs within 0.5 h (90 °C) to oligomers (Si_2 to Si_5; 88%) and hydrosilylation products (12%).[64a] The electronic effect of *p*-substituents in $(p\text{-}XC_6H_4)_2SiH_2$ has not been examined although condensation of examples where $X = p$-MeO and *p*-Cl in the presence of Cp_2TiPh_2 have been reported.[25] However, very poor coupling yields were obtained from $(p\text{-}ClC_6H_4)_2SiH_2$ consistent with the problems of halogenated organic substituents at silicon described earlier.

Although Ph_2SiH_2 (or Ar_2SiH_2) does not couple past the disilane stage (or only a few % of the trisilane is observed under forcing conditions) this is not the case if the two phenyl groups are tied together to form heterocycles such as silafluorene and 9,10-dihydro-9-silaanthracene.[64a] Silafluorene reacts with quantitative conversion after 2 h at r.t. with $Cp_2ZrCl_2/2^nBuLi$ in toluene to give disilane as the major product with some trisilane ($Si_2/Si_3 \sim 6.5/1$). A ratio of $Si_3/Si_2 = 0.45$ was obtained from silaanthracene after 2 days at 90 °C in the presence of $Cp_2ZrCl_2/2^nBuLi$ but that ratio is > 7 (99% conversion) after 10 h with Cp_2ZrMe_2 at 90 °C.

Therefore, reduction of steric hindrance allows the formation of oligomers higher than the disilane.

Just as primary alkylsilanes couple more slowly and give considerably shorter chains than observed in the condensation of $PhSiH_3$, dialkylsilanes couple with difficulty. Only traces of oligomers were obtained from reaction of dialkylsilanes in the presence of $Cp_2MCl_2/^n2BuLi$.[48] However, when a mixture of norbornene and Pr_2SiH_2 were reacted with $Cp_2TiCl_2/2^nBuLi$ in toluene at 90 °C rapid reaction took place to give $H(Pr_2Si)_xH$ ($x = 2$, 3) and hydrosilylation products in a 3:1 ratio. After 4 days the ratio of oligomers to hydrosilylation products remained the same but the ratio of Si_2/Si_3 changed from 5.0 to 2.2. One of the few other studies involving a dialkylsilane was the reaction of Bu_2SiH_2 in the presence of $Cp_2Ti(OPh)_2$.[47] When catalytic amounts of $Cp_2Ti(OPh)_2$ were heated with neat Bu_2SiH_2 at 110 °C for 30 min. the products $Bu_2Si(H)(OPh)$, $Bu_2Si(OPh)_2$ (total of 5%), and $H(Bu_2Si)_2H$ (4.4%) were observed in addition to unreacted monosilane. It is possible that longer reaction times could produce further conversion of the monosilane to oligomers since the phenoxide ligands from the catalyst precursor would have been consumed. Harrod and co-workers examined the reaction of excess $BuMeSiH_2$ with Cp_2TiMe_2 and observed only the complex $[Cp_2Ti(\mu\text{-}SiBuMeH)(\mu\text{-}H)TiCp_2]$ with no further transformation to other Ti(III) containing species as was observed in the reaction of Ph_2SiH_2 and $PhMeSiH_2$.[12] The stability of the adduct obtained from dialkylsilanes may contribute to the lack of dehydrocoupling in this instance. With either Cp_2TiMe_2 or Cp_2ZrMe_2, no coupling of $BuMeSiH_2$ was observed under all conditions of concentration or temperature that were attempted.[19] The reaction of $BuMeSiH_2$ with Cp_2ZrMe_2 produced only a symmetrical dimer with the presumed structure $[Cp_2Zr(SiBuMeH)]_2$ in contrast to the unsymmetrical dimers formed from either Ph_2SiH_2 or $PhMeSiH_2$.[19] Tilley and co-workers have also demonstrated the stoichiometric replacement of a $Si(SiMe_3)_3$ ligand in $CpCp^*Hf[Si(SiMe_3)_3]Cl$ in reaction with the secondary silanes, Ph_2SiH_2 and $PhMeSiH_2$, similar to those that they reported with primary silanes.[41,42] Presumably this would be the first stage in a cycle leading to dehydrocoupling of secondary silanes although this has not been reported by the Tilley group.

As a last comment, an attempt to dehydrocouple the labeled secondary silane, $PhMeSiD_2$, to give $D(PhSiMe)_xD$, with $Cp_2ZrCl_2/2^nBuLi$ demonstrated another process that was promoted by this catalyst system.[50] Analysis of the oligomer mixture produced revealed that although each oligomer had approximately two deuterium atoms (determined by mass spectroscopy), the label had scrambled between the SiH and CH (methyl group) positions as determined by ^1H and ^2H NMR spectroscopy.

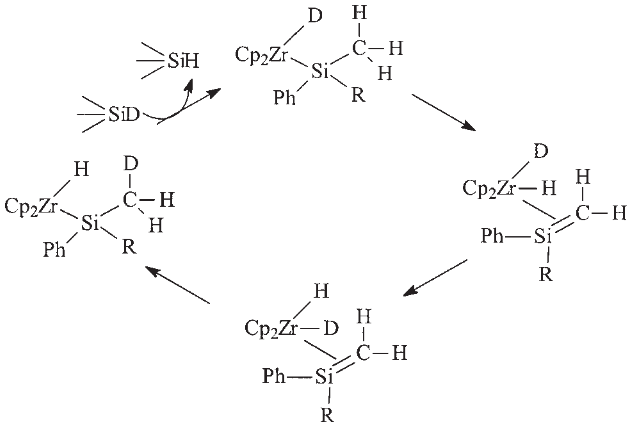

FIG. 7. Mechanism for deuterium scrambling in reaction of $PhMeSiD_2$ with $Cp_2ZrCl_2/2^nBuLi$.[50]

The deuterium scrambling is slower than silicon–silicon bond formation. The scrambling of the deuterium label was not present in the products produced with the Ti and Hf catalyst systems although loss of a portion of deuterium label from the terminal SiD(H) positions did occur. Only a minimum scrambling of the deuterium label was observed in the condensation of $PhEtSiD_2$ (all 3 metals in Cp_2MCl_2) and of $PhCH_2(Me)SiD_2$ (Cp_2ZrCl_2). The results can be interpreted in terms of a β-hydride elimination as shown in Fig. 7.

D. *Tertiary Silanes*

There are no conditions yet reported for the coupling of tertiary silanes with organic substituents. The attempted condensation of $PhMe_2SiH$ with $Cp_2TiCl_2/2^nBuLi$/norbornene for 45 h at 90 °C resulted in consumption of 25% of the starting material but only the formation of hydrosilylation product.[64a] Although Ph_2MeSiH and Cp_2MX_2 (M = Ti, Zr, Hf; X = F, OPh, NMe_2) appear to transfer hydride to the metal center, no silicon–silicon coupling products were observed.[45] Neither Me_3SiH nor Et_3SiH react with $CpCp^*Hf[Si(SiMe_3)_3]Cl$, thus no dehydrocoupling would be observed.[41,42]

The disilane, $Me_3SiSiMe_2H$ reacts in the presence of Cp_2MMe_2 (M = Ti, Zr) to give the oligomeric product $Me_3Si(SiMe_2)_nSiMe_2H$ and the monomer, Me_3SiH[10,18] although this is probably not a dehydrocoupling reaction. After 20 h at 130 °C (M = Ti) the oligomer mixture with $n = 1$ to 7 were identified by GCMS. In a related reaction with Cp_2ZrMe_2 at r.t., a white solid identified as $Cp_2Zr[SiMe_2SiMe_3]Me$ formed. Reaction of

$(Me_{11}Si_6)Me_2SiH$ with Cp_2MMe_2 (M = Ti, Zr) at 80 °C for 2 days produced 5% of disilane $[(Me_{11}Si_6)Me_2Si]_2$ and 2–3% $Si_6Me_{11}H$ (and unreacted starting material).[14] Cyclohexasilanes with hydrogen bonded to one or two ring atoms ($Si_6Me_{11}H$ and 1,4-$Si_6Me_{10}H_2$) did not react with Cp_2MMe_2.[14] Thus, $(Me_{11}Si_6)Me_2SiH$ may be the only tertiary silane where coupling, albeit in small yields, has been successfully accomplished with a metallocene catalyst.

E. *Hydride Terminated Disilanes and Oligomers*

One of the unique features of metallocene promoted dehydrocoupling is the faster reaction of 1,2-disubstituted disilanes than that of the analogous monosilane.[3*l*,19] The faster reaction, in the case of $H(PhSiH)_2H$, was attributed originally to a dihydrocoupling of the disilane to give even numbered oligomers, since odd numbered oligomers were not observed in the reaction mixtures (Cp_2MMe_2 promoted reactions). The $Cp_2^*HfH_2$ catalyzed reaction of $H_2PhSiSiPhH_2$ occurs faster than that of $PhSiH_3$ and in this case, odd numbered oligomers were observed.[30] In a later report, Harrod again utilized $H(PhSiH)_2H$ with Cp_2MMe_2 (M = Ti, Zr; 20 °C) and using GP chromatograms demonstrated the presence of both even- and odd-numbered chains in the product mixtures.[79] The presence of odd-numbered chains from a disilane suggests that another process competes with the direct dehydrocoupling of two disilanes. This additional process was eventually assigned to reaction of the metal catalyst with the Si–Si bond providing monosilane that could then react with the disilane as will be described in the following paragraphs.

There are two general types of hydride-terminated disilanes that have been studied: those in which the substituents at each silicon are the same (symmetrical), and those where the two silicon centers are different (unsymmetrical). The symmetrical disilanes that have been studied include $H(RSiH)_2H$ (R = Me;[9,18,24,46,86,70,84] Ph[11,19,27,30,79,84]) and $H(RSiMe)_2H$ (R = Me,[10,18,24] Bu,[53] Ph[53]). The unsymmetrical disilanes include $H_2PhSiSiMeH_2$,[84] $HPh_2SiSiPhH_2$,[53] $HPh_2SiSiPhMeH$,[53] $HPhMeSiSiPrMeH$,[53] $HPhMeSiSiMe_2H$,[53] and $HMe_2SiSiMeH_2$.[24,70]

The reactions of Cp_2MMe_2 and Cp_2MBu_2 with $H(Me_2Si)_2H$, $H(MeSiH)_2H$ and the previously described $Me_3SiSiMe_2H$ (Section IV.D) as well as the co-polymerization of $PhSiH_3$ with $H(MeSiH)_2H$ have been studied by Hengge and co-workers.[9,10,18] The products were identified primarily by GCMS but in some cases by ^{29}Si NMR spectra of reaction mixtures. A unique feature of the reaction of $H(MeSiH)_2H$ was the formation of branched as well as linear oligomers (from Si_3 to Si_7) determined in the early stages of the condensation (2 h at r.t.). The presence of $[Si(Si_3)]$ units in the products was verified by ^{29}Si NMR data. The polymerization of $H(MeSiH)_2H$ is slow with Cp_2TiMe_2 (several weeks to form a solid polymer) but rapid with Cp_2ZrMe_2 when a solid polymer formed in less than an hour. The polymer is pyrophoric in air and has the approximate composition, $(MeSiH_{0.58})$, indicating that cross-linking has occurred.[10,18] If the initial reaction involves, at least in part, reaction of the catalyst with the Si–Si bond of the disilane, $MeSiH_3$ would be generated. Subsequent reactions then would lead to $H(MeSiH)_xH$ and the formation of cross-linked polymer would parallel the results observed by Harrod for the condensation of $MeSiH_3$ described in Section IV.B.[8] The reaction of $H(Me_2Si)_2H$ with the same catalysts gave $HMe_2Si(SiMe_2)_{n-1}SiMe_2H$ and $(n-1)Me_2SiH_2$. Again, this suggests reaction of the catalyst with the Si–Si bond of the disilane to give Me_2SiH_2, and condensation to linear oligomers. At 130 °C for 2 days, $H(Me_2Si)_2H$ and Cp_2TiMe_2 gave oligomers with up to 10 silicon centers.[18] Since the product oligomers were determined by GC and GC-MS, this actually represents the limit of the measurement and not necessarily the limit of the chain length. The reaction of $H(MeSiH)_2H$ with Cp_2TiF_2 gave an insoluble solid after 3 days at r.t.[46] The condensation of $H(MeSiH)_2H$ and the unsymmetrical disilane, $H_2PhSiSiMeH_2$ with $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$, $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (L = THF, py), and *rac*-(EBTHI)M(η^2-$Me_3SiC{\equiv}CSiMe_3$) (M = Ti, Zr) produced similar results. The reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ with $H(MeSiH)_2H$ produced oligomers with even and odd numbers of Si atoms in approximately the same amounts suggesting that the disilane is cleaved. After about 2 days at r.t., an insoluble cross-linked polymer was produced. With the Zr analogs, more branched oligomers are observed initially and insoluble polymer was produced. The M_w values of the polymer produced (after 7 days at 40 °C) from $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ was 16,000 with an $M_n = 2900$ ($P_D = 5.5$) that is probably cross-linked through the MeSiH units. The EBTHI complexes seem to effect Si–H activation preferentially whereas the Cp_2M based complexes preferentially activate the Si–Si bonds. With the unsymmetrical disilane, $H_2MeSiSiPhH_2$, Si–Si cleavage dominates and new silyl groups are added preferentially to the phenyl-substituted end of the disilane. The EBTHI complexes react similarly but also give significant amounts of the disproportionation products, Ph_2SiH_2 and Ph_3SiH.[46] These disproportionation products are also obtained in the condensation of $H(PhSiH)_2H$ and in this case the highest M_w polysilane was also obtained from $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ but was only 1800 ($M_n = 1400$).[84]

The co-condensation of $H(MeSiH)_2H$ and $HMe_2SiSiMeH_2$ with $Cp_2ZrCl_2/LiAlH_4$[70] and with $Cp_2Zr(CH_2SiMe_3)_2$[24] have also been reported in patents. In the case of the former catalyst the polymer produced had a $M_w = 9760$ and $M_n = 2810$. The polydispersity (3.5) again suggests that cross-linking may have occurred. The polymers were used to generate SiC.

In the studies performed by Hengge and co-workers, the monosilanes that could form from Si–Si cleavage of the starting disilane would not be observed in the GC traces. If Si–Si bond cleavage occurs, then using unsymmetrical disilanes should give two different monosilanes and if the monosilanes are sufficiently non-volatile, could be detected in GC traces. Coupling of the monosilanes with the original disilane should give two different sets of two trisilanes. The presence of two monosilanes and four trisilanes would provide more definitive support for the cleavage of the disilane. The reaction of $HPh_2SiSiPhMeH$ with $Cp_2MCl_2/2^nBuLi/$*cis*-cyclooctene provided both Ph_2SiH_2 and $PhMeSiH_2$ as well as two sets of the trisilanes $Ph_4Me_2Si_3H_2$ and $Ph_5MeSi_3H_2$. The trisilanes were isolated by distillation and characterized by ^1H NMR spectroscopy.[53] The rate of reaction with the titanium catalyst system (80 °C) as indicated by the consumption of the phenyl-substituted disilanes after 1 h was similar for the three cases, $HPhMeSiSiMe_2H$, $H(PhSiMe)_2H$, and $HPh_2SiSiPhMeH$ (~75%). The product distribution showed initial formation of monosilanes and trisilanes followed by the slow formation of higher oligomers. The SiH coupling of the disilane to give tetrasilane was also observed to take place simultaneously in some cases. The oligomer series, $H(PhSiMe)_xH$ ($x = 2, 3, 4$) was examined and only the disilane reacted rapidly at the Si–Si bond. Only a minor cleavage reaction was observed with the trisilane and cleavage was absent in the tetrasilane.[53] However, this was not the case for $H(MeSiH)_xH$ ($x = 3, 4$) in the presence of Cp_2ZrMe_2, the results of which contributed to Hengge's β-bond elimination proposal[20] nor for the reaction of $H(PhSiH)_3H$ with $Cp^*_2HfH_2$ at 80 °C where after 2 h the product distribution was $PhSiH_3$ (20%) and $H(PhSiH)_xH$ ($x = 2$ (22%), 3 (46%), 4 (12%)) as determined by ^1H NMR spectroscopy.[30]

F. *Bis-silanes*

There are several reports of the condensation of bis-silanes of the type $H_3Si–X–SiH_3$ (primary silanes) and $H_2RSi–X–SiR'H_2$ (secondary silanes) principally with the aim of producing polymers that would be precursors to silicon carbide ceramic material. The polymers would, in principle, have repeating units of the type $[H_2SiSiH_2–X]_n$ or $[HRSiSiR'H–X–]_n$. The linking units (X) tend to be aromatic or alkyl groups.

Tilley and co-workers studied the condensation of p-$(H_3Si)_2C_6H_4$, m-$(H_3Si)_2C_6H_4$, 1,3,5-$(H_3Si)_3C_6H_3$, 4,4′-$(H_3Si)_2C_6H_4C_6H_4$, and 2,5-$(H_3Si)_2C_4H_2S$ in the presence of $[CpCp^*ZrH_2]_2$ in C_6H_6.[31,32] The products were insoluble in organic solvents and did not melt or decompose when heated to 300 °C. From combustion analyses and integration of CRAMPS solid state ^1H NMR spectra, considerable cross-linking was determined. Since dehydrocoupling would give $–SiH_2–SiH_2–$ linked by organic groups, cross-linking of such "secondary silane" units would not be surprising. The stoichiometric reactions of 1,4-$(H_3Si)_2C_6H_4$ and 2,5-$(H_3Si)_2C_4H_2S$ with $CpCp^*Hf[Si(SiMe_3)_3]Cl$ afforded bimetallic complexes $CpCp^*Hf(Cl)(SiH_2XSiH_2(Cl)HfCp^*Cp$.[41] Condensation of $H_3SiCH_2CH_2SiH_3$ with $Cp_2ZrCl_2/2^nBuLi$ also gave insoluble polymer in short time periods.[61] Occasionally, samples of the polymer produced were pyrophoric. Addition of solvent and the use of the catalyst system known to promote dehydrocoupling more slowly $[(C_5H_4SiMe_3)_2HfCl_2/2^nBuLi]$ produced insoluble material as did other primary silane precursors such as $(H_3SiCH_2CH_2)SiR_2$ (R = Me, Ph) and $(H_3SiCH_2CH_2CH_2)_2SiMe_2$.[61] Including a longer linker as in bis(1-sila-3-butyl)benzene produced an insoluble polymer (Cp_2TiCl_2/Red-Al) along with a soluble portion that had an approximate DP of 11.[67] Condensation of $C_6H_5CH(SiHe_3)_2$ with Cp_2MCl_2/Red-Al (M = Ti, Hf) gave both redistribution and dehydrocoupling products but the polymer was primarily an insoluble material with mp > 300 °C. Redistribution was not observed when $Cp_2MCl_2/2^nBuLi$ was employed as the catalyst.[51] High yields of polymer were produced from 1,4-$(H_3Si)_2Si_6Me_{10}$ with Cp_2MMe_2.[14] The polymers had M_w values of 4200 (M = Ti) and 10,500 (M = Zr) and had melting points ≥ 360 °C. It is probable that condensation of the primary bis-silanes will be accompanied by some redistribution (possibly generating SiH_4) as well as further reaction of the SiH bonds in the silicon linking units in the polymer.

The use of secondary carbosilanes, $H_2PhSi(CH_2)_xSiPhH_2$ ($x = 1, 2, 3$) and $(H_2PhSiCH_2CH_2)_2SiMe_2$ gave polymers ($Cp_2ZrCl_2/2.2^nBuLi$) that were soluble in common organic solvents and with M_w values up to 12,000.[61] A related study of $(H_2MeSi)_2CH_2$ with $Cp_2ZrCl_2/2^nBuLi$ and with Cp_2TiCl_2/2MeLi produced only low molecular weight polymer ($M_w = 1200$ to 1600).[59]

The carbosilane monomer, $H_2MeSiCH_2CH_2SiH_3$, contains both a secondary and a primary silicon center. After about 48 h with Cp_2TiMe_2 or $Cp_2TiCl_2/^nBuLi$ at r.t. the dehydrocoupling reaction occurred at the primary silane center to give a polysilane with a substituent at each silicon center that contained a tether to the secondary silane center. The initial polymer had a M_w of approximately 1000. After another 72 h at r.t., the secondary silane centers had begun to react and partially cross-linked soluble polymer was produced ($M_w \sim 32{,}900$ with $M_n = 3260$). Heating for a short period at 50 °C produced highly cross-linked, insoluble polymer.[13] The complex $Cp_2Ti(OPh)_2$ was also found to be active for the condensation and cross-linking of this monomer.[47] In a related study, a series of carbosilanes were produced by hydrosilylation of $VinSiCl_3$ with $PhMeSiH_2$ and Ph_2SiH_2 followed by reduction to give a mixture of $HRR'SiCH_2CH_2SiH_3$ and $HRR'SiCH(CH_3)SiH_3$. The condensation of the mixture in the presence of $Cp_2TiCl_2/^{n}BuLi$ at 70 °C gave the oligomers $H[HRR'Si–X–SiH]_nH$ ($n = 12–15$) with no evidence of cross-linking.[56] In this case, the tether contained a tertiary silane center which was unlikely to couple to generate a cross-linked polymer.

V

CHARACTERIZATION OF POLYSILANES PRODUCED FROM DEHYDROCOUPLING

One of the most important properties is the M_w and/or M_n values and these have been included in Table III and selected examples are also cited in the discussion presented in Sections IV.A and IV.B. The range for M_w values is from about 1000 to 20,000 and M_n values up to about 10,000 have generally been determined by GPC relative to polystyrene standards. Harrod has proposed a relationship between the molecular weight measured by GPC against polystyrene standards and the chain length.[95] If this equation is a reasonable estimate, then the highest chain lengths reported from dehydrocoupling contain about 125 silicon atoms. In some cases the ratio between polymer and oligomers (mainly cyclic material) has been determined by GPC as well. The signals for SiH resonances in the ^1H NMR spectrum of the oligomers and polymers derived from $PhSiH_3$ tend to be found between 4 and 5 ppm and it is customary to obtain the ratio between linear and cyclic material from integration of the signals below 4.8 ppm in the ^1H NMR spectrum relative to resonances above this value.[17,30]

A reasonable expectation for a transition metal catalyzed process would be the ability to control the microstructure of the product and in this case the polysilane, $H(RSiH)_xH$, that is produced. An unusual selectivity seemed to be apparent in the condensation of $PhSiH_3$ by bis(indenyl)- and bis(tetrahydroindenyl)zirconium dimethyl catalysts and was originally attributed to stereoregulation in the polymerization but was later proposed to be due to an unusual selectivity in the production of cyclics.[36,79] In an earlier report[17] of the condensation of $PhSiH_3$ with *rac*-(EBI)$ZrCl_2/2^{n}BuLi$

(Class 4, Table I), as well as $Cp_2Zr(H)Cl$ (Class 2, Table I), a stereoregular polymer was assigned to the $H(PhSiH)_xH$ product based on ^{29}Si NMR data that exhibited a resemblance to the known *all trans*-$(PhSiH)_6$ which would be a model for a syndiotactic sequence of adjacent silicon centers. However, both Harrod[79] and Corey[71] demonstrated that the $H(PhSiH)_xH$ polymer was actually atactic. Harrod and co-workers studied the condensation of $PhSiH_3$ with (*S*,*S*)-[1,2-bi(η^5-tetrahydroindenyl)ethane]titanium binaphtholate/2^{n}BuLi (Class 5, Table I) and the cation-like systems, Cp_2HfCl_2/2^{n}BuLi/$B(C_6F_5)_3$ and $CpCp^*ZrCl_2$/2^{n}BuLi/$B(C_6F_5)_3$ (both in Class 8, Table I) and Grimmond and Corey examined $(Cp^R)_2MCl_2$ and $CpCp^RMCl_2$ ($M = Ti$, Zr; $Cp^R = C_5H_4C(Me)_2CH(Me)_2$) in combination with ^{n}BuLi (Class 4, Table I). Both groups utilized ^{29}Si NMR spectroscopy in the analysis of the structure of the polymer. In the Harrod study the stepwise oligomerization of $PhSiH_3$ to Si_2 through Si_5 was observed and assignment of the peaks to the stereoisomers of Si_4 and Si_5 oligomers was possible. For the longer oligomers/polymers the ^{29}Si resonances fell into three relatively distinct regions at δ (ppm) 58–59 (terminal SiH_2Ph groups), 59–63 (internal SiHPh), and 64–65 (penultimate SiHPh groups).[79] In the Grimmond/Corey analysis by ^1H and $^{29}Si\{^1H\}$ DEPT 135 ° NMR spectroscopy, the main resonances at δ −59 to −63 ppm could be simulated with 20 separate peaks and the rr, mm and mr triad regions were assigned. A Bernoullian statistical analysis indicated a syndioselective probability (1-Pm) of 0.55 during the propagation of the pseudochiral chain.[71] Even the use of the chiral enantiopure Group 4 metallocene dichlorides, $Cp(Cp^{Si*})ZrCl_2$, $(Cp^{Si*})_2ZrCl_2$ ($Cp^{Si*} = C_5H_4Si(CH_3)_2$-(1*R*)-*endo*-(+)-$OC_{10}H_{17}$), as catalyst precursors (with ^{n}BuLi) provided only polymer with an atactic microstructure[55] as was also observed when $(Cp^N)_2ZrCl_2$/2^{n}BuLi was employed as the catalyst system.[73] The condensation of (p-$H_3CC_6H_4$)SiH_3 with both chiral and achiral zirconocenes, Cp_2ZrCl_2, $Cp(Cp^{Si*})ZrCl_2$, $(Cp^{Si*})_2ZrCl_2$ (in combination with ^{n}BuLi) provided $H[(p\text{-}H_3CC_6H_4)SiH]_xH$ (M_n values ranging from 1600 to 2000) and analysis of $^{29}Si\{^1H\}$ DEPT, ^1H and $^{13}C\{^1H\}$ NMR spectra indicated that products had a predominantly atactic microstructure. Thus, the chiral substitution of the zirconocene rings had no effect on the stereogrowth of the polysilane.[54] Reliable integration of the $^{13}C\{^1H\}$ NMR data for the *p*-Me group could not be obtained because the signals were nearly coincident. However, at 346 K the Me groups were sufficiently resolved to replicate the peaks by deconvolution techniques. The meso and racemic stereoreplication probabilities were equivalent indicating an atactic polymer as was concluded from the ^{29}Si NMR data. Thus, to quote Harrod: “There is no evidence to support the involvement of the metal center in determining the stereochemistry at silicon during the group 4 metallocene catalyzed dehydrocoupling of phenylsilane''.[79]

Although NMR spectroscopy is the tool of preference in the characterization of the polysilanes produced from dehydrocoupling, there are also characteristic $\nu_{(SiH)}$ bands in the infrared spectrum. A strong band about 2100 cm^{-1} is found for the tertiary SiH centers and is somewhat lower in frequency than the primary silane monomers. A second band at 910 cm^{-1} has been assigned to the bending mode of a SiH_2 group. Such a band is absent in tertiary silanes. The band near 910 cm^{-1} is indicative of the terminal SiH_2R group in the polysilane. The relative intensities of the 2100 and 910 cm^{-1} bands change with molecular weight.[6a] Although Harrod and co-workers have used mass spectroscopy to characterize polysilylenes with up to 10 silicon centers this method does not appear to be practical (as yet) for polysilanes with longer chains.[6a]

The condensation of secondary silanes that have two different groups produced oligomers where the silicon centers are chirotopic. As the chain lengthens the number of diastereomers increases with 2 stereoisomers for the disilane (one meso and one *d,l* pair), 3 for the trisilane (2 meso and one *d,l* pair) and 6 for the tetrasilane (two meso forms and four *d,l* pairs). The ^1H NMR spectrum for the methyl region of $H(PhSiMe)_2H$ showed two doublets of equal intensity corresponding to the disilane. The trisilane, $H(PhSiMe)_3H$ exhibited 4 doublets (terminal SiMe) of equal intensity and 3 singlets in a 1:2:1 ratio (internal SiMe) that correspond to a statistical distribution of diastereomers. The SiMe signals of $H(PhSiMe)_4H$ overlap to such an extent that it was not possible to determine whether a statistical mixture of diastereomers were present.[48] Thus, it is not clear whether diastereomeric induction occurs in the growth of the oligomers produced from secondary silanes (at least those from $PhMeSiH_2$) or if the mixture is ''atactic'' by analogy to the polysilanes produced from $PhSiH_3$. It has been possible to analyze the $^{19}F\{^1H\}$ spectrum of $F(PhSiMe)_4F$ (produced from mixture of $H(PhSiMe)_4H$ isomers and $CuCl_2/CuI/KF$) in terms of the presence of 6 diastereomers and 6 diastereomers were observed in the HPLC trace of the fluorine terminated tetrasilane but it is not yet clear whether a statistical distribution of diastereomers is present.[103]

An *ab initio* study of the geometries, polarizabilities, and rotational barriers of $H(PhSiH)_nH$ oligomers has been reported.[104] The trends in polarizabilities for isotactic and syndiotactic oligomers with $n = 4$–8 were extrapolated to the infinite polymer limit.

The reaction chemistry of the polysilanes (particularly those formed from $PhSiH_3$) have been studied to a limited extent and will only be mentioned briefly here. The polysilanes, $H(RSiH)_nH$, obtained from dehydrocoupling are air-sensitive producing a siloxane-type structure for the polymer backbone.[105] A free radical mechanism was proposed on the basis of model studies performed on $(Me_3Si)_2(Me)SiH$. An important aspect of this study was the finding that GPC data do not distinguish the polysilane and the oxidized material and thus cannot be used to evaluate the extent of oxidative degradation. Both IR and/or NMR spectroscopy could be successfully used to follow the course of the oxidation.[105] Waymouth and co-workers reported the free-radical halogenation of $H(PhSiH)_nH$ by CCl_4 or CBr_4[106] as well as the free-radical hydrosilylation of X=CHR ($X = CH_2$, O) promoted by AIBN (2,2′-azo(bisisobutyronitrile)].[107] Greater than 84% of the SiH bonds were chlorinated at r.t. after 28 h and after 5 days, 95% of the SiH bonds were converted. The hydrosilylation reaction allowed the introduction of tethers to the silicon that terminated in functional groups such as COOMe, OH, CO_2H, and NMe_2. The degree of substitution varied from 73% to 93%. The free radical reactions studied by Waymouth and co-workers did not appear to degrade the polysilane chains. Another type of substitution of the SiH units in the polysilane chain was initiated by Cp_2TiMe_2 which promotes the reaction of NH_3 and $H(PhSiH)_nH$ in toluene at 95 °C to give a new polymer of approximate composition, $–(PhSiNH_2)_x–$ with a molecular weight about 2.5 times that of the starting material.[108] Harrod has also described the reaction of a mixture of cyclohexene and $PhSiH_3$ where polymerization of the silane occurs faster than hydrosilylation (with Cp_2TiMe_2) and after the polysilane is produced, cyclohexyl groups are introduced into approximately 50% of the SiH groups.[3p] One of the more interesting applications of poly(hydrosilane)s is the stabilization of polypropylene during multiple extrusion.[105] Poly(hydrosilane)s have also been employed as radical-based reducing agents for organic halides.[109]

VI

DEHYDROCOUPLING INITIATED BY METALS OTHER THAN GROUP 4

The majority of studies that involve "intentional" dehydrocoupling reactions involve metallocenes of Group 4. However, as stated in the introduction, the first recognized example for dehydrocoupling was in 1973 utilizing Wilkinson's catalyst.[1] It is probable that there were earlier examples of silicon oligomer products in uncharacterized material when electron-rich complexes were studied as hydrosilylation catalysts. There are now reports of the use of a range of metals (other than Group 4) that promote dehydrocoupling of hydrosilanes and these cases are summarized in Table V. Many of the papers cited in Table V are preliminary

TABLE V

DEHYDROCOUPLING OF HYDROSILANES BY METALS OTHER THAN GROUP 4

Group	Complex	Silane	Ref.
5	Cp_2V, Cp_2VMe_2	$PhSiH_3$: di- and trisilanes	6b
	Cp_2NbH_3, Cp_2TaH_3	$PhSiH_3$[a]	6b
6	Cp_2Cr	$PhSiH_3$	6b
	Cp_2MH_2 (M = Mo, W)	$PhSiH_3$[a,b]	6b
7	$Ph_3SiMn(CO)_5$	HD_4: disilane	109
8	$Fe(CO)_5/\Delta$	$(Me_3Si)_3SiH$: disilane	110a
	$Fe(CO)_2[P(OPh)_3]_2H(SiMe_2Ph)$	$PhMe_2SiH$: disilane	110b
	$Fe(dppe)_2(CH_2{=}CH_2)$	$(EtO)_3SiH$: disilane	111
	$FeCl_3$/Li/THF or DME/Δ	$MePhSiH_2$: dimer through tetramer	90
		^{n}OctylSiH_3: $(^n\text{Octyl})_2SiH_2$	90
	$FeCl_3/WCl_6$/Li/THF or DME/Δ	$MePhSiH_2$: dimer through tetramer	90
		$PhCH_2SiH_3$: $(PhCH_2)_xSiH_{4-x}$ ($x = 2, 3$)	90
	$[\{(p\text{-tolyl})_3P\}_3RuCl_2]$	$PhSiH_3$: $SiH_4 + Ph_2SiH_2$	112[c]
9	$ClRh(PPh)_3$	$PhMeSiH_2$, Ph_2SiH_2, $PhSiH_3$, Et_2SiH_2: dimers, oligomers, and disproportionation	1
		Et_2SiH_2, $PhMeSiH_2$: disilanes	113
		Silaanthracene, Ph_2SiH_2: di- and trisilanes	114
		Ph_2SiH_2, $MePhSiH_2$, Et_2SiH_2, $(n\text{-Hex})_2SiH_2$: di- and trisilanes	115
		1,2-disubstituted disilanes: polymers	116
	fac-$(Me_3P)_3Rh\{Si(OMe)_3\}_2H$	$(MeO)_3SiH$: dimer	117
	$\{[(C_6H_{11})_3P]_2RhCl\}_2$	$HexSiH_3$: MW, 1380	118
	$[\{Pr^i_2PCH_2CH_2PPr^i_2\}Rh]_2(\mu\text{-}H)$	Ph_2SiH_2: dimer	119
		p-$TolSiH_3$: dimer + redistribution	120
		n-$BuSiH_3$: di- through pentasilane	120
	$[PPh_2CH_2CH_2SiMe_2]Rh(PMe_3)_2$	$PhMe_2SiH$: dimer	121
	$[IrMe_2Cp^*PMe_3]/2[Cp_2Fe]PF_6$	$PhMe_2SiH$: disilanes[d]	122
10	Ni^*/PPh_3[e]	Ph_2SiH_2, $PhMeSiH_2$: di- to tetrasilane	123
	$[\eta^3{:}\eta^1\text{-}Ind(CH_2)_2NMe_2)Ni(PPh_3)][BPh_4]$[f]	$PhSiH_3$: disilane	124
	$(1\text{-}MeInd)Ni(PPh_3)Cl + AgBF_4$, $AlCl_3$, MAO, or LAH	$PhSiH_3$:[g] MW's from 700 to 4400	125
	$(1\text{-}Me\text{-}Ind)Ni(PR_3)Me$ (R = Ph, Cy, Me)	$PhSiH_3$: MW's of linears from 370–1800	126
	$Pd(allyl)_2Cl_2$	1,2-disubstituted disilanes: polymers	116
	$Pd(dba)_2$	1,2-disubstituted disilanes: polymers	116
	$Pt(cod)_2$	Et_2SiH_2: MW from 2100–39,000	127,128
		$MeHexSiH_2$: MW from 6800–25,000	128
		$[(CH_2)_xSi]H_2$ ($x = 3,4$, multimodal; 5 oligomers)	128
		$PhMeSiH_2$[h]	128
		Silafluorene: multimodal	128

(*Continued*)

TABLE V
Continued

Group	Complex	Silane	Ref.
	$(Me_2PhP)_4Pt$	$HSiMe_2Ph$: dimer	129
	$(Ph_3P)_2Pt(H_2C{=}CH_2)$	$PhMeSiH_2$, Et_2SiH_2: dimers	113
	$(Ph_3P)_2PtCl_2$	Et_2SiH_2/hexane: dimer[i]	113
	$(Me_3P)_2PtCl_2$	$PhMe_2SiH$: dimer	129
	$(Ph_3P)_2PtI_2$	Et_3SiH: dimer	130
	$H_2PtCl_6 \cdot 6H_2O$	$C_6H_{13}SiH_3$: dimer through pentamer[j]	131
Ln	$Cp^*_2NdCH(SiMe_3)_2$	$PhSiH_3$: MW's from 520 to 4800	132
		$HexSiH_3$: MW's from 500 to 900	132
		$MeSiH_3$: MW's from 500 to 7300	133
	$Cp^*_2LaCH(SiMe_3)_2$ [k]	$PhSiH_3$: DP, 4–9	134
Ac	$Cp^*_2UMe_2$	$PhSiH_3$: oligomer	6b
	$Cp^*_2ThMe_2$	$PhSiH_3$: dimer	6b
Al	Red-Al	$[C_4Ph_4Si]H_2$: MW 4100–4600	135
	Super-Hydride	MW 5800	135

[a] No dehydrocoupling observed.

[b] Reaction with hydrosilanes forms isolable complexes of $Cp_2Mo(H)(SiR_3)$ but not the W-analog; also complexes made from $H_2SiMePh$, H_2SiPh_2, $HSiPh_3$.

[c] Early patents claimed $H(PhSiH)_xH$ as the product.[112b,]

[d] No coupling observed with Ph_2MeSiH, Ph_3SiH.

[e] Activated Ni prepared from NiI_2/Li/))))).

[f] No coupling observed with $[(\eta^3{:}\eta^0\text{-Ind}(CH_2)_2NMe_2)Ni(PPh_3)Cl]/AgBF_4$.

[g] Reactions run in toluene or methylene chloride.

[h] Redistribution.

[i] Rates of dehydrocoupling to the dimer and hydrosilylation of the olefin are about equal.

[j] Since the reaction was run in the presence of O_2, the products are probably siloxanes (see text).

[k] Other complexes utilized were Cp^*_2LnR (Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$ and $[Me_2Si(C_5Me_4)_2]NdCH(SiMe_3)_2$), Cp^*_2Sm, and $Cp^*_2Sm(THF)_2$.[134]

communications with little follow through in terms of full papers, thus information is sparse. The majority of the successful dehydrocoupling examples come from Rh, Ir, and Pt complexes and these metals will be covered separately.

A. *Results from Rh, Ir, Pd, and Pt Complexes*

The first publication devoted to dehydrocoupling was published in 1973 and involved the use of $(Ph_3P)_3RhCl$ (Wilkinson's catalyst) and the generation of oligomers from $PhMeSiH_2$, Ph_2SiH_2, and Et_2SiH_2.[1] However, disproportionation products produced from the phenyl-substituted monosilanes were also present and indicated one of the competitive reactions that occur with the use of Pt group metals.

One major use of electron-rich metal complexes has been as pre-catalysts to promote hydrosilylation reactions.[136] Brown-Wensley has studied the competition of dehydrocoupling and hydrosilylation reactions in equimolar mixtures of Et_2SiH_2 and 1-hexene as promoted by selected electron-rich catalysts: $(Ph_3P)_2Pt(C_2H_4)$, H_2PtCl_6, $(Ph_3P)_2PtCl_2$, $Pt(COD)Cl_2$, $(Ph_3P)_3RhCl$, $[Rh(CO)_2Cl]_2$, $CpRh(C_2H_4)_2$, $RhCl_3$, $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$, and $[Pd(allyl)Cl]_2$.[113] In all of these cases, both Si–Si bond formation and hydrosilylation occurred although hydrosilylation dominated in all cases except for $(Ph_3P)_2Pt(C_2H_4)$ and $(Ph_3P)_2PtCl_2$ where the rates of the two processes were very similar. It is interesting to note that even with H_2PtCl_6, a traditional hydrosilylation catalyst, Si–Si bond formation still occurs even in the presence of an olefin. The reaction of $PhMeSiH_2$ and $(EtO)_3SiH$ produced predominantly disproportionation products (Ph_2MeSiH and $(EtO)_4Si$, respectively) with $(Ph_3P)_2Pt(C_2H_4)$. Tertiary silanes did not dehydrocouple as was the case observed for the metallocene complexes of Group 4. The rhodium catalyst, $(Ph_3P)_3RhCl$, was found to be the most effective catalyst for dehydrocoupling. Another important observation reported by Brown-Wensley was that either O_2 or H_2O could cause the formation of siloxanes. For instance, when $(Ph_3P)_3RhCl$ or $(Ph_3P)_2Pt(C_2H_4)$ were added to a mixture of 1 mmol each of Et_3SiH, 1-hexene and ROH ($R = Et$ or H) the rate of formation of Si–O bonds was 10 to 100 times faster than hydrosilylation.[113] Thus, a second "competitive" problem in using Pt group metals as catalysts for dehydrocoupling is the facile oxygenation of Si–Si bonds by $(Ph_3P)_3RhCl$ and $(Ph_3P)_2Pt(CH_2{=}CH_2)$. A workup procedure that precludes oxygen and water will be necessary for the successful isolation of the silicon oligomer or polymer.

No oligomers higher than a disilane were reported in the Brown-Wensley study although disilanes and trisilanes were produced from both $PhMeSiH_2$ and Et_2SiH_2 (in addition to disproportionation products) in the earliest report of the use of $(Ph_3P)_3RhCl$ to promote dehydrocoupling.[1] Disproportionation products dominated with $(Ph_3P)_3RhCl$ at higher temperatures. At 80 °C in C_6H_6, after 0.5 h, 57% of $PhMeSiH_2$ was consumed and the ratio of measureable disproportionation products to disilane was ~ 7.9.[137] After 24 h the mass balance showed that a volatile disproportionation component, $MeSiH_3$, was lost from the reaction mixture. Although reaction of Ph_2SiH_2 with catalytic quantities of $(Ph_3P)_3RhCl$ provided disilane in addition to disproportionation products,[1] silaanthracene (the two phenyl groups of Ph_2SiH_2 are "tied" together in the ortho position by a CH_2 group) provided about a 1:1 mixture (by weight) of disilane and trisilane and *no* disproportionation products (83% conversion of the starting monomer).[114] Siloxane products were also observed and several conditions were attempted before the siloxane byproducts could be reduced to less than 5% of the product mixtures. All the products were isolated (radial chromatography) and characterized including the X-ray structure of the trisilane. One could conclude, at least tentatively, that the mechanistic pathway from reactants to products when $(Ph_3P)_3RhCl$ is used as a catalyst will contain at least one step that has a higher barrier as a result of steric hindrance from substituents at silicon. Similar results were discussed earlier in the reactions of silaanthracene in the presence of Cp_2MMe_2 (M = Ti, Zr).

A technique for suppressing the formation of disproportionation products was recently published by Rosenberg and co-workers.[115] If the H_2 produced in the dehydrocoupling of neat Ph_2SiH_2 was removed by a rapid stirring technique using flat-bottomed vials as reaction vessels, the redistribution reaction could be reduced to less than 10% of the product mixture. On a scale with 5 mL of Ph_2SiH_2, sparging of the silane with N_2 in the presence of 0.2 mol% $(Ph_3P)_3RhCl$ provided $HPh_2SiSiPh_2H$ in ~80% yield after approximately 2 h (toluene was added to keep the mixture mobile). Reactions of Et_2SiH_2 and $(^nHex)_2SiH_2$ were slower and produced disilane as the major product (reactions were not taken to complete consumption of the monomer) but *no* redistribution products were observed in these dialkylsilane cases. All the reactions were conducted in a drybox.

Another rhodium catalyst used for the dehydrocoupling of silanes where details of the work have been published involves the dimer, $[\{^iPr_2PCH_2CH_2P^iPr_2\}Rh]_2(\mu\text{-}H)_2$.[119,120] The reactions were conducted in a bomb open to a nitrogen manifold to allow for escape of the hydrogen produced. In this case, reaction of both a primary and a secondary silane were examined. The secondary silane, Ph_2SiH_2 in toluene was treated with the dimer (Si/Rh = 100), degassed and heated to 60 °C for 18–24 h to give 71–77% conversion to the disilane as determined by ^1H NMR spectroscopy.[119] The condensation of *p*-tolylsilane was also studied and after 2 days at r.t. (Si/Rh = 100), with the same rhodium dimer only 36% consumption of the monomer had occurred. The major product was $H[(p\text{-}Tol)SiH]_2H$ but the remainder included the disproportionation products, $(p\text{-}Tol)_xSiH_{4-x}$ ($x = 2, 3$) and $H_2(p\text{-}Tol)SiSi(p\text{-}Tol)_2H$.[120] In the condensation of $^nBuSiH_3$ which was conducted under conditions where the headspace in the reaction bomb was evacuated several times or open to a manifold to allow H_2 to escape, 63% conversion of the monomer occurred to give oligomers from Si_2 to Si_5. The two diastereomers of Si_4 were observed in a 5:1 ratio.[120] Another rhodium dimer, $\{[(C_6H_{11})_3P]_2RhCl\}_2$, has been used to form polysilane ($M_w = 1380$) from $HexSiH_3$ although in this case the details of the workup are unknown.[118]

The last examples in this section represent possibilities that might be utilized in future studies employing electron-rich metals. The complex, Rh[(κ^2*Si,P*)-$Me_2Si(CH_2)_2PPh_2](PMe_3)_2$, reacts spontaneously with a six-fold excess of $HSiMe_2Ph$ to generate $RhH(SiMe_2Ph)$[(κ^2*Si,P*)-$Me_2Si(CH_2)_2PPh_2](PMe_3)_2$. After an additional 20 h, $PhMe_2SiSiMe_2Ph$ and RhH_2[(κ^2*Si,P*)-$Me_2Si(CH_2)_2PPh_2](PMe_3)_2$ were observed in 91% yield each.[121] Coupling of $PhMe_2SiH$ with [$Cp^*IrMe_2(PMe_3)$] in combination with the one-electron oxidant, [$Cp_2Fe]PF_6$, gave a 71% yield of the disilane, $PhMe_2SiSiMe_2Ph$. The ratio of Si/Ir/Fe was 400/1/2.4, thus this represents a catalytic dehydrocoupling process. Neither Ph_2MeSiH nor Ph_3SiH, gave dehydrocoupling products with the Ir/Fe combination.[122] The iridium complex, $(Ph_3P)_2(OC)IrCl$, produced only redistribution products with $PhMeSiH_2$ (80 °C for 1 h in C_6H_6), however, the reaction of the tertiary silane, HMeBzSiOSiBzMeH ($Bz = CH_2C_6H_5$) gave both products of redistribution ($BzMeSiH_2$, $BzMe_2SiH$, Bz_2MeSiH, and Bz_2SiH_2) and minor coupling of the redistributed products ($HBzMeSiSiBzH_2$ and HBzMeSiSiBzMeH) in addition to siloxane oligomers that were not identified.[137] Another iridium complex, Ir(CN)(CO)(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) reacted with two equivalents of Et_3SiH to give almost immediately the oxidative addition product, $IrH(CN)(SiEt_3)(CO)$(dppe), which reacted further to give eventually ~95% of the Et_3Si group as $Et_3SiSiEt_3$ (reactions were performed in an NMR tube and the disilane was not isolated).[138] Minor coupling of tertiary silanes was also reported under somewhat forcing conditions with $(Me_2Ph)_4Pt$ and $(Me_3P)_2PtCl_2$.[129] Reaction of an equimolar mixture of $(Ph_3P)_2PtI_2$ and $HSiEt_3$ in toluene at 110 °C provided $(Ph_3P)_2PtHI$ (51%) and $Et_3SiSiEt_3$ (70%).[130] Collectively, these results suggest that it may be possible to design an electron-rich complex that would promote the coupling of tertiary silanes.

The reaction of primary silanes with electron-rich metal complexes appear to give low molecular weight material. Previously mentioned were the following examples: ^{n}BuSiH$_3$/[{^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$}Rh]$_2$(μ-H)$_2$[120] and ^{n}HexSiH$_3$/{[$(C_6H_{11})_3P]_2RhCl\}_2$.[118] One other example was described briefly involving the addition of $H_2PtCl_6 \cdot 6H_2O$ (as well as Wilkinson's catalyst) to ^{n}HexSiH$_3$.[131] However, since reactions were run in air, it is highly likely that the oligomer products that were described were actually siloxanes and not silicon oligomers. Since the reactions of primary silanes do not appear to provide polysilanes, are there any indications that molecular weights at least in the range of those observed for metallocenes have been achieved? A preliminary report has appeared that 1,2-disubstituted disilanes provided polymers with molecular weights up to 190,000 with the complexes $(Ph_3P)_3RhCl$, $Pd(allyl)_2Cl_2$, and $Pd(dba)_2$.[116] This would represent one of the highest molecular weights achieved by dehydrocoupling, if the claim is valid. Another study reported the use of Pt(cod)$_2$ to promote the dehydrocoupling of the secondary silanes, Et_2SiH_2 and $^nHexMeSiH_2$ in toluene at 55–80 °C over a 4-day period. During the polymerization the reaction mixture was subjected to freeze-pump thaw cycles at regular intervals in order to remove accumulated hydrogen. Polymodal mixtures were obtained with M_w values ranging from $\sim$2000 to $\sim$40,000. Silacyclopentane and silacyclohexane also gave polymodal products on heating with Pt(cod)$_2$ at 55 °C for 48 h. Reaction of $PhMeSiH_2$, however, gave extensive redistribution to Ph_3SiH, Ph_2MeSiH, $PhMe_2SiH$, and/or Me_3SiH in line with the results reported with other electron-rich complexes.[128]

As stated earlier, disilanes are sometimes reported as byproducts in hydrosilylation reactions. A number of halide complexes of Nb, Ru, Ir, Pd, and Pt were utilized in the reaction of Et_3SiH with benzylidene aniline and Et_3SiSiH_3 was observed as a byproduct in yields up to 38%.[139] However, since the aim of these studies is usually hydrosilylation, it is somewhat difficult to identify where disilanes (or other oligomers) are byproducts and the example just mentioned is unlikely to be the only one but could provide clues for complexes for future development.

The mechanism for dehydrocoupling utilizing electron-rich complexes has not yet been established. The most commonly proposed route involves oxidative addition of the hydrosilane to the metal center followed by reductive elimination of two silyl groups to form the Si–Si bond related to that proposed by Curtis and Epstein.[140]

B. *Ni Complexes*

Ni complexes are included in a separate category as they seem to demonstrate a different type of reactivity compared to the metals discussed in the previous section. The first example of a heterogeneously catalyzed dehydrogenative coupling of hydrosilanes was reported from Ni* (produced from NiI_2 and Li dispersion in THF in the presence of ultrasonic waves). In the presence of 1 mol% each of Ni* and PPh_3 in THF, $PhMeSiH_2$ gave $H(PhMeSi)_xH$ ($x = 2(20\%)$, 3(40%), 4(25%); GC yields) and the minor disproportionation product, Ph_2MeSiH ($<3\%$). The reaction was believed to occur through oxidative addition of the monosilane to nickel metal. In the absence of Ph_3P yields were lower but the role that the phosphine played was unknown.[123]

Zagarian and co-workers have examined the condensation of $PhSiH_3$ for the three closely related nickel complexes: (1-MeInd)Ni(PPh$_3$) Cl + an additive,[125] (1-MeInd)Ni(PR$_3$)Me (R = Ph, Cy, Me)[126] and

[(η^3:η^1-IndCH$_2$CH$_2$NMe$_2$)Ni(PPh$_3$)][BPh$_4$].[124] The complex, (1-MeInd)Ni (PPh$_3$)Cl, was activated by three different types of reagents. Addition of AgBF$_4$ produced H(PhSiH)$_n$H with $M_w = 2017$ and $M_n = 1469$ after 24 h. Use of methylalumoxane gave similar results. Reactions were run in CH$_2$Cl$_2$ (or toluene) in contrast to conditions normally employed for the metallocene catalysts of Group 4. In fact, reactions could be run at –40 °C, and after 1 day the M_w value was 4400 ($M_n = 2500$). Generally, molecular weights seemed to improve with longer time periods. Concentrated solutions of the silane gave intractable polymers suggesting cross-linking involving the backbone Si–H groups. Another strategy to an active catalyst involved addition of LiAlH$_4$ to (1-MeInd)Ni(PPh$_3$)Cl which probably generates a neutral Ni–H species. The M_w values after 1 day were <1000, but rose to 3600 ($M_n = 1.6$) after 7 days. A one pot synthesis of the polysilane was achieved by addition of LiAlH$_4$ (1.3 equivalents) to PhSiCl$_3$ (1 equivalent) in ether, then adding (1-MeInd)Ni(PPh$_3$)Cl. In this case, after 4 days the yield of the polymer was 80% with $M_w = 7565$ although the polydispersity was high (4.9). In this last experiment the excess LAH may have produced an anionic nickel hydride species but attempts to isolate a Ni–H species failed.[125] With the (1-MeInd)Ni(PR$_3$)Me pre-catalyst and neat PhSiH$_3$ only oligomers formed.[126] For the PMe$_3$ (R = Me) complex, reaction was rapid with nearly quantitative conversion of PhSiH$_3$ over a few hours and material that solidified in about 2–3 days. A combination of NMR and GPC techniques revealed about a 2:3 ratio of cyclic ($n = 5$–7) to linear ($n = 7$–10) components. Adding toluene and running the reaction at −35 °C provided a greater proportion of the linear component but had little effect on the chain length. Increasing the reaction temperature also resulted in longer linear chains with some increase in cyclic material. The Ni–Me catalyst precursor gave polysilanes with narrow polydispersities (~1.1 to 1.5). The stoichiometric reaction of PhSiH$_3$ with (1-MeInd)Ni(PR$_3$)Me gave CH$_4$ and no PhMeSiH$_2$ (the type of product obtained from the dimethylmetallocenes) and implies the formation of (1-MeInd)Ni(PR$_3$)SiPhH$_2$. The authors proposed that a σ-bond metathesis reaction between the starting nickel complex and PhSiH$_3$ gave rise to the nickel–silyl. The presence of 1-phenylsilyl-3-methylindene (and PMe$_3$) in the catalytic reaction mixtures suggested a reductive elimination of the (1-MeInd) and SiH$_2$Ph ligands from the metal to give a Ni(0) species. To test the notion that Ni(0) could be a catalyst for dehydrocoupling the reaction of Ni(PMe$_3$)$_4$ with excess PhSiH$_3$ was examined and although ~60% cyclic polysilane was produced, the linear portion exhibited an M_w value (after 6 days) similar to that achieved with (1-MeInd)Ni(PMe$_3$)Me.[126] In a last, but related variation, the cationic complex, [(η^3:η^1-IndCH$_2$CH$_2$NMe$_2$)Ni(PPh$_3$)][BPh$_4$], was shown to effect only the dimerization of PhSiH$_3$ (% conversion not specified). The combination of $[(\eta^3:\eta^0\text{-IndCH}_2\text{CH}_2\text{NMe}_2)\text{Ni(PPh}_3)\text{Cl}]$ and $AgBF_4$ failed to initiate the dehydrocoupling of $PhSiH_3$.[124]

C. *Electron Poor Metallocenes of Groups 5 and 6, Lanthanides and Actinides*

The Group 4 metallocenes that promote dehydrocoupling have been described earlier in Section II. Relatively soon after Harrod's first publication on the Cp_2MMe_2 ($M = Ti$, Zr) promoted dehydrocoupling, he published a survey of the reaction of $PhSiH_3$ with other metallocene type complexes from Groups 4–6 as well as a uranium and thorium analog.[6b] The results from the Group 4 complexes were covered in Section 2 and included $CpMMe_3$, Cp^*MMe_3 ($M = Ti$, Zr; giving traces of oligomers), and $(MeCp)_2MMe_2$, $CpCp^*MMe_2$, $Cp^*_2MMe_2$ ($M = Ti$, Zr; giving $\geq 80\%$ yield of oligomers). Both Cp_2V and Cp_2VMe_2 produced only disilane and trisilane from $PhSiH_3$ in contrast to the metallocenes of Group 4. The formation and separation of the disilane and trisilane produced from Cp_2V was described. No silicon oligomers were reported from Cp_2Cr or from Cp_2MH_2 ($M = Mo$, W) although $Cp_2Mo(H)(SiH_2Ph)$ was formed and isolated.[6b]

The last grouping of metallocene type complexes comes from the lanthanides and actinides. Tanaka and co-workers reported the use of $Cp^*_2NdCH(SiMe_3)_2$ to promote the polymerization of $PhSiH_3$[132] and $MeSiH_3$.[133] Polymerization was promoted by heating and at 130 °C for 2 days, the polysilane isolated had a M_w of 1600 and a M_w/M_n of 1.9. Hexylsilane reacts more slowly as was observed with the metallocenes of Group 4 and even after 13 days at 160 °C, the M_w of the polymer was < 1000. The field desorption mass spectrum was consistent with $H(^n\text{HexSiH})_nH$ with $n = 2$ to 10.[132] The condensation of $MeSiH_3$ in the presence of $Cp^*_2NdCH(SiMe_3)_2$ ($Si/Nd = 440$ in benzene; reactions conducted in an autoclave) was also studied and at temperatures ≤ 70 °C only oligomers were observed.[133] However, at 90 °C polymerization took place and the M_w of the polymer produced after 2 days was 7300 ($M_w/M_n = 5.0$) with a CH_3/SiH ratio $= 1.0$ by ^1H NMR integration. At higher temperatures only insoluble material formed. The results are similar to those reported by Harrod for the condensation of $MeSiH_3$ with Cp_2MMe_2 ($M = Ti$, Zr) although the polydispersities of the polysilane produced from this catalyst (see Section IV.B) tended to be higher than those reported with $Cp^*_2NdCH(SiMe_3)_2$.

Marks and co-workers also utilized $Cp^*_2NdCH(SiMe_3)_2$ for condensation of $PhSiH_3$ as well as the La, Sm, Y, and Lu analogs plus

$[Me_2Si(C_5Me_4)_2]NdCH(SiMe_3)_2$, Cp^*_2Sm, and $Cp^*_2Sm(THF)_2$.[134] All the complexes were highly active catalysts for dehydrocoupling of $PhSiH_3$ although the molecular weights of the polysilane were reported only for $Cp^*_2LaCH(SiMe_3)_2$ and were ≤ 1000. Upon addition of $PhSiH_3$ to $Cp^*_2LnCH(SiMe_3)_2$, quantitative elimination of $H_2C(SiMe_3)_2$ was observed. From NMR measurements of the initial phases of the reaction, small oligomers were observed and results were similar to those observed from Group 4 catalysts. Kinetic parameters were measured and supported four-centered intermediates such as those proposed by Tilley for Group 4 metallocenes.

In Harrod's original report of the screening of metallocenes as dehydrocoupling catalysts, $Cp^*_2MMe_2$ ($M = U$ and Th) was studied and although these actinides did promote the reaction of $PhSiH_3$, only dimers or small oligomers were produced.[6b]

D. *Miscellaneous Other Metal Complexes*

The manganese complex, $Ph_3SiMn(CO)_5$ has been used to promote hydrosilylation of olefins both thermally and photochemically. With HD_4 and pentene, and 0.1 mol% of $Ph_3SiMn(CO)_5$, thermal activation gave a 20% yield of D_4–D_4 but none from photochemical activation.[109] A few complexes of iron, $Fe(CO)_5$,[110a] $Fe(CO)_2[P(OPh)_3]_2H(SiMe_2Ph)$,[110b] and $Fe(dppe)_2(CH_2{=}CH_2)$[111] have been reported to couple tertiary silanes but few details are available.

Although a transition metal was not involved, the dehydrocoupling of the *secondary* hydrosilane, 1,1-dihydrotetraphenylsilole, to polymers with M_w values ranging from ~ 4000 to ~ 6000 (polydispersities ranged between 1.1 and 1.2) in the presence of catalytic quantities of Red-Al, L(N or K)-Selectride or Super-Hydride has been reported.[135a] This is the only currently published example of polymeric material produced from a secondary silane. It is interesting that this secondary silane is a heterocyclic system where steric interactions (from substituents at silicon) have been reduced, although the fact that there are phenyl groups on the α-carbon, makes this a rather extraordinary result.

VII

CONCLUSION

Homodehydrocoupling is only one reaction of hydrosilanes that is promoted by transition metal complexes. In the development of pre-catalysts for the specific reactions that lead to Si–Si bond formation, Group 4 metallocene derivatives of several variations (summarized in Table I) have been examined. Three approaches to a catalytic system have been developed starting with Cp_2MMe_2, $CpCp^*M[Si(SiMe_3)_3]X$, and $Cp_2MCl_2/2^nBuLi$. These were later expanded into complexes with substituted Cp-rings and in the presence of other activators especially those that lead to cationic (or cation-like) metallocene systems. The benchmark silane used to determine the efficiency of the dehydrocoupling process is $PhSiH_3$ which provides the polysilane, $H(PhSiH)_xH$. Reactions are normally run without solvent and at room temperature to minimize formation of cyclic byproducts. M_w values up to $\sim 20{,}000$ have been observed in some cases and the polydispersities tend to fall below a value of 2 and in general, the polymers are linear. Significant cross-linking in $H(PhSiH)_xH$ is observed only in the condensation of $PhSiH_3$ with the cationic complex $CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3$ since the complex also promotes redistribution to generate Ph_2SiH_2 and SiH_4. It is the incorporation of SiH_4 into the chain that most likely produces the cross-linking. Cross-linking is also observed in the condensation of $MeSiH_3$. Steric problems in the condensation of hydrosilanes is obvious when rates of reactions of primary silanes are compared to those of secondary silanes which couple to give only oligomers with metallocene pre-catalysts and with one exception, tertiary silanes do not react. Control of the microstructure in the polymers $H(RSiH)_xH$ remains a challenge for the future as the current material produced from metallocene catalysts is atactic. The most widely accepted mechanism for dehydrocoupling of hydrosilanes by metallocenes of Group 4 is the σ-bond metathesis sequence proposed by Tilley.

The use of metal complexes other than those of Group 4 is not well explored and this may be due to the promotion by such metals of competitive reactions of the hydrosilane particularly the redistribution of groups at silicon. However, the major problem will be the metal promoted formation of siloxanes in the presence of either oxygen or water. Electron-rich metal complexes do not appear to be useful for the condensation of primary silanes to polymeric material although condensation to oligomers has been observed. The exception is the use of indenyl complexes of nickel(II) where polymers similar to those obtained from Cp_2MMe_2 ($M = Ti$, Zr) have been obtained from $PhSiH_3$. In contrast to metallocene complexes however, there are several examples where electron-rich metals have promoted the coupling of tertiary silanes.

The monosilanes that produce polymeric material tend to be limited. Thus far, primary arylsilanes are the only well documented silanes that react to provide polymer. Primary alkylsilanes couple more slowly and tend to give relatively short chains (chain lengths up to about 12 silicon atoms).

As the bulk of the substituents on silicon increases, the shorter become the chains in the coupled product, to the limit of disilane. This "limit" occurs for both primary and secondary silanes. One difference between the metallocene (Group 4) promoted dehydrocoupling reactions and that of metals such as Rh or Pt, is the difficulty in the condensation of dialkylsilanes from the former grouping. Dialkylsilanes condense in the presence of metallocene catalysts only if a hydrogen acceptor (such as an olefin) is present. An interesting exception to the condensation of a secondary silane center comes from the reactions of hydrogen terminated disilanes such as 1,2-dimethyldisilane which forms polymers from both metallocene promoted reactions as well as with Rh and Pd complexes.

The future challenges in this area will be the development of catalyst sytems that promote the formation of higher molecular weight material and that also have the ability to control the microstructure of the polymer. Other features for new catalyst systems would involve the ability to distinguish between primary, secondary, and tertiary centers and couple both alkylsilanes and arylsilanes efficiently. To achieve these goals will require a better understanding of the mechanistic pathways for dehydrocoupling than is currently available.

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Organoelement Compounds Possessing Al–Al, Ga–Ga, In–In, and Tl–Tl Single Bonds

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I

INTRODUCTION

Compounds possessing isolated element–element single bonds between main-group elements are quite common for the fourth to seventh main groups, examples are Si–Si (Si_2Me_6), As–As (As_2I_4), or Se–Se bonds (elemental selenium). In contrast to this wide area of chemistry, comparable and well characterized dinuclear compounds with the elements boron, aluminum, gallium, indium, and thallium remained extremely rare until the last decades of the twentieth century. The main problem in the synthesis and isolation of persistent dielement derivatives of the type $R_2E–ER_2$ ($E = B$, Al, Ga, In, Tl) arose from disproportionation reactions which generally proceed by the precipitation of the elements $E^{\pm 0}$ and the formation

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of products of the trivalent elements E^{3+}. Such a reaction is favored by the coordinative unsaturation of the central atoms, which allows the bridging of the E–E bonds as a possible initiating step of decomposition.

The first examples of non-delocalized E–E bonds between elements of the third main group were obtained with boron in the monomeric boron subhalides $X_2B–BX_2$ (X = F, Cl, Br, I), in tetraalkoxydiboranes $B_2(OR)_4$, or in tetraaminodiboranes $B_2(NR_2)_4$.[1–3] Although the homologous compounds E_2X_4 (X = halogen) of the heavier elements have an identical experimental formula, they adopt different structures which do not contain E–E bonds. Instead, these subhalides were identified as mixed valent E(I)–E(III) species of the type $E^+[EX_4]^-$. They gave compounds containing Ga–Ga or In–In bonds only on treatment with donor ligands (L) and by co-ordinative saturation of the central atoms in the adducts $X_2(L)E–E(L)X_2$. These and related compounds are described in more detail in the following sections.

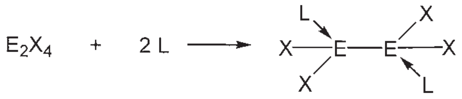
The syntheses of organoelement derivatives containing E–C beside the E–E bonds proved to be even more difficult than the syntheses of halides or alkoxides, and it was not before 1980 that the first tetraalkyldiboranes(4) $R_2B–BR_2$ were isolated. They were obtained by the reactions of subvalent precursor molecules with suitable alkyllithium compounds and required steric shielding by bulky substituents to prevent decomposition.[4,5] The first authenticated tetraalkyldialane(4) containing an Al–Al single bond was published in 1988.[6] Since then this particular area of organoelement chemistry has developed to a huge field of activities, and is still of current interest. This review is focused on the syntheses and physical properties of compounds possessing localized Al–Al, Ga–Ga, In–In, and Tl–Tl single bonds. The first polyhedral cluster molecules containing aluminum, gallium, and indium atoms in lower oxidation states were isolated in the course of these research activities. They require a more delocalized approach in understanding their bonding and are completely ignored here. This topic has been reviewed several times before in recent literature.[7] In addition, intermetallic phases are beyond the topic of this review and are not discussed here.

II

FORMATION OF E–E SINGLE BONDS BY COORDINATION OF SUBHALIDES

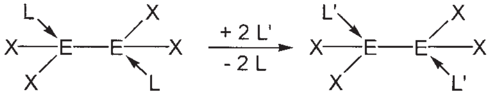
Reactions of elemental gallium or indium with the corresponding trihalides afforded compounds for which elemental analyses verified the composition EX_2. Such a fragment would have an unpaired electron, so that owing to the diamagnetism of the products the occurrence of E–E bonds was suggested,[8] which, however, could be verified only for the boron subhalides $X_2B–BX_2$.[1] Spectroscopic and crystallographic investigations in the fifties of the last century[9] revealed that the corresponding subhalides of the heavier elements adopt differing structures containing the mixed valent ionic species $E[EX_4]$. The tetrahedral $[EX_4]^-$ anions have Ga or In atoms in an oxidation state +3 with normal E–X bond lengths, while the monovalent Ga^+ and In^+ counterions show only weak van der Waals contacts to halogen atoms.[10] E–E bonds resulted only on treatment of these subhalides with neutral or anionic donors to yield the adducts $X_2(L)E–E(L)X_2$ containing co-ordinatively saturated atoms in an oxidation state +2.[11] Mixed valent aluminum compounds $Al[AlX_4]$ have not been characterized unambiguously so far, and donor stabilized subhalides possessing Al–Al bonds (see below) were published only recently more than twenty years later than their heavier homologues.

Essentially three methods were employed for the synthesis of adducts of the gallium or indium subhalides E_2X_4 (X = Cl, Br, I). The first and most important route comprises the direct treatment of the corresponding mixed valent species with organic donors at low temperature [Eq. (1)]. A vast number of different ligands such as ethers (dioxane, THF),[12–18] amines (trialkylamines, pyridine),[14,16–21] thioethers,[14,17,18,22] triethylphosphane,[21] or dimethylsulfoxide[18] were employed for the formation and stabilization of the E–E bonds. Ligand exchange is the second important method to be discussed here [Eq. (2)]. It is employed in those cases in which the direct treatment of the mixed valent species with a particular ligand causes disproportionation.[14,17,22] The third method starts with compounds InX, which contain indium in an oxidation state +1. On addition of donors disproportionation reactions occurred, which in particular cases stop at the intermediate oxidation state +2 [Eq. (3)].[23–25] A remarkable carbene complex was generated by that route, in which two Arduengo type carbenes [:CN(Mes)C_2H_2N(Mes), Mes = Mesityl] are attached to the In atoms of In_2Br_4.[23]



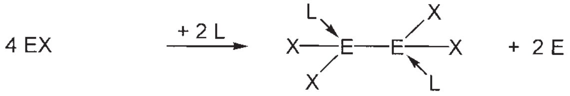
(1)

E = Ga, In L = organic donor
X = Cl, Br, I



(2)

E = Ga, In   L = dioxane
X = Cl, Br, I   L' = pyridines



(3)

E = Ga; X = I (see text)
E = In; X = Cl, Br, I

Similar gallium(I) halides GaX are available only by sophisticated high temperature methods.[26] Ultrasonic treatment of a suspension of elemental gallium and iodine in toluene afforded, however, a pale green powder,[27] which seems to be a mixture of different subhalides, but behaves as gallium monoiodide GaI in many reactions. Addition of the donors triethylphosphane or trimethylamine yielded the corresponding adducts of Ga_2I_4.[28,29] Further, more specialized procedures for the synthesis of those adducts comprise the oxidation of elemental gallium or indium with Et_3AsI_2 and $n$$Pr_3PI_2$, respectively, which give the products in high yield [Eq. (4)],[30,31] or the anodic oxidation of gallium in the presence of hexamethylphosphoric triamide.[32]

(4)

E = Ga, R = Et, E' = As
E = In, R = *n*Pr, E' = P

Facile routes for the convenient syntheses of similar complexes of the aluminum(II) subhalides do not exist at all. These compounds $[X_2(L)Al–Al(L)X_2$ ($X = Cl, Br, I$; $L = NMe_2SiMe_3$, OEt_2, PEt_3, MeOPh)] were obtained in low yields by the treatment of metastable solutions of aluminum monohalides AlX with the corresponding donor substances similar to the reactions described in Eq. (3).[33–35] Al_2Cl_4 was supposed to be formed from elemental Al and $AlCl_3$ at 120 °C in a solvent, however, it was not isolated in a pure form and was characterized on the basis of some not really specific reactions.[36] In view of the results obtained recently with respect to the synthesis and stability of aluminum subhalides,[33–35] it seems to be rather implausible that indeed considerable concentrations of a subhalide had formed. Quantum-chemical calculations

TABLE I

STRUCTURALLY CHARACTERIZED COMPOUNDS $X_2(L)E–E(L)X_2$ (E = Al, Ga, In; X = HALOGEN) STABILIZED BY ORGANIC DONOR MOLECULES (E–E BOND LENGTHS IN pm; STRETCHING VIBRATIONS $\nu_{E–E}$ IN cm^{-1})

	E–E	$\nu_{E–E}$	Ref.
$(Me_3SiMe_2N)Cl_2Al–AlCl_2(NMe_2SiMe_3)$ **1**	257.3(5)	–	33
$(Me_3SiMe_2N)Br_2Al–AlBr_2(NMe_2SiMe_3)$ **2**	256.4(4)	–	33
$(MeOPh)Br_2Al–AlBr_2(MeOPh)$ **3**	252.7(6)	510	34
$(Et_2O)I_2Al–AlI_2(OEt_2)$ **4**	252(2); 253.1(1)	–	33
$(Et_3P)I_2Al–AlI_2(PEt_3)$ **5**	254.6(3)	–	33
$(dioxane)Cl_2Ga–GaCl_2(dioxane)$ **6**	240.6(1)	238	12
$[(dioxane)Cl_2Ga–GaCl_2(dioxane)]_\infty$ **7**	238.3(1)	–	13
$[(Me_2N)_3PO]Cl_2Ga–GaCl_2[OP(NMe_2)_3]$ **8**	239.2(1)	–	32
$(pyridine)Cl_2Ga–GaCl_2(pyridine)$ **9**	240.3(1)	223	14
$(4Me\text{-}pyridine)Cl_2Ga–GaCl_2(4Me\text{-}pyridine)$ **10**	241.5(2)	214	19,14
$(Me_3N)Cl_2Ga–GaCl_2(NMe_3)$ **11**	242.1(1)	–	37
$(dioxane)Br_2Ga–GaBr_2(dioxane)$ **12**	239.5(6)	168	38,14
$(pyridine)Br_2Ga–GaBr_2(pyridine)$ **13**	242.1(3)	163	22,39
$(Et_3N)I_2Ga–GaI_2(NEt_3)$ **14**	249.8(7)	–	29
$(Et_3P)I_2Ga–GaI_2(PEt_3)$ **15**	243.6(2)	–	28
$(Et_3As)I_2Ga–GaI_2(AsEt_3)$ **16**	242.8(7)	–	30
$(THF)_2Cl_2In–InCl_2(THF)_2$ **17**	271.5(1)	180	24
$L'Br_2In–InBr_2L'$ **18**	274.4(1)	–	23
$(TMEDA)Br_2In–InBrI(TMEDA)$ **19**	277.5(2)	131	40,20
$(nPr_3P)I_2In–InI_2(PnPr_3)$ **20**	274.5(3)	–	31

L' = carbene, $:CN(Mes)C_2H_4N(Mes)$.

revealed that the compound with an Al–Al bond ($Cl_2Al–AlCl_2$) is not the favorable one, instead, the mixed valent species similar to the Ga or In subhalides with two or three bridging Cl atoms [$Cl_2Al^{III}(\mu\text{-}Cl)_2Al^I$; $ClAl^{III}(\mu\text{-}Cl)_3Al^I$] are energetically favored.[36]

Often, these adducts were characterized by vibrational spectroscopy, and Raman spectroscopic investigations were particularly informative and indicative for the occurrence of E–E bonds. Some E–E stretching vibrations $\nu_{E–E}$ are summarized in Table I. They nicely show the expected dependency of $\nu_{E–E}$ on the atomic masses of the respective elements and on the masses of the substituents. Some compounds were further characterized by nuclear quadrupole resonance spectroscopy, which gave indications for phase transfer processes and for the extent of electron transfer from the ligands to Ga or In atoms.[15,16] Most helpful for the discussion of the constitution and conformation of these subhalides are the results of X-ray crystal structure determinations. The E–E bond lengths (Table I) reflect the general trend in third main-group chemistry. While as expected the In–In distances are the longest in this series (~275 pm), the Ga–Ga bonds (~240 pm) are considerably shorter than the bonds between the lighter Al atoms (~255 pm). Reasons for this behavior, which impressively verifies the particular properties of gallium in comparison with its homologues, are discussed in more detail in Section VI. There is a nice series of homologous adducts of Ga_2I_4 coordinated by NEt_3 (**14**), PEt_3 (**15**), and $AsEt_3$ (**16**). A continous decrease of the Ga–Ga bond lengths (249.8, 243.6, and 242.8 pm) was observed with an unusually long bond for the amino adduct. The bond angles I–Ga–I change in the reverse direction (101.8, 107.6, and 109.0°, respectively). That alteration has been explained by a decreasing donor strength in the series $N > P > As$ with an approach to an sp^2 hybridized Ga atom for the $AsEt_3$ ligand.[28] Furthermore, steric repulsion, due to the short Ga–N bond may be strongest for the NEt_3 ligand, should result in a lengthening of the Ga–Ga bond.

Generally, the co-ordination numbers of the Al and Ga atoms are four. Only one exception was observed in the polymeric isomer (**7**) of the dioxane adduct of Ga_2Cl_4, where the bidentate dioxane ligands bridge two Ga–Ga moieties. The co-ordination numbers of the gallium atoms increase from four in **6** to five in **7**. Two of the four structurally characterized indium compounds have co-ordination numbers of five at their central atoms, which may be favored by their large covalent radius. Two THF molecules are attached to the indium atoms in **17**, while TMEDA acts as a bidentate ligand in **19**. The carbene adduct **18** has In–C donor–acceptor bonds which are elongated (226 pm on average[23]) compared to normal In–C single bonds of alkylindium derivatives. In most compounds $X_2(L)E–E(L)X_2$ the expected ethane like conformation was observed with the organic donor ligands in *trans*-arrangement. Exceptions are the isotypic dioxane adducts **6** and **12**, which adopt an eclipsed conformation with the oxygen atoms opposite to chlorine or bromine atoms. The smallest torsion angles across the Ga–Ga bonds are 13° on average in both derivatives (Cl–Ga–Ga–O in **6** and Br–Ga–Ga–O in **12**).

Three cluster compounds are worth mentioning in context with the particular topic described here. The subhalides $Al_{22}Cl_{20}(L)_{12}$ (L = THF, THP) and $Al_{22}Br_{20}(L)_{12}$ (L = THF) possess cluster cores formed by icosahedra of twelve Al atoms.[41,42] Ten of these cluster atoms are terminally attached to $AlX_2(L)$ substituents (X = Cl, Br) via Al–Al single bonds. The Al–Al bond lengths are 254.9, 255.2, and 252.6 pm, respectively, and correspond well to those detected for the aluminum(II) subhalides **1** to **5** (Table I).

TABLE II

STRUCTURALLY CHARACTERIZED COMPOUNDS CONTAINING THE ANIONS $[X_3E–EX_3]^{2-}$ (E = Ga, In) (E–E BOND LENGTHS IN pm; E–E STRETCHING VIBRATIONS $\nu_{E–E}$ FROM RAMAN DATA IN cm^{-1})

	E–E	$\nu_{E–E}$	Ref.
$[Cl_3Ga–GaCl_3][NMe_4]_2$ **21**	239.0(2)	233	43–47
$[Cl_3Ga–GaCl_3][Ph_3PH]_2$ **22**	240.4(2); 240.7(1)	233	48–50
$[Cl_3Ga–GaCl_3]Li_2$ **23**	239.1(1)	–	51
$[Br_3Ga–GaBr_3][NPr_4]_2$ **24**	241.9(5)	164	52,46
$[Br_3Ga–GaBr_3]Li_2$ **25**	240.4	–	53
$[Br_3Ga–GaBr_3]Ga_2$ **26**	242.7(4); 243.9(6)	163	54–56
$[I_3Ga–GaI_3]Li_2$ **27**	242.8(2)	–	51
$[I_3Ga–GaI_3]Ga_2$ **28**	238.5(5)	125	57–60
$[Br_3In–InBr_3]K_2$ **29**	267(1)	139[a]	61,62
$[Br_3In–InBr_3]In_2$ **30**	268.8; 271.6	139	63–65
$[Br_3In–InBr_3]In_3Br$ **31**	270.7 (av.)	139	66–69

[a] Detected with the $[NBu_4]^+$ salt.

Beside organic donor ligands halide anions (X = Cl, Br, I) were employed to stabilize E–E single bonds. Anions of the type $[X_3E–EX_3]^{2-}$ were formed in which E is restricted to the elements gallium and indium. Compounds characterized by X-ray crystal structure determinations (**21–31**) are summarized in Table II. Since the organoelement aspect of these hexahalides is rather peripheral, it has not been dealt with in detail here. The E–E bond lengths (Ga–Ga ~240 pm; In–In ~270 pm) are similar to those given in Table I for the neutral adducts with organic ligands. Same holds for the E–E stretching vibrations determined by Raman spectroscopy. Interestingly, the gallium compounds seem to be stable enough to exist even in water solution.[70] A fluorine compound $[Ga_2F_6]^{2-}$ was mentioned in literature.[71] However, its real existence has not been supported by a thorough characterization.

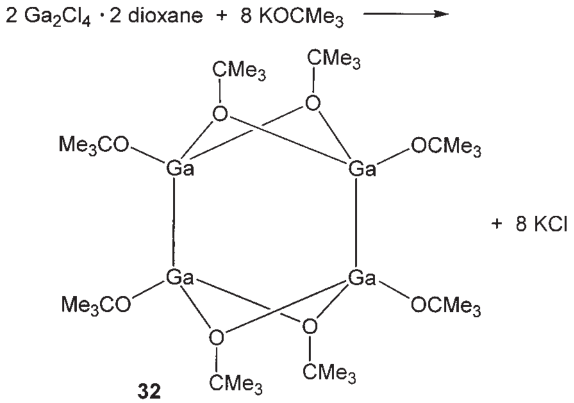
III

CHALCOGEN ATOMS COORDINATING E–E BONDS

Only homoleptic compounds are considered here, compounds bearing miscellaneous ligands including elements of Group 15 to 17 are discussed in Section V. Several inorganic compounds such as Al_7Te_{10}, GaS, or In_6Se_7

are known in which Al–Al, Ga–Ga, or In–In bonds are coordinated by chalcogen atoms (examples and further details are given in Refs. 72–81). In contrast, dielement compounds bearing organic ligands such as alcoholates or thioalcoholates are extremely rare. The anodic oxidation of elemental indium in the presence of thiols was reported to afford insoluble diindium compounds of the type $(RS)_2In–In(SR)_2$ ($R = C_5H_{11}$, 2-$C_{10}H_7$).[82] The products were characterized by mass spectroscopy, elemental analysis, and some chemical reactions. The oxidation of elemental gallium or indium with tetrahalogeno-*o*-benzoquinone in the presence of the neutral donor phenanthroline was supposed to yield compounds with E–E bonds coordinated by chelating catecholato ligands. Attempts to grow single crystals of the products for crystal structure determinations failed.[83]

A structurally authenticated digallium(II) compound (**32**) exclusively co-ordinated by alcoholate groups was obtained by the reaction of $Ga_2Cl_4(dioxane)_2$ **6** with $KOCMe_3$ [Eq. (5)].[84] The product $(Me_3CO)_2Ga–Ga(OCMe_3)_2$ forms a dimer in the solid state possessing two Ga–Ga bonds and four tetracoordinated gallium atoms. The Ga–Ga bonds [248.3(1) pm] are lengthened compared to those of the subhalides described before (Tables I and II). The structure may be derived from a strongly distorted cube of which two opposite edges are Ga–Ga bonds, while two edges remain open. Thus, it differs strongly from that of other dimeric dielement compounds such as $[R(X)E–E(X)R]_2$ (X = halogen, E = Ga, In), which usually adopt a Realgar type arrangement of the central cage atoms (see Section VI.D). The most obvious difference between both types of structures is the arrangement of the Ga–Ga bonds, which are parallel in **32**, while they are perpendicular to one another in the remaining cages.



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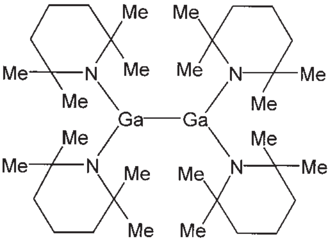
(5)

A dithallium species, $[Tl–Tl]^{4+}$, representing a rare example of a dithallium(II) compound with a Tl–Tl single bond, was detected in a matrix of oxygen atoms formed by an oxomolybdato phase ($Tl_{0.8}Sn_{0.6}Mo_7O_{11}$).[85] The Tl–Tl bond length [284.0(3) pm] is similar to that observed for elementorganic dithallium(II) compounds discussed below.

IV

HOMOLEPTIC DIELEMENT COMPOUNDS WITH PNICOGEN ATOMS COORDINATED TO E–E BONDS

Tetraaminodigallium compounds $(R_2N)_2Ga–Ga(NR_2)_2$ were obtained by the treatment of $Ga_2Cl_4(dioxane)_2$ with the corresponding lithium amides similar to the route given in Eq. (5). Terminal monodentate amido groups were observed in the tetramethylpiperidino derivative **33**,[86] while a chelating coordination was obtained with the diamide $Me_2C[CH_2N(Li)SiMe_3]_2$ (**34**).[84] A similar synthesis starting with two-fold lithiated di(*tert*-butyl)diazabutadiene gave compound **35** with an unsaturated chelating ligand.[87] The formation of a benzannelated compound of that type by the same route has been claimed, however, no experimental details have been published so far.[88] The interest in diaza heterocycles similar to **35** was stimulated by attempts to synthesize compounds which have low coordinated gallium atoms in an oxidation state +1 and which are similar to imidazole based Arduengo carbenes.[89,90] Another route for the synthesis of **35** starts with $GaCl_3$ [Eq. (6)]. Reduction of the digallium(III) intermediate with potassium yielded **35**, which by further reduction was transferred to the carbene analogue not shown here. A third method for the synthesis of those 1-galla(II)-2,5-diazole derivatives containing Ga–Ga bonds comprises the irradiation of a η^1-pentamethylcyclopentadienylgallium compound. Reduction of the Ga atoms occurred by the homogeneous cleavage of the Ga–Cp* σ-bond [Eq. (7)].[91]



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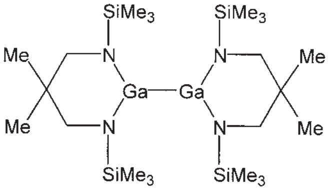

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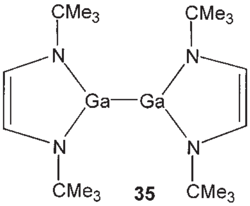

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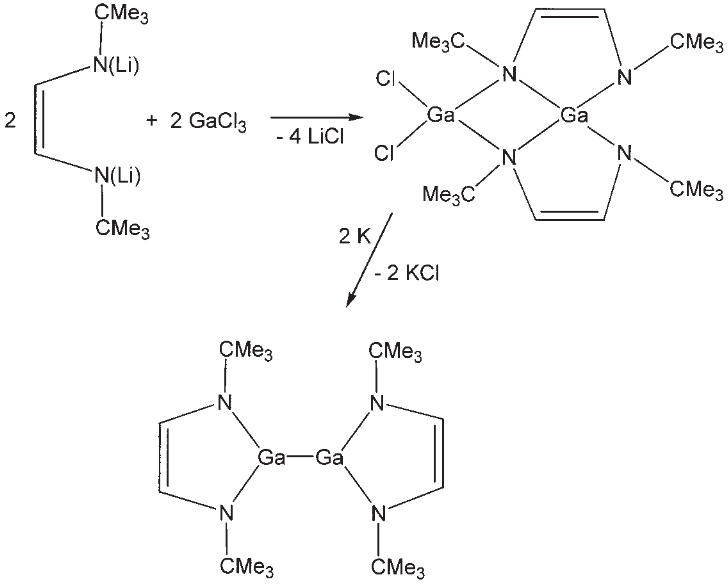

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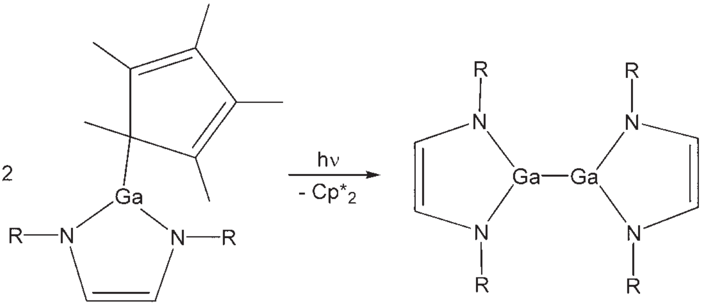
(6)



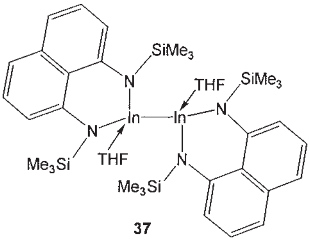
(7)

R = -2,6-iPr$_2$-C_6H_3 (**36**)
-2,6-Et_2-C_6H_3

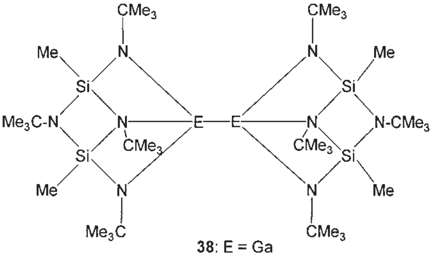
Crystal structure determinations of the compounds **33–36** revealed coordinatively unsaturated, tri-coordinated Ga atoms. They show different conformations across the Ga–Ga bonds with an ideal staggered arrangement of the substituents observed only for **34** and **35** (torsion angle 90°). The planes of the heterocycles in **33** are tilted by an angle of 31° indicating a considerable approach to planarity. Variable torsion angles between 42 and 59° were determined for the relatively irregular molecular structure of **36**. The orthogonal geometry was calculated to be the most favorable one for all digallium compounds independent of the nature of the substituents.[91] However, the barrier of rotation diminishes on going from alkyl or silyl groups to NH_2 or the chelating $HNC(H){=}C(H)NH$ ligand. The Ga–Ga bond lengths [252.5(1) pm (**33**); 238.5(1) pm (**34**); 233.3(1) pm (**35**); 234.82(2) pm (**36**)] differ considerably. The longest one was observed for compound **33**, in which the gallium atoms were terminally coordinated by amido groups. Much shorter distances were found for the diheterocyclic derivatives in which the Ga–Ga bonds connected two rings. They were even shorter than in the subhalides discussed before. The Ga–Ga distances correlated to the N–Ga–N angles, which systematically became smaller on going from **33** to **36** (118°; 109°; 90°; 89°). The alteration of the bond lengths surely does not indicate any contribution of π-bonding. Already the experimentally observed molecular conformations clearly exclude such an assumption. Quantum-chemical calculations[91] showed an increase of the contribution of the s-orbitals to the Ga–Ga bonds, when alkyl groups were replaced by the more electronegative amido ligands. A further increase of the s-character results upon coordination of chelating ligands and the formation of heterocycles, which effect small N–Ga–N angles. Thus, the short Ga–Ga bonds in compounds **35–36** were deduced merely to an increased s-contribution to the Ga–Ga bond. The rather long Ga–Ga distance in **33** may further be influenced by some steric repulsion between the bulky substituents.

To the best of my knowledge, similar compounds containing In–In bonds and coordinatively unsaturated In atoms have not been published thus far. Owing to the larger covalent radius of In, the formation of adducts with higher coordination numbers than three is preferred. This is nicely demonstrated with the derivative **37**, which is quite similar to the tetraamides discussed before, but has an additional THF molecule coordinated to each In atom.[92] Compound **37** is formed by the reaction of the corresponding dilithium diamide with InBr and disproportionation. Chelating ligands coordinated by three or four donor atoms [nitrogen (**38–40**) or nitrogen and phosphorus (**41**, **42**)] to the gallium(II) or indium(II) atoms were employed in several cases for stabilizing

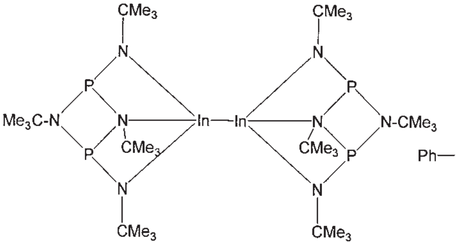
E–E bonds (E = Ga, In).[93–95] Examples are shown with compounds **37–42**. The synthesis of these compounds succeeded by the reduction of the corresponding element(III) chlorides with activated alkali metals (**38**, **39**, **41**, **42**)[93,95] or by the reaction of InBr with the lithiated ligand under disproportionation (**40**).[94] The Ga–Ga [252.1(1) pm **41**] or In–In distances [276.8(1) pm **39**; 277.20(4) pm **40**; 276.2 pm **42**] are longer than those observed for subhalides of these elements (Tables I and II). A rather long In–In bond (324 pm) has been determined by EXAFS in a phthalocyanine complex, in which the indium atoms are coordinated by the four nitrogen atoms of the heterocyclic ligand, two nitrogen atoms of a TMEDA ligand and the indium atom of the second half of the molecule.[96] Raman spectroscopy revealed an emission at 110 cm^{-1} assigned to the In–In bond, which was interpreted in terms of an only weak bonding interaction.



37



38: E = Ga
39: E = In



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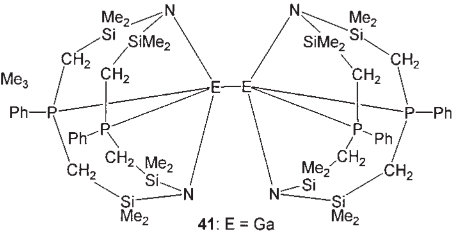
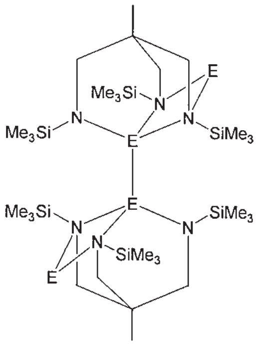
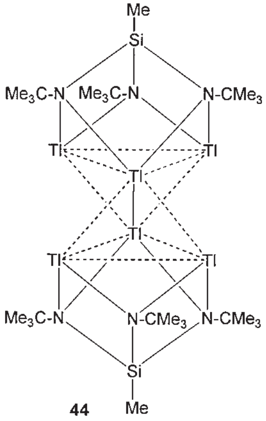


41: E = Ga
42: E = In

An analogous homoleptic tetraamido dialuminum compound containing an Al–Al bond has not yet been reported. Tl–Tl interactions have been discussed for some amidothallium(I) derivatives containing pairs or chains of Tl atoms, very long Tl–Tl distances (> 340 pm) indicate, however, rather weak direct Tl–Tl contacts. Some examples are given in References.[97–99] A Tl–Tl single bond exhibiting a very short Tl–Tl distance [273.4(2) pm] was found for the thallium(II) compound **43**, in which each Tl(II) atom is coordinated by a tripodal trisamido ligand.[99] Compound **43** was obtained by the reaction of TlCl with the corresponding lithium trisamid. An isostructural diindium derivative exists, which surprisingly has a longer E–E distance [280.7(1) pm].[99] A relatively short Tl–Tl distance [316.7(8) pm] was also observed for compound **44**.[100] However, the oxidation state +1 of all Tl atoms actually excludes the formulation of an isolated Tl–Tl σ-bond comparable to that of **43**. Several longer Tl–Tl contacts (346 pm) were detected and may indicate some delocalization leading to a more cluster like situation.[7]



43: E = In, Tl



44

V

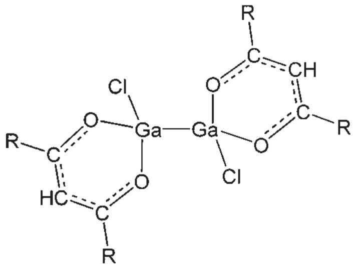
HETEROLEPTIC DIELEMENT COMPOUNDS COORDINATED BY MISCELLANEOUS DONOR ATOMS OF GROUP 15–17

All compounds containing at least one E–C σ-bond are discussed in the next section, and only those molecules are considered here which have different donor atoms of the Groups 15–17 of the periodic table. All compounds may be derived from the subhalides of Al, Ga, and In by replacing two halogen atoms by chelating bidentate ligands. Treatment of $Ga_2Cl_4(THF)_2$ with sodium β-diketonates afforded digallium compounds (**45**) in which the Ga–Ga bonds are coordinated by two Cl atoms and two acetylacetonato ligands.[101] Coordinative saturation was achieved with coordination numbers of four at the Ga atoms, which is required to obtain stable molecules and to prevent decomposition by disproportionation. These compounds do not adopt *trans* conformations as might be expected from steric and electrostatic considerations. Instead, the torsion angles Cl–Ga–Ga–Cl of 123.4° (R = Me) and 130.1° (R = CMe_3) indicate an anticlinal arrangement of the Ga–Cl bonds.

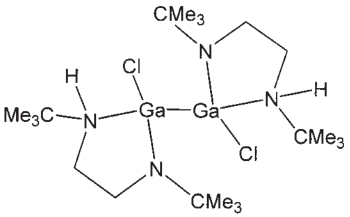
Similar diindium dihalides bearing catecholato ligands were postulated to occur in the solid state, while in solution dissociation should give rise to EPR active indium(I) and indium(III) semiquinone species.[102] Sufficient experimental data for the concise characterization and identification of the solids have not been published. A mixed coordination by O and N atoms has been reported for the digallium compound $Ga_2Cl_2L_2$ with L = Me_3C–O–$SiMe_2$–N–CMe_3, which was characterized by molar mass determination and NMR spectroscopy only.[103]

Reaction of $GaCl_3$ with Me_3C–NH–C_2H_4–NH–CMe_3 in the presence of two equivalents of $LiCMe_3$ resulted in a remarkable redox process which afforded the digallium(II) compound **46** in low yield.[104] The chelating ligand is coordinated by an amido and an amino nitrogen atom resulting in quite different Ga–N distances of 187.6(2) and 210.3(2) pm, respectively. The Ga–Ga bond length is 244.8(1) pm, and a synclinal arrangement of the Ga–Cl bonds was observed (torsion angle Cl–Ga–Ga–Cl 82.9°). Reduction of di(*tert*-butyl)-diazabutadiene by "GaI" (see above) gave the compound **47**, in which the Ga–Ga bond is coordinated by two radical diazabutadienide monoanions.[105] Ga–Ga bond length [242.3(1) pm] and molecular conformation (torsion angle I–Ga–Ga–I 72.8°) are similar to those of the previously described compound **46**. The Ga–Ga distance is strongly elongated compared to that of the diazabutadiene adducts **35** and **36** (233.3 and 234.8 pm) discussed before, which have a co-ordination number three at their central Ga atoms.

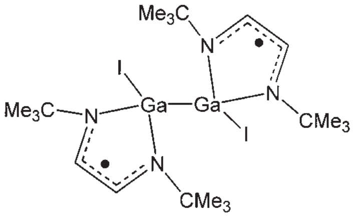
A diindium(II) compound (**48**) similar to **47** containing radical diazabutadienide ligands attached to In was obtained on a similar route by treating InCl with a diaryldiazabutadiene.[23] The In–In bond length is 272.8(1) pm in a centrosymmetric structure exhibiting an ideal *trans*-arrangement of both halogen atoms. The *trans*-conformation was also observed for the β-diketiminato diindium compound **49**. The In–In bond length of 283.4(1) pm[106] is longer than that of the diazabutadiene derivative **48**, which nicely correlates to the differences between the N–In–N bond angles. The longer bond of **49** is in accordance with the larger bond angle 87° (78° in **48**, see discussion before). The azaallyl adducts **50** (E = Al, Ga, In) were obtained by the reduction of the corresponding element(III) halides with alkali metals or by the reaction of the lithium compound with InBr followed by disproportionation.[107] The ligands are coordinated in a chelating fashion by one N and one C atom with long E–C distances. The E–E bond lengths [Al–Al 259.3(2) pm; Ga–Ga 244.5(9) pm; In–In 272.8(4) pm] reflect the generally observed trend with the shortest distance detected for the Ga compound. The torsion angles across the E–E bonds (X–E–E–X) decrease steadily on going from aluminum to indium (145.9°, 133.9°, and 129.4°, respectively).



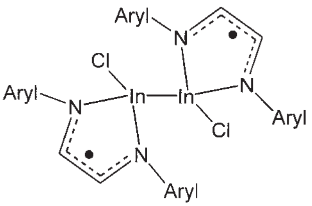
45: R = Me, CMe$_3$



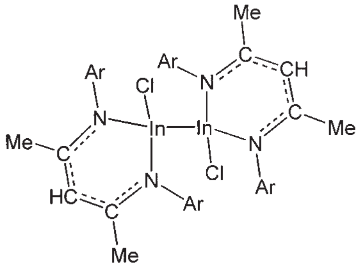
46



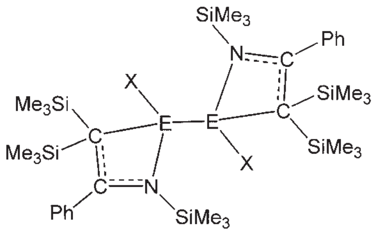
47



48 (Aryl =
2,6-iPr$_2$C$_6$H$_3$

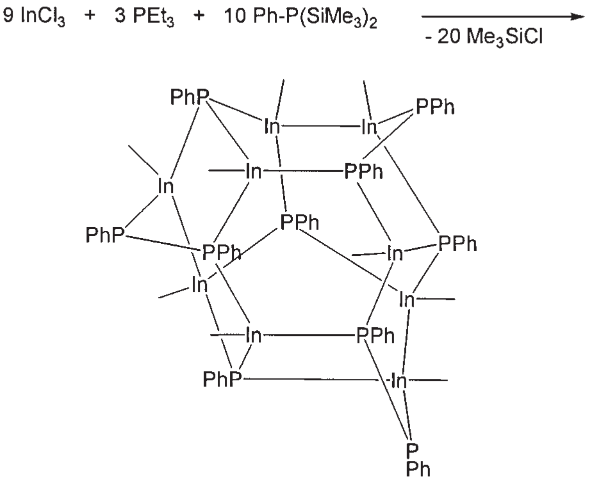


49: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$



50 E = Al, X = Cl, I
E = Ga, X = Cl
E = In, X = Br

The rather complicated In–P framework of **51** was obtained by the reaction of indium(III) chloride with PhP(SiMe$_3$)$_2$ in the presence of triethylphosphane [Eq. (8)].[108] Apparently, a complex redox process occurred, in the course of which P atoms were oxidized by the formation of three P–P bonds, while six In atoms were reduced from +3 to +2 accompanied by the formation of three In–In bonds. The indium(II) atoms are coordinated by a terminal Cl atom, two P atoms and the second In atom of the In–In bond. The In–In (averaged 274 pm) and P–P bond lengths (averaged 222 pm) represent localized single bonds.



(8)

$[(InCl)_3\{(Cl)InIn(PEt_3)\}_3(P\text{-}Ph)_4(P_2Ph_2)_3Cl]$

51

VI

DIELEMENT COMPOUNDS CONTAINING E–C OR E–Si BONDS

A. *Neutral Tetraalkyl, Tetraaryl, and Tetrasilyl Dielement Compounds*

The formation of alkylelement compounds containing Al–Al single bonds had been claimed several times before the first structurally authenticated example was synthesized and published in 1988.[6] A chain of three aluminum atoms in an oxidation state +2 and +1 was proposed to occur in the alkyl amino compound $Al_3(CH_3)_3(NMe_2)_2$,[109] while the occurrence of direct bonding interactions between even four Al atoms was suggested for $Al_4B(NMe_2)_3(CH_3)_6$.[110] Both compounds are said to be formed by the treatment of tetrakis(dimethylamino)diborane(4) possessing a B–B bond with dimeric trimethylaluminum. These reactions seem to be rather strange, because they involve the reduction of an aluminum(III) species, which normally requires strong reducing agents, by a boron(II) compound. The characterization of the products is poor, and the suggestions of their structures are essentially based on hydrolysis experiments, which yield certain quantities of elemental hydrogen. From the absence of an IR absorption in the characteristic range of Al–H groups above 1500 cm^{-1}, it was concluded that the formation of H_2 had been caused by the presence of aluminum in unusually low oxidation states. It was stated earlier[111] that the proposed structures are suspect and that presumably mixtures of unknown products had formed.

The synthesis of iBu$_2$Al–AliBu$_2$ was reported in 1976.[112] It should have been formed by the reduction of Cl–AliBu$_2$ with potassium and was isolated as a brown, highly viscous fluid which was not purified further. Elemental analysis and hydrolysis was taken as an evidence for the occurrence of an Al–Al bond. As is shown below, the isolation of stable tetraorganyldialanes requires strong steric shielding by bulky substituents in order to kinetically prevent decomposition. Thorough investigations into the true structure of the product showed that, as expected, disproportionation occurred and that a dialane(4) derivative was not present. The main product was identified as the KCl adduct of triisobutylaluminum, K[ClAliBu$_3$]. This compound is easily available by the specific reaction between AliBu$_3$ and KCl and shows the same NMR data as the oily product obtained by the reduction of ClAliBu$_2$ with potassium. Further evidence for the identity of both products came from their chemical behavior in secondary reactions. The almost quantitative formation of an 18-crown-6 complex and of a triphenylphosphane adduct of AliBu$_3$ was observed upon treatment with crown ether or with triphenylphosphane.[7a,113] As a remarkable by-product of that reduction the cluster compound K$_2$[Al$_{12}$$iBu_{12}$] was reproducibly isolated in small quantities. It is an analogue of *closo*-dodecaborate(2-), $[B_{12}H_{12}]^{2-}$, and its molecular core comprises an almost undistorted icosahedron of twelve Al atoms.[114] Despite its doubtful existence and insufficient characterization "tetraisobutyldialane(4)" was employed in secondary reactions, and the formation of products containing aluminum in low oxidation states was claimed.[115,116] However, the characterizations of the products are absolutely insufficient, and the suggested structures have not been verified reasonably in any case. Tetraneopentyldialane(4) was supposed to be formed as an intermediate, but its existence is speculative and was not verified by suitable methods.[117]

Stable homoleptic tetraorganyldielement compounds characterized by crystal structure determinations are summarized in Table III. Their syntheses succeeded by three methods: (i) Reduction of element(III) compounds by alkali metals; (ii) treatment of subhalides with the corresponding alkyllithium compounds; (iii) reactions of particular silanides

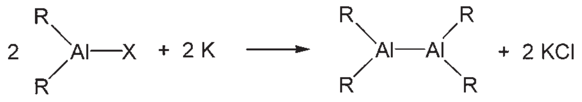
TABLE III

TETRAALKYL, TETRAARYL, AND TETRASILYL DIELEMENT(4) COMPOUNDS (E–E DISTANCES IN pm; TORSION ANGLES τ IN degree; E–E STRETCHING VIBRATIONS $\nu_{E–E}$ IN cm^{-1})

	E–E	τ	$\nu_{E\text{-}E}$	Ref.
$[(Me_3Si)_2CH]_2Al–Al[CH(SiMe_3)_2]_2$ **52**	266.0(1)	4.3	373	6
$[(Me_3Si)_2CH]_2Ga–Ga[CH(SiMe_3)_2]_2$ **53**	254.1(1)	4.9	268	118
$[(Me_3Si)_2CH]_2In–In[CH(SiMe_3)_2]_2$ **54**	282.8(1)	6.7	–	119
$(2,4,6\text{-}i Pr_3C_6H_2)_2Al–Al(2,4,6\text{-}i Pr_3C_6H_2)_2$ **55**	264.7(3)	44.8	–	120
$(2,4,6\text{-}i Pr_3C_6H_2)_2Ga–Ga(2,4,6\text{-}i Pr_3C_6H_2)_2$ **56**	251.5(3)	43.8	–	121
$[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ga–Ga[2,4,6\text{-}(CF_3)_3C_6H_2]_2$ **57**	247.9(1)	–	–	122,123
$(2,4,6\text{-}i Pr_3C_6H_2)_2In–In(2,4,6\text{-}i Pr_3C_6H_2)_2$ **58**	277.5(2)	48	–	124
$[2,4,6\text{-}(CF_3)_3C_6H_2]_2In–In[2,4,6\text{-}(CF_3)_3C_6H_2]_2$ **59**	274.4(2)	94.1	–	122
$[(Me_3C)_3Si]_2Al–Al[Si(CMe_3)_3]_2$ **60**	275.1(2)	90	–	125,126
$[(Me_3Si)_3Si]_2Ga–Ga[Si(SiMe_3)_3]_2$ **61**	259.9(4)	80	–	127
$[(Me_3C)_3Si]_2In–In[Si(CMe_3)_3]_2$ **62**	292.8(3)	87.0	–	126,128
$[(Me_3C)_2PhSi]_2In–In[SiPh(CMe_3)_2]_2$ **63**	293.8(1)	79.9	–	126
$[(Me_3Si)_3Si]_2In–In[Si(SiMe_3)_3]_2$ **64**	286.8(1)	78.6	–	129
$[(MeC)_3Si]_2Tl–Tl[Si(CMe_3)_3]_2$ **65**	296.1(1)	89.6	–	126,128
$[(Me_3C)_2PhSi]_2Tl–Tl[SiPh(CMe_3)_2]_2$ **66**	288.1(2)	82.2	–	126
$[(Me_3Si)_3Si]_2Tl–Tl[Si(SiMe_3)_3]_2$ **67**	291.4(1)	78.1	78	130

with element(III) derivatives by electron transfer. The first method [Eq. (9)] comprises the reduction of dialkyl- or diarylaluminum halides with potassium in *n*-hexane, which was the preferred route for the synthesis of few known dialanes(4) (**52** and **55**).[6,120] The digallium compound **57** was obtained by a similar method.[122] Most dielement compounds were synthesized by the reaction of subhalides of Ga or In with the corresponding alkyllithium derivatives, and most suitable starting materials are gallium(II) and indium(II) halides already containing E–E bonds (Table I, [Eq. (10)]).[118,119,121,122,124,127] In some cases, however, indium(I) and thallium(I) halides or amides were employed, and the dielement compounds were formed by the disproportionation of unstable organoelement(I) intermediates [Eq. (11)].[122,126,128,130] The third method comprises the unexpected reduction of element trihalides by triorganosilanides [Eq. (12)]. Tri(*tert*-butyl)silyl sodium reacted with $AlBr_3$ and ECl_3 ($E = In$, Tl) by the formation of tetrasilyldielement(II) compounds.[126] These reactions may have proceeded via radical intermediates, and as a secondary product hexakis(*tert*-butyl)disilane was isolated. In contrast, $GaCl_3$ gave the remarkable radical $R_2Ga–GaR^{\bullet}$ (VI,C).[131–134] In one case, $LiSi(SiMe_3)_3$ was reported to give a diindium compound (**64**) by reaction with $InCl_3$ in low yield.[129] The tetrasilyldigallane(4) $[\{(Me_3C)_3Si\}_2Ga–Ga(SiMe_3)Si(CMe_3)_3]$

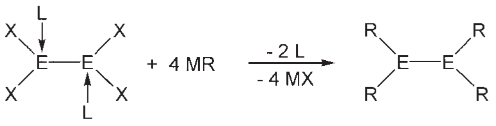
has a trimethylsilyl group and three $Si(CMe_3)_3$ substituents attached to its Ga–Ga bond and was obtained by the reaction of $SiMe_3Cl$ with the corresponding sodium salt $[Na(THF)_3Ga_2R_3]$ $[R = Si(CMe_3)_3]$ (see Section VI.C). It has not been characterized by crystal structure determination up to now.[131]



(9)

X = Cl, Br

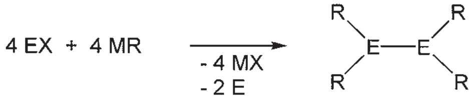
52: R = $CH(SiMe_3)_2$
55: R = 2,4,6-$i$$Pr_3C_6H_2$



(10)

E = Ga, In
X = Cl, Br
L = dioxane, TMEDA
M = Li, MgBr

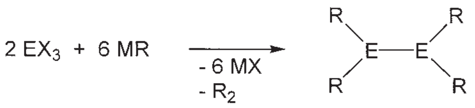
53: E = Ga, R = $CH(SiMe_3)_2$
54: E = In, R = $CH(SiMe_3)_2$
56: E = Ga, R = 2,4,6-$i$$Pr_3C_6H_2$
57: E = Ga, R = 2,4,6-$(CF_3)_3C_6H_2$
58: E = In, R = 2,4,6-$i$$Pr_3C_6H_2$
61: E = Ga, R = $Si(SiMe_3)_3$



(11)

E = In, Tl
X = Br, $N(SiMe_3)_2$
M = Li, Na, Rb

59: E = In, R = 2,4,6-$(CF_3)_3C_6H_2$
62: E = In, R = $Si(CMe_3)_3$
63: E = In, R = $SiPh(CMe_3)_2$
65: E = Tl, R = $Si(CMe_3)_3$
66: E = Tl, R = $SiPh(CMe_3)_2$
67: E = Tl, R = $Si(SiMe_3)_3$



(12)

E = Al, In, Tl
X = Cl, Br
M = Li, Na

60: E = Al, R = $Si(CMe_3)_3$
62: E = In, R = $Si(CMe_3)_3$
64: E = In, R = $Si(SiMe_3)_3$
65: E = Tl, R = $Si(CMe_3)_3$

Important structural parameters of homoleptic tetraorganyldielement(4) compounds are summarized in Table III. Interestingly, the comparison of homologous compounds, e.g., the bis(trimethylsilyl)methyl derivatives **52–54** or the triisopropylphenyl compounds **55**, **56**, and **58**, shows that the Al–Al single bonds are longer than the bonds between the heavier Ga atoms by 12 pm on an average (~5%). The shorter Ga–Ga bonds may be caused by the relatively small covalent radius of gallium. It is the first element behind the first transition metal period, and hence some contraction of the electron shell may result. Furthermore, electrostatic effects may influence the bond properties to a considerable extent, because gallium is more electronegative than aluminum. Thus, a lower charge separation has to be expected for the Ga–C compared to the Al–C bonds, which results in lower positive charges located at the central Ga atoms. As a consequence, elongation of the E–E bonds by electrostatic repulsion may be considerably stronger in the dialuminum compounds. The expected continuous increase of the E–E bond lengths was finally observed for the series Ga–Ga, In–In, and Tl–Tl. Only one exception was found for the compounds **63** [In–In 293.8(1) pm] and **66** [Tl–Tl 288.1(2) pm; $R = SiPh(CMe_3)_2$]; no explanation was given in the respective reference.[126] Furthermore, the E–E bond lengths depend on the kind of substituents. The alkyl groups $CH(SiMe_3)_2$ gave longer distances than the aryl substituents $i\mathrm{Pr}_3C_6H_2$ and $(CF_3)_3C_6H_2$, the last, most electron withdrawing one gave the shortest bonds. The longest E–E distances were observed with silyl groups attached to the central Al, Ga, In, or Tl atoms.

The dependence of the E–E bond lengths on the nature of the substituents has been explained merely by steric effects. However, it seems more likely that a balanced interaction of steric effects, charge separation, electrostatic repulsion, rehybridization etc., causes the observed variation. In contrast to the amido compounds discussed above, a specific correlation between the E–E bond lengths and the bond angles (C–E–C or Si–E–Si) does not exist. The different influence of alkyl and silyl substituents was investigated by quantum-chemical calculations.[91]

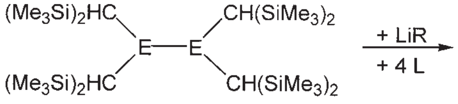
Theory predicted (see below) that the staggered arrangement of the substituents is the energetically most favorable one. However, the experimentally determined torsion angles across the E–E bonds (Table III) show a more or less strong deviation from that conformation in many cases. The bis(trimethylsilyl)methyl compounds **52–54**, for instance, possess an almost planar molecular E_2C_4 core with torsion angles close to 0°, which at a first glance seems to be most unfavorable. That unusual structure may be caused by the particular symmetry of the $CH(SiMe_3)_2$ groups, which favors an arrangement with the hydrogen atom attached to the α-carbon atom of the first ligand pointing between both trimethylsilyl groups of the neighboring ligand. Owing to such an arrangement of all substituents, the four α–C–H bonds are almost exactly in the molecular plane, and the C–Si bonds to the inner carbon atoms adopt an optimum position for which hyperconjugation with the empty p-orbitals of the central atoms could be expected. The torsion angles between these Si–C σ-bonds and the empty p-orbitals do not become larger than 30°. Thus, the singular molecular conformation may be stabilized by steric interactions and may further be favored by some electronic contributions. Indeed, there are indications from UV/Vis spectroscopy that electronic delocalization may occur. The molecular structure should result in chemically different substituents; however, no splitting of resonances was observed in the NMR spectra even at low temperature.[6,118,119] In contrast, the tri(isopropyl)phenyl compounds **55**, **56**, and **58** adopt a conformation which is intermediate between an ideal staggered or eclipsed form and have torsion angles of 44–48°. An approach to the ideal staggered form was observed for the remaining compounds, in particular the silyl derivatives show torsion angles near 90°.

All these dielement compounds are colored, with the color strongly depending on the atomic masses of the elements and on the substituents. The alkyl derivatives are pale yellow (**52**, Al–Al), yellow (**53**, Ga–Ga), and orange-red (**54**, In–In), almost the same holds for the aryl derivatives **55–59**. The silyl compounds have red to dark green colors. A bathochromic shift was observed for the characteristic absorptions in the UV/Vis spectra of all homologous compounds on going to the heavier element, furthermore shifts to longer wavelengths correlate to the increasing torsion angles R–E–E–R across the E–E bonds.

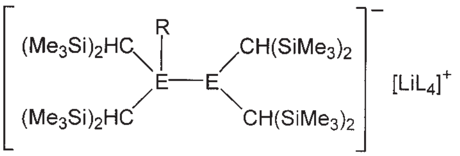
Quantum-chemical calculations on the model compounds dialane(4) Al_2H_4[36,135–143] and digallane(4) Ga_2H_4[91,136,138] were conducted in great number. The most stable configurations are not those involving an E–E single bond, but the mixed-valent ionic forms $E^+[EH_4]^-$ containing an atom of the element in an oxidation state +1 coordinated to the anion by bridging a face or an edge of the EH_4 tetrahedron. Both coordination modes have comparable energies. The molecules $H_2E–EH_2$ possessing an E–E bond were calculated to be considerably less stable. Their staggered D_{2d} form is energetically slightly more favored than the planar, eclipsed (D_{2h}) one, however, the rotation barriers are small. Only few alkyl or aryl substituted compounds were calculated, such as $Me_2Al–AlMe_2$,[33] $Ph_2Al–AlPh_2$,[144] and $Me_2In–InMe_2$.[145] The obtained E–E distances are in very good agreement with those determined by crystal structure determinations. Tetraphenyldialane(4) was analyzed with respect to its preferred conformation. Once again the most favorable structure is the staggered form with a torsion angle C–Al–Al–C of 85°, which significantly deviates from the angle of 44.8° experimentally determined for the tetraaryl derivative **55**. A compound bearing miscellaneous substituents, [Cp*(H)Al–Al(H)Cp*], was investigated by quantum-chemical methods. It has an η^5-Cp* ligand and an overall *trans*-bent configuration.[146]

B. *Dielement(5) and Dielement(6) Compounds*

The tetraalkyl, tetraaryl, and tetrasilyl dielement(4) compounds described in the preceding chapter contain tri-coordinated Al, Ga, In, or Tl atoms and hence are potentially useful as bifunctional Lewis acids. The monoadducts **68** and **69** still possessing intact Al–Al bonds were formed by the reaction of tetraalkyldialane(4) **52** with methyllithium[147] or lithium bromide[148] in the presence of the chelating ligand TMEDA for the complexation of the lithium ions [Eq. (13)]. Ethyllithium[149] and *tert*-butyllithium[147] afforded the hydrido compound **70** by β-elimination. Analogous gallium or indium compounds could not be isolated so far. Ethyllithium, for instance, reduced the gallium compound and afforded a radical anion containing a 1e-Ga–Ga π-bond.[150] The alkynido derivatives **71** (E = Ga) and **72** (E = In, [Eq. (13)]) were obtained by the treatment of the dielement(4) compounds **53** and **54** with lithium alkynides.[151] These reactions, too, are nice examples for the different behavior of the aluminum compound and its heavier homologues, which despite their narrow structural relationship often result in the formation of different secondary products. Under conditions similar to those required for the formation of **71** and **72**, the insertion of the alkynido group into the Al–Al bond was observed, which resulted in the isolation of a three-membered AlC_2 heterocycle with an exocyclic tri-coordinated Al atom and some evidence for a non-classical bonding situation.[152]



52: E = Al
53: E = Ga
54: E = In



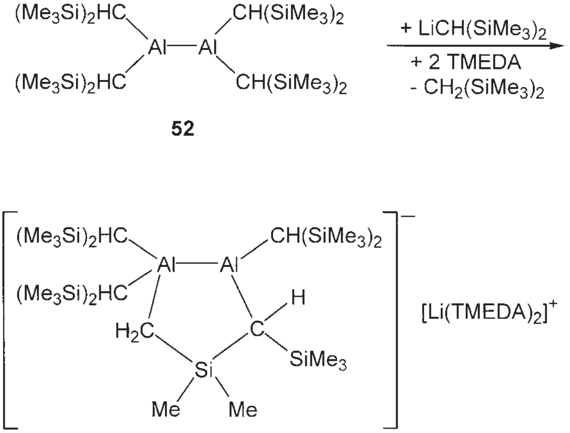
(13)

68: E = Al, R = CH_3, L = 1/2 TMEDA
69: E = Al, R = Br, L = 1/2 TMEDA
70: E = Al, R = H, L = 1/2 TMEDA
71: E = Ga, R = C≡C−Ph, L = THF
72: E = In, R = C≡C−Ph, L = 1/2 TMEDA

As schematically shown in Eq. (13), the additional ligands unexpectedly do not occupy a bridging position between both third main-group atoms via 3c-2e bonds, and even the bromine atom does not bond to the second atom of the E–E bond by one of its lone pairs. Instead, a terminal coordination was determined, and coordination numbers of three and four are realized on neighboring Al, Ga, or In atoms. The reason for that behavior may be a balanced bonding situation. The E–E distances would allow the formation of bridges, because they are close to those observed for $(AlMe_3)_2$ or for dimeric hydrides of these elements.[153] However, the presence of the E–E bond would result in acute bond angles E–E–R in the bridged molecules. On the other hand, some stabilization may arise from hyperconjugation, because the bis(trimethylsilyl)methyl groups attached to the tri-coordinated atoms adopt an arrangement similar to that described above with an optimum position of the α–C–Si bonds to overlap with the empty p-orbitals.

The substituents of the coordinatively saturated, tetra-coordinated atoms are arranged in a less ordered fashion. The bromine derivative **69** is unstable in solution and dissociates by the formation of its constituents. The Al–Br bond is long (248 pm) compared to values usually observed (220 to 230 pm), indicating weak coordinative bonding. The remaining derivatives do not show a similar dramatic elongation of their E–R bonds. The E–E distances are only slightly changed compared to those of the starting compounds (Table III; **69**: 264.3(4); **70**: 266.7(3); **71**: 255.8(1); **72**: 285.34(4) pm). Only the methyl derivative **68** shows a strong lengthening of its Al–Al bond from 266.0(1) to 275.2(3) pm, which is in accordance with its low stability in solution at room temperature. Owing to the particular structures of compounds **68–72** chemically different $CH(SiMe_3)_2$ substituents should result in the NMR spectra. With the exception of **68**, however, fast exchange processes led to one resonance at room temperature, and only at very low temperatures the expected splitting was observed.

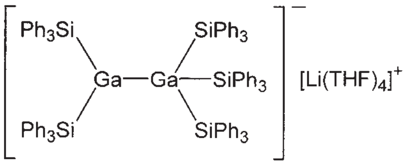
Deprotonation of the dialuminum compound **52** with the sterically highly shielded base $LiCH(SiMe_3)_2$ afforded the remarkable heterocyclic dialanate(5) **73**, in which the Al–Al bond is part of an Al_2C_2Si ring [Eq. (14)].[149] Clearly, the formation of an adduct is prevented here by steric repulsion. Instead, the base attacks a methyl group at the periphery of the molecule to yield a carbanion which is stabilized by a co-ordinative interaction with one of the Al atoms to give the non-planar five-membered ring. Once again the Al–Al bond length [266.5(3) pm] corresponds well to that of the starting compound **52**. The protons in α-position to the tri-coordinated aluminum atom show an extreme difference of their chemical shifts of 1.75 ppm. This is caused by their different arrangement with respect to the empty p-orbital. One ($\delta = -1.27$, ring) is parallel to that orbital, while the other one ($\delta = 0.48$, intact substituent) is localized in its nodal plane.



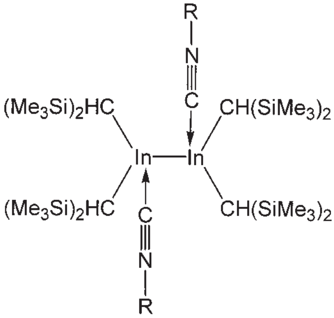
73

(14)

A pentasilyldigallanate(5) (**74**) was obtained in low a yield by the reaction of "GaI" (see above) with $LiSiPh_3$.[154] The Ga–Ga distance [254.6(7) pm] is slightly shorter than that of the tetrakis[tris(trimethylsilyl)silyl] derivative **61** (Table III), which has been explained by a stronger steric repulsion between the much bulkier substituents of **61**. As expected, the dielement(5) compounds **68–73** show the longer terminal bonds at the saturated, tetra-coordinated central atoms, only in the diindium derivative **72** the difference is negligibly small. Interestingly, the reverse was observed for the pentasilyldigallium compound **74**, for which the longest Ga–Si bonds were found at the tri-coordinated gallium atoms. Quantum-chemical calculations conducted on the model compound $[Ga_2H_5]^-$ revealed a significant contribution of hyperconjugation, in particular between the Ga–Ga σ-bond and the antibonding orbitals of the Ga–H bonds at the tri-coordinated Ga atom. The interaction weakens the Ga–H bonds at this position and hence was taken as an explanation for the particular structural parameters of **74**. Further quantum-chemical calculations on $[E_2R_5]^-$ anions were reported in References 140 and 154.



74



75: R = CMe_3, Ph

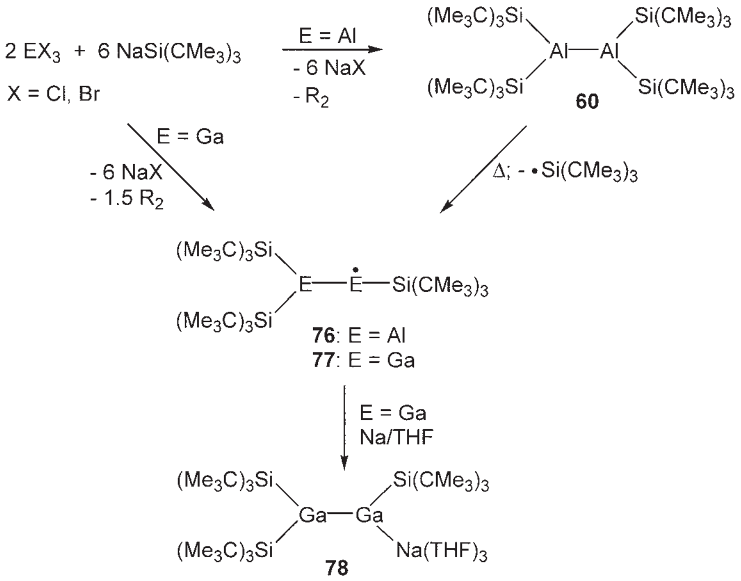
While the addition of one ligand to an atom of the E–E bonds in tetraorganyl dielement(4) compounds is quite common now, structurally authenticated bisadducts involving both Lewis-acidic central atoms are extremely rare. The formation of those adducts containing two anionic ligands such as carbanions may be strongly disfavored because of electrostatic repulsion and by the accumulation of negative charge in the hypothetical products. Nevertheless, the syntheses of those bisadducts were claimed in literature, however, the characterization was poor in all cases. In 1936 the reaction of $GaMe_3$ with Na in liquid nitrogen was reported to yield hexamethyldigallanate(6) $[Me_3Ga–GaMe_3]^{2-}$, the product was characterized by the secondary reaction with NH_4Br and the evolution of H_2.[155]

The similar reaction of triisobutylaluminum with potassium should give $K_2[i\text{Bu}_3\text{Al–Al}i\text{Bu}_3]$, which was characterized by a protolysis reaction and NMR spectroscopy.[156] A reinvestigation showed that actually the aluminum(III) compound $K[\text{Al}i\text{Bu}_4]$ had formed, which has identical chemical shifts in the NMR spectra compared to those reported for the hypothetical dialanate(6).[157] The formation of elemental hydrogen upon hydrolysis in all these doubtful cases may be caused by finely dispersed elemental aluminum. Brown substances were generally obtained in these reactions which require a thorough and repeated purification to finally isolate the pure and colorless products. The dialane(4) $i\mathrm{Bu}_2\mathrm{Al}$–$\mathrm{Al}i\mathrm{Bu}_2$ and its true constitution were discussed in Section VI.A. Nevertheless, several reports exist which formulate the rather doubtful adducts of that compound with THF[156] and hydride ions.[158] The last ones have been identified as aluminum(III) hydrides in Reference 159. Quantum-chemical calculations on the model compound $[H_3Ga–GaH_3]^{2-}$ verified an ethane like geometry for these dianions with weak Ga–Ga single bonds.[160,161] Furthermore, different structures of the B_4H_{10} analogous adducts of $H_2Ga–GaH_2$ with two equivalents of BH_3 or GaH_3 were calculated by *ab initio* methods. Similar energies were obtained for the butterfly structure known for the boron compound and for those molecules which have the ligands in a terminal arrangement with non-supported Ga–Ga bonds and tetra-coordinated Ga atoms in their molecular centers.[162]

The coordination of both atoms of an E–E single bond by Lewis-bases has been represented so far only by the singular isonitrile adducts **75**. They were obtained by the reaction of the diindium compound **54** with an excess of phenyl and *tert*-butyl isonitrile.[163] The In–In bond lengths [284.8(1) pm in both cases] are only slightly lengthened compared to that of the starting compound (282.8 pm), while the In–C bonds to the isonitrile ligands are very long (>240 pm) indicating a weak coordinative bonding. Accordingly, the products dissociate completely upon dissolution in isonitrile free solvents. The expected ethane-like staggered arrangement with the isonitrile groups in *trans* positions (schematically shown in **75**) was observed for the *tert*-butyl derivative. In contrast, an eclipsed conformation with neighboring aromatic groups was determined for the phenyl compound. The structure may be caused by an interaction between both parallel phenyl rings (shortest C–C distance 371 pm). Also these reactions with isonitriles reflect the very interesting differences in the chemical behavior in the homologous series of the tetraalkyldielement(4) compounds **52–54**. While the larger indium atoms gave the bisadducts with retention of the In–In bond and no evidence for an insertion reaction, one or two isonitrile carbon atoms were inserted into the Al–Al or Ga–Ga bonds of the dialuminum and digallium homologues upon treatment with isonitriles even at low temperature.[164]

C. *Trisilyldielement Compounds—Radicals and Anions*

As mentioned before (Section VI.A, [Eq. (12)]), the reactions of $AlBr_3$ or $InCl_3$ with $NaSi(CMe_3)_3$ afforded tetrasilyl compounds possessing Al–Al or In–In bonds (**60** and **62**). Interestingly, the corresponding digallium derivative could not be isolated under similar conditions, instead a trisilyldigallium radical (**77**, [Eq. (15)]) had spontaneously been formed by the homolytic cleavage of a Ga–Si bond.



(15)

A similar product was obtained with aluminum on warming of the corresponding tetrasilyldielement(4) compound to 50 °C [Eq. (15)].[131–134] At a first glance, these remarkable radicals are strongly related to the tetraorganyl compounds and are worth mentioning here. However, EPR spectroscopy revealed that the unpaired electron occupies a π-orbital and that the E–E bond may best be described by some multibonding interactions. Thus, the detailed discussion of these compounds is beyond the topic of this review. Same holds for an anionic derivative (**78**, [Eq. (15)]) obtained by the reduction of **77** with sodium.[131] Quantum-chemical calculations on $[Al_2H_3]^-$ verify that interpretation.[140,165]

D. *Organodielement Halides*

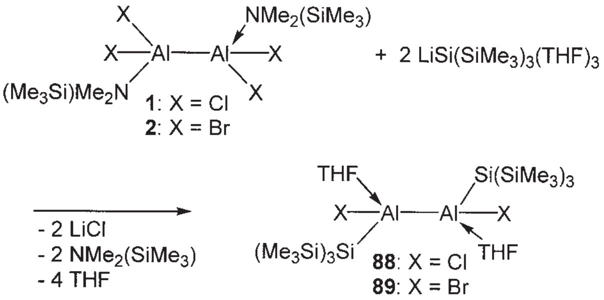
Structurally characterized dielement halides containing E–E and E–C or E–Si bonds are summarized in Table IV. Three different types of compounds may be distinguished: (i) Derivatives which are monomeric even in the solid state and contain coordinatively unsaturated, tri-coordinated

TABLE IV
ORGANODIELEMENT HALIDES (E–E DISTANCES IN pm)

		E–E	Ref.
$\{(Me_3Si)_3C\}(I)Ga–Ga(I)\{C(SiMe_3)_3\}$ **79**	monomeric	240.1(1)	166
$(tBu_3C_6H_2)(Cl)Ga–Ga(Cl)(tBu_3C_6H_2)$ **80**	monomeric	243.8(6)	167
$(Dipp_2C_6H_3)(I)Ga–Ga(I)(Dipp_2C_6H_3)$ **81**	monomeric	249.3(2)	168,169
$(Trip_2C_6H_3)(I)Ga–Ga(I)(Trip_2C_6H_3)$ **82**	monomeric	248.2(2)	169
$[(tBu_3Si)(Cl)Ga–Ga(Cl)SitBu_3)]_2$ **83**	dimeric	254.7 (av.)	170
$[\{(Me_3Si)_3Si\}(Cl)Ga–Ga(Cl)\{Si(SiMe_3)_3\}]_2$ **84**	dimeric	250.5 (av)	127
$[\{(Me_3Si)_3Si\}(Br)Ga–Ga(Br)\{Si(SiMe_3)_3\}]_2$ **85**	dimeric	251.5	171
$[\{(Me_3Si)_3C\}(Cl)In–In(Cl)\{C(SiMe_3)_3\}]_2$ **86**	dimeric	282.4 (av.)	172
$[\{(Me_3Si)_3C\}(Br)In–In(Br)\{C(SiMe_3)_3\}]_2$ **87**	dimeric	284.5 (av.)	172
$[\{(Me_3Si)_3Si\}(Cl)(THF)Al–Al(THF)(Cl)\{Si(SiMe_3)_3\}]_2$ **88**	adduct	258.8(2)	173
$[\{(Me_3Si)_3Si\}(Br)(THF)Al–Al(THF)(Br)\{Si(SiMe_3)_3\}]_2$ **89**	adduct	262.8(2)	173
$[(tBu_3C_6H_2)(Cl)Ga–GaCl_3][Li(THF)_4]$ **90**	adduct	242.2(3)	167
$[\{(Me_3Si)_3Si\}Br_2Ga–GaBr_2\{Si(SiMe_3)_3\}][Li(THF)_2]_2$ **91**	adduct	247.7(1)	174
$[\{(Me_3Si)_3Si\}I_2Ga–GaI_2\{Si(SiMe_3)_3\}][Li(THF)_2]_2$ **92**	adduct	249.7(4)	174
$\{(NMe_2)_2C_6H_3\}(Cl)In–In(Cl)\{(NMe_2)_2C_6H_3\}$ **93**	adduct	271.6(1)	175

central atoms (**79–82**) must be stabilized by very bulky substituents;[166–169] (ii) Sterically less shielded compounds give dimers via four E–X–E bridges (**83–87**);[127,170–172] (iii) Stabilization may also be achieved by adduct formation and saturation of the central Group 13 atoms with donors such as halide ions, ether molecules, or amino groups (**88–93**).[173–175]

An obvious access to these organodielement halides is the treatment of subhalides already containing the E–E bond with two equivalents of an organolithium compound. As an example the reaction of the dialuminum subhalides **1** and **2** with $LiSi(SiMe_3)_3$ is shown in Eq. (16).[173] In these cases the molecules are stabilized by co-ordination of a THF ligand to each Al atom of the E–E bond. The dimeric digallium compound **84** was obtained by a similar route starting with $Ga_2Cl_4(dioxane)_2$ **6**.[127] A stable adduct is not formed here, dimerization occurred instead with all chlorine atoms adopting a bridging position. The very bulky tri(*tert*-butyl)phenyl group of the monomeric compound **80** prevented the dimerization by steric shielding. Compound **80** was obtained by the reaction of **6** with the corresponding aryllithium derivative in a 1 to 2 molar ratio, equimolar quantities of the starting materials yielded the LiCl adduct **90**.[167] A dianionic adduct with two bromine atoms (**91**) attached to each Ga atom of the Ga–Ga bond was realized by the reaction of $LiSi(SiMe_3)_3$ with $Ga_2Br_4(dioxane)_2$ **12**.[174] Both lithium counter ions are coordinated by two bromine atoms and two THF molecules.



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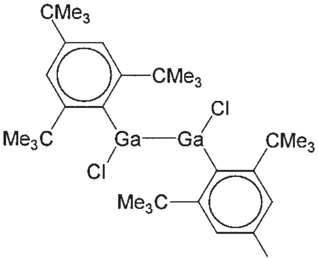

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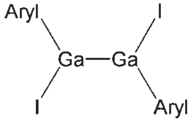
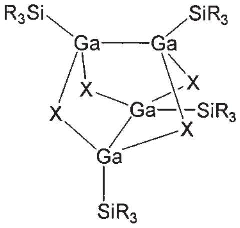
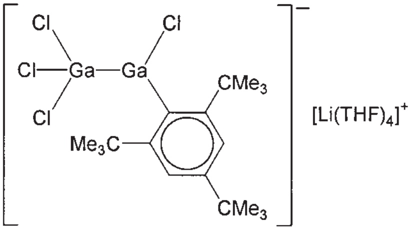


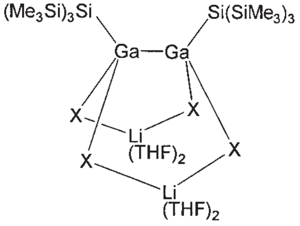
81: Aryl = 2,6-Dipp$_2$C$_6$H$_3$,
Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$
82: Aryl = 2,6-Trip$_2$C$_6$H$_3$,
Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$



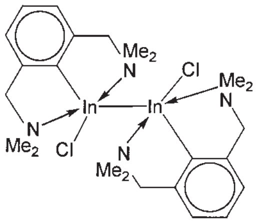
83: X = Cl, R = CMe$_3$
84: X = Cl, R = SiMe$_3$
85: X = Br, R = SiMe$_3$



90



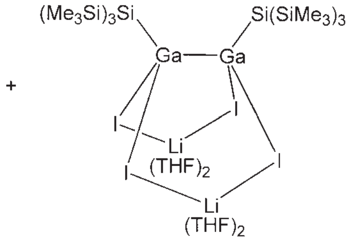
91: X = Br
92: X = I



93

The second method often employed for the synthesis of diorganodielement halides starts with the subhalides GaBr or "GaI". The dielement compounds result from disproportionation, and most of these products were isolated in low yields only. The synthesis of the lithium iodide adduct **92** starting with "GaI" is shown in Eq. (17).[174] Elemental gallium and a gallium(III) compound were formed as by-products. The same procedure was employed for the synthesis of the monomeric digallium diiodides **81** and **82**, which bear the bulky aryl substituents 2,6-bis(2,6-diisopropylphenyl)phenyl ($\mathrm{Dipp_2C_6H_3}$) or 2,6-bis(2,4,6-triisopropylphenyl)phenyl ($\mathrm{Trip_2C_6H_3}$).[168,169] The dimeric compound **85** was obtained by the reaction of the corresponding silyllithium derivative with metastable GaBr.[171]

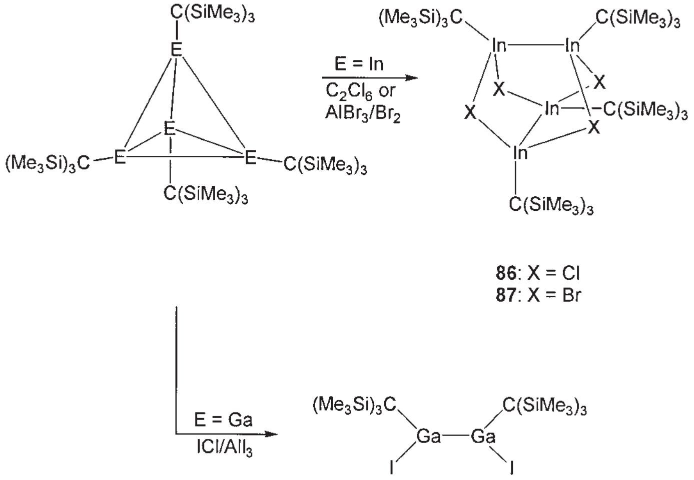
$$\text{"GaI"} + \mathrm{Li(THF)_3Si(SiMe_3)_3} \longrightarrow \mathrm{Ga} + [\mathrm{(Me_3Si)_3Si{-}GaI_3}][\mathrm{Li(THF)_3}]$$



(17)

92

Careful oxidation of clusters formed by the elements gallium and indium in an oxidation state +1 such as $\mathrm{E_4[C(SiMe_3)_3]_4}$ (E = Ga, In) offers another facile route for the synthesis of organoelement subhalides in reasonable yields. Suitable reagents are halogen donors such as $\mathrm{C_2Cl_6}$, mixtures of the halogens with the corresponding aluminum halides or ICl in the presence of $\mathrm{AlI_3}$ [Eq. (18)].[166,172] The formation of dimers (**86** and **87**) with all halogen atoms in bridging positions was observed for the larger In atoms, while monomers (**79**) were detected with the smaller Ga atoms. The reduction of an organoelement(III) dihalide by an alkali metal was used in one case only (**83**). Compound **83** may be considered as an intermediate product, and indeed, further reduction with excess sodium or potassium afforded the cluster compounds $\mathrm{Ga_4R_4}$ and $\mathrm{[Na(THF)]_2Ga_4R_4}$ [$\mathrm{R = Si(CMe_3)_3}$].[170] The dilithium salt of diisopropyl aminoborole was used as a reducing agent in a similar reaction of an organoindium(III) dichloride. The monomeric product (**93**) is stabilized by the intramolecular coordination of the indium atoms by two nitrogen atoms of the substituents.[175]



86: X = Cl
87: X = Br

79

(18)

The E–E distances (Table IV) are intermediate between those of the dielement tetrahalides (Table I) and those of the corresponding tetraorganyldielement(4) derivatives (Table III). As expected, the shortest distances were detected for the monomers. A slight lengthening of the E–E bonds results on going from chlorine to bromine or iodine. Three of the four known monomeric digallium dihalides (**80–82**) are planar in the solid state, which may be caused by steric repulsion between the very bulky substituents. Interestingly, the alkyl compound **79** shows a staggered conformation with a torsion angle I–Ga–Ga–I of 93.3°. Thus, the Ga–I bond at one gallium atom is almost ideally perpendicular to the plane around the second gallium atom and is parallel to the empty p-orbital of the second atom. In accordance with results of quantum-chemical calculations[166] that particular conformation gave the shortest Ga–Ga distance (240.1 pm) of these dihalides. Hyperconjugation across the Ga–Ga bond does not seem to be important here as a stabilizing effect. The E_4X_4 cages of the dimeric compounds show some similarities to the structure of the As_4S_4 cage of the mineral Realgar. In contrast to the more or less intensively colored tetraorganyldielement(4) compounds **52–67** most of the dihalides **83–93** possessing tetracoordinated central atoms are colorless.

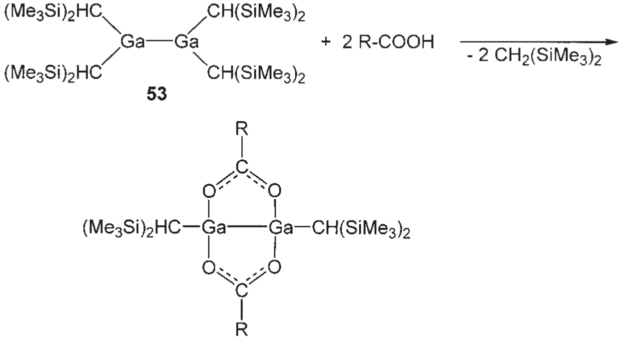
E. *Dialkyldielement Compounds Containing Oxo or Sulfur Ligands*

Substituent exchange reactions with the tetraalkyldielement compounds **52–54** by retention of the E–E bonds should open an easy access to further dielement derivatives. However, whenever these dielement compounds were treated with alcohols or amines to replace an alkyl group, the formation of H_2 and the cleavage of the E–E bonds by oxidation of the central atoms was observed. Finally, proton donors were employed which possess chelating residues in order to stabilize the E–E bonds by coordinative saturation of the central atoms. Once again, the aluminum(II) and indium(II) atoms of **52** and **54** were oxidized.[176] The dialuminum derivative **52** and one equivalent of benzoic acid gave the product $R_2Al(\mu\text{-}H)(\mu\text{-}O_2C\text{–}Ph\text{–}O,O')AlR_2$ [$R = CH(SiMe_3)_2$], in which both Al atoms are bridged by a hydride anion and a carboxylato ligand, while a cage compound, $RIn(\mu\text{-}O_2C\text{–}Ph\text{–}O,O')_4InR$, with four benzoato ligands bridging two indium(III) atoms was obtained by the treatment of diindane(4) **54** with an excess of benzoic acid.[176] In contrast, substituent exchange by retention of the Ga–Ga bond succeeded when digallane(4) **53** was treated with carboxylic acids, which once again gives a very nice evidence for the particular role of gallium in third main-group chemistry.

Complete consumption of the yellow digallium starting compound **53** was only achieved when two equivalents of the carboxylic acids were employed, and two alkyl groups of different gallium atoms were replaced by chelating carboxylato ligands in all cases [(Eq. (19)].[177–180] The colorless products **94–99** were isolated in almost quantitative yields (up to 95%), and as a remarkable difference to the dialuminum or diindium compounds the cleavage of the Ga–Ga bond was not observed even as a minor side reaction. No differences in synthesis or thermal stability of the products occurred with respect to the kind of the acid employed. Thus, steric shielding does not play a determining role, instead, the disproportionation as a possible route for decomposition is prevented by the coordinative saturation of the Ga atoms.

Molecular structures, unusual for main group chemistry, were determined in which the Ga–Ga bonds are bridged by both of the carboxylato ligands. Ga–Ga distances in a very narrow range at about 238 pm resulted, which are short even compared to those observed for the subhalides summarized in Tables I and II. Clearly, an essential part of the shortening of the Ga–Ga bonds in comparison to that of the starting compound **53** (254 pm) is caused by the bridging with the carboxylato groups. The molecules are not flat, as schematically shown in Eq. (19), but the carboxylato ligands are almost ideally perpendicular to one another with O–Ga–O angles of about 91 to 93°. Furthermore, the C–Ga–Ga–C groups approach linearity with Ga–Ga–C angles of approximately 160°.

As was shown by quantum-chemical calculations,[180] the orbitals at gallium involved in the Ga–O interactions essentially possess p-character. Thus, in a rough approach the bonding of these compounds may be described by sp-hybridized Ga atoms leading to a high s-character in the Ga–Ga bonds, which is in accordance with the shortening detected experimentally. Two p-orbitals remain at each gallium which are perpendicular to the Ga–Ga bond and determine the arrangement of the carboxylato ligands. Clearly, that particular structure is forced by the small bite of the carboxylato ligands. The terminal coordination of the gallium atoms by carboxylato groups was calculated to be rather unfavorable, in particular owing to the high energy required for the deformation of the O–C–O angle. The rigidity of the carboxylato group would result in close contacts between its inner carbon atom and the gallium atom, both of which bear a partial positive charge. Thus, considerable electrostatic repulsion may occur and may favor the observed constitution. The molecule containing bridging carboxylato groups was calculated to be 117 kJ/mol more favored than that with terminal groups. The diacetato derivative **94** is an excellent starting material for the synthesis of further digallium compounds by lithium acetate elimination (see below).

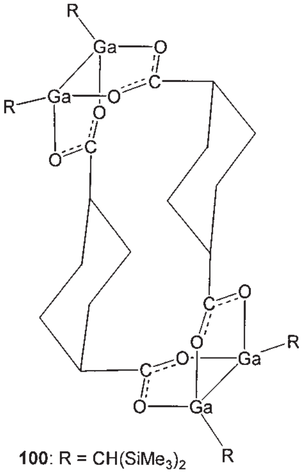


(19)

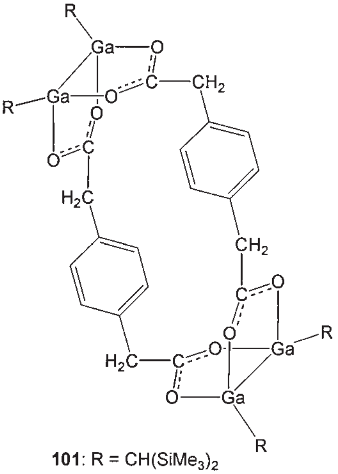
94: R = CH_3 **97**: R = C_6H_5
95: R = CMe_3 **98**: R = 4-Br-C_6H_4
96: R = Adamantyl **99**: R = 3,5-$C_6H_3Me_2$

Bifunctional dicarboxylic acids show a similar high selectivity upon reaction with the digallium compound **53**. Two bis(trimethylsilyl)methane molecules were released per each formula unit of **53**, and macrocycles with the dicarboxylato ligands bridging two or four digallium moieties were isolated in high yields (~80%). The structural motifs around the Ga–Ga bonds are indistinguishable from those of the dinuclear compounds **94–99** described before, hence the perpendicular arrangement of the carboxylates at the Ga–Ga bonds control the molecular self-assembly and the formation of the macrocycles. The degree of oligomerization and the nuclearity of the heterocycles formed depend on the rigidity of the backbone of the dicarboxylates. If they are flexible and not strictly linear, dimers are formed containing two Ga–Ga bonds, such as observed for cyclohexane dicarboxylic acid (**100**), phenylene diacetic acid (**101**), or the oligomethylene bridged dicarboxylic acids (**102** and **103**).[179] Rigid back bones like that of ferrocene dicarboxylic acid (**104**)[181] or muconic acid (**105**)[182] gave octanuclear macrocycles possessing four Ga–Ga bonds and up to 44 atoms in the ring (**106**, naphthalene dicarboxylic acid[183]). These reactions open the route for the facile synthesis of very large macrocycles containing cavities with diameters of more than to 2 nm. Usually, solvent molecules are enclosed in the heterocycles giving nice supramolecular aggregates. These large macrocycles may be suitable to act as hosts for organometallic molecules, for instance, after further functionalization.

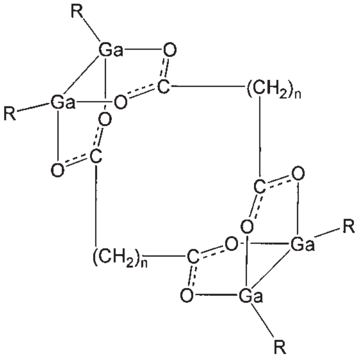
The carboxylates may be considered as three-atomic chelating ligands. A four-atomic chelate may be derived from tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), and indeed that acid gives a clean reaction with the tetraalkyldigallium compound **53** by the release of two equivalents of bis(trimethylsilyl)methane and formation of the yellow compound **107** in high yield. The tropolonato ligands adopt a terminal position at each Ga atom of the Ga–Ga bond [244.9(1) pm],[184] which is lengthened compared to the bonds of the bridged carboxylato derivatives described above by about 7 pm and which is in the expected range of unsupported bonds in dialkyldigallium compounds. Squaric acid may be described as bifunctional analogue of tropolone, and an octanuclear macrocycle (**108**), similar to **104–106**, was obtained on reaction with digallane(4) **53**.[182] Two pentane molecules were enclosed in its cavity.



100: R = $CH(SiMe_3)_2$

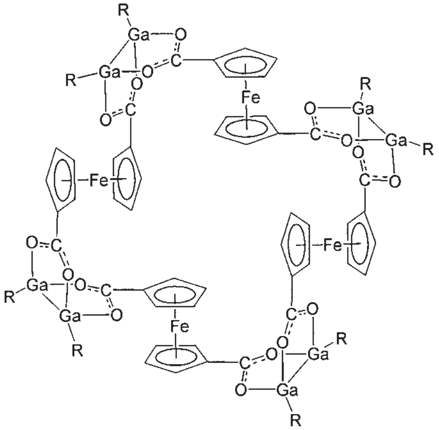


101: R = $CH(SiMe_3)_2$

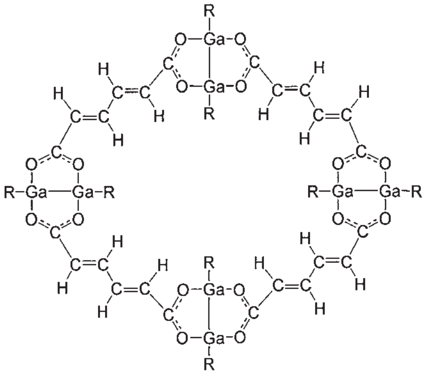


102: R = $CH(SiMe_3)_2$, n = 4
103: R = $CH(SiMe_3)_2$, n = 6

The Ga–Ga bonds (245.5 pm on average) of **108** are lengthened compared to those of the carboxylato bridged compounds by about 7 pm, which may be caused by the larger bite between the coordinating oxygen atoms. Furthermore, the Ga–Ga–C angles (139.7° on average) verify the more relaxed bonding situation and deviate from linearity more than those of the carboxylato compounds **95** to **106**.

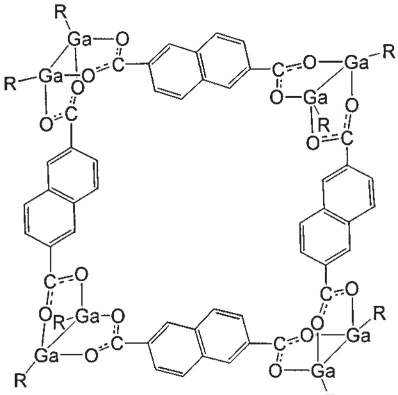


104: R = $CH(SiMe_3)_2$



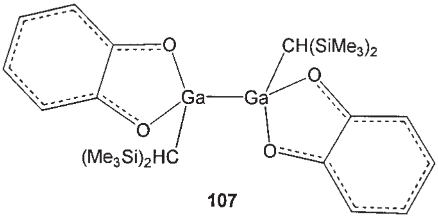
105: R = $CH(SiMe_3)_2$

Acetylacetonates, which have delocalized electronic π-systems including the atoms O_2C_3, form five-atomic chelates. Dialkyldigallium compounds (**109** and **110**) containing these ligands terminally attached to both Ga atoms of the Ga–Ga bonds are easily available by the reaction of dibenzoyl- or dipivaloylmethane with **53** similar to the reactions of the carboxylic acids shown in Eq. (19).[185,186] Centrosymmetric molecules were formed with the substituents in *trans* arrangement



106: R = CH(SiMe$_3$)$_2$

The Ga–Ga bond lengths are in the expected range (244 pm) for unsupported bonds bearing two alkyl groups beside two electronegative ligands. Different coordination modes were observed for the two analogous digallium compounds bearing the ligands imidotetraphenyldiphosphinate (**111**) or the corresponding sulfur derivative imidotetraphenyldithiodiphosphinate (**112**).[187]



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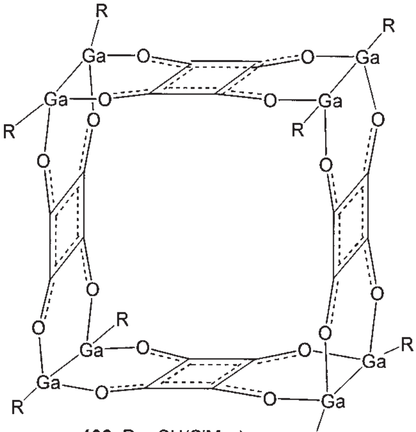
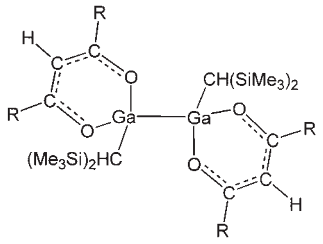
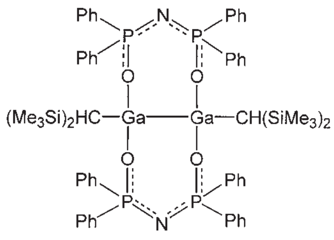


108: R = CH(SiMe$_3$)$_2$

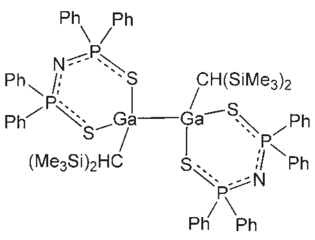
The oxo ligands adopt a bridging position, while a terminal arrangement was determined for the sulfur compound **112**. The O–Ga–Ga–O torsion angle of **111** (32°) verifies a strong deviation from the ideal eclipsed conformation observed for the carboxylato compounds. A synclinal conformation with a C–Ga–Ga–C torsion angle of –47.5° was found for compound **112**. The Ga–Ga bond lengths differ by about 4 pm with the shortest distance detected for the bridged compound (245.6(1) and 249.9(1) pm, respectively). The synthesis of **111** succeeded by treatment of the tetraalkyldigallium compound with the free acid. The product was, however, isolated in 27% yield only, and a mononuclear compound which was formed by the cleavage of the Ga–Ga bond was obtained as a main-component. This verifies the empirical rule that the stronger acids give the best results with respect to the substituent exchange, while surprisingly the weaker acids favor the cleavage of the Ga–Ga bond. Accordingly, the sulfur starting compound, the anion of which is less stabilized by delocalization and which is a weaker acid than the oxygen compound, does not give the substitution product with an intact Ga–Ga bond at all. The sulfur compound **112** was finally obtained by the reaction of the diacetatodigallium derivative **94** with the lithium salt of the ligand by precipitation of lithium acetate.



109: R = Ph
110: R = CMe$_3$



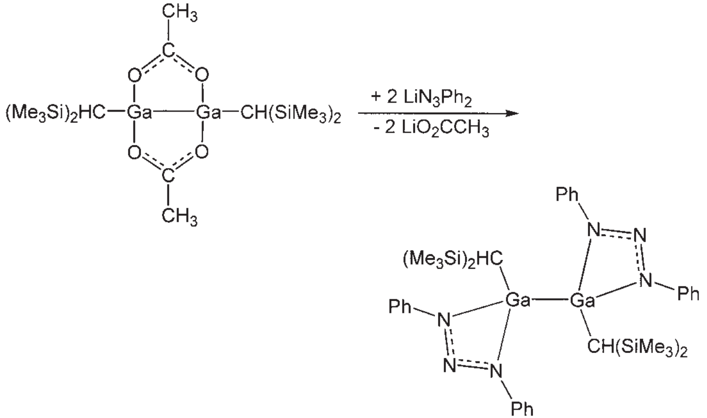
111



112

F. *Dialkyldielement Compounds Containing Nitrogen Ligands*

In accordance with the empirical rule just cited, the digallium compound **53** reacted with the very weak proton donor diphenyltriazene HN_3Ph_2 to yield a mixture of the products of substitution [$(Ph_2N_3)RGa$–$GaR(N_3Ph_2)$, **113**] and of Ga–Ga bond cleavage [$R_2Ga(N_3Ph_2)$].[188] The digallium compound **113** was subsequently obtained by the specific reaction of the di(μ-acetato)digallium compound **94** with LiN_3Ph_2 in an almost quantitative yield [Eq. (20)].[178] In contrast to the bridging carboxylato groups the chelating ligand diphenyltriazene is terminally attached to each Ga atom of the Ga–Ga bonds. The preference of the bridging coordination of carboxylato ligands is caused by the relatively large O–C–O angle (~ 125°), by the high energy which is required for its deformation, and by the electrostatic repulsion between the positively charged Ga and carboxylato C atoms (see above). Owing to the lone electron pair at the central N atom, the N–N–N angle is smaller even in the free triazenido ligand (114.6°), and the terminal coordination (angle N–N–N of the coordinated ligand 105.9°) requires a deformation energy of only 13 kJ/mol. Thus, a more relaxed bonding situation with an approach to sp^3-hydridized Ga atoms is realized.[178] The unsupported Ga–Ga bonds of **113** are longer than those of the carboxylato bridged molecules by about 8 pm [245.8(1) pm].[188] The higher flexibility of the triazenido group compared to the rigid backbone of the carboxylato ligand is further demonstrated by the structure of compound **114**, which was obtained by a reaction according to Eq. (20) with a 1 to 1 molar ratio of the starting compounds.[178] In that case, the resulting arrangement of the chelating ligands is determined by the strongly preferred coordination mode of the carboxylato group, and the triazenido ligand adopts also a bridging position across the Ga–Ga bond.



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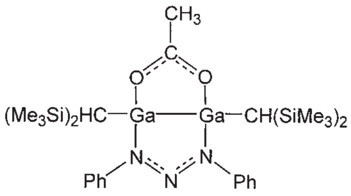

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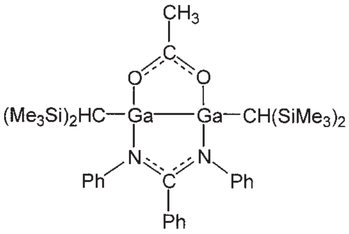

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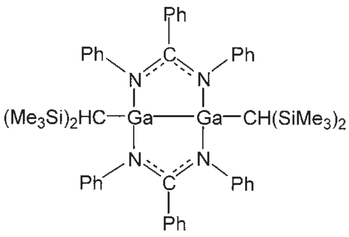

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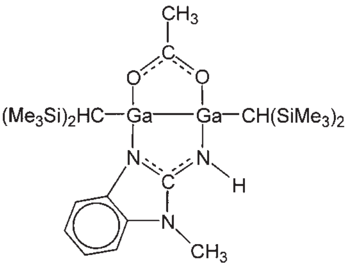

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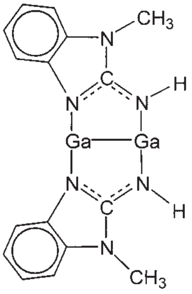
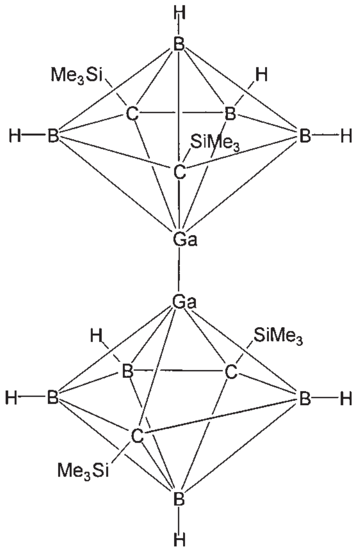


118

The facile route for the synthesis of digallium compounds bearing different ligands according to Eq. (20) was employed for the synthesis of further derivatives (**114–118**).[178,186] Compound **118** exists in *cis*/*trans* isomeric forms, the *cis* compound is shown here. The *trans* form with the phenylene groups on different sides of the molecule is thermally favored and was obtained as the major product on heating of the reaction mixture to 90 °C. These compounds (**113–118**) show the broad applicability of the substitution of Ga–Ga bonds and the great variability of accessible structures. It may be an interesting task for future work to introduce chiral ligands.

G. *Third Main-Group Elements and Hydrogen Atoms as Ligands*

In very few cases only the atoms of the E–E bonds are coordinated by third main-group elements. The reaction of 2,4-dicarba-*nido*-hexaborate(2-) with dimeric $(Me_3CGaCl_2)_2$ yielded a digallium compound (**119**) in a low yield, which has the Ga atoms coordinated by carbaborato ligands in an η^5-fashion with all Ga–C or Ga–B distances in a narrow range.[123] The Ga–Ga bond [234.0(2) pm] is very short. It is one of the shortest bond lengths reported for a Ga–Ga single bond in this review (233.3 pm in **35**), which was explained by a relatively low steric repulsion. However, it seems to be more probable that the hybridization of the Ga atoms with a high s-character in the E–E bond or a reduced electrostatic repulsion may cause that unusual shortening. So far, detailed quantum-chemical calculations are not available.



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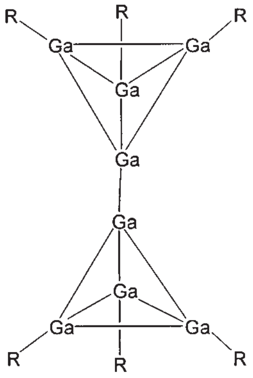
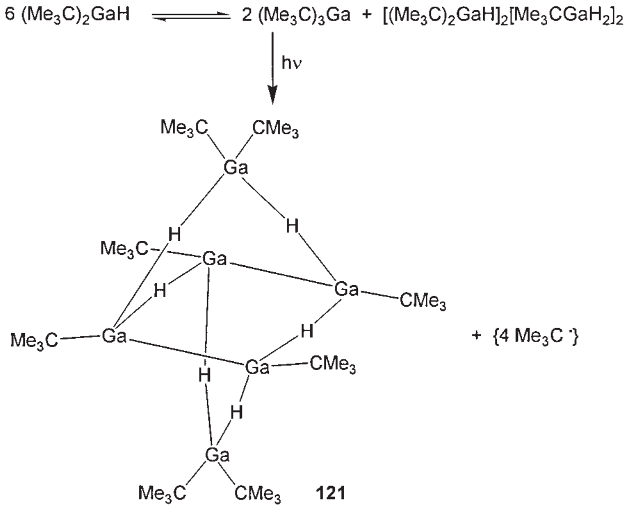


120: R = $C(SiMe_3)_3$

The second example of an E–E bond surrounded by Group13 elements is found in compound **120**, in which two tetrahedral Ga_4 clusters are connected by a Ga–Ga single bond.[189] This compound was obtained in small quantities by the reaction of the labile halide GaBr with the corresponding alkyllithium derivative. The Ga–Ga σ-bond [261.4(1) pm] in the core of the molecule is rather long and almost indistinguishable from the Ga–Ga distances in the clusters, which are in a narrow range between 260 and 265 pm. Force constants obtained by quantum chemical calculations verify a relatively weak Ga–Ga bond compared to that of Ga_2H_4, for instance. Weaker force constants were obtained for the Ga_4 clusters, in which the Ga–Ga interactions are determined by delocalized molecular orbitals.[189] The destabilization of the inner Ga–Ga single bond in **120** has been explained by the delocalization of electron density within both tetrahedral cluster fragments. Furthermore, steric repulsion between the bulky substituents may give some contribution to the experimentally observed lengthening.

A Ga–Ga bond coordinated by H atoms was found in compound **121**, which was synthesized by irradiation of a solution of $[(Me_3C)_2GaH]_3$ [Eq. (21)].[190] That hydride partially dismutates in solution to give the sesquihydride $[(Me_3C)_2GaH]_2[Me_3CGaH_2]_2$ and $Ga(CMe_3)_3$.[191] The mechanism of the formation of **121** is unclear, but homolytic cleavage of Ga–C bonds may initiate the reaction. The structure of **121** comprises a cage of six Ga and six H atoms. Two Ga–Ga bonds are connected by two H atoms to give a six-membered Ga_4H_2 heterocycle. Opposite Ga atoms of the ring are bridged by $(Me_3C)_2GaH_2$ ligands. The Ga–Ga distances are rather long (264.0 pm) although steric repulsion seems to be of negligible importance here. Some delocalization may be indicated here, and indeed a similar, but not identical structure was calculated for the isoelectronic *hypho*-borane B_6H_{14}.



121

(21)

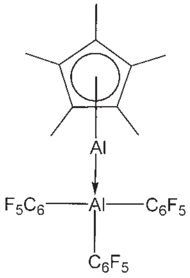
Ga–Ga and Tl–Tl bonds coordinated by manganese atoms were supposed to occur in some carbonylmanganese complexes.[192,193]

VII

E–E BONDS IN E^I–E^{III} ADDUCTS

Several monomeric organoelement(I) compounds of the elements Al, Ga, In, and Tl in an oxidation state +1 were described in recent literature. Examples are ECp*,[194] E–$C(SiMe_2R)_3$,[195] or tris(pyrazolyl)borate complexes of Group 13 elements.[196] These compounds have a lone electron pair at their central atoms and are suitable to act as Lewis-bases. Thus, a further method for the synthesis of compounds containing E–E single bonds comprises the treatment of those monomers with Lewis-acidic, coordinatively unsaturated compounds ER_3 of these elements in an oxidation state +3. RE → ER_3 adducts (**122–127**) were formed the E–E bonds of which may be described by strong donor–acceptor interactions. The products **122–125** were obtained by direct treatment of the element(I) derivatives ECp* with the corresponding element(III) compounds,[197,198] while the trispyrazolylhydroborato compounds **126** and **127** were formed by redox processes. The potassium salt of the borato ligand reacted with the subhalide "GaI" (see above) to yield **126** as a by-product of the gallium(I) complex not coordinated by GaI_3,[199] while it gave **127** upon treatment with InI_3.[200] The E–E distances [Al–Al 259.1(2) pm (**122**); Ga–Ga 242.45(3) (**123**), 243.7(2) (**124**), 250.6(3) pm (**126**); In–In 274.8(4) pm (**127**)] are shorter than those given in Table III for the symmetric tetraalkyl or tetraaryl dielement derivatives, but correspond well to those given in Table IV for organodielement compounds bearing at least two electronegative halide ligands. The cyclopentadienyl compounds are not linear, and the angles E–E–X (X = centroid of the η^5-cyclopentadienyl ring) deviate more or less significantly from the ideal value of 180°.

Obviously, these adducts RE → ER_3 are valence isomers of the tetraorganyl dielement compounds R_2E–ER_2. The reason for the occurrence and stability of these different molecular structures was investigated by quantum-chemical calculations.[137,201,202] Compared to the normal symmetric forms, the donor–acceptor compounds are electronically stabilized by π-donor groups (η^5-Cp*) or by coordinative saturation of one Ga or In atom by chelating ligands. A very bulky σ ligand should also be able to stabilize these forms, however, no such compound has been isolated so far. A complex of Al atoms with trimethylaluminum, which was also reported to contain an Al–Al bond and may occur in deposition processes of aluminum starting with $AlMe_3$, was detected by laser fluorescence technique and further investigated by *ab initio* calculations.[203] A semi-bridging methyl group and Al–Al bond lengths of 271–275 pm were predicted.



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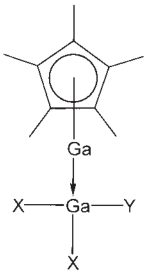
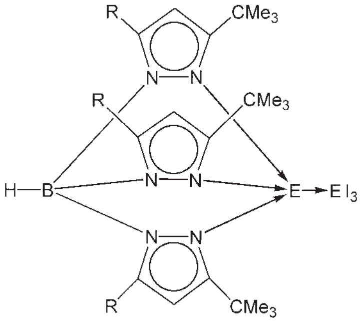


123: X = Cl, Y = η^1-Cp*
124: X = I, Y = η^1-Cp*
125: X = Y = CMe_3



126: E = Ga, R = CMe_3
127: E = In, R = H

VIII

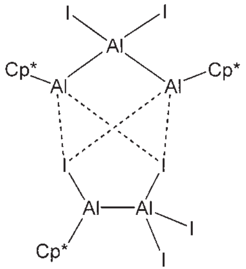
CHAINS AND RINGS

Branched and unbranched chains of Ga or In atoms embedded in inorganic matrices of O or Se atoms were reported in literature several times.[204–210] They are not discussed in detail here. The cluster compound $Al_4Cp^*_4$ reacted with AlI_3 to yield product **128**, in which an Al_2 moiety and an Al_3 chain possessing two Al–Al single bonds are connected by iodine atoms.[211] The formation of **128** was described by the insertion of monomeric AlCp* fragments into three Al–I bonds of the iodine bridged dimer $(AlI_3)_2$. The Al–Al bond lengths are in a narrow range between 252.2(7) and 253.8(7) pm and similar to those observed for some subhalides given in Table I. Owing to *ab initio* calculations, **128** was described as a contact ion pair. It decomposes slowly at room temperature by disproportionation to yield elemental aluminum.

Al atoms tetrahedrally surrounded by four Al atoms and connected to these atoms by Al–Al single bonds were observed for both constituents of the compound $[Al_5Br_8(THF)_4]^-[Al_5Br_6(THF)_6]^+$ (**129**).[212] The eight terminal Al atoms differ markedly in their coordination modes, six are coordinated by two Br atoms and one THF molecule, while two of the cation are attached to one Br atom and two THF molecules. The Al–Al distances observed for the anion and cation show only negligible differences and correspond well to those of the subhalides $(L)X_2Al–AlX_2(L)$ given in Table I. Compound **129** was obtained in a low yield by cocondensation of metastable AlBr with toluene and THF. It is stable up to 100 °C. The corresponding gallium–chlorine compound does not crystallize isostructurally, but has molecules of the composition $Ga_5Cl_7(OEt_2)_5$ (**130**).[213] The structure of the salt-like aluminum derivative **129** may be derived from that of **130** by the shift of one halogen atom from one formula unit to another. The inner Ga atom of **130** has an oxidation state of ±0, the terminal ones have +2 [three $GaCl_2(OEt_2)$ units] and +1 [one $GaCl(OEt_2)_2$ unit]. Owing to the different oxidation states, the Ga–Ga distances differ slightly, the shorter ones were observed for the bonds to the Ga^{II} atoms (about 242 pm). The remaining bond length is 245 pm. Compound **130** was obtained by a route similar to the synthesis of **129**, starting with metastable GaCl. The solid decomposes above 0 °C.

The easily available subhalide "GaI" (see above) has often been employed for the synthesis of unusual secondary products. Treatment with PEt_3 yielded the trigallium derivative $Ga_3I_5(PEt_3)_3$ (**131**) in moderate yield, which contains a chain of three Ga atoms.[28] Each Ga atom is coordinated by a triethylphosphane ligand, and the oxidation states are +2 (terminal Ga atoms) and +1 (inner Ga atom). The Ga–Ga bond lengths (245.6 pm on average) are as expected.

A chain of three Ga atoms was also determined for the silyltrigallium derivative **132**, which was obtained by the treatment of the trisilyldigallium monoanion **78** [Eq. (15)] with 18-crown-6.[131] According to the different chemical environment of the Ga atoms, the lengths of the Ga–Ga bonds differ [249.4(1) and 256.9(2) pm]. The shorter one belongs to the bond involving the formally anionic Ga atom, which further shows a secondary interaction to a methyl substituent of the GaR_2 group. A chain of three Ga atoms enclosed in a four-membered, butterfly shaped Ga_3Si heterocycle was found in the ionic silyl compound **133**.[214] The Ga–Ga distances are in the expected range (254.1 pm on average). It was obtained in a small yield upon treatment of the subhalide $Ga_2Cl_4(dioxane)_2$ **6** with the corresponding silyllithium compound.



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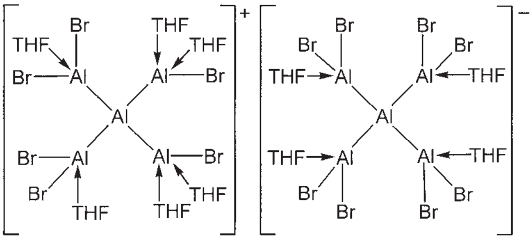

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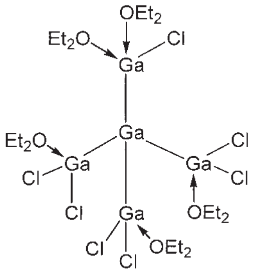
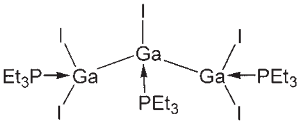
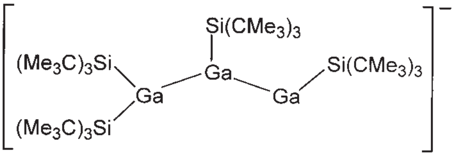


130



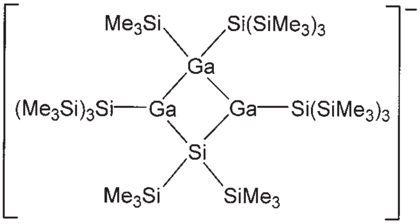
131

The trigallium compound **134** was isolated in a very low yield starting with "GaI" and triphenylgermyllithium.[154] It possesses a quite remarkable molecular structure, in which a gallium atom not attached to further ligands bridges two trigermylgallium moieties to yield a linear chain of three Ga atoms (angle Ga–Ga–Ga 178.8°). Despite the unusual coordination of the inner Ga atoms, the Ga–Ga distances (254.2 pm on average) do not deviate from the standard value. A further trigallium compound was postulated to be formed by the treatment of a highly shielded arylgallium dichloride [Aryl = 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$] with P(SiMe$_3$)$_3$.[215] The bulky aryl group of the inner Ga atom seems to be replaced by a hydrogen atom, and the terminal Ga atoms are bridged by two PH$_2$ groups. In contrast to all trigallium compounds mentioned so far, a non-symmetric Ga$_3$ chain was determined exhibiting a normal (251.5 pm) and a rather long Ga–Ga distance (277.8 pm).



$[Na(18\text{-crown-}6)(THF)_2]^+$

132



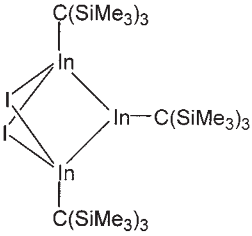
$[Li(THF)_4]^+$

133

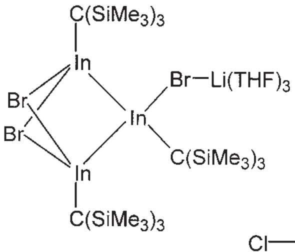
$[(Ph_3Ge)_3Ga\text{-}Ga\text{-}Ga(GePh_3)_3]^-$

$[Li(THF)_4]^+$

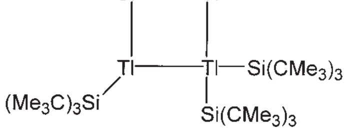
134



135

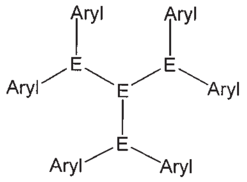


136

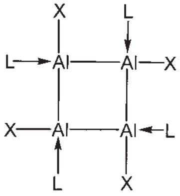


137

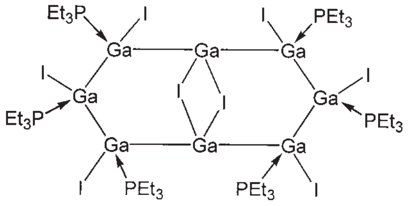
Organoelement halides containing chains of three In or Tl atoms were reported with three compounds (**135** to **137**). Compound **135** was isolated in a high yield by the partial oxidation of the tetraindium cluster $In_4[C(SiMe_3)_3]_4$ with a mixture of I_2/AlI_3.[216] It contains two coordinatively saturated terminal In atoms bridged by two iodine atoms, and one central unsaturated metal atom. The bromine compound **136** is a minor by-product of the synthesis of the starting tetraindium cluster.[217] Its structure is quite similar to that of the iodine compound **135**, but has all three In atoms with a coordination number of four. The thallium compound **137** was obtained by the reaction of $TlCl_3$ with the corresponding silylsodium derivative; and it crystallized as black crystals in a quite low yield after storing of a solution at –25 °C for six months.[218] In all three cases the lengths of the E–E single bonds correspond well to standard values (In–In: 281.5 and 282.1 pm, respectively, on average; Tl–Tl 291.8 pm).



Aryl = 2,4,6-triisopropylphenyl
138: E = Ga
139: E = In



140: X = Br, L = NEt_3
141: X = I, L = PEt_3
142: X = I, L = NEt_3



143

Star-like tetraelement compounds (**138** and **139**) containing a central coordinatively unsaturated Ga or In atom attached to three dialkylelement groups in a planar environment were obtained by the oxidation of the corresponding anions with dry air (**138**)[219] or by treatment of the tetraaryldiindium starting compound **58** with elemental lithium (**139**).[124]

The Ga–Ga (247.6 pm) and In–In bond lengths (269.6 pm) are shorter than those of corresponding tetraaryldielement derivatives containing isolated E–E single bonds.

Rings exclusively formed by E–E single bonds with the heavier elements of the third main-group are very rare (**140–142**).[220–222] They were obtained by the treatment of metastable solutions of aluminum monohalides with donor ligands or by ligand exchange in low yields. Each Al atom of the rings has a coordination number four, and the donor ligands occupy alternating positions above and below the molecular plane. In accordance with quantum-chemical calculations[220,223] the square rings are planar, and the Al–Al distances (260 to 265 pm) are significantly longer than those observed for the corresponding subhalides **1–5** (Table I) containing aluminum atoms in an oxidation state +2. This lengthening may simply be explained by the larger covalence radius of the Al atoms in an oxidation state of +1 in **140–142** compared to that of the higher valent atoms in **1–5**. The shortest distance was observed for the phosphane adduct **141**, which may be caused by a lower positive charge at the central Al atoms compared to that expected for the amino derivatives and, as a consequence, a lower electrostatic repulsion. An eight-membered octagallium ring was observed for compound **143**, which was obtained by cocondensation of metastable GaI and triethylphosphane.[29] It contains a planar ring. Six gallium atoms are coordinated by iodine atoms and phosphane ligands, while the two remaining ones in opposite positions are bridged by two iodine atoms. The Ga–Ga distances (247 pm on average) are longer than those of most of the subhalides given in Table I. Partial oxidation of **153** and insertion of two oxygen atoms in two opposite Ga–Ga bonds gave a Ga_8O_2 heterocycle in which two tetragallium chains are bridged by oxygen.[29]

IX

CONCLUDING REMARKS

Compounds containing E–E single bonds between the heavier elements of Group 13 received considerable interest in the last decades and developed to a broad field in current organoelement chemistry with a multitude of different formulas and types of structures. The first synthesis of a tetraalkyldielement(4) derivative in 1988 marked the starting point for many aspects of that chemistry and influenced the further development of organoelement chemistry with aluminum, gallium, indium, and thallium in unusual oxidation states to a considerable extent. Some of the first cluster compounds possessing these elements in an oxidation state +1 were obtained by disproportionation of unstable organodielement intermediates in the course of systematic investigations into their properties.[7] That development culminated in the recent syntheses of sterically highly shielded element(I) derivatives which form dimers in the solid state. These products may be expected to possess E–E double bonds similar to diborenes, however, they have only weak E–E bond strengths and may best be described by two donor–acceptor bonds in accordance with their non-linear structures.[168,169]

The tetraorganyldielement(4) compounds themselves proved to be quite interesting not only owing to their novel molecular structures, but also because they have singular chemical properties with a broad applicability in secondary reactions.[224] Electron transfer gave radical anions containing 1e–E–E π-bonds and planar molecular skeletons with short E–E bond lengths. The transfer of a second electron to obtain an E–E double bond obviously gave unstable species and only secondary products of decomposition reactions could be isolated. Insertion reactions were observed in great number with a broad variety of substrates such as chalcogen atoms, isonitriles, diazomethanes, carbenes, and many others. Metathesis reactions may be suitable for the synthesis of many secondary products, however, only the reaction between digallium and ditellurium compounds yielding a monomeric triorganogalliumtelluride has been described so far. Those three types of reactions which proceed under retention of the E–E bonds were discussed in this chapter. These are the substituent exchange, the deprotonation of substituents and the formation of adducts. Investigations into the chemical reactivity of these dielement compounds are still of interest in current literature. Thus, this chemistry is far from being at its end, and further interesting results are to be expected in the near future.

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The (Butadiene)zirconocenes and Related Compounds

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I

INTRODUCTION

1,3-Butadiene, the parent conjugated diene, can in principle attain two planar conformations, namely *s-trans*-butadiene and *s-cis*-butadiene. In reality, the majority of the acyclic 1,3-butadiene derivatives exhibit global conformational minima that are at least close to the *s-trans*-diene situation.[1,2] For butadiene itself the *s-trans*-C_4H_6 conformer is more stable than the *s-cis*-isomer by ca. 3–4 kcal mol^{-1}, although the *s-trans*- $\leftrightarrows$ *s-cis*-butadiene interconversion is kinetically rapid ($\Delta G^{\neq} \approx 7$ kcal mol^{-1}). Consequently, reactions via the less favorable conformations are not uncommon (e.g., the Diels-Alder reaction) (Scheme 1).

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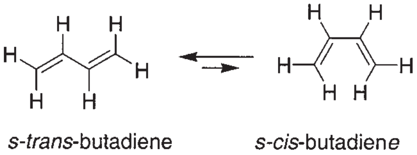
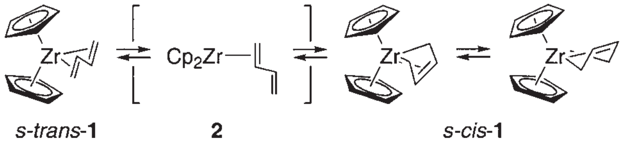


SCHEME 1



SCHEME 2

(Butadiene)metal complexes have a great importance in organic synthesis and in organometallic chemistry, and especially in catalysis.[3] Many important catalytic conversions of conjugated dienes involve their (conjugated diene)metal complexes as starting materials or essential intermediates. The majority of (η^4-butadiene)transition metal complexes exhibit structures that contain a cisoid arrangement of the butadiene C_4-unit attached at the metal center. Therefore, it was a remarkable incident that the first example of a transoid (η^4-butadiene)metal complex was prepared, isolated, and characterized in 1980.[4] Dinuclear [(*s*-*trans*-butadiene)M_2L_n]-type complexes with bridging transoid C_4H_6 ligands had been known before, but [(*s*-*trans*-η^4-butadiene)$ZrCp_2$], independently discovered by G. Erker's and A. Nakamura's groups, appeared to be the first mononuclear transition metal complex that contained a transoid butadiene conformer that was bonded to a single d-metal atom through all its four conjugated diene carbon centers (for structural details see Chapter 4).

The [(*s*-*trans*-diene)$ZrCp_2$] complex (*s*-*trans*-**1**) equilibrates with the [(*s*-*cis*-diene)$ZrCp_2$] isomer (*s*-*cis*-**1**) via a reactive high lying (η^2-butadiene) metallocene intermediate (**2**) [$\Delta G^{\neq}$ (*s*-*trans*-**1** → *s*-*cis*-**1**, 283 K) $= 22.7 \pm 0.3$ kcal mol^{-1}]. Syntheses of the (butadiene)zirconocene system carried out under kinetic control invariably led to pure *s*-*trans*-**1**, whereas a ca. 1:1 equilibrium of *s*-*trans*-**1** and *s*-*cis*-**1** was obtained under conditions of thermodynamic control.[5,6] The σ^2,π-structured *s*-*cis*-**1** isomer undergoes a dynamic "ring-flip" automerization process (see Scheme 2) that is rapid on the NMR time scale [$\Delta G^{\neq}_{\text{autom}} = 12.6 \pm 0.5\,\text{kcal}\,\text{mol}^{-1}$].[5]

The earlier work on the (butadiene) Group 4 metallocenes and related systems was reviewed by Erker *et al.*[6] and by Yasuda *et al.*[7] in 1985. In the meantime the (butadiene)metallocenes have found a widespread use, especially in organic and organometallic synthesis,[8] and, more recently, in catalysis.[9] A variety of selected topics from those fields of studies and applications has been reviewed with regard to more specialized aspects.[10,11] In this account we wish to discuss a variety of current trends and developments in (conjugated diene)metallocene chemistry and try to outline the various pathways that have led to them. This review does, therefore, not attempt to provide a complete coverage of structural and chemical details but rather give a (necessarily subjective) overview of the current state and development of a field, that has rapidly expanded and extended to neighboring areas during the recent years.

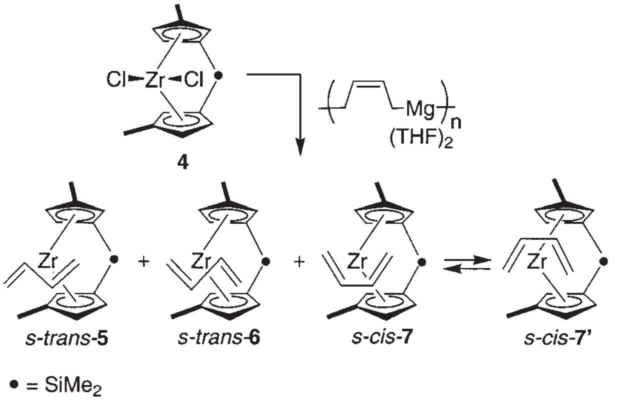
II

THE UNIQUE (*s-trans*-η^4-CONJUGATED DIENE)METAL COMPLEX FAMILY

It is well known that *s-trans*-butadiene can serve as a bridging ligand in binuclear [(μ-η^2,η^2-C_4H_6)M_2L_n]metal complexes.[12] However, since the original discovery in 1980[4] there has been an increasing number of structurally, chemically, and spectroscopically well characterized mononuclear (*s-trans*-conjugated diene)metal complex systems reported in the literature.[11]

The clear structural characterization of the transoid butadiene ligand of the (*s-trans*-η^4-butadiene) Group 4 metallocenes has met with difficulties right from the beginning. The (*s-trans*-η^4-C_4H_6)M moiety represents an element of chirality. Thus, *s-trans*-**1** has an idealized C_2-symmetry and is chiral. In the crystal of *s-trans*-**1** and of many related examples there is a positional disorder of the central butadiene carbon atoms due to an enantiotopic superposition that has hampered detailed structural description. In addition, several other examples suffered from a *s-trans*-/*s-cis*-isomer disorder in the crystal that led to additional difficulties of describing the (*s-trans*-η^4-butadiene) ligand geometry in such complexes with the desired accuracy. Therefore, the structural description of the (*s-trans*-butadiene)zirconocenes had to rely for many years on the sufficiently precise X-ray crystal structure determination of a derivative, namely [(*s-trans*-η^4-1,4-diphenylbutadiene)$ZrCp_2$] (**3**).[13]

We have recently used a "stereochemical trick" to solve this pending structural problem. The anellation of the chiral (*s-trans*-η^4-C_4H_6)M subunit with a chiral bent metallocene leads to the formation of a pair of diastereomeric (*s-trans*-butadiene)metallocene complexes. Crystals of a single diastereomer were obtained that were free from the otherwise so often observed disorder phenomena. The actual example was prepared by



SCHEME 3

treatment of the chiral (*rac*) zirconocene dichloride **4** (see Scheme 3) with butadiene–magnesium to yield a mixture of the stereoisomers *s-trans*-**5**, *s-trans*-**6**, and the equilibrating *s-cis*-**7** isomers. The X-ray crystal structure analysis of the pure (M)(p-S)(*s-trans*-η^4-butadiene)[$Me_2Si(C_5H_3CH_3)_2$]Zr isomer (**5**) revealed the typical data of the (*s-trans*-η^4–C_4H_6)Zr subunit, e.g., featuring a characteristic C1–C2–C3–C4 torsional angle of $\theta = 124.3(4)^\circ$ and ligand bond angles of 122.3(4)° (C1–C2–C3) and 123.4(4)° (C2–C3–C4).[14] Table I shows a comparison of additional typical bonding features (Fig. 1).

The butadiene ligand in the Group 4 metallocene complexes is very reactive towards olefins attached at the Cp rings. A typical example is the system **9** that instantaneously reacts further to yield **10** when generated from **8** (see Scheme 4). In contrast, the unsaturated (butadiene)ansa-metallocene complexes *s-cis*-**13** and *s-trans*-**13** are stable when prepared from **12** under similar conditions.[15] Complex **12** was obtained by a ring closing olefin metathesis reaction from **11**.

The Group 5 metal complex analogues of the Group 4 (butadiene)metallocenes are cations. The favored [(*s-trans*-η^4-butadiene)$TaCp_2$]$^+$ cation complex **16** was prepared in the following way: treatment of [(butadiene) $CpTaCl_2$] (**14**) with two equivalents of CpNa gave the [(η^2-butadiene)(η^1-Cp)(η^5-Cp)$_2$Ta] complex **15**. Subsequent removal of a Cp-anion equivalent from **15** by treatment with [Cp_2ZrMe]$^+$ (with formation of [Cp_3ZrCH_3][16]) then gave the stable [(*s-trans*-η^4-C_4H_6)$TaCp_2$]$^+$ cation complex **16** (with [$CH_3B(C_6F_5)_3$]$^-$ counteranion).[17] The NMR features of *s-trans*-**16** are very similar to those of *s-trans*-**1**. The analogous [(*s-trans*-η^4-butadiene) TaCp*Cp]$^+$ cation system (**19**) was prepared in a similar way by means of chloride abstraction from **18** (Scheme 5).[18]

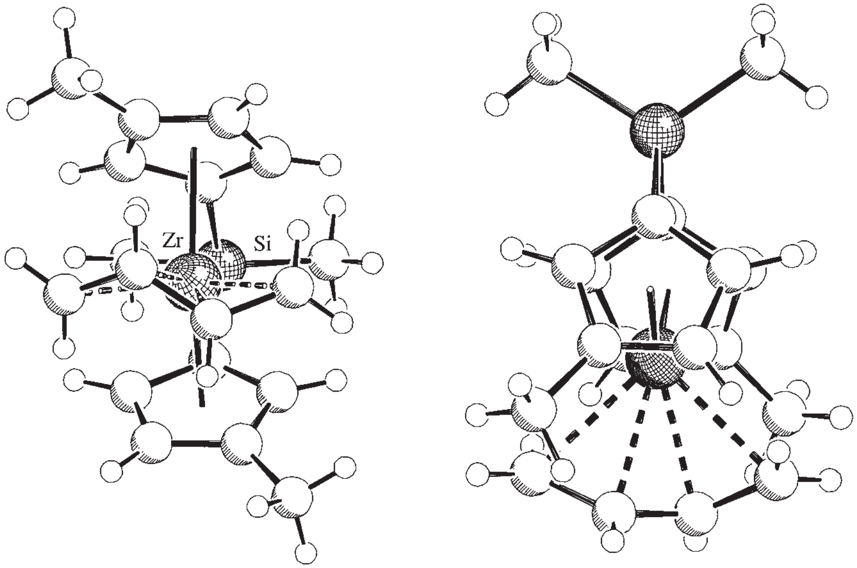
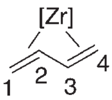
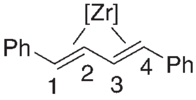


FIG. 1. Two views of the molecular structure of the (*s-trans*-η^4-butadiene)zirconocene complex **5**.

TABLE I

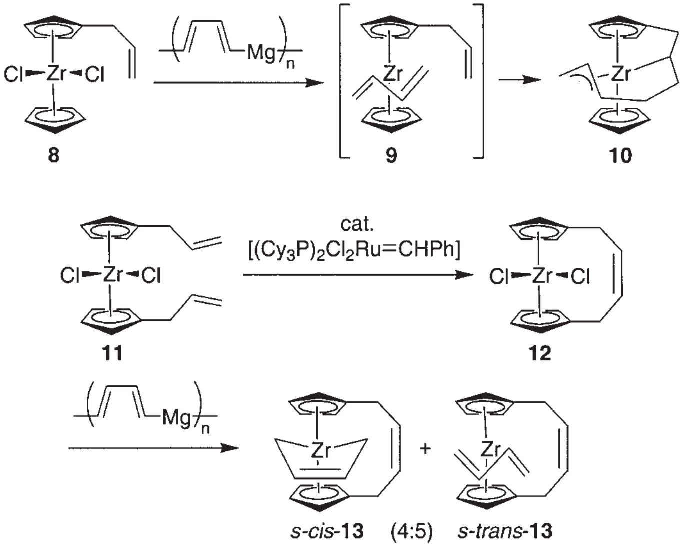
A COMPARISON OF CHARACTERISTIC STRUCTURAL DATA OF TYPICAL (*s-trans*-η^4-BUTADIENE)METALLOCENE COMPLEXES[a,b]

	 (**5**)[14]	 (**3**)[13]
Zr–C1	2.453(3)	2.50(1)
Zr–C2	2.352(3)	2.37(1)
Zr–C3	2.338(3)	2.39(1)
Zr–C4	2.455(3)	2.51(1)
C1–C2	1.402(5)	1.41(2)
C2–C3	1.393(5)	1.44(2)
C3–C4	1.364(6)	1.39(2)
θ[c]	124.3(4)	126.2(2)

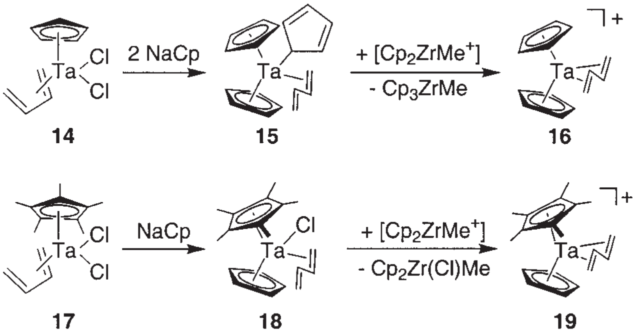
[a] Bond lengths in Å.

[b] For **3** averaged data of the two crystallographically independent molecules are given.

[c] C1–C2–C3–C4 torsional angle.



SCHEME 4

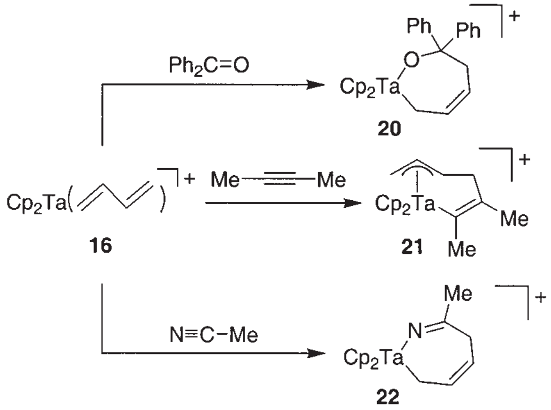


cations with [$CH_3B(C_6F_5)_3^-$] anions

SCHEME 5

The (butadiene)tantalocene cations add a variety of unsaturated reagents (alkenes, alkynes, nitriles, or ketones) similarly as do the neutral (butadiene)zirconocenes to yield the typical metallacyclic reaction products (for selected examples see Scheme 6)[17–19] (Fig. 2).

Ernst *et al.* have described similarly structured Cp_2Ta-pentadienyl systems,[20] and Bazan *et al.* have synthesized a neutral [(*s-trans*-η^4-butadiene)



SCHEME 6

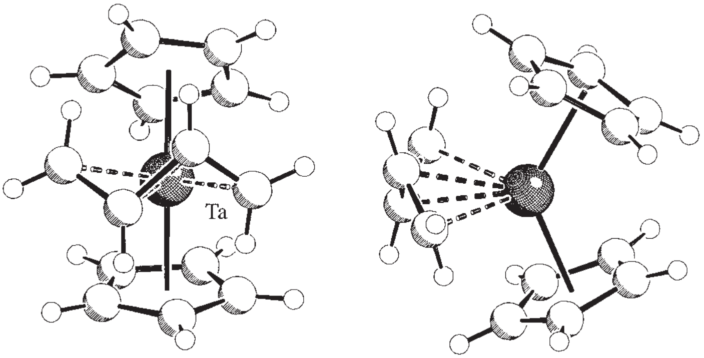
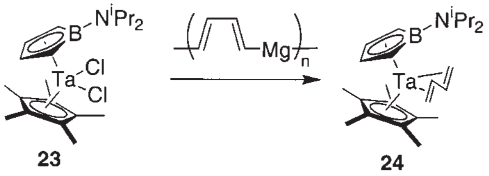


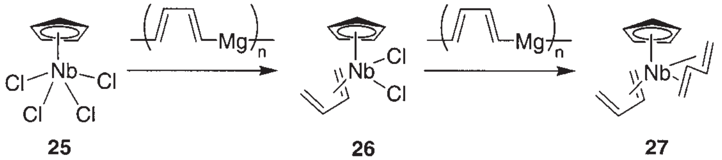
FIG. 2. Front and side view of (*s-trans*-η^4-butadiene)tantalocene cation in **16**.



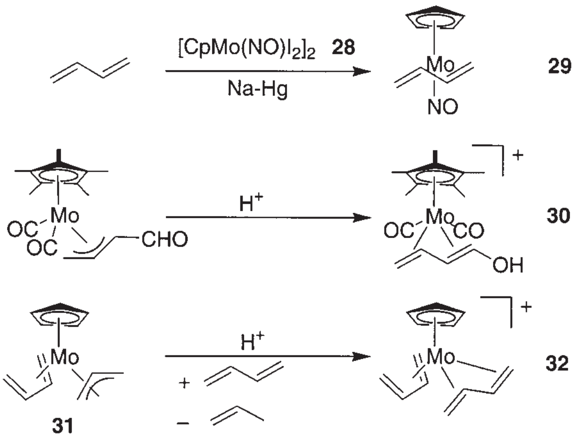
SCHEME 7

Ta($C_4H_4BNR_2$)Cp] analogue (**24**)[21] of the [(*s-trans*-η^4-butadiene) $TaCp_2]^+$ cations (Scheme 7).

Another way of constructing neutral analogues of **16** lies in the use of the [$CpM^{(V)}$(butadiene)] subunit as a framework that in itself is isolobal to the $[Cp_2M^{(V)}]^+$ backbone.[22] Attachment of a second butadiene unit



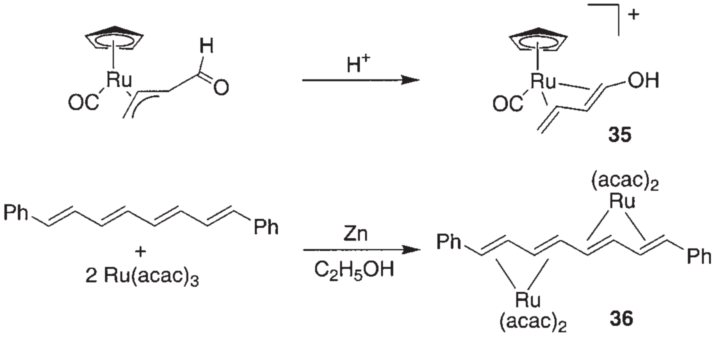
SCHEME 8



SCHEME 9

to the former indeed leads to stable [(*s*-*trans*-diene)M(η^4-C_4H_6)Cp] systems of niobium or tantalum (see Scheme 8).[23,24]

A combination of this principle of molecular (butadiene)metal complex construction[11] consequently leads to the (*s*-*trans*-η^4-butadiene) Group 6 metal complexes depicted in Scheme 9. Reduction of e.g., [CpMo(NO)I_2]$_2$ (**28**) with sodium amalgam in the presence of a series of conjugated dienes gave the stable [(*s*-*trans*-η^4-diene)MoCp(NO)] complexes **29** (some characterized by X-ray diffraction) as described by Legzdins *et al.*[25,26] In some cases the *s*-*cis*-isomers were found as kinetic products. Treatment of **28** with butadiene–magnesium (followed by thermolysis) also eventually led to the formation of the systems **29**. These complexes add alkynes to form similar products[27] as described for the tantalum complexes in Scheme 6. Green *et al.* have described protonolytic pathways to analogously structured functionalized [(*s*-*trans*-diene)Mo]$^+$ cation complexes (e.g., **30** in Scheme 9).[28,29] Consequently, the cationic bent metallocene surrogate [Cp(butadiene)Mo]$^+$ also binds an additional butadiene ligand in the *s*-trans-η^4-fashion to form [(*s*-*trans*-η^4-butadiene)Mo(butadiene)Cp]$^+$ **32**,



SCHEME 10

as was demonstrated by Poli *et al.*[30] Thermolysis of the starting material **31** eventually leads to the formation of [(*s*-*trans*-η^4-butadiene)Mo(Cp)(η^3-allyl)] (**33**).[31] Herrmann *et al.* described a related neutral [(*s*-*trans*-η^4-butadiene)ReCl$_2$(Cp*)] complex (**34**).[32]

Green has also used the method of H$^+$ addition to a –CHO-substituted (allyl)metal complex for the preparation of (*s*-*trans*-diene) complex derivatives of a Group 8 metal. The Ru complex **35** was synthesized in that way.[33] Stable [(*s*-*trans*-η^4-conjugated diene)Ru(acac)$_2$] isomers have been described[34] and related [(*s*-*trans*-η^4-diene)Ru(trispyrazolylborate)Cl] systems are stable and isolable.[35] Eventually, Mashima *et al.* have described the reaction of all-*trans*-1,8-diphenyloctatetraene with [Ru(acac)$_3$] under reducing conditions. A dimetallic complex (**36**) was isolated and characterized by X-ray diffraction, that contained a linear array of two (*s*-*trans*-η^4-diene)Ru subunits[36] (see Scheme 10).

III

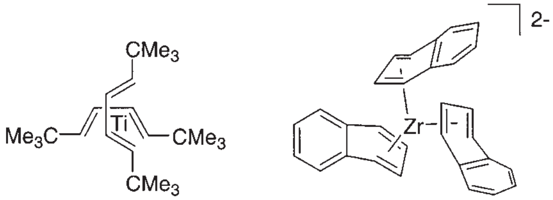
SYNTHESES AND STRUCTURAL PROPERTIES OF (BUTADIENE) GROUP 4 METAL COMPLEXES

Butadiene complexes are ubiquitous in the organometallic chemistry of the middle and late transition metals. This is still different for the Group 4 metals where conjugated dienes are not among the most commonly encountered ligand types, although the number of such titanium, zirconium, or hafnium complexes is increasing. In this chapter we will describe a variety of (butadiene) Group 4 metal complex types that vary with regard to the presence of their additional κ- and π-ligands.

A. *Cyclopentadienyl-free (Butadiene)M(IV) Complexes*

Homoleptic (conjugated diene) Group 4 metal complexes are rather rare. Cloke *et al.* used the metal vapor technique to prepare a "butadiene sandwich" titanium complex. The complex [(η^4-1,4-di-*tert*-butylbutadiene)$_2$Ti] (**37**) was prepared by co-condensation of electron-beam vaporized Ti with the substituted conjugated diene ligand. The (*s-cis*-η^4-diene)$_2$Ti complex was characterized spectroscopically.[37] (Arene)$_n$M(IV) complexes can show similar structural features with the individual naphthalene or anthracene ligands being η^4-coordinated and thus serving as substituted butadiene ligands. Treatment of [ZrCl$_4$(THF)$_2$] with excess naphthalene-potassium yields the "ate complex" [tris(naphthalene)Zr]$^{2-}$ dianion (**38**) that was isolated as a dark red crystalline solid. The X-ray crystal structure analysis revealed an (idealized) C_{3h}-symmetrical structure.[38] Treatment of [TiCl$_4$(dmpe)] with potassium anthracene gave a related neutral [(η^4-anthracene)$_2$Ti(dmpe)] complex. Bis(cyclooctatetraene)Ti and -Zr complexes can show a similar bonding pattern with one of the cyclic polyene ligands being η^4-bonded. [(η^4-1,4-bis(trimethylsilyl)cot)(η^8-1,4-bis(trimethylsilyl)cot)]Ti is a typical example[40] (Scheme 11).

Fryzuk *et al.* have used the monoanionic bidentate [(^{i}Pr$_2$PCH$_2$SiMe$_2$)$_2$N]$^-$ ("PN$_2$")-ligand for stabilizing the *s-cis*-η^4-butadiene ligand at zirconium or hafnium.[41,42] Treatment of **39** [M = Zr or Hf] with butadiene–magnesium gave the diene complex **40** that exhibits a similar dynamic behavior as is known from the (*s-cis*-conjugated diene)metallocene family.[43] The hafnium complex **40b** reacts further with allylmagnesium chloride to eventually yield the CC-coupling product **41**. A related tetradentate dianion "P$_2$N$_2$"-ligand gave the [("P$_2$N$_2$")Zr(*s-cis*-η^4-butadiene)] complex



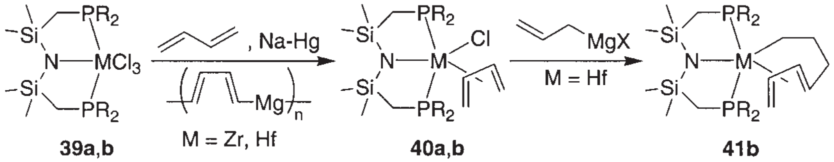
37 **38**

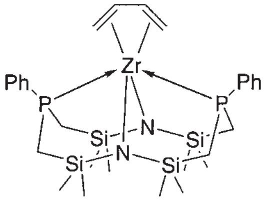
SCHEME 11

42 that was also characterized by an X-ray crystal structure analysis[44] (Scheme 12).

A variety of new ligand designs and ligand combinations were used in attempts to mimic some properties of the ubiquitous bent metallocene environment at the early metal centers; consequently, some of these systems were used in the further development of butadiene–zirconium chemistry. The pyridine based chelate zirconium dichloride complex **43** cleanly formed the butadiene complex **44** upon treatment with butadiene–magnesium. Its structure shows that the C_4H_6 is arranged perpendicular to the chelate ligand plane. Complex **44** inserts one equivalent of an alkene or alkyne to form the metallacyclic π-allyl system **45**[45] (Scheme 13).

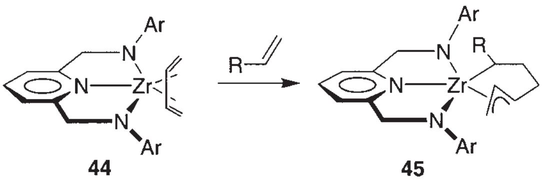
[$TiMe_2(dmpe)_2$] reacts with $AlEt_3$ and butadiene to yield a stable [(*s*-*cis*-η^4-C_4H_6)$_2$Ti(dmpe)] complex.[46] In the absence of the Al-reagent *trans*-[$TiMe_2(dmpe)_2$] eliminates one equivalent of dmpe at −20 °C to form the butadiene addition product [(butadiene)$TiMe_2$(dmpe)].[46] A similar system was described that was obtained in a one pot reaction



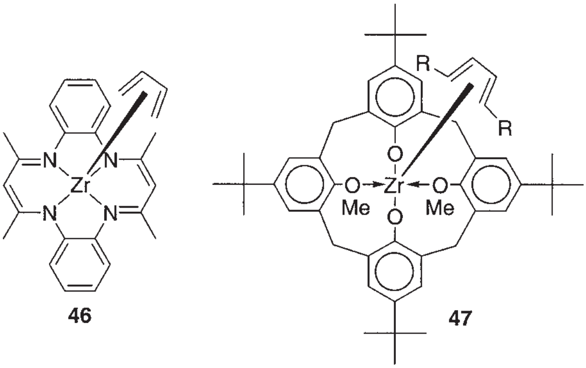


42

Scheme 12



Scheme 13



46 **47**

SCHEME 14

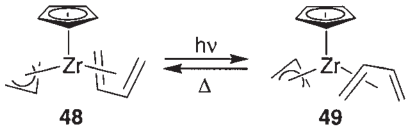
by treatment of $HfCl_4$ with PMe_3 and 2,3-dimethylbutadiene with sodium-amalgam. The [*trans*-$(PMe_3)_2HfCl_2$(*s*-*cis*-η^4-dimethylbutadiene)] product was isolated in ca. 50% yield.[47]

Floriani *et al.* have prepared (*s*-*cis*-η^4-butadiene) complexes at chelate dianion-Zr frameworks. The [(tetraaza[14]annulene)$ZrCl_2$] systems [(tmtaa) $ZrCl_2$] yields **46** upon treatment with butadiene–magnesium.[48] The related [Zr]Cl_2 complex of a calix[4]arene derivative similarly yields conjugated diene complexes upon treatment with the respective butadiene–magnesium reagents. In contrast to the corresponding [(1,4-diphenylbutadiene)$ZrCp_2$] system, which favors an *s*-*trans*-diene arrangement, the corresponding [(calix[4]arene)Zr(diene)] complex (**47**, R = Ph) features a *s*-*cis*-η^4-conjugated diene geometry[49] (Scheme 14).

B. *Mono(cyclopentadienyl)(diene)zirconium Derivatives*

We had previously shown that the reaction of [Cp(allyl)$ZrCl_2$] with butadiene–magnesium gave the "supine–supine" [(*s*-*cis*-η^4-butadiene)(η^3-allyl) (η^5-cyclopentadienyl)Zr] isomer **48**.[50] Photolysis of **48** selectively gave the isomer **49**, in which both open π-ligands had become stereochemically inverted. A theoretical analysis[51] has revealed that in this reaction the butadiene ligand "ring-flip" is probably taking place concertedly with the rapid allyl inversion[52] at zirconium (Scheme 15, Fig. 3).

The change to substituted allyl ligands influences the **48** $\leftrightarrows$ **49** equilibrium in the corresponding hafnium systems.[53] Silver *et al.* have used the specific deprotonation at related methylallyl derivatives to generate the conjugated diene ligand in the coordination sphere of the metal.



SCHEME 15

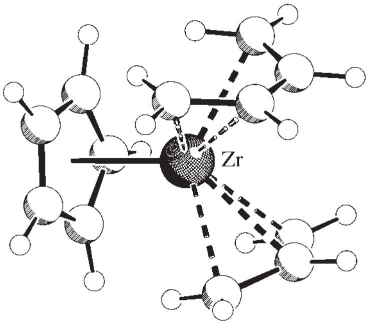
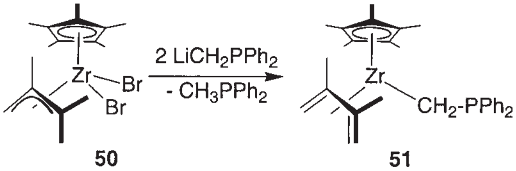
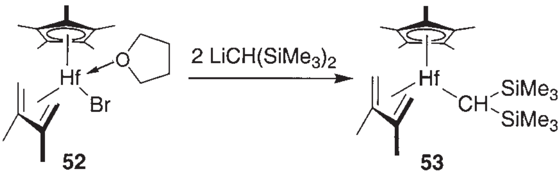


FIG. 3. Molecular geometry of **48**.



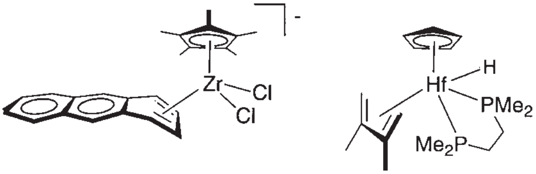
SCHEME 16



SCHEME 17

The reagent $LiCH_2PPh_2$ has been very useful for effecting such a transformation[54] (Scheme 16).

The $[Cp^*(\eta^4\text{-diene})MX]$ ($M = Zr$, Hf) complexes readily form "four-coordinate" adducts with neutral Lewis base ligands (e.g., THF or pyridine). Treatment of such stabilized adducts with Li–R reagents leads to the formation of the corresponding alkyl complexes (e.g., **53**). Some of these systems insert ethylene to form oligomeric chains[55] (Scheme 17).



54 **56**

SCHEME 18

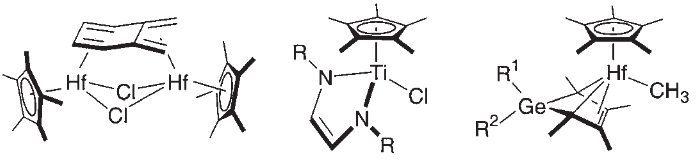
[Cp*ZrCl$_3$] reacts with [Mg(anthracene)(THF)$_3$] to yield the [η^4-anthracene)Cp*ZrCl$_2$]$^-$ anion complex **54** (with [Mg$_2$(μ-Cl)$_3$(THF)$_6$]$^+$ countercation).[56] Treatment of [CpZrCl(dmpe)$_2$] with butadiene yields [CpZrCl(*s*-*cis*-η^4-butadiene)(dmpe)] (**55**).[57] Subsequent reaction of such systems (M = Zr, Hf) with hydride ("Red-Al®") leads to [CpM(H)(butadiene)(dmpe)] (**56**), which rapidly insert terminal alkenes to give the corresponding [CpM(-CH$_2$CH$_2$R)(*s*-*cis*-η^4-butadiene)(dmpe)] systems[58] (Scheme 18).

[Cp(η^5-2,4-dimethylpentadiene)Ti(PR$_3$)] adds acetonitrile to the open π-ligand (with loss of the PR$_3$ donor) to yield a substituted Cp(diene)Ti system (isolated as a dimer).[59] *o*-Quinodimethane serves as a very reactive conjugated diene.[60] Therefore, it is not surprising that it has served as a ligand in a variety of metal complex systems.[61] Royo *et al.* have prepared a variety of Group 4 metal complexes of *o*-quinodimethane, many of them using this C$_8$H$_8$ unit as a bridging ligand.[62] A structurally very interesting example is the system **57**.[63]

1,4-Diazadienes are electronically quite different from the normal conjugated diene systems. Nevertheless, they often form metal complexes that structurally resemble their diene metal complex analogues. In some cases, such as the [Cp*Ti(1,4-diazadiene)Cl] complex **58** even the dynamic behavior of the corresponding Cp*Ti(diene) complexes is mimicked.[64] Siloles and Germoles are reactive cyclic 1,3-dienes that form the respective early metal complexes (a typical example is **59**) by various pathways starting from more structurally complicated germolyl metal complex systems[65] (Scheme 19).

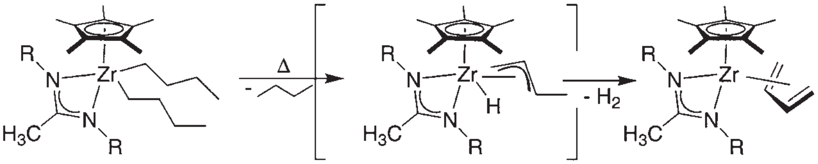
Some nitrogen ligands can stabilize the Cp*M(butadiene) moiety considerably. Sita *et al.* have used the stabilizing ability of an acetamidinato ligand to induce a novel synthetic entry into Cp*M(butadiene)L chemistry. When the [di-(*n*-butyl)Zr(acetamidinato)Cp*] complex **60** was heated, it eliminated H$_2$ along with one equivalent of *n*-butane to yield the butadiene complex **62** (probably via the intermediate **61**)[66] (Scheme 20).

The Si$_1$-or C$_1$-bridged Cp/amido Group 4-derived "constrained geometry" Ziegler-Natta catalysts have found a widespread interest in the



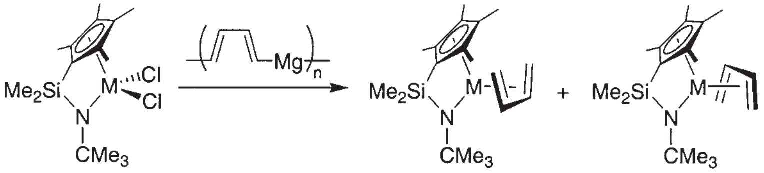
57 **58** **59**

Scheme 19



60 **61** **62**

Scheme 20



63 ("supine") **64** ("prone")

M = Zr: 85 : 15
M = Ti : 6 : 95

Scheme 21

recent years.[67,68] In some of the silanediyl-bridged Cp/amido catalyst systems the respective (*s*-*cis*-η^4-butadiene)metal complexes were used as specific catalyst precursors. Marks *et al.* have prepared a (*s*-*cis*-η^4-2,4-hexadiene)[Ti] complex of this type that was characterized by X-ray diffraction.[69] We have prepared and characterized the butadiene-containing parent compounds spectroscopically and by X-ray crystal structure analyses. The reaction of [{(C$_5$Me$_4$)SiMe$_2$NCMe$_3$}ZrCl$_2$] (**63**) with the butadiene–magnesium reagent gave the supine oriented (butadiene) "constrained geometry" system **64** as the major product (see Scheme 21), whereas the "prone" oriented [(butadiene)(Cp*SiMe$_2$NCMe$_3$)M] complex was clearly favored in the case of titanium.[70] The [(butadiene)(CpSiMe$_2$NCMe$_3$)Ti] analogue also showed a "prone"-type structure.[71]

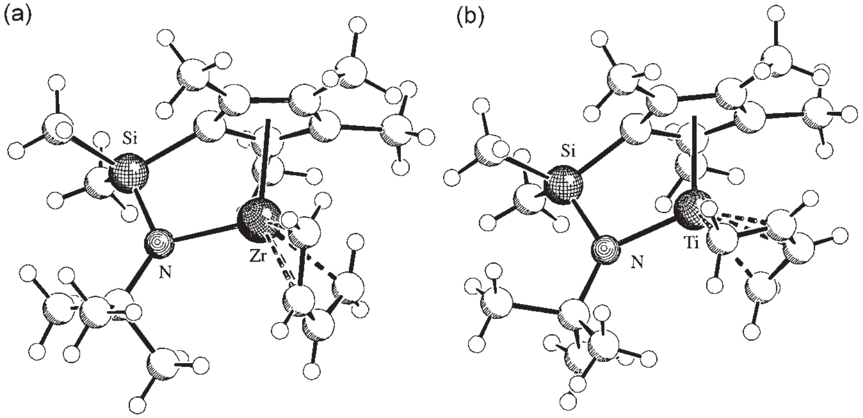


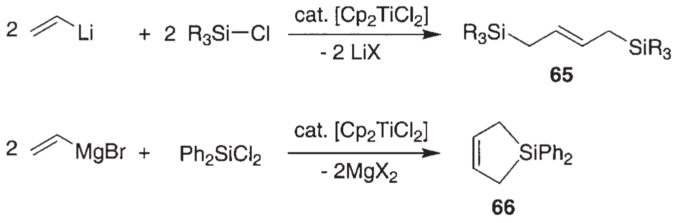
FIG. 4. A comparison of the "supine" and "prone"-type structures of the complexes **64** (supine, M = Zr (a): Zr–C1: 2.300(5) Å, Zr–C2: 2.459(5) Å; prone, M = Ti (b): Ti–C1: 2.180(6) Å, Ti–C2: 2.260(7) Å).

In this series the corresponding [(butadiene)($CpSiMe_2NCMe_3$)Zr] complex contains a metal center of markedly increased Lewis-acidity. In the crystal it forms a cyclotetrameric structure with one of the terminal butadiene–CH_2 groups of each C_4H_6 ligand found bridging between two zirconium centers[71] (Fig. 4).

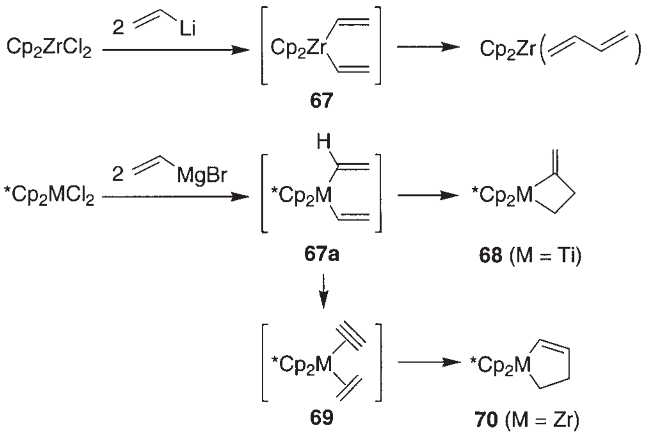
C. *The* (*s-cis-*η^4*-Butadiene*)*metallocenes*

In most cases that were reported in the literature so far, the (*s-cis*-η^4-diene)metallocene complexes (and their *s-trans-* counterparts), were synthesized by treatment of the respective bent metallocene dichloride precursor with a suitable conjugated-diene-magnesium reagent. However, in a few cases alternative entries and procedures have been developed and described. None of these has found such a widespread application as the original procedure, but some interesting chemistry has evolved among those methods.

Thiele and Beckhaus reacted zirconocene dichloride with two molar equivalents of vinyl lithium. The expected divinylzirconocene product proved not to be stable under the applied reaction conditions. It was initially not even observed as an intermediate but reacted further by σ-ligand coupling to give a good yield of the stable (butadiene)zirconocene (see Scheme 23).[72] This coupling reaction was actually used synthetically to



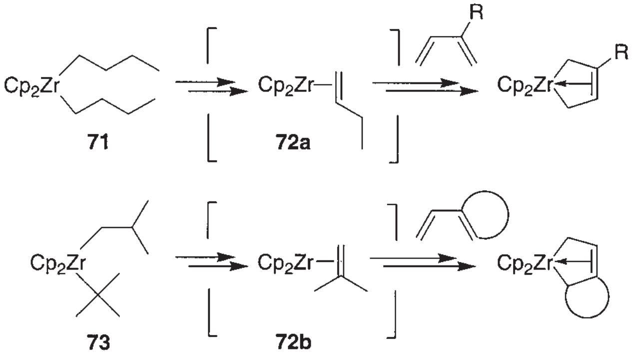
Scheme 22



Scheme 23

couple vinyl lithium with trialkylsilylchloride—catalyzed by Cp_2TiCl_2—to yield the C_4 product **65**, probably via a [(butadiene)$TiCp_2$] intermediate. Similarly, the silacyclopentene product **66** was obtained by [Cp_2TiCl_2]-catalyzed coupling of two $CH_2{=}CHMgX$ equivalents with Ph_2SiCl_2[73] (see Scheme 22).

In the case of the reaction of [Cp_2*$HfCl_2$] with the vinyl-Grignard reagent, Thiele and Beckhaus were actually able to isolate the (divinyl) hafnocene product (**67a**).[74] However, in the corresponding (permethyl)titanocenes and -zirconocenes two different types of products were formed (see Scheme 23). These were shown to originate from H-transfer pathways[75] that were successfully competing with the previously observed σ-ligand coupling pathway. The scope of these competition pathways was shown to depend on the substitution pattern at the Cp-ligands of the open, unbridged metallocenes.[76] (Butadiene)metallocene formation is, however, favored at ansa-metallocene frameworks.[76,77]



SCHEME 24

Originally we had prepared (butadiene)ZrCp$_2$ by trapping *in situ* generated zirconocene with butadiene. We had generated the reactive metallocene photolytically by UV irradiation of diphenylzirconocene.[4a] Meanwhile, equally effective but more convenient methods of generating [Cp$_2$Zr] and its congeners by thermally induced methods are available.[78] Negishi has employed the "dibutylzirconocene-method" to prepare a variety of (butadiene)zirconocenes from [Cp$_2$ZrCl$_2$], *n*-butyl lithium and the appropriate conjugated diene.[79] Generating the metallocene by treatment of [Cp$_2$ZrCl$_2$] with two molar equivalents of *tert*-butyl lithium has also been applied for the synthesis of (conjugated diene)zirconocenes.[80] Trapping experiments showed that (η^2-alkene)metallocene complexes (**72**) should be considered as the essential reactive intermediates in these reactions[80] (Scheme 24).

Even non-conjugated di-olefins may be used in these systems as precursors for the (conjugated diene)metallocene synthesis. They become isomerized under the reaction conditions at the bent metallocene system.[81] Even vinylcyclopropanes yield the corresponding (1,3-diene)metallocene complexes when treated with the reagent **71**. The three-membered ring is readily opened under the typical reaction conditions.[82]

The (*s-cis*-butadiene) Group 4 metallocenes adopt a σ^2,π-type structure. The actual strength of the π-bonding component and, hence, the metallacyclopentene character of the complexes depends very much on the substitution pattern of the diene ligand[6] and it is also strongly influenced by the nature of the bent metallocene unit. These various influences were recently analyzed for some ansa-metallocene/1,3-diene combinations by means of computational chemistry,[83,84] and the results were compared with the dynamic features ($\Delta G^{\neq}_{\text{inv}}$ of the "ring-flip" inversion process, solid state structural features, and PE-spectra of selected examples). The (butadiene)zirconocene ring inversion process was also investigated in the solid state.[85]

A rather simple structure/activation energy correlation ($\Delta G^{\neq} = -ax_o^4$) was found for a series of (*s*-*cis*-η^4-1,3-diene)metallocenes whose characteristic structural parameters and ring inversion activation barriers had been reported in the literature.[86]

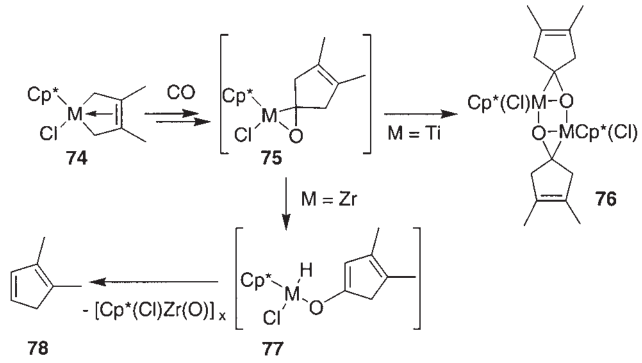
IV

STOICHIOMETRIC USE OF THE (BUTADIENE)METALLOCENES

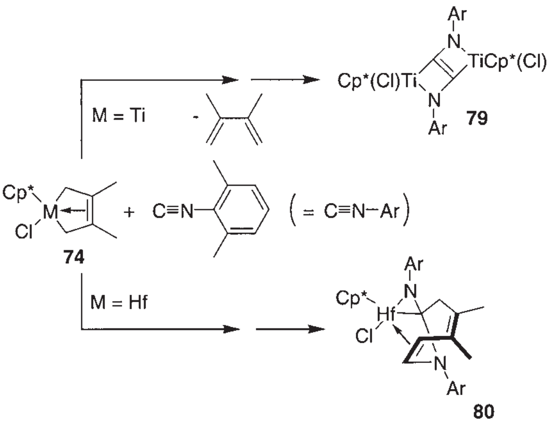
A. *Reactions with Small Organic Molecules*

The (1,3-diene)M^{IV} complexes can react in various competing ways with carbon monoxide. It had been known that the butadiene ligand can be expelled upon treatment of the (*s*-*cis*/*s*-*trans*-butadiene)zirconocene mixture with CO to form [$Cp_2Zr(CO)_2$]. It is likely that this reaction takes place starting from the transoid isomer (or a reactive [(η^2-butadiene) $ZrCp_2$] intermediate resulting from it), whereas the remaining cisoid isomer incorporates a CO molecule to eventually yield 3-cyclopentenone. A zirconium enolate was suggested as an intermediate of this branch of the overall reaction scheme.[6] In the case of the related [Cp*(Cl) Zr(1,3-diene)] complexes, the reaction goes beyond that stage. After CO insertion, a subsequent deoxygenation is eventually observed to yield [Cp*(Cl)Zr(O)]$_x$ and the corresponding cyclopentadiene (**78**).[87] A (η^2-ketone) metal complex is probably involved along this pathway. In the case of the titanium system this was actually isolated as a dimer[87,88] (**76**) (of a typical structure[89]) and characterized by X-ray diffraction (Scheme 25).

Isonitriles often undergo multiple insertions into metal–carbon bonds,[90] in contrast to carbon monoxide. Therefore, it is not surprising that reactions of (diene) Group 4 metal complexes with aryl- or alkylisonitriles may have a different outcome. Thus, the (*s*-*cis*-η^4-2,3-dimethylbutadiene) titanium complex **74a** (M = Ti) reacts with 2,6-xylylisocyanide by replacement of the diene ligand and isonitrile coupling to yield **79**, whereas the corresponding hafnium complex **74c** (M = Hf) inserts two equivalents of the arylisocyanide to give the unusually structured diene/isonitrile coupling product **80** (see Scheme 26).[91]



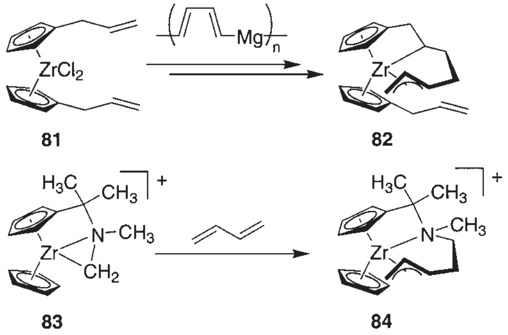
SCHEME 25



SCHEME 26

(Butadiene)zirconocenes insert one equivalent of α-olefins, alkynes, and similar reagents into a Zr–C bond to form seven-membered metallacyclic π-allyl complexes. This often observed reaction also takes place intramolecularly by coupling a pendant olefinic group, that is attached to a Cp-ring, with the butadiene ligand.[92] A typical example is depicted in Scheme 27. Imines sometimes show alkene-like reactivities. The cationic (η^2-iminium)zirconocene complex **83** readily reacts with butadiene or isoprene following a similar CC-coupling pathway to yield **84**[93] (Fig. 5).

Similarly, the coupling of two conjugated dienes has been reported to take place at CpTi-derived complexes to yield linear C_8-products.[94]



SCHEME 27

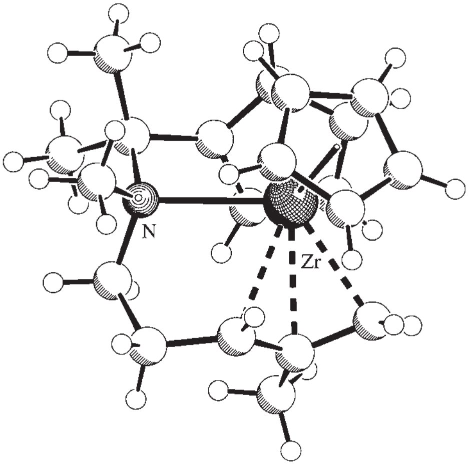
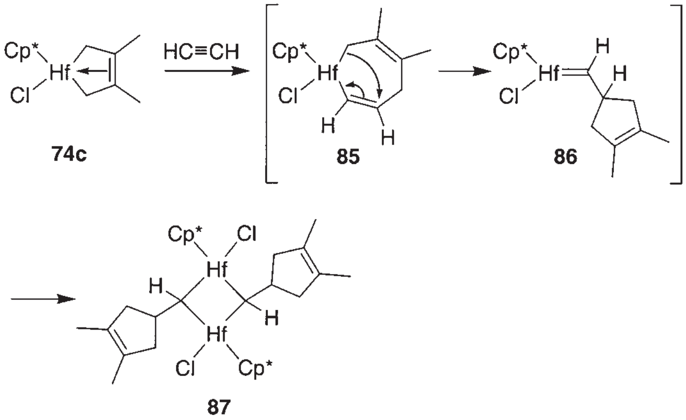


FIG. 5. A view of the molecular structure of complex **84a** (cation only), obtained by coupling of **83** with isoprene.

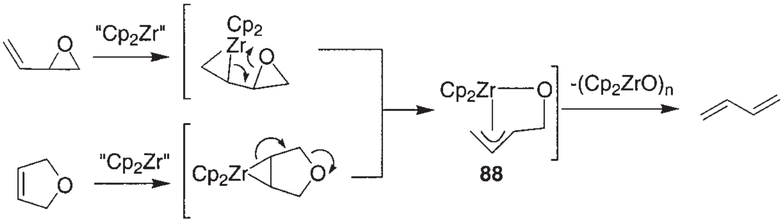
Bis(aryloxy)Ti(butadiene) systems react with a variety of α-olefins to form linear C_6-coupling products.[95]

[(2,3-Dimethylbutadiene)HfCp*(Cl)] (**74c**) reacts with one molar equivalent of acetylene to yield the unusual product **87**. This is probably formed by a conventional butadiene/alkyne coupling at the Group 4 metal center, followed by an intramolecular alkene insertion into the adjacent hafnium to carbon σ-bond. The resulting alkylidene complex (**86**) then rapidly dimerizes to yield the observed final product (see Scheme 28), that was characterized by X-ray diffraction.[96]

Vinyloxiranes react with the "Negishi-reagent" [Cp_2ZrBu_2] by means of deoxygenation to yield conjugated dienes. This reaction is likely to



Scheme 28

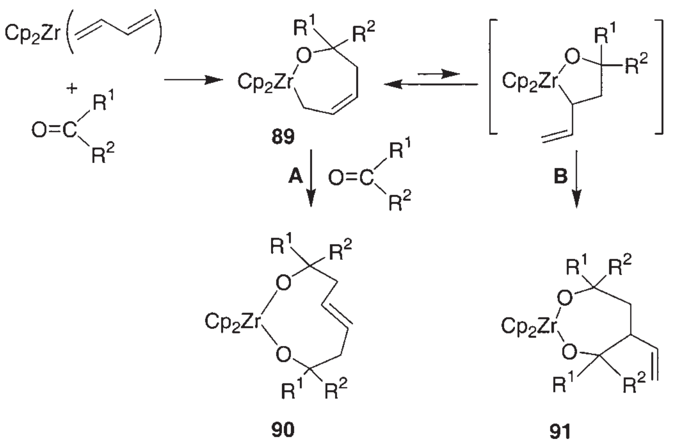


Scheme 29

involve the π-allyl-metallaheterocyclic intermediate (**88**) that is cleaved to form $[(Cp_2ZrO)_n]$ and the organic product[97] (Scheme 29).

B. *Template Reactions*

(Butadiene)zirconocene reacts readily with a great variety of organic carbonyl compounds to yield seven-membered metallacyclic addition products (**89**).[98] In many cases a second ketone, aldehyde, or heterocumulene equivalent is subsequently inserted.[99–102] Usually a linear 1,4-carbon–carbon coupling product is obtained (**90**) (pathway **A** in Scheme 30), but in a few cases involving special steric features (e.g., diphenylketene[102] or benzophenone[103]) a competing pathway is favored leading to the respective 1,2-coupling product between the conjugated diene and two molecules of the organic carbonyl compound (Scheme 30, pathway **B**). Subsequent



SCHEME 30

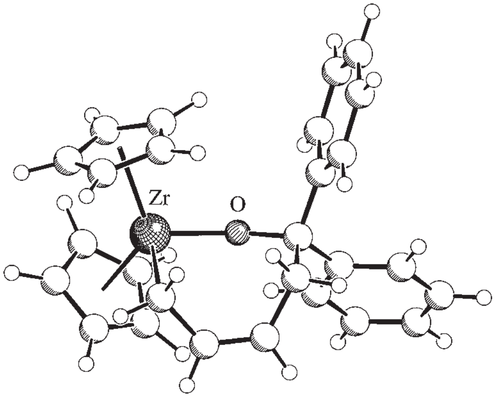
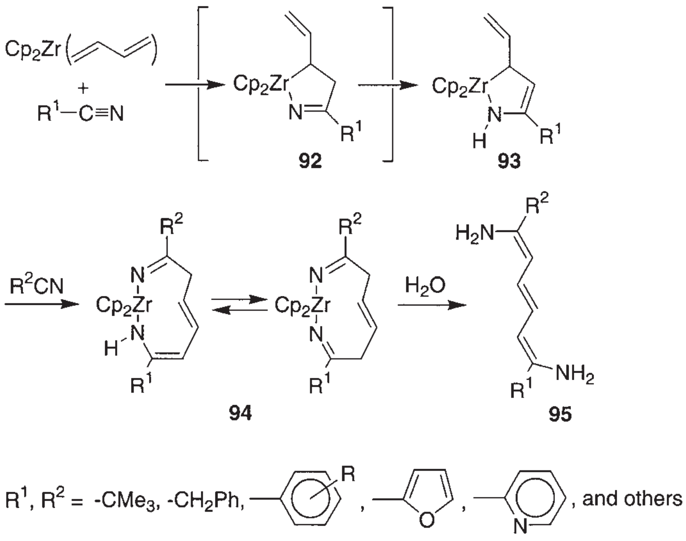


FIG. 6. Molecular structure of an example of the compounds **89** ($R^1 = R^2 = Ph$).

hydrolysis yielded the various types of diol products, some of which were useful building blocks in organic synthesis (Fig. 6).

Nitriles react with (butadiene)zirconocenes in similar ways; however, some important details of the reaction course are different in these cases. A variety of aryl-, hetaryl-, or alkylcyanides add cleanly to the [(butadiene) $ZrCp_2$] reagent. It is likely that **92** is the initial CC-coupling product. Under typical reaction conditions this is not stable but rapidly undergoes a tautomerization reaction to yield the isomer **93**. This can rapidly react further with a second equivalent of the nitrile reagent to



SCHEME 31

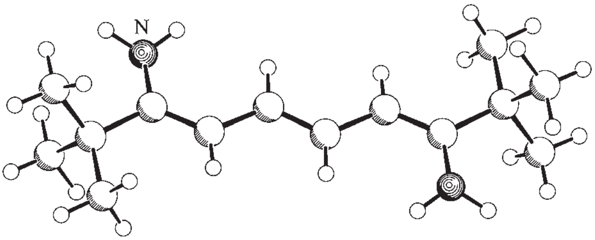
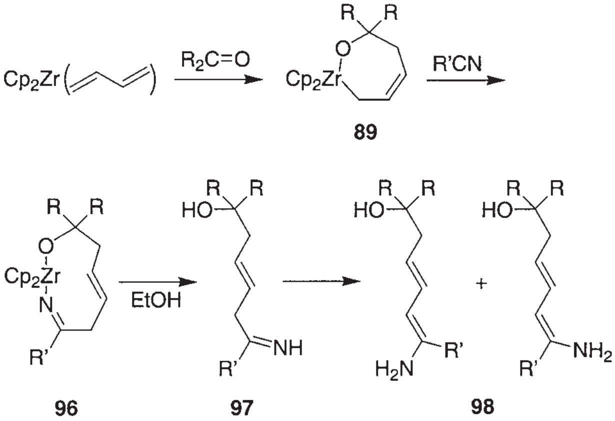


FIG. 7. A view of the conjugated primary enamine product **95a**.

form a 1,4-bis-addition product. Under typical reaction conditions a mixture of a pair of tautomeric nine-membered diazazirconacycles is obtained (**94a** $\leftrightarrows$ **94b**), that both exhibit a *trans*-C=C double bond inside the nine-membered metallacyclic ring system (see Scheme 31). Subsequent hydrolysis makes the unique 1,6-disubstituted 1,6-diaminohexa-trienes (**95**) readily available on a preparative scale. The primary enamines **95** are stable at ambient conditions; they are thermodynamically favored over their respective imine tautomers.[104–106]

The conjugated primary enamines **95** exhibit planar frameworks with alternating C=C double and C–C single bonds between their C(sp^2) atoms. Conjugation extends through the C(NH_2) center to the attached aryl ring systems which generally are oriented close to coplanar with the



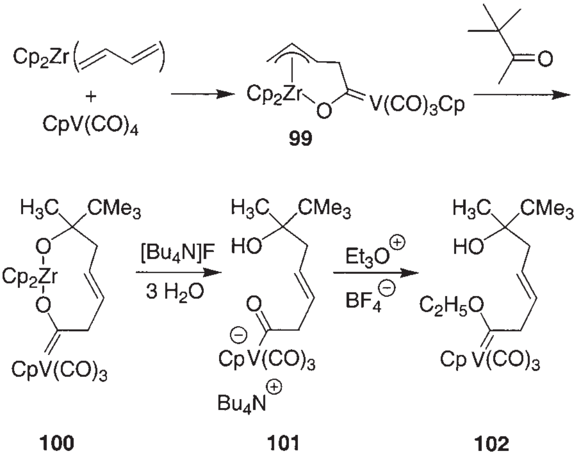
Scheme 32

central conjugated 1,6-diamino-1,3,5-hexatriene system. Figure 7 shows the molecular structure of the stable primary enamine product (**95a**) obtained by 1,4-coupling of two molecules of pivalonitrile with butadiene at the zirconocene template, followed by hydrolysis.[104]

The seven-membered metallacycles **89** (formed by ketone addition to [(butadiene)ZrCp_2] cleanly add a nitrile molecule at elevated temperatures to yield the respective nine-membered metallacyclic products **96**. Their hydrolysis then yields the 6-hydroxy-substituted non-conjugated unsaturated imines **97** under kinetic control. Within a few hours at room temperature these rearrange to the thermodynamically favored primary dienamine products **98**.[107] In this case the thermochemical diene conjugational energy makes the primary dienamines more stable than their conjugated imine tautomers (Scheme 32).

C. *Zirconoxycarbene Complexes*

(Butadiene)zirconocene reacts with metal carbonyls in a similar way as with ketones. Carbon–carbon coupling between a butadiene terminus and the carbonyl carbon atom occurs readily to yield a metallacyclic product, only that generally a metallacyclic π-allyl metallocene system is obtained from the reactions with metal carbonyls.[8] Sometimes, O-zirconated Fischer-type carbene complexes are readily formed in this way that cannot be easily obtained by other routes. A typical example is the



SCHEME 33

zirconoxycarbene vanadium complex **99** that was formed by treatment of $CpV(CO)_4$ with the (butadiene)$ZrCp_2$ reagent.[108]

Group 4 metaloxycarbene complexes of various transition metals throughout the Periodic Table were synthesized by means of the "(butadiene)metallocene method".[8,109,110] The initial products can be reacted further, e.g., with ketones or aldehydes to yield the respective nine-membered metallacyclic systems. These have been modified in various ways. A typical example is shown in Scheme 33. The zirconoxyvanadium carbene complex **99** was reacted with methyl-*tert*-butylketone to yield **100**. Subsequent hydrolysis (with $Bu_4NF \cdot 3H_2O$) gave the zirconium-free acylmetallate system (**101**) that was converted to a conventional Fischer-type (alkoxycarbene)vanadium complex (**102**) by treatment with Meerwein's reagent.[111] Fischer carbene complexes of other metals were also synthesized by this specific route[112] (Figs. 8 and 9).

The zirconoxycarbene complexes undergo a variety of typical Fischer-carbene reactions. Typically, unsaturated nine-membered zirconoxy-carbene complexes such as **103** are readily deprotonated in the α-position to the carbene carbon atom. The stereochemistry of the subsequent alkylation reaction is very efficiently controlled by the remote stereogenic center at C2, resulting in an effective 1,5-asymmetric induction[113] (Scheme 34, Fig. 10).

Once the butadiene/metal-carbonyl/ketone (or aldehyde or nitrile) template coupling at the Group 4 bent metallocene unit has been carried out and subsequent modifications have been made, the corresponding

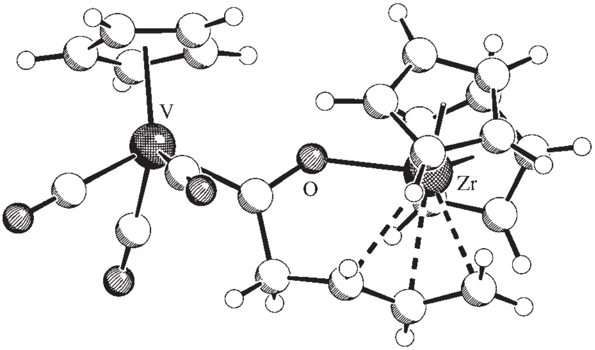


FIG. 8. Molecular structure of the vanadium carbene complex **99**.

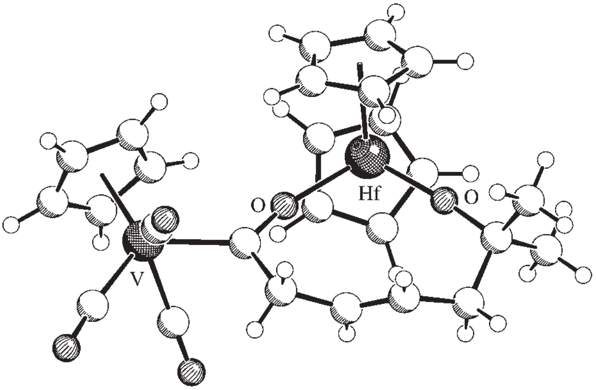
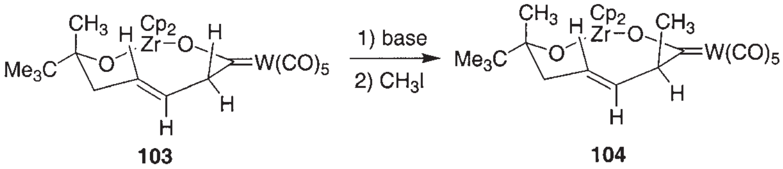


FIG. 9. A projection of the molecular structure of an example of a nine-membered metallacyclic Group 4 metaloxycarbene complex (**100a**, Hf/V).



SCHEME 34

functionalized organic products are set free by means of a two step one pot reaction. The zirconium template is removed by hydrolysis followed by oxidative cleavage of the carbene complex by treatment with a mild oxidizing reagent such as pyridine-*N*-oxide.[114] Schemes 35 and 36 show two typical examples. The ε-hydroxy-*trans*-3-hexenoic

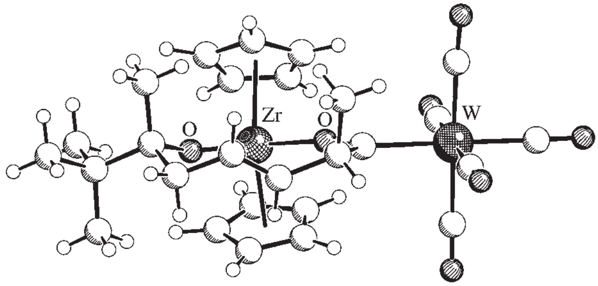
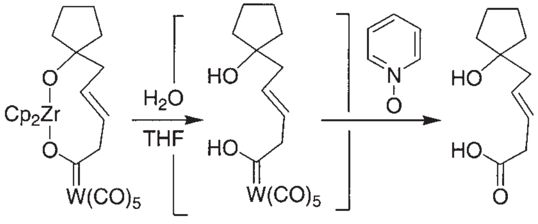
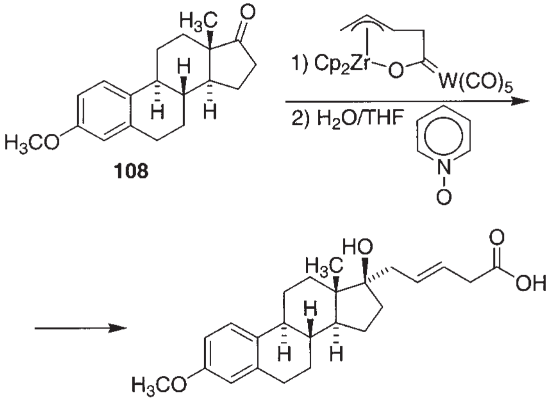


FIG. 10. Molecular structure of the zirconoxycarbene tungsten complex **104** obtained by diastereoselective alkylation of **103**.



105 **106** **107**

SCHEME 35



109

SCHEME 36

acid **107** obtained by this method from (butadiene)zirconocene, hexa(carbonyl)tungsten, and cyclopentanone uses its characteristic orientation of two functional group for forming a ribbon-like supramolecular aggregate structure in the solid state (see Fig. 11).[115] Various other types of organic aggregate structures were constructed by this synthetic approach

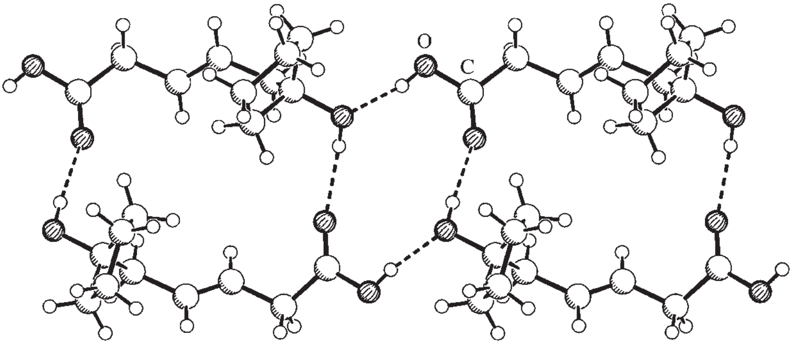


FIG. 11. A view of the ribbon-like hydrogen-bonded super-structure of the 6-hydroxy-*trans*-3-hexenoic acid **107** in the crystal.

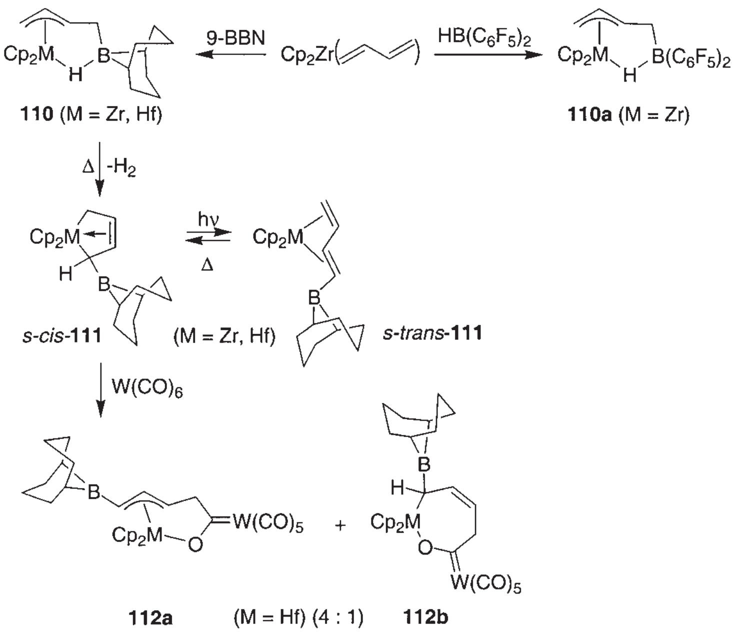
using different ketone components in our organometallic template synthesis.[116]

The (butadiene)zirconocene template coupling reaction has found application in organic synthesis. Coupling of [(butadiene)$ZrCp_2$] with $[W(CO)_6]$ followed by the reaction of the steroid ketone 3-methoxy-1,3,5(10)-trien-17-one (**108**) gave the corresponding metallacyclic zirconoxycarbene tungsten complex (that was actually isolated and characterized by X-ray diffraction[114]). Subsequent hydrolysis/oxidative cleavage furnished the corresponding steroid derivative (**109**) as a single diastereomer. Several variants and derivatives of **109** were prepared using the synthetic techniques described above.[116]

D. *Coupling Reactions with Selected Main Group Element Reagents*

(Butadiene)zirconocene selectively adds boranes HBR_2 to form (π-allyl)zirconaheterocyclic products (e.g., **110**, see Scheme 37).[117] Upon heating borylation of the butadiene ligand takes place with formation of the (*s-cis*/*s-trans*-borylbutadiene)zirconocenes **111**.[118] The borylated (butadiene)metallocenes undergo similar reactions as the parent $[(C_4H_6)ZrCp_2]$ system. Thus complex **111** ($M = Hf$) reacts with $[W(CO)_6]$ to yield a 4:1 mixture of the metaloxycarbene tungsten complexes **112a** and **112b**.[119]

An iminoborane adds to [(butadiene)$ZrCp_2$] in a similar way as does a nitrile (see above) to yield the metallaheterocycle **113**.[120] Similarly, (butadiene)zirconocene adds $AlCl_3$ (and related $XAlR_2$ compounds). The resulting $AlCl_3$ addition product (**114**) features an unusual 1,2-η^2-allyl-coordination of the resulting ligand to the zirconium center (see Fig. 12)[121] (Scheme 38).



SCHEME 37

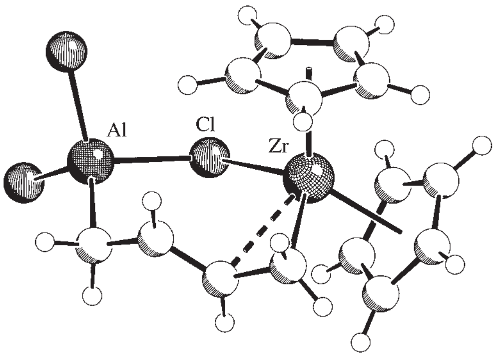
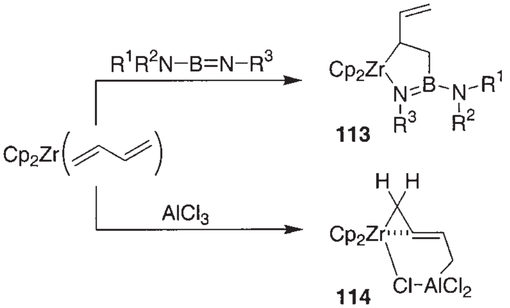


FIG. 12. Molecular structure of the (butadiene)zirconocene/$AlCl_3$ addition product **114** (Zr–C1: 2.348(2) Å, Zr–C2: 2.525(3) Å, Zr · · · C3: 3.04 Å).

[(Butadiene)$ZrCp_2$] and substituted derivatives have been used as reagents for the synthesis of Group 5 element heterocycles. Thus, treatment of **1** with $RAsCl_2$ gave [Cp_2ZrCl_2] and the corresponding dihydroarsole.[122] Binger *et al.* have used the butadiene ligand to stabilize a



SCHEME 38

(cot)Hf building block. Treatment with the phosphaalkyne $Me_3C–C\equiv P$ resulted in the displacement of the C_4H_6 ligand with consecutive formation of phosphaalkyne coupling products.[123]

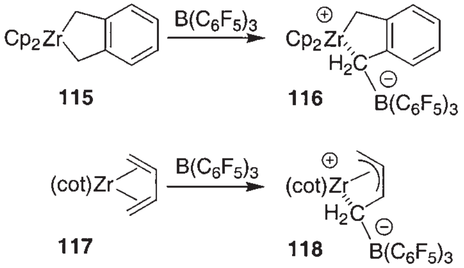
V

(BUTADIENE)ZIRCONOCENES IN CATALYSIS

A. *Stoichiometric Models and Side Reactions*

The strong Lewis acid tris(pentafluorophenyl)borane adds to many (conjugated diene)zirconium complexes to form isolable dipolar ("betaine")-type complexes. Typical examples are the systems **116** and **118**, that were obtained by treatment of the corresponding [(*o*-quinodimethane)zirconocene] (**115**) or the [(η^8-cyclooctatetraene)(*s*-*cis*-η^4-butadiene)zirconium] (**117**) precursors, respectively (Scheme 39).[61] A variety of closely related metallocene and constrained geometry betaine systems have been found to be very active homogeneous single-component Ziegler-Natta α-olefin polymerization and co-polymerization catalysts,[9,124] as will be discussed in the following chapters of this article. However, some of these dipolar addition products are unstable with regard to subsequent reactions that involve ligand redistribution processes at boron. These will first be discussed since some such reactions may provide us with valuable information about potential deactivation pathways of such catalytic systems, and some of the observed reaction pathways represent principally very interesting chemical features of their own right (Fig. 13).

Bochmann *et al.* have shown that the half-sandwich [(2,3-dimethylbutadiene)(^{R}Cp)ZrMe] complex **119** eliminates methane above



SCHEME 39

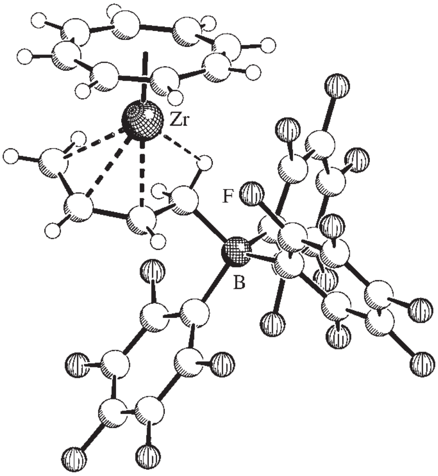
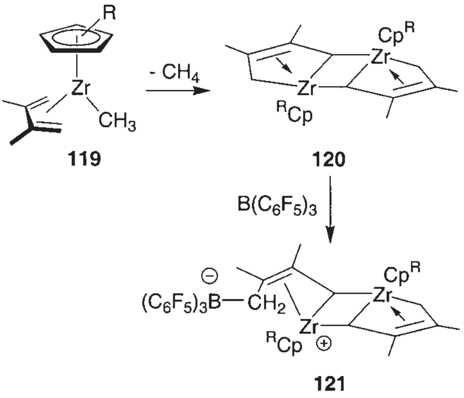


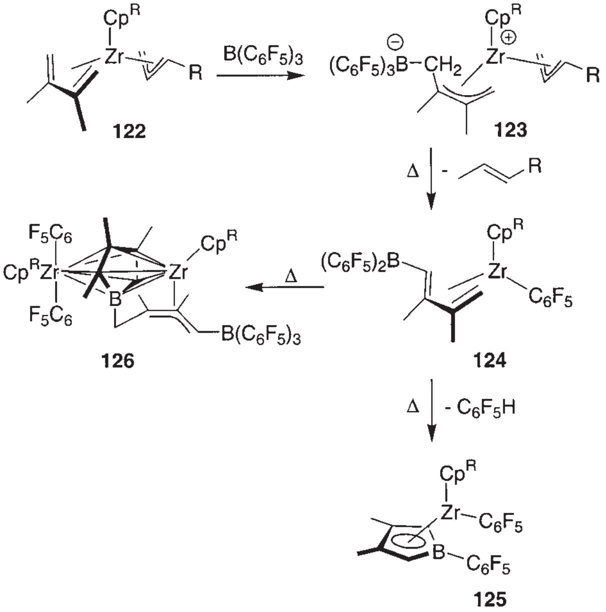
FIG. 13. A view of the molecular structure of the dipolar complex **118** (Zr–C1: 2.588(5) Å, Zr–C2: 2.450(4) Å, Zr–C3: 2.266(4) Å, Zr· · ·C4: 2.614(4) Å, Zr–C(cot)average: 2.403(3) Å).

0 °C to form the dinuclear (butadienyl)zirconium system **120**. Treatment with $B(C_6F_5)_3$ leads to the formation of a mono-addition product (**121**), even in the presence of excess borane. Complex **121** (Scheme 40) shows only a marginal ethene polymerization activity. This led to the notion that such formation of dimeric zirconium complexes might represent desactivation pathways in homogeneous Ziegler-Natta catalyst chemistry.[125]

The corresponding substituted [(R-allyl)(diene)(^{R}Cp)Zr] systems **122** add $B(C_6F_5)_3$ to form the mono-nuclear addition products **123**. These loose one equivalent of the corresponding alkene subsequently with formation of the stable (boryl-butadiene)Zr-C_6F_5 complexes (**124**) that are formed by a pentafluorophenyl migration from boron to zirconium.[126–128] Upon warming, a cleavage of C_6F_5H takes place from **124** with ring

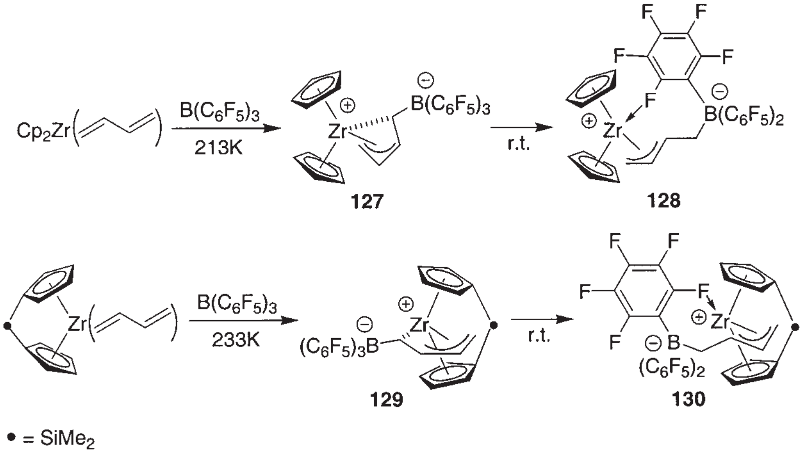


Scheme 40



Scheme 41

closure of the remaining Ar–B(diene) fragment to form the corresponding (η^5-borole)Zr complex **125** (see Scheme 41).[129,130] Thermolysis of the (boryl-butadiene)zirconium complex **124** at higher temperature eventually leads to a cleavage of all three –C_6F_5 groups from one boron atom



SCHEME 42

with formation of the unusually structured borole-bridged triple-decker di-zirconium complex **126**.[131,132]

B. *The (Butadiene)zirconocene Route to Active Ziegler-Natta Catalyst Systems*

The [(*s-cis*/*s-trans*-η^4-butadiene)zirconocene] mixture reacts cleanly with $B(C_6F_5)_3$. At 213 K, i.e., under kinetic control, the addition of the strong boron Lewis acid is observed to take place at a terminal carbon atom of the butadiene ligand to form the cisoid zirconocene–butadiene–borate betaine complex **127**. At ambient temperature this rapidly rearranges to the stable transoid isomer **128** (see Scheme 42).[133] The (*s-cis*/*s-trans*-η^4-butadiene)*ansa*-zirconocene mixture of isomers reacts analogously with $B(C_6F_5)_3$, however, the isomerization of the kinetically formed cisoid betaine isomer (**129**) to the thermodynamic product (**130**) requires a considerably higher activation energy [$\Delta G^{\neq}_{\text{isom}}$ (298 K) = 21.5 ± 0.5 kcal mol^{-1}).[134] (Figs. 14 and 15.)

The solid state structures of the complexes **128** and **130** (and several additional examples) show the presence of an *E*-[$(C_6F_5)_3B$–CH_2]-substituted distorted π-allyl ligand at zirconium. Most characteristic is the pronounced coordination of an *ortho*-F(C_{Ar}) fluorine atom from one of the C_6F_5-rings to the strongly electrophilic zirconium center. The resulting Zr–F(C_{Ar}) interaction spans ca. 2.4 Å (**128**: 2.423(3) Å, **130**: 2.408(2) Å) with a Zr–F–C angle of ca. 140° (**128**: 140.0(3)°, **130**: 142.6(2)°).[135] This Zr–F(C_{Ar})

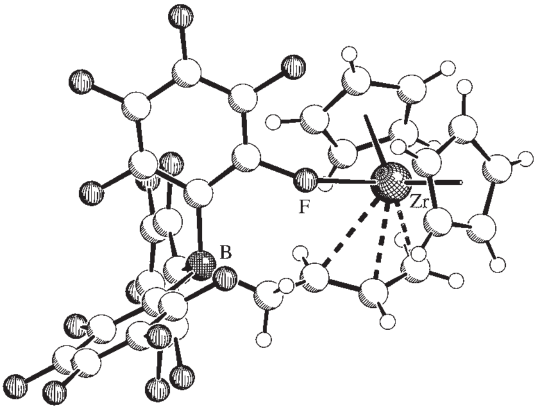


FIG. 14. A view of the molecular geometry of the parent zirconocene–butadiene–$B(C_6F_5)_3$ betaine complex **128**.

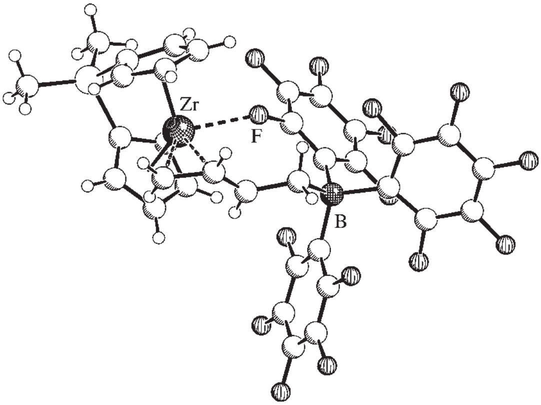
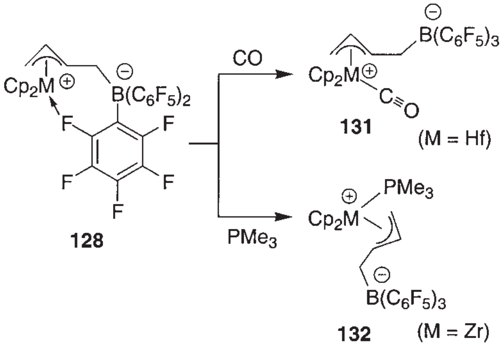


FIG. 15. Molecular structure of dipolar ansa-metallocene/C_4H_6/$B(C_6F_5)_3$ coupling product **130**.

interaction is also present in solution. It is indicated by a ^{19}F NMR resonance of the respective fluorine nucleus (at low temperature) that is shifted to very negative δ-values (**128**: δ-213, **130**: δ-220) relative to the remaining *ortho*-fluorine resonances.[133,135]

The Zr–F(C_{Ar}) interaction is rather weak (see below). It is easily cleaved by the addition of a suitable two-electron donor such as CO or an isonitrile. The formation of the dipolar [(carbonyl)hafnocene-C_4H_6–$B(C_6F_5)_3$] betaine system (**131**)[133] from **128a** (M = Hf), or the adduct **132** that was obtained by treatment of **128** (M = Zr) with PMe_3, are typical examples.[136] The ansa-zirconocene-derived betaine **130** forms similar



SCHEME 43

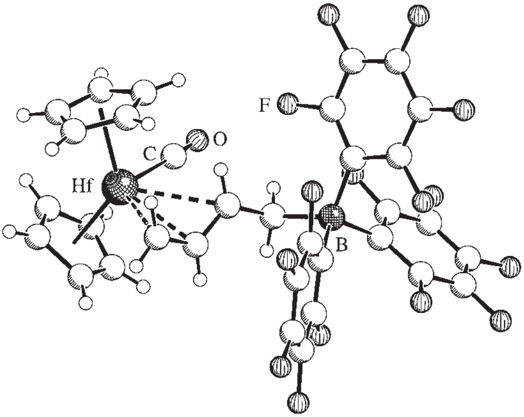


FIG. 16. Molecular geometry of the dipolar carbonyl hafnium complex **131**.

adducts with e.g., PMe_3 or pyridine with cleavage of the Zr–F(C_{Ar}) bond.[83] (Scheme 43, Figs. 16 and 17.)

The new reasonably strong Lewis acid (*N*-pyrrolyl)$B(C_6F_5)_2$ (**133**) also adds to the diene ligand of (butadiene)zirconocene.[137,138] In this case a dipolar product (**134**) is obtained that exhibits a similar structure as e.g., the $[Cp_2Zr–C_4H_6–B(C_6F_5)_3]$betaine **128**, however, here it is the π-system of the pyrrolyl substituent at boron that coordinates to the zirconium center. From the dynamic NMR spectra a bond strength of ca. 15 kcal mol^{-1} was estimated for the pyrrolyl···Zr π-interaction in complex **134**.[137] This is slightly stronger than the Zr–F(C_{Ar}) interaction in e.g., **128** (Scheme 44, Fig. 18).

The relative stabilities of the cisoid and transoid [metallocene–C_4H_6–$B(C_6F_5)_3$]betaines may vary depending on the steric bulk of the metal

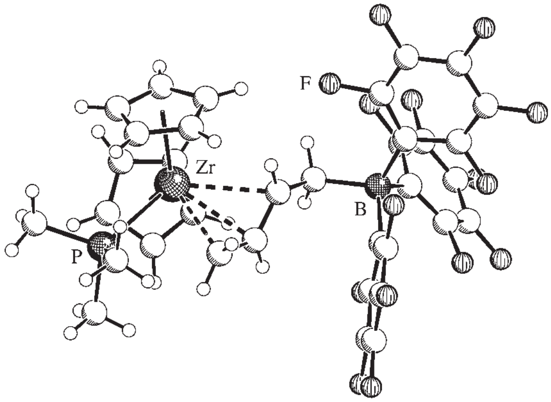
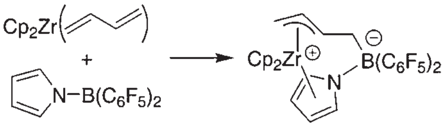


FIG. 17. Molecular structure of the dipolar trimethylphosphine zirconium complex **132**.



133 **134**

SCHEME 44

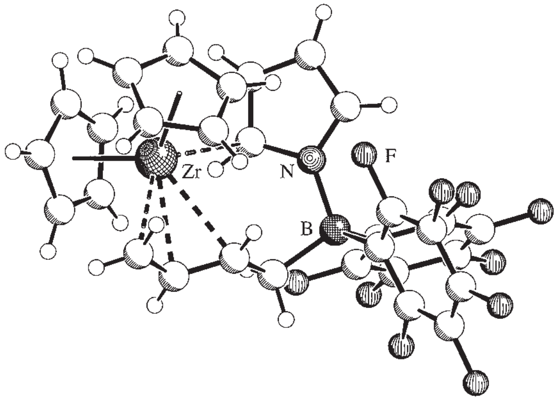
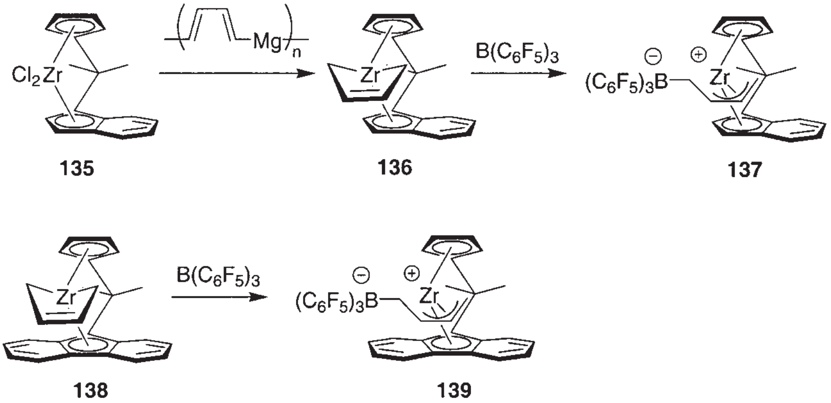


FIG. 18. Molecular structure of **134**, featuring a pyrrolyl· · ·Zr π-interaction (Zr–C5: 2.723(3) Å).

complex component and on its electronic features. Typically, the asymmetric (C_1) ansa-zirconocene dichloride system **135** forms a single [(*s-cis*-η^4-butadiene)metallocene] isomer (**136**) when treated with butadiene–magnesium. Addition of $B(C_6F_5)_3$ occurs rapidly to selectively yield the cisoid [metallocene–C_4H_6–$B(C_6F_5)_3$] complex **137** (see Scheme 45).[134]



SCHEME 45

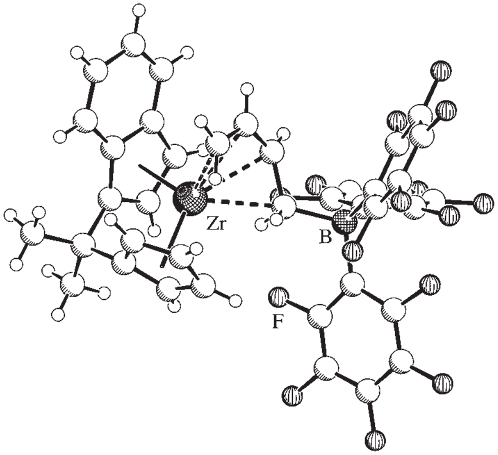
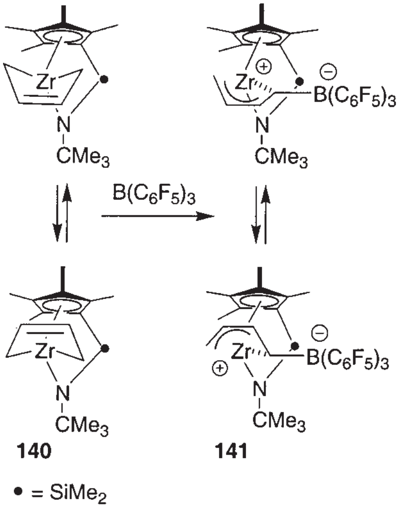


FIG. 19. Molecular structure of complex **137** featuring an internal C4· · ·Zr ion pair interaction (C4–Zr: 2.498 (2) Å).

The specific geometry of the Z-configurated [$(C_6F_5)_3B–CH_2$]-allyl ligand prohibits the formation of a stabilizing Zr–F(C_{Ar}) interaction; instead these systems feature a pronounced internal [B]–CH_2/Zr ion pair interaction (see Fig. 19). The fluorenyl-derived ansa-metallocene system **139** shows a similar structural behavior.[134]

The "constrained geometry" (Cp*/amido)zirconocene butadiene system exhibits a pair of equilibrating [(*s-cis*-C_4H_6)Zr($C_5Me_4SiMe_2NCMe_3$)] isomers (**140**) that add $B(C_6F_5)_3$ to yield a pair of Z-[{$B(C_6F_5)_3BCH_2$-π-allyl}Zr]



Scheme 46

betaine systems (**141**, see Scheme 46).[139] Cowley *et al.* have characterized a variety of such Ti and Zr systems by X-ray diffraction.[140]

Increasingly, steric bulk leads to an opening of the metallocene–butadiene–borate betaine structure. A typical example is the complex [Cp^*_2Zr–C_4H_6–$B(C_6F_5)_3$] **142a**. The very bulky bis(pentamethylcyclopentadienyl)Zr complex attains a very distorted σ,π-allyl-type structure (see Fig. 20) with no interaction remaining between Zr and the pendant [–CH_2–$B(C_6F_5)_3$] end of the butadiene/$B(C_6F_5)_3$ ligand.[141]

The structure of complex **142a** may serve as a model to illustrate the dynamic features that are characteristic of the dipolar [zirconocene–C_4H_6–$B(C_6F_5)_3$] systems in solution. As a typical example, the parent betaine system **128** (see Scheme 42) shows 15 separate ^{19}F NMR signals only at low temperature. Warming the sample above 233 K leads to coalescence of the respective pairs of signals. From the dynamic ^{19}F NMR spectra an activation barrier to cleavage of the Zr–F(C_{Ar}) interaction of $\Delta G^{\neq}(233\ \text{K}) = 8.1 \pm 0.4\ \text{kcal mol}^{-1}$ was obtained. This value is probably close to the actual Zr–F(C_{Ar}) bond dissociation energy in **128**. A variety of other examples of this class of compounds shows similar $\Delta G^{\neq}_{\text{Zr–F(diss)}}$ activation energies.[134,135] Further increasing of the monitoring temperature leads to the observation (by ^{1}H–^{13}C NMR spectroscopy) of an enantiomerization process of the complexes by means of a dynamic $\pi \leftrightarrows \sigma \leftrightarrows \pi$ interconversion of the allyl moiety.[142] The activation barrier of this process is strongly dependent on the structure of the bent metallocene

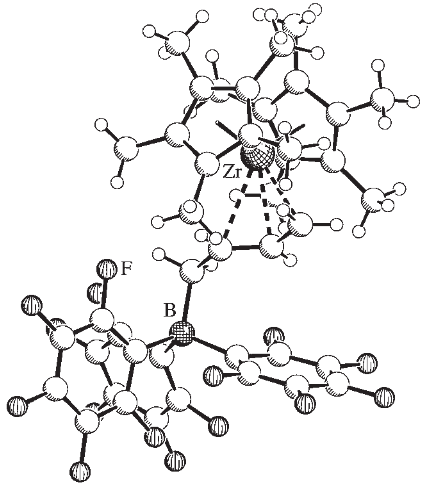
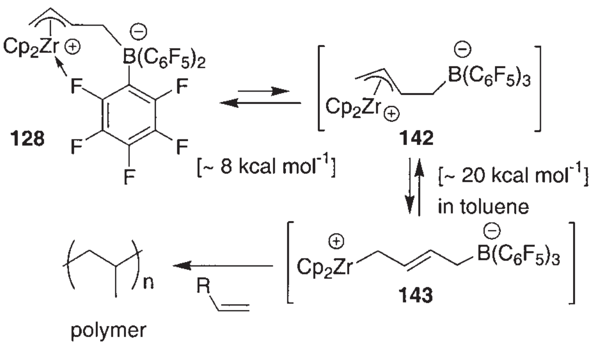


FIG. 20. A view of open betaine structure of [Cp^*_2Zr-σ,π–C_3H_4–CH_2–$B(C_6F_5)_3$] (**142a**) (Zr–C1: 2.337(4) Å, Zr–C2: 2.488(4) Å, Zr–C3: 2.722(4) Å, Zr ⋯ C4: 3.854(4) Å).

used and on the actual reaction conditions. For the parent compound **128** $\Delta G^{\neq}_{\mathrm{m(solv)}} \approx 20\ \mathrm{kcal\ mol^{-1}}$ was obtained from the dynamic ^{1}H NMR spectra in pure toluene for this allyl inversion process.[139] In d_8-THF the σ-allyl intermediate is considerably stabilized and a much lower $\Delta G^{\neq}_{\mathrm{m(THF)}} \approx 9.5\ \mathrm{kcal\ mol^{-1}}$ was observed.[135] Even the presence of α-olefins has a measurable effect on the barrier of this process [$\Delta G^{\neq}_{\mathrm{m(propene)}} \approx 16.5\ \mathrm{kcal\ mol^{-1}}$ for **128**]. The corresponding enantiomerization barriers are much lower for the ansa-zirconocene betaine system **130** (see Scheme 42) with values of $\Delta G^{\neq}_{\mathrm{m(toluene)}} = 14.7\ \mathrm{kcal\ mol^{-1}}$ and $\Delta G^{\neq}_{\mathrm{m(1-butene)}} = 13.2\ \mathrm{kcal\ mol^{-1}}$.[139] The dynamic features of these complexes indicate that a reactive σ-allyl betaine isomer (**143**) is within easy energetic reach and the $\Delta G^{\neq}$ values place its formation within the energetic range of the α-olefin polymerization process. Therefore, it was expected that the [zirconocene–butadiene–$B(C_6F_5)_3$] systems are homogeneous single component Ziegler-Natta α-olefin polymerization catalysts. Practically all of the [(butadiene)metallocene/$B(C_6F_5)_3$] adducts and their related "constrained geometry" systems are excellent olefin polymerization catalysts that equal or even exceed their conventional $^{R}Cp_2MCl_2$/MAO or [$^{R}Cp_2MCH_3{}^{+}$] congeners in catalyst activities. Consequently, some of these systems seem to have found applications–the [(butadiene)metallocene/$B(C_6F_5)_3$] systems have been most valuable for a variety of mechanistic studies that have helped to increase the current knowledge about the often very fast and at the same time very selective



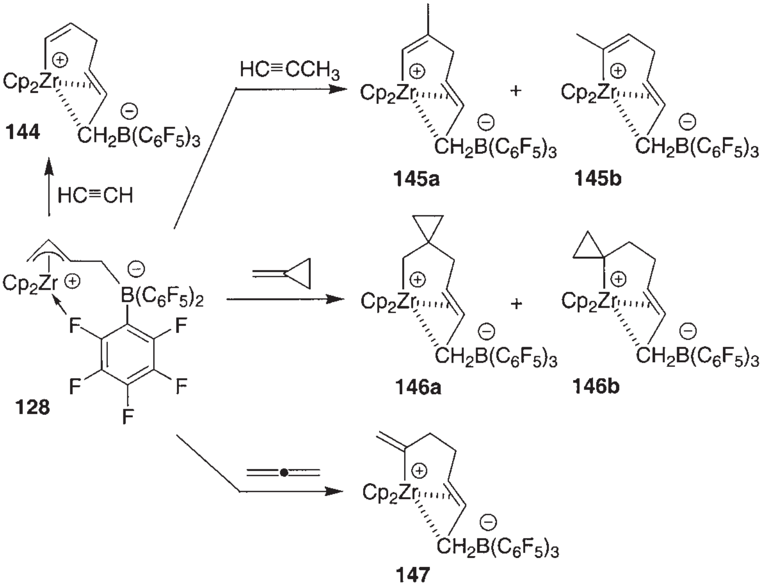
SCHEME 47

carbon–carbon coupling processes effected by the homogeneous Ziegler-Natta catalysts.[143]

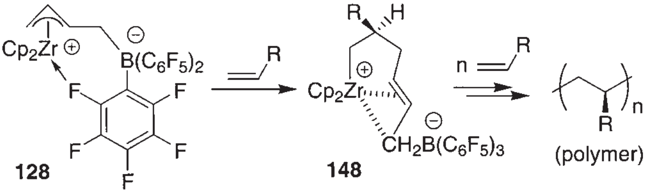
C. *Mechanistic Studies*

At low temperature the betaine system **128** reacts with a variety of alkenes and alkynes to yield mono-insertion products. These systems are rather unstable. So far they could not be isolated, but their composition was unequivocally established by low temperature NMR spectroscopy. Out of the **128** ⇆ **142** ⇆ **143** equilibrium (see Scheme 47), complex **128** adds one equivalent of acetylene to form **144** (see Scheme 48). With propyne a mixture of the two regioisomers **145a** and **145b** is formed. Similarly, the reactive olefin methylenecyclopropene adds regio-unselectively to yield the respective α- and β-regioisomers of **146**. In contrast, allene adds cleanly to give a single insertion product (**147**) that features the methylene group in the α-position to the metal.[144]

α-Olefins also insert cleanly and regioselectively; in this case only the products **148** are formed that carry the substituents R in the β-carbon atom of the resulting metallacyclic ring system.[144] The products **148** are of special interest as they probably represent the primary alkene insertion intermediates of the α-olefin polymerization sequence initiated at the single component Ziegler-Natta catalysts **128** (and its congeners). This initial stoichiometric olefin insertion and coupling reaction, therefore, represents one of the closest chemical models[145] for the actual repetitive alkene carbon–carbon coupling steps at the active metallocene polymerization catalysts that can be used for specific experimental studies towards a more profound understanding of the fundamental



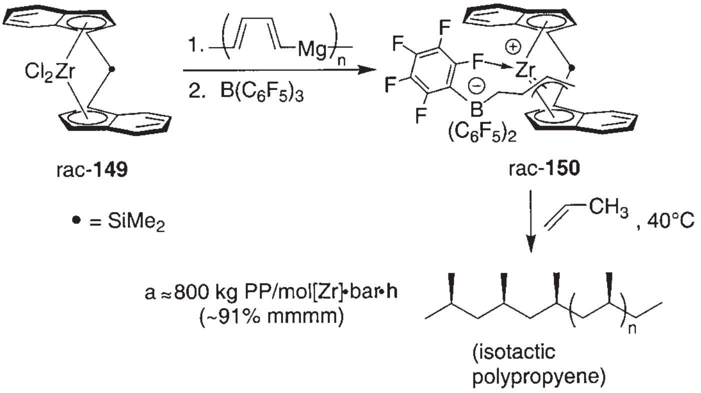
SCHEME 48



SCHEME 49

principles that govern the reactivity and selectivity patterns at this important class of alkene polymerization catalysts.

The systems **148** are very sensitive. They can usually only be observed in a rather narrow "temperature window"; being formed at ca. −20 °C, most of these systems are persistent up to ca. 0 °C before they are decomposed or react further with added excess olefin to form the respective polymer (see Scheme 49). The "extra-stabilization" that makes these initial mono-olefin insertion products actually experimentally observable as intermediates probably results from a favorable internal coordination of the C=C double bond of the C_4H_6 section and an internal ion pair interaction of the $–CH_2–[B]$ terminus with the electrophilic zirconium center.[144]



SCHEME 50

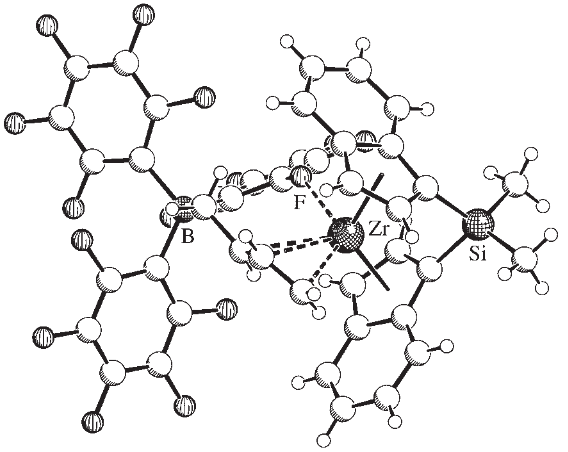
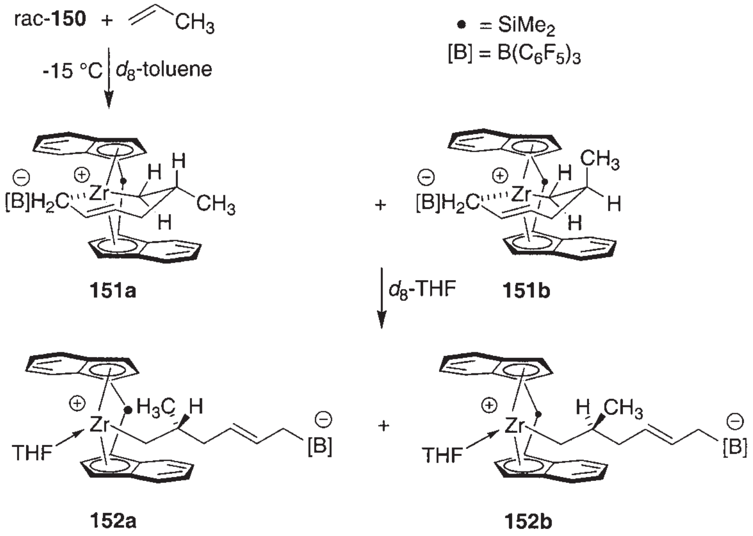


FIG. 21. A view of the molecular structure of the single component metallocene Ziegler-Natta catalyst rac-**150** (Zr–C1: 2.343(7) Å, Zr–C2: 2.485(6) Å, Zr–C3: 2.635(6) Å, Zr–F(C_{Ar}): 2.483(3) Å).

A stereochemical Ziegler-Natta study was based on this chemistry. *Rac*-[{Me_2Si(1-indenyl)$_2$}$_2ZrCl_2$] (*rac*-**149**) was reacted with butadiene–magnesium. The resulting [(*s*-*cis*-η^4-butadiene)metallocene] complex was then treated with $B(C_6F_5)_3$ to yield *rac*-**150** (see Scheme 50 and Fig. 21). Complex **150** is a very reactive single component Ziegler-Natta catalyst that gives an isotactic (>90% mmmm) high molecular weight polypropylene, when treated with propene in toluene solution at +40 °C.[146]

The reaction of *rac*-**150** with propene at −15 °C in d_8-toluene gave a mixture of two stereoisomeric olefin-mono-insertion products (**151a** and

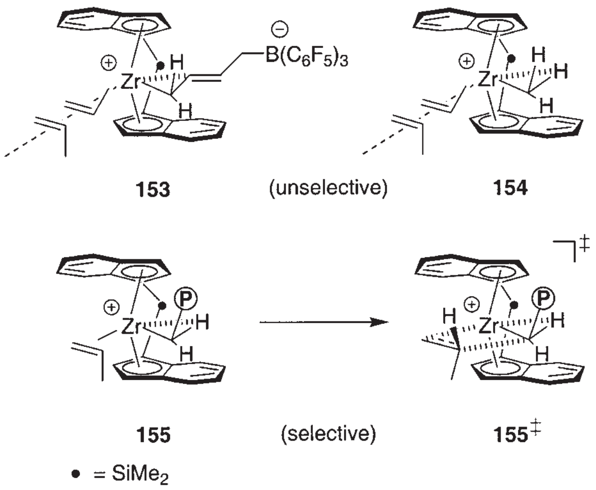


Scheme 51

151b) in 60:40 ratio. Subsequent opening of the ring system by treatment with d_8-THF (with destruction of the element of planar chirality) yielded the open-chain products **152a** and **152b**, again in a 60:40 ratio (see Scheme 51).[146]

This meant that the first propene insertion reaction at the chiral ansa-metallocene catalyst proceeded stereo-unselectively, whereas all subsequent 1-alkene CC-coupling reactions at the same catalyst were taking place with a very high diastereoselectivity. Brintzinger *et al.* obtained an analogous result from a different type of experiment using the same ansa-metallocene framework.[147] This probably indicates that the stereochemical control of the isotactic polypropylene formation is not achieved by a direct interaction of the chiral metallocene framework with the incoming prochiral α-olefin, but by a mechanism that involves the growing polymer chain. It is likely that the stereochemical information is transferred from the metallocene backbone onto the growing polymer by means of a “relay mechanism” that involves the α-carbon of the growing hydrocarbon chain as a chiral auxiliary,[145d,146] which becomes consumed and newly built up in every single olefin insertion step (see Scheme 52).

It is likely that the stereochemically decisive influence between the respective substituents at the front of the bent metallocene wedge takes place in the actual transition state ($\mathbf{155}^{\neq}$) of the insertion. By a detailed kinetic study using the unique chemical and spectroscopic features of the **128** → **148** transformation we could ascertain that the actual

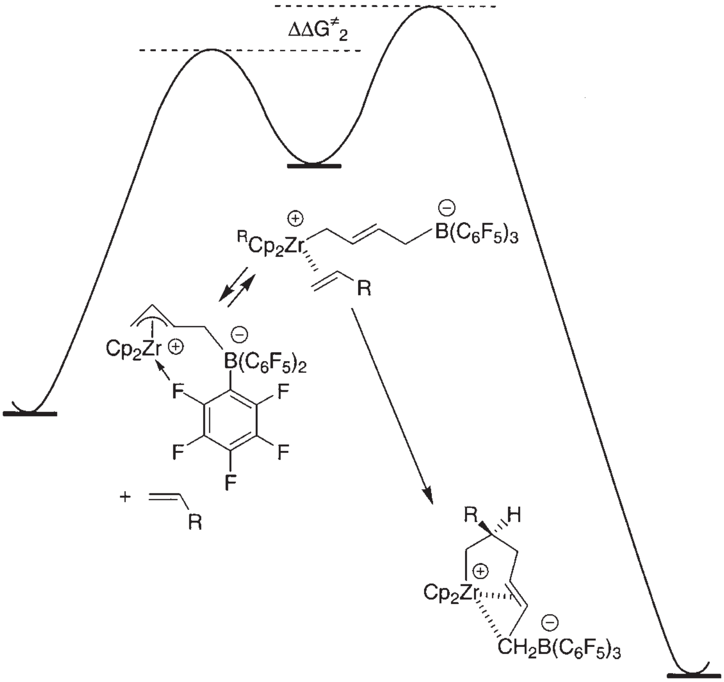


Scheme 52

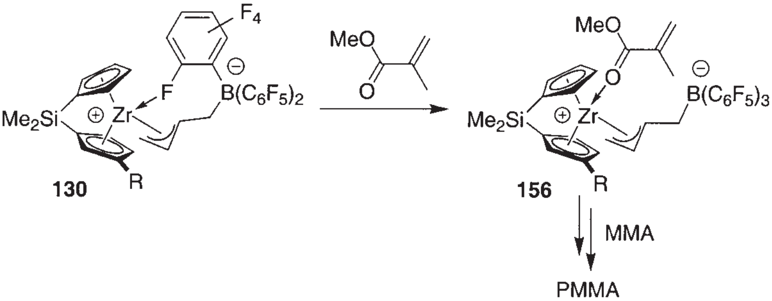
insertion step is overall rate and selectivity determining.[139,148] It is likely from that study that the 1-alkene addition is taking place in a pre-equilibrium step which was found to be more or less pronounced in the case of three representative examples, namely an open non-bridged zirconocene, a Me_2Si-bridged ansa-zirconocene, and a Me_2Si-linked Cp*/amido "constrained geometry"-type catalyst system. The activation energy difference between olefin addition and actual olefin insertion ($\Delta G_2^{\neq}$ in Scheme 53) was found between 0.7 and 3.0 kcal mol^{-1} in these systems using the mono-olefin insertion reaction at the respective [metallocene–butadiene–$B(C_6F_5)_3$]betaine model systems.[139]

At the end of the initiation period in these systems, chain transfer takes place to an incoming α-olefin, liberating a large oligomeric-modified $[H–(CH_2–CHR)_n–C_4H_6–B(C_6F_5)_3]^-$ anion that was actually detected in several cases by negative ion electrospray-MS.[124] This technique was also used to detect some uncommon reaction features of the oligomer formation during the initation period of a butadiene–betaine-"constrained geometry" catalyst system.[124]

The (butadiene) ansa-zirconocene-derived complexes **130** (^{R}Cp, R = H, Me, cyclohexyl, isopropyl, *tert*-butyl) are active catalysts for the polymerization of methylmethacrylate.[149] The isotacticity of the resulting PMMA increases rapidly with increasing bulk of the attached substituents.[150] The initial intermediate (**156**) of the polymerization reaction was observed by NMR spectroscopy[124,149] (Scheme 54).



SCHEME 53



SCHEME 54

(Butadiene) Group 4 metal complexes and (allyl) complex systems derived thereof have also been suggested as reactive intermediates at various homogeneous Group 4 metal complex-catalyzed conjugated diene polymerization reactions.[151]

VI

CONCLUDING REMARKS

(Butadiene)zirconocene was the first organometallic system for which the unique *s-trans*-η^4-coordination of a conjugated diene to a single transition metal center was observed. Its specific bonding features together with the remarkable rearrangement to the (*s-cis*-η^4-butadiene)zirconocene isomers, and the analysis of their dynamic features, significantly contributed to the understanding of the specific coordinative features of the bent metallocenes and disclosed a variety of other metal complex fragments with similar or related properties throughout the Periodic Table. As a consequence, examples of the remarkable (*s-trans*-η^4-1,3-diene) coordination were found for many other d-block elements subsequently.

The chemistry of the (1,3-diene)metallocenes and related compounds has grown remarkably. It has found many interesting applications in organometallic chemistry as well as in organic synthesis, where the (butadiene)metallocene family has turned out to provide interesting and reliable building blocks for the preparation of interesting new metal-containing as well as metal-free products.

Most interesting current uses and applications of the (butadiene)metallocenes are probably observed in the field of homogeneous catalysis. The easy formation of the (1,3-diene)$M^{IV}L_n$-derived homogeneous single component Ziegler-Natta catalysts has stimulated quite a variety of detailed experimental investigations toward a more detailed understanding of essential reaction steps that take place at these fascinating organometallic catalyst systems.

(Butadiene)metallocene chemistry has reached some maturity; but judging from its rapidly advancing recent development it is likely that members of this organometallic complex family will significantly contribute to finding solutions for a variety of pendant problems, be it in the ongoing development of advanced catalyst systems, of finding viable synthetic entries to novel organic or organometallic materials or other areas of current interest.

VII

APPENDIX: ABBREVIATIONS

acac	acetylacetonate, pentane-2,4,dionate
cod	cycloocta-1,5-diene
cot	cyclooctatetraene

Cp	η^5-cyclopentadienyl, η^5-C_5H_5
Cp*	η^5-pentamethylcyclopentadienyl, η^5-C_5Me_5
Calix[4]arene	$(t\mathrm{BuC_6H_4OMe})_2(t\mathrm{BuC_6H_4O})_2(\mathrm{CH_2})_4$ dianion
dmpe	1,2-bis(dimethylphosphino)ethane
PN_2	$\mathrm{N(SiMe_2CH_2PiPr_2)_2}$ anion
Red-Al®	$\mathrm{Na[H2Al(OCH_2CH_2OMe)]}$
tmtaa	tetramethyltetraaza[14]annulene dianion

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Borylenes as Ligands to Transition Metals

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I

INTRODUCTION

In the ongoing[1] course of his groundbreaking work on boron subhalides, Timms reported in 1967 on the preparation of fluoroborylene F–B[2,3] from elemental boron and BF_3 at high temperatures of about 2000 °C. Almost 20 years later, West generated the silylborylene Ph_3Si–B[4] by irradiation of $(Ph_3Si)_3B$ in hydrocarbon matrices at $-196\,^{\circ}C$. In both cases the borylenes turned out to be highly reactive species, which could only be obtained in the gas or solid phase by applying rather drastic conditions. Likewise, a number of reports appeared over the years, for which, from the nature of trapping products, borylenes might be assumed as intermediates in the condensed phase and at ambient temperature. However, structural or spectroscopic proof for the existence of the proposed borylenes in solution, which were assumed to be generated photochemically[5] or by reduction of suitable dihaloboranes,[6–9] could not be provided. In particular, the system $MeBBr_2/C_8K$[10–15] as a source for methylborylene Me-B was challenged by other authors.[16]

The synthesis of borylenes is as yet restricted to the aforementioned high and low temperature techniques, respectively. Related hypovalent compounds of other p-block elements, e.g., Al,[17] C,[18–22] and Si,[23–28] however,

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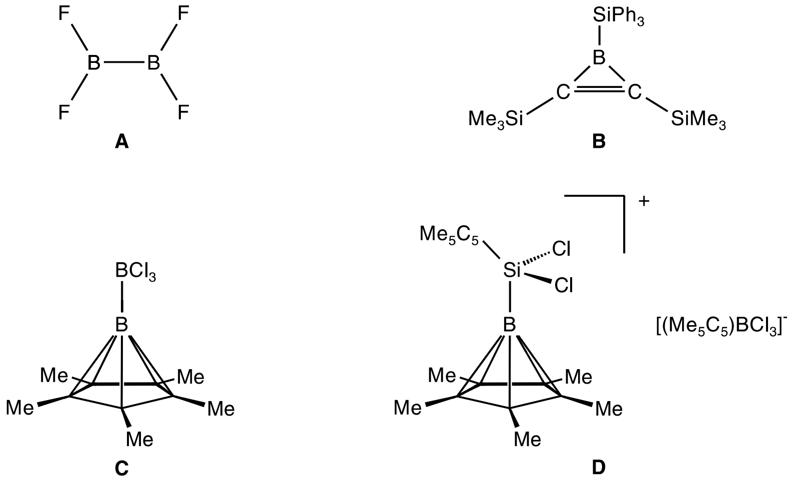


FIG. 1. Trapping products of various borylenes R–B.

are well known to exist as monomers in the condensed phase and at ambient temperature. Probably due to the elaborate experimental requirements associated with the synthesis of borylenes, their chemistry is only poorly developed. In the course of their investigations Timms and West reported on a few successful trapping reactions of their borylenes, e.g., the insertion of B-F into a boron–fluorine bond of BF_3 yielding B_2F_4[3] (A) and the reaction of Ph_3Si-B with bis(trimethylsilyl)acetylene affording the corresponding borylene[4] B. In addition, Jutzi[29,30] and Siebert[31] succeeded in fully characterising some derivatives of the hypothetical (η^5-cyclopentadienyl)borylene, which in contrast to its higher homologues of the type $[(\eta^5\text{-}C_5Me_5)E]_n$ (E = Al,[32] Ga,[33] In,[34] Tl[35]) is not known as a free molecule. Compounds like C and D were obtained from the reaction of $(\eta^5\text{-}C_5Me_5)_2Si$ with suitable boranes and are best described as *nido*-pentacarbahexaboranes(6).[31] (Fig. 1)

Since 1990 the chemistry of transition metal complexes of boron experienced a renaissance during which it became for the first time possible to generate and stabilize borylenes in the coordination sphere of various transition metals. Likewise, many short lived and labile species were successfully stabilised as ligands to transition metals, e.g., CS,[36] cyclobutadiene,[37] and $HP(OH)_2$[38]—a hitherto unknown tautomer of hypophosphorous acid—to name only a few. Transition metal complexes of boron are characterized by electron-precise two-center, two-electron (2c–2e) bonds linking the boron atom to the metal center. Thus, they significantly differ from all other classes of compounds with direct metal–boron interactions i.e., borides,[39–41] metallaboranes,[42–44] and complexes with π-bonded boron containing ligands.[45–52]

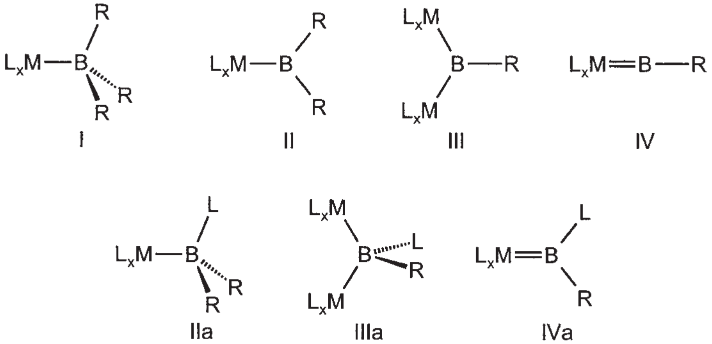


FIG. 2. Different coordination modes for boron-centered ligands.

Due to vigorous research on transition metal complexes of boron since 1990,[53–56] a variety of different coordination modes for boron-centered ligands has been realized, allowing for a systematic classification of those compounds (Fig. 2). Depending on the coordination number of boron and the number of metal–boron bonds one can distinguish between borane-(I), boryl-(II), and bridged (III) as well as terminal borylene complexes (IV). Borane complexes can be understood as Lewis acid–base adducts of basic metal centers and acidic boranes BR_3 resulting in a fourfold coordination of the boron atom. Boryl complexes, however, show boron in coordination number three which is achieved by linking a BR_2 group to a metal center. The borylene ligand R–B can adopt two different coordination modes: either bridging between two metal centers with three coordinate boron or terminal to one metal center with formation of a formal metal–boron double bond and a decrease of the coordination number to two. Provided the boron atom in II–IV is still Lewis-acidic, there is the possibility of adding a suitable base L, which results in the formation of the corresponding adducts of boryl-(IIa) and both bridged (IIIa) and terminal (IVa) borylene complexes. Examples for all types of compounds I–IV have been already described in the earlier literature between 1963 and 1970 albeit without structural confirmation.[57] The spectroscopic data reported for these compounds conflict with more recent findings and the proposed constitution of those complexes was disproved to some extent.

The significant interest that the prospects of transition metal complexes of boron received over the past few years is not only due to a hitherto unknown type of metal–boron linkage. Boryl complexes in particular became a highly rewarding target due to their potential application for the functionalisation of hydrocarbons. They are well known to be key intermediates in the metal catalysed hydroboration and related reactions,[58–65] and more recently gave access to functionalised alkanes by photochemically induced C–H activation.[66–68] The realization of both bridged and terminal borylene complexes is one of the most recent achievements in this field. In comparison to boryl complexes and the homologous group 13 elementdiyl complexes,[69] however, they are still exceptionally rare. Thanks to their close relationship to pivotal organometallics such as carbene, vinylidene, and especially carbonyl complexes, they have nevertheless been the subject to considerable interest.[70–73] In particular, the nature of the metal–boron linkage was subject to many theoretical studies (*vide infra*), which still outnumber the experimental reports by far.

II

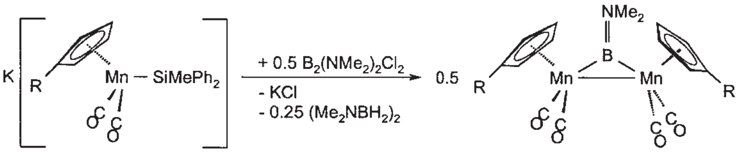
BRIDGED BORYLENE COMPLEXES

The first report of a structurally authentic borylene complex dates back to 1995 and describes a dinuclear manganese complex with a bridging borylene moiety (*vide infra*). Thus, being known for somewhat longer than their terminal counterparts, the chemistry of bridged borylene complexes has developed to greater extent. Although there are still less than 20 compounds of the type III and IIIa known, different methods have been developed for their synthesis and their reactivity has been studied in detail to some extent, especially with respect to substitution reactions at the metal coordinated borylene ligand.

A. *Synthesis*

1. From Diboranes

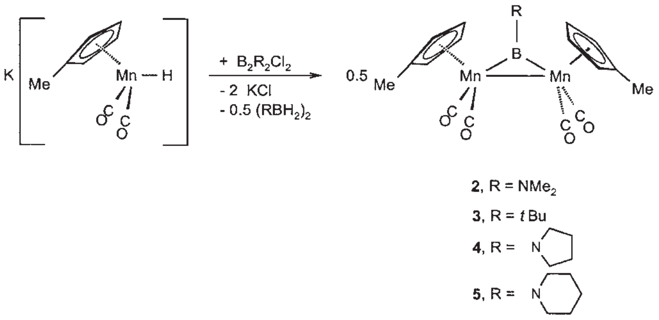
Hartwig, Norman, Marder and others have shown since the early 1990s that diboranes(4) of the type $X_2B–BX_2$ ($X = OR$, F) are excellent precursors for the facile synthesis of a broad range of mono-, bis-, and trisboryl complexes *via* oxidative addition with cleavage of the boron–boron bond.[74–85] Subsequently, we could demonstrate that 1,2-dihalodiboranes(4) undergo salt elimination reactions with transition metal carbonylates without cleavage of the boron–boron bond, thus furnishing the first examples of diborane(4)yl complexes $[L_xM\{B(R)–B(R)X\}]$ ($X = Cl$, Br, I), which are characterized by a η^1-coordinated $R_2B–B(R)$-ligand.[86–90] Our attempts at that time to realise a η^2- or side-on coordination mode for the diborane(4) ligand by reacting $ClB(NMe_2)–B(NMe_2)Cl$ with $K[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(SiMePh_2)]$ ($R = H$, Me) as a synthetic equivalent for a dianionic transition metal complex[91] resulted in the unexpected formation [Eq. (1)] of the first borylene complexes [μ-B(NMe$_2$){(η^5-C$_5$H$_4$R)Mn(CO)$_2$}$_2$] (**1**, R = H; **2**, R = Me).[92]



(1)

1, R = H
2, R = Me

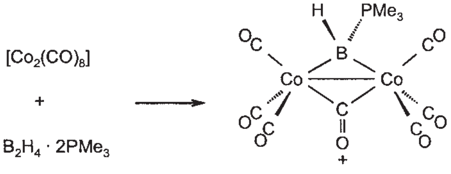
The dinuclear borylene complexes **1** and **2** are the products of a non-stoichiometric and obviously complex reaction involving the cleavage of the boron–boron bond and formation of a corresponding diborane(6) derivative (Me$_2$N–BH$_2$)$_2$—the origin of the hydrogen and the fate of the metal-bound silyl group, however, remained unclear.[92] A significant improvement of this synthesis was achieved by employing the related hydride complex K[(η^5-C$_5$H$_4$R)MnH(CO)$_2$] as a precursor furnishing the complexes **1** and **2** in much higher yields up to 80% as products of a stoichiometric reaction according to Eq. (2). In this case, a hydrogen transfer from manganese to boron occurred and resulted in the formation of (Me$_2$N–BH$_2$)$_2$ as the second boron-containing product of this reaction. Our further studies have shown that the cleavage of the boron–boron bond in the starting diboranes(4) contributes decisively to the formation of the bridged borylene complexes, since no products with B–Mn bonds were formed from related monoboranes R$_2$NBCl$_2$.[93] In addition to complexes **1** and **2** we could obtain further bridged borylene complexes of the type [μ-BR{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**3**, R = *t*Bu; **4**, R = N(C$_4$H$_8$); **5**, R = N(C$_5$H$_{10}$))[88,92,93] from the reactions of K[(η^5-C$_5$H$_4$Me)MnR(CO)$_2$] (R = H, SiMePh$_2$) with the corresponding diboranes(4).



(2)

2, R = NMe$_2$
3, R = *t*Bu
4, R =
5, R =

In 1998 Shimoi succeeded in another approach to bridged borylene complexes again *via* cleavage of a diborane(4).[94] Reaction of $[Co_2(CO)_8]$ with $B_2H_4 \cdot 2PMe_3$ yielded the cobalt borylene complex $[\mu\text{-}BH(PMe_3)(\mu\text{-}CO)\{Co(CO)_3\}_2]$ (**6**) according to Eq. (3). The fragmentation of the 1,2-bis(trimethylphosphane)diborane(4) into $BH_3 \cdot PMe_3$ and $BH \cdot PMe_3$ and liberation of one CO group led to **6**, which is a very remarkable compound as it represents the only example of a complex in which the parent borylene B–H is stabilized within the coordination sphere of a transition metal. In addition, complex **6** is also the only base stabilized bridged borylene complex as yet.

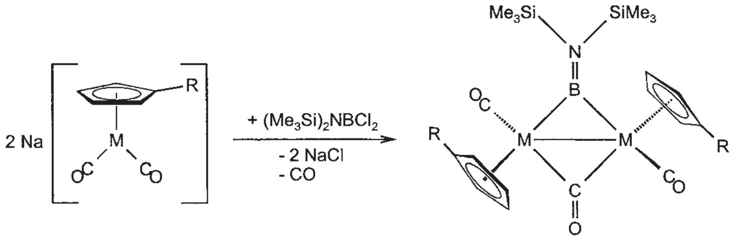


6 $BH_3 \cdot PMe_3$, CO

(3)

2. From Monoboranes

The aforementioned syntheses of dinuclear borylene complexes are very specific and restricted to the two systems discussed. In order to gain a more general access to bridged borylene complexes, we investigated reactions of aminodihaloboranes with anionic transition metal compounds in a 1 : 2 ratio. According to Eq. (4) the bridged borylene complexes $[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_4R)Fe(CO)\}_2]$ (**7**, R = H; **8** = Me)[95] and $[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**9**)[96] were obtained from $(Me_3Si)_2NBCl_2$ and $Na[(\eta^5\text{-}C_5H_4R)M(CO)_2]$ (M = Fe, R = H, Me; M = Ru, R = H) with salt elimination and loss of one carbonyl ligand.



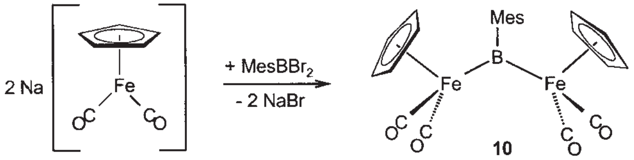
(4)

7, R = H, M = Fe
8, R = Me, M = Fe
9, R = H; M = Ru

The formation of the iron borylene complexes **7** and **8** was observed under all conditions applied, however, the synthesis of the corresponding ruthenium analogue **9** depends on the reaction conditions and stoichiometry.

For example, only an excess of Na[(η^5-C_5H_5)Ru(CO)$_2$] and slow addition of the borane led to **9** as the sole product. Interestingly, sterically less demanding amino(dichloro)boranes such as Me_2NBCl_2 reacted in both cases with substitution of only one boron–bonded chloride and formation of the corresponding boryl complexes. This result was attributed to the electron withdrawing effect of the silyl groups, which in the case of $(Me_3Si)_2NBCl_2$ make the boron center more electrophilic and hence, more susceptible to nucleophilic attack of the carbonylate.[95,96]

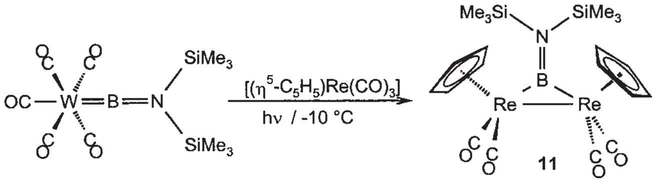
More recently, Aldridge further exploited this approach for the synthesis of [μ-BMes{(η^5-C_5H_5)Fe(CO)$_2$}$_2$] (**10**) [Eq. (5)] which represents a rare example of a structurally authentic complex with an unsupported borylene ligand B–R (R = alkyl, aryl, silyl). Interestingly, the formation of **10** is not accompanied by CO liberation although rather harsh conditions had to be applied.[97]



(5)

3. By Borylene Transfer

In the course of our investigations on the reactivity of terminal borylene complexes we found that the borylene ligand B–R can be transferred between different metal centers upon photolysis (*vide infra*). This method was not only exploited for the synthesis of novel terminal borylene complexes but also provided access to [μ-B{N(SiMe$_3$)$_2$}{(η^5-C_5H_5)Re(CO)$_2$} (**11**) according to Eq. (6).[98] Although complex **11** represents the rhenium analogue of **1** all former attempts to obtain this product by the corresponding salt elimination reaction of K[(η^5-C_5H_5)ReR(CO)$_2$] (R = H, SiMePh$_2$) with mono- or diboranes(4) had failed,[99–101] thereby demonstrating that the photochemically induced intermetallic borylene transfer is a valuable synthetic alternative for borylene complexes which cannot be obtained by other methods.



(6)

B. *Reactivity*

Despite the fact that a variety of synthetic methods for the generation of bridged borylene complexes is now at hand, their chemistry is still not explored in detail. In the case of [μ-B(NMe$_2$){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**2**) and related manganese borylene complexes, however, we could show that these species undergo a variety of substitution reactions at the metal coordinated borylene ligand with retention of the metal boron linkages. In agreement with computational studies (*vide infra*) we found the aminoborylene complexes **1** and **2** to be extremely unreactive toward nucleophilic substitutions at the bridging boron center. Stability against both air and moisture is the consequence and these compounds can be obtained even in high yields up to 80% by an aqueous work-up under air.[88,93] Treatment of **2** with an excess of gaseous HCl, however, provided the chloroborylene complex [μ-BCl{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**12**), which due to its increased reactivity served as starting material for further substitution reactions at the borylene center.

Protic reagents such as primary amines, alcohols, and water led to the corresponding substituted borylene complexes [μ-BX{(C$_5$H$_4$Me) Mn(CO)$_2$}$_2$] (**13**, X = NH*t*Bu; **14**, X = NHPh; **15**, X = OMe; **16**, X = OEt; **17**, X = O*i*Pr; **18**, X = OH) in high yields of up to 94% (Fig. 3).[100,102] It should be noted that due to the kinetic lability of the metal–boron bond such reactions at the boron center with retention of the M–B linkage are very rare for both boryl- and borylene complexes and were observed subsequently by Roper only in the case of one particular boryl complex.[103]

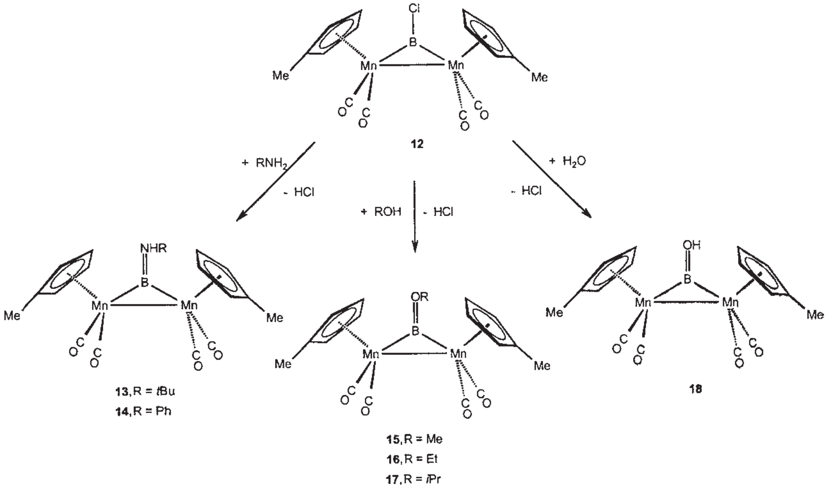
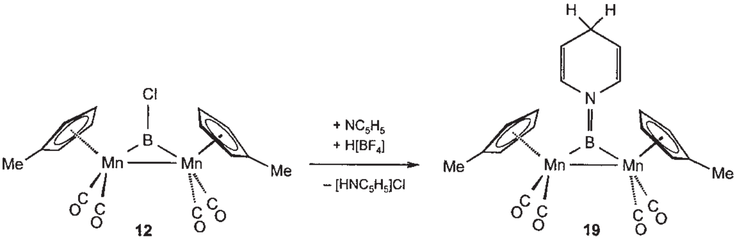


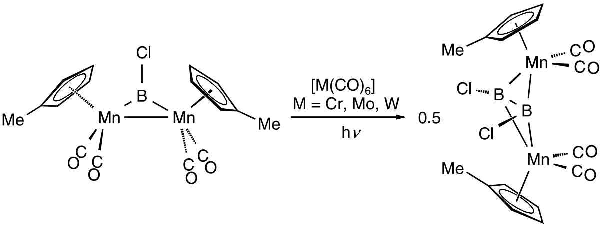
FIG. 3. Substitution reactions at a metal coordinated borylene ligand.

Further reactions of the chloroborylene complex **12** with protic reagents such as H[BF_4] in the presence of pyridine yielded the aminoborylene complex [1-(μ-B)-4-H(NC_5H_5{(C_5H_4Me)Mn$(CO)_2$}$_2$] (**19**) as the product of an unprecedented formal 1,4-hydroboration of pyridine [Eq. (7)].[104] Experiments with deuterated solvents and reagents proved the starting complex **12** to be the source for the hydride that attacks at the 4-position of the pyridine ring, thus accounting for yields being always lower than 50%.



(7)

In the course of our studies on the photochemically induced borylene transfer we found terminal borylene complexes of the type [$(OC)_5M=B=NR_2$] (M = Cr, Mo, W) to be an unprecedented source for the aminoborylene BNR_2 at ambient temperatures and in condensed phases (*vide infra*). Preliminary studies, however, showed that the photochemistry of bridged borylene complexes differs significantly from that of their terminal counterparts. Irradiation of the bridged chloroborylene complex **12** in the presence of [$M(CO)_6$] (M = Cr, Mo, W) resulted not in the formation of a [$(OC)_5M=B$–Cl] species (M = Cr, Mo, W) with borylene transfer, but yielded the novel dimetalla-*nido*-tetraborane [B_2Cl_2{(η^5-$C_5H_4CH_3$)Mn $(CO)_2$}$_2$] (**20**) according to Eq. (8), thus establishing the first synthetic link between electron-precise borylene complexes and electron-deficient metallaboranes. Computational studies and X-ray data proved **20** to exhibit a dicyclobutadiene- or butterfly geometry, which as a structural motif was without precedent in metallaborane chemistry.[105] While the aforementioned hexacarbonyls served only as a rather poor CO source, the use of gaseous CO under the same conditions led to the metallaborane **20** in much higher yields.[105]



12 **21**

(8)

C. *Spectroscopic and Structural Aspects*

It is well established for boryl complexes [L_xM–BR_2] (II) that the introduction of a metal–boron linkage gives rise to significantly deshielded ^{11}B-NMR signals with respect to those of the borane precursors.[53–56] Due to the presence of two metal–boron bonds all bridged borylene complexes are characterized by shifts to even lower field in the ^{11}B-NMR spectra. All amino- and oxoborylene complexes that incorporate a B–N or B–O π-component, are characterized by corresponding resonances between $\delta = 100$ and 120 (Table I). Complexes **3** and **10** display bridging alkyl- and arylborylene ligands, respectively, which are free of ligand-boron π-interaction, and thus, even more deshielded signals are observed down to $\delta = 170.0$. In contrast to the aforementioned species with three co-ordinate boron centers the base-stabilized borylene complex [μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**6**) is characterized by a significantly shielded ^{11}B-NMR resonance at $\delta = 17.5$ due to an increased coordination number of four.

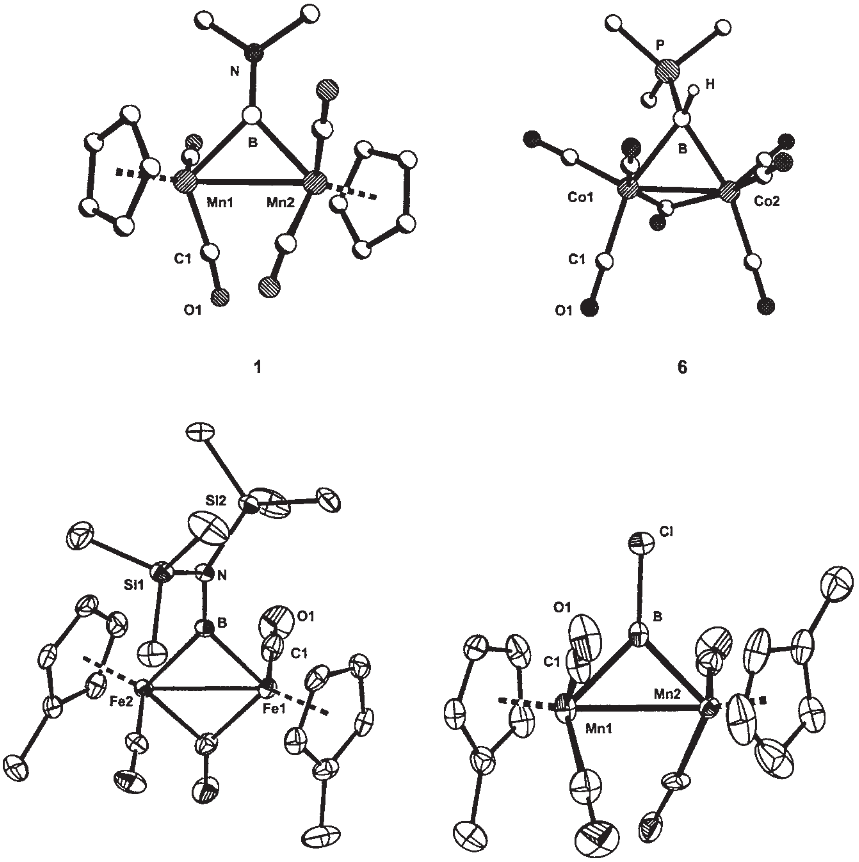
X-ray structural data are available for [μ-B(NMe$_2$){(η^5-C$_5$H$_5$)Mn(CO)$_2$}$_2$] (**1**), [μ-B{N(SiMe$_3$)$_2$}(μ-CO){(η^5-C$_5$H$_4$Me)Fe(CO)}$_2$] (**8**), [1-(μ-B)-4-H(NC$_5$H$_5$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**19**), [μ-BCl{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**12**), [μ-BOEt{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**16**), [μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**6**), and [μ-BMes{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$] (**10**) (Figs. 4 and 5). The aminoborylene complexes **1**, **8**, and **19** exhibit a central isosceles triangle made up by the boron and the two metal atoms with metal–metal and metal–boron distances (Table I) which are in the expected range for corresponding single bonds. In all cases, short boron–nitrogen distances establish the presence of the corresponding double bonds. It should be noted, however, that the bulky N(SiMe$_3$)$_2$ substituent in **8** due to its increased spatial requirements is twisted by 53.7(1)° with respect to the Fe–B–Fe plane. Hence, in connection with the extended B–N distance of 141.2(4) pm, a somewhat less effective backbonding from nitrogen to boron can be assumed. The overall molecular structure data of bridged borylene complexes resemble those of the isoelectronic vinylidene[106,107] or corresponding bridged methylene complexes,[108–110] which can be considered as dimetallacyclopropane derivatives. The related manganese complexes **12** and **16** with bridging chloro- and ethoxyborylene ligands show a very similar structural motif with respect to the central B–Mn$_2$ moiety and unobtrusive B–Cl and B–O distances, respectively. Although being related to the aforementioned iron and manganese species, the solid state structure of the mesitylborylene complex **10** shows some characteristic differences. Firstly, as already observed in corresponding gallium and indium complexes,[111–113] the absence of a constraining metal–metal bond

TABLE I

Compounds	Synthesis	*d*(M–B)	δ	Ref.
[μ-B(NMe$_2$){η^5-(C$_5$H$_5$)Mn(CO)$_2$}$_2$] (**1**)	b	203(1)	103.0	92,93
[μ-B(NMe$_2$){η^5-(C$_5$H$_5$)Mn(CO)$_2$}$_2$] (**1**)	–	204.9*	y	117
[μ-B(NMe$_2$){η^5-(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**2**)	b	x	102.8	92,93
[μ-B*t*Bu{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**3**)	b	x	170.0	92,93
[μ-B{N(C$_4$H$_8$)}{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**4**)	b	x	100.3	88
[μ-B{N(C$_5$H$_{10}$)}{(η^5-(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**5**)	b	x	101.1	88
[μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**6**)	b	211.2(9) 210.8(11)	17.5	94
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){(η^5-C$_5$H$_5$)Fe(CO)}$_2$] (**7**)	a	x	118.4	95
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){(η^5-C$_5$H$_4$Me)Fe(CO)}$_2$] (**8**)	a	200.7(3) 200.2(3)	119.1	95
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){(η^5-C$_5$H$_5$)Ru(CO)}$_2$] (**9**)	a	x	105.9	96
[μ-BMes{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$] (**10**)	a	209.1(10)	158.0	108
[μ-B{N(SiMe$_3$)$_2$}{(η^5-C$_5$H$_5$)Re(CO)$_2$} (**11**)	c	x	100.4	98
[μ-BCl{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**12**)	e	203.9(11)	133.5	150
[μ-B(NH*t*Bu){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**13**)	e	x	102.4	102
[μ-B(NHPh){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**14**)	e	x	107.6	102
[μ-B(OMe){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**15**)	e	x	98.8	102
[μ-B(OEt){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**16**)	e	198.8(2) 202.1(2)	97.6	102
[μ-B(O*iPr*){(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**17**)	e	x	96.5	100
[μ-B(OH){(η^5-C$_5$ H$_4$Me)Mn(CO)$_2$}$_2$] (18)	e	x	101.6	102
[1-(μ-B)-4-H(NC$_5$H$_5$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$ (**19**)	e	202.3(5)	111.9	104
[(OC)$_4$Fe–B(η^5-C$_5$Me$_5$)] (**21**)	a	201.0(3)	−35.3	122
[(OC)$_5$W=B=N(SiMe$_3$)$_2$] (**22**)	a	215.1(7)	86.6	123
[(OC)$_4$Fe=B=N(SiMe$_3$)$_2$] (**23**)	a	x	88.2	123
[(OC)$_5$Cr=B=N(SiMe$_3$)$_2$] (**24**)	a, c	199.6	92.3	123,98
[(OC)$_5$Cr=B–Si(SiMe$_3$)$_3$] (**25**)	a	187.8(10)	204.3	136
[Os(=BNHC$_9$H$_6$N)Cl$_2$(CO)(PPh$_3$)$_2$] (**26**)	d	x	y	147
[Os(=BNHC$_9$H$_6$N)Cl(I)(CO)(PPh$_3$)$_2$] (**27**)	e	205.5(8)	51.7	147
[Os{=BCl(NHC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**28**)	d	x	y	149
[Os{=BOEt(NHC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**29**)	e	206.6(5)	52.1	149
[Os{=BCl(NMeC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**30**)	e	x	x	149
[(η^5-C$_5$Me$_5$)Fe(CO)$_2$=BMes][BAr$^f{}_4$] (**31**)	d	179.2(8)	145.0	149
[(η^5-C$_5$H$_5$)(OC)$_3$V=B=N(SiMe$_3$)$_2$] (**32**)	c	197.1(8)	98.3	105
[(OC)$_5$W=B=N(SiH$_3$)$_2$] (**33**)	–	215.2*	y	133,134
[(OC)$_4$Fe–B(η^5-C$_5$H$_5$)] (**34**)	–	196.2*	y	133,134
[Os{B(OEt)NHC$_9$H$_6$N}Cl(CO)(PPh$_3$)$_2$] (**35**)				
[Os{=BCl(NMeC$_5$H$_4$N)}H(CO)(PPh$_3$)$_2$] (**36**)	e	207.8(4)	84.6	148
[Os{=BOEt(NMeC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**37**)	e	x	53.2	148
[Os{=BOEt(NMeC$_5$H$_4$N)}MeCN(CO)(PPh$_3$)$_2$][SbF$_6$] (**38**)	e	x	54.6	148

Abbreviations: a, from monoboranes; b, from diboranes(4); c, by borylene transfer; d, from boryl complexes; e, from borylene complexes; x, no X-ray data available; y, no ^{11}B-NMR data available.

*Geometry from *ab initio* calculation.

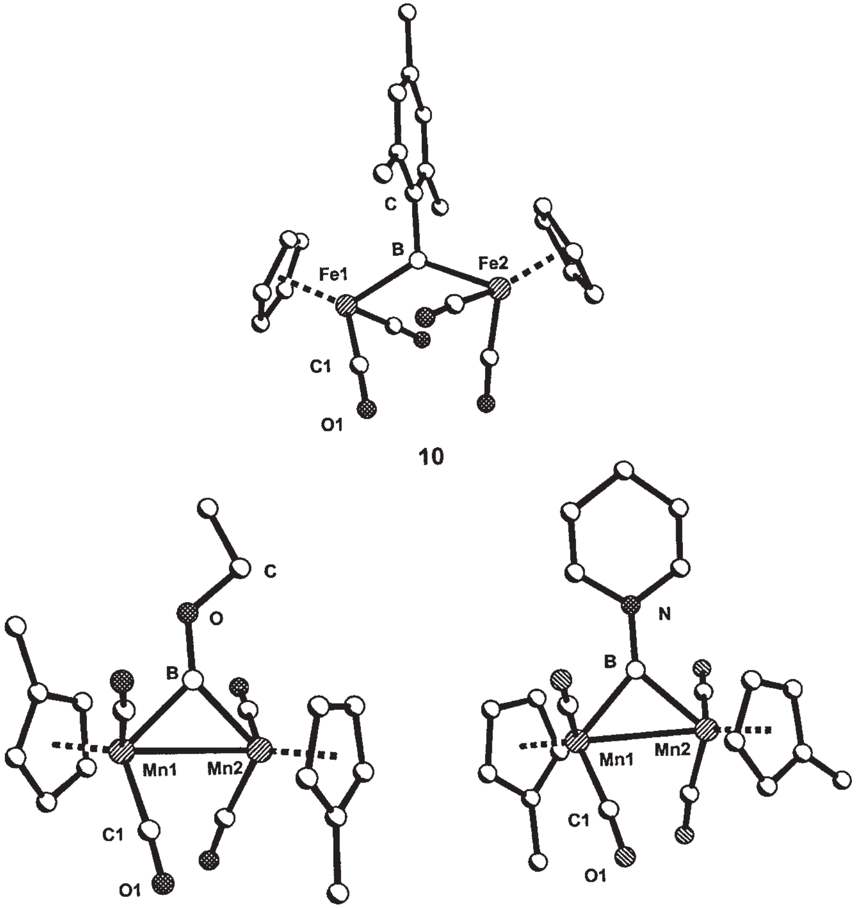


1 **6**

8 **12**

FIG. 4. Structure of selected bridged borylene complexes in the crystal.

leads to a significantly wider Fe–B–Fe angle with respect to complexes where the bridging borylene ligand is part of a three membered metallacycle. Secondly, the Fe–B distances are ~ 9 pm longer than in the corresponding aminoborylene complex **8**. This result is somewhat surprising as one could expect a stronger Fe–B π-backbonding for the former complex, thus compensating for the missing ligand by increased boron π-interaction (*vide infra*). However, the rather long Fe–B bonds reflect the increased steric demands of the boron bound mesityl ligand with respect to the amino groups.



10

16 **19**

FIG. 5. Structure of selected bridged borylene complexes in the crystal.

The tetrahedrally coordinated boron center in the base stabilized complex **6** shows the expected increase of the metal–boron distances, which thus range between those of cobalt boryl complexes[114,115] and cobaltaboranes.[116]

Recently, the borylene complex [μ-B(NMe$_2$)\{(η^5-C$_5$H$_5$)Mn(CO)$_2$\}$_2$] (**1**) was subject to detailed computational studies and the theoretically predicted and the experimentally derived structural parameters were found to be in very good agreement (Table I).[117] Density functional theoretical studies have concluded that borylenes BX can be viable ligands in the design of transition metal complexes, which are thermodynamically stable with respect to a homolytic metal–boron bond dissociation. On one hand, the high thermodynamic stability is traced back to the good σ-donor and π-acceptor properties of BX ligands owing to the σ- and π-orbital energies. On the other hand, the high polarity and the small HOMO–LUMO gap of the uncoordinated BX ligand suggest a low kinetic stability. Increasing the HOMO–LUMO gap by complexation also increases the kinetic stability to a certain extent, but the imbalance between σ-donation and π-acceptance leads to a positive charge on BX and makes a nucleophilic attack at the co-ordinated fragment more favorable. In the complex **1** the kinetic stability is enhanced by steric protection of the reactive frontier orbitals of the $BNMe_2$ ligand by complexation at a bridging site and additionally by bulky methyl substituents. The binuclear $Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ fragment reduces also the build-up of positive charge at $BNMe_2$, as it is an excellent π-donor with just the right frontier orbitals to restore the M–$BNMe_2$ σ-donation and π-back donation balance.

In agreement with these findings aminoborylene complexes of the type $[\mu\text{-}BR_2\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ (**1**) proved to be inert toward air and water and to undergo nucleophilic substitutions at the boron center with retention of the electronically stabilized Mn_2B-skeleton (*vide supra*).

III

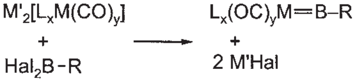
TERMINAL BORYLENE COMPLEXES

A. *Synthesis*

1. From Monoboranes

Salt elimination reactions between anionic transition metal complexes, usually carbonylates of the type $M'[L_xM(CO)_y]$, and main group element halides $HalER_z$ have a pivotal role in organometallic chemistry for the synthesis of species $[L_x(OC)_yM\text{-}ER_z]$ with transition metal element bonds.[118,119] More recently, corresponding salt elimination reactions employing boron halides $HalBR_2$ and Hal_2BR have become a very facile method for the synthesis of boryl[53–56] and bridged borylene complexes (*vide supra*). It should be noted, though, that in the case of certain combinations between metal carbonylates and haloboranes a nucleophilic attack of CO oxygen atoms at the boron center with formation of oxycarbyne complexes was observed as an alternative reaction path to the expected synthesis of boryl complexes.[89,120,121]

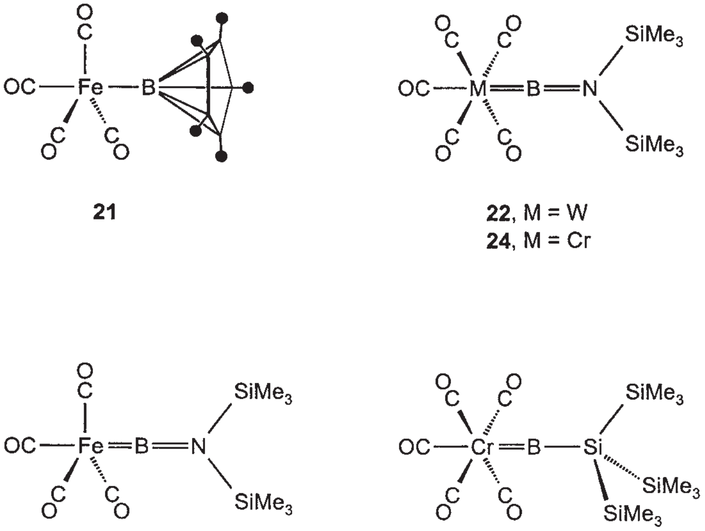
An extension of this synthetic approach to dianionic carbonylates and suitable dihaloboranes [Eq. (9)] gave access to the first structurally authentic terminal borylene complexes [(OC)$_4$Fe-B(η^5-C$_5$Me$_5$)] (**21**)[122] and [(OC)$_5$W=B=N(SiMe$_3$)$_2$] (**22**),[123] which Cowley and we reported in 1998 (Fig. 5).



$$\begin{matrix} M'_2[L_xM(CO)_y] \\ + \\ Hal_2B\text{-}R \end{matrix} \longrightarrow \begin{matrix} L_x(OC)_yM{=}B\text{–}R \\ + \\ 2\ M'Hal \end{matrix} \qquad (9)$$

By applying the corresponding precursors K$_2$[Fe(CO)$_4$] and Na$_2$[Cr(CO)$_5$] we also obtained the related aminoborylene complexes [(OC)$_4$Fe=B=N(SiMe$_3$)$_2$] (**23**)[123] and [(OC)$_5$Cr=B=N(SiMe$_3$)$_2$] (**24**)[123] (Fig. 6), the latter of which was subsequently characterized by X-ray structure analysis.[124]

The formation of **21**–**24** implies that the boron center in such terminal borylene complexes requires stabilization by a ligand that is both sterically demanding and electron releasing. Evidently, the η^5-C$_5$Me$_5$ and the N(SiMe$_3$)$_2$ substituents provide sufficient steric shielding and π-electron stabilization. In the case of the former, however, an alternative point of view may be applied, namely that the electron deficiency of the boron center is relieved by its incorporation into a non-classical polyhedral skeleton. Thus,



21

22, M = W
24, M = Cr

23

25

Fig. 6. Terminal borylene complexes from salt elimination reactions.

compound **21** is best described as a *nido*-borane[31,125,126] like the related main group element derivatives of the η^5-C_5Me_5 borylene **C** and **D** (*vide supra*).

According to our experience with the formation of classical transition metal–boron bonds by salt elimination reactions, the aminoborane $Br_2B{=}N(SiMe_3)_2$ appeared to be the most promising borane precursor for the synthesis of terminal aminoborylene complexes because of the increased electrophilicity of the boron center in comparison to the corresponding (dialkylamino)boranes, hence, facilitating the nucleophilic substitution of the halides by transition metals.[95,96] Despite numerous efforts[99–101] and the vast amount of various haloborane precursors at hand, all attempts to obtain corresponding complexes $[(OC)_xM{=}B{=}NR_2]$ from any other aminoborane $Hal_2B{=}NR_2$ have so far failed, thus emphasising the particular significance of $Br_2B{=}N(SiMe_3)_2$ for the synthesis of terminal borylene complexes. The lack of success of salt elimination reactions with dianionic metal carbonylates according to Eq. (9) appears to extend to common alkyl- and aryl(dihalo)boranes Hal_2B–R,[99–101] thus hampering the isolation of terminal borylene complexes of the type $[(OC)_xM{=}B{-}R]$. These compounds, however, are of particular interest, since here, the boron center is both coordinatively and electronically unsaturated and thus, displays a very unusual bonding situation in regard to boron chemistry, in which only a very few methyleneboranes of the type $(Me_3Si)_2C{=}B{-}R$ (R=Me, *t*Bu, 2,3,5,6-tetramethylphenyl, 2,4,6-trimethylphenyl) are known.[127–131] Due to their obvious significance[70] for the understanding of metal–boron bonding alkyl- and arylborylene complexes $[(OC)_xM{=}B{-}R]$ had been already subjected to several theoretical studies[132–135] before we could report the first experimental proof for such a compound in 2001.[136] The use of the sterically demanding silylborane $Cl_2B{-}Si(SiMe_3)_3$ furnished the fully characterized $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**25**) as the first terminal borylene complex with a boron center which is both coordinatively and electronically unsaturated (Fig. 6). In contrast to its rather stable amino-analogue $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**24**) the silylborylene complex **25** proved to be extremely sensitive towards air and moisture and shows significant decomposition in solution and even in the solid state after several hours at ambient temperature. The enhanced sensitivity of **25** is obviously due to the lack of ligand-to-boron π-interaction as the steric requirements of the $Si(SiMe_3)_3$ are arguably equal or even greater than that of the $N(SiMe_3)_2$ group in **24**.

2. From Boryl Complexes

Silyl and germyl complexes with suitable functionalities were successfully used as precursors for the synthesis of compounds with corresponding transition metal element multiple bonds.[137–145] Due to the aforementioned

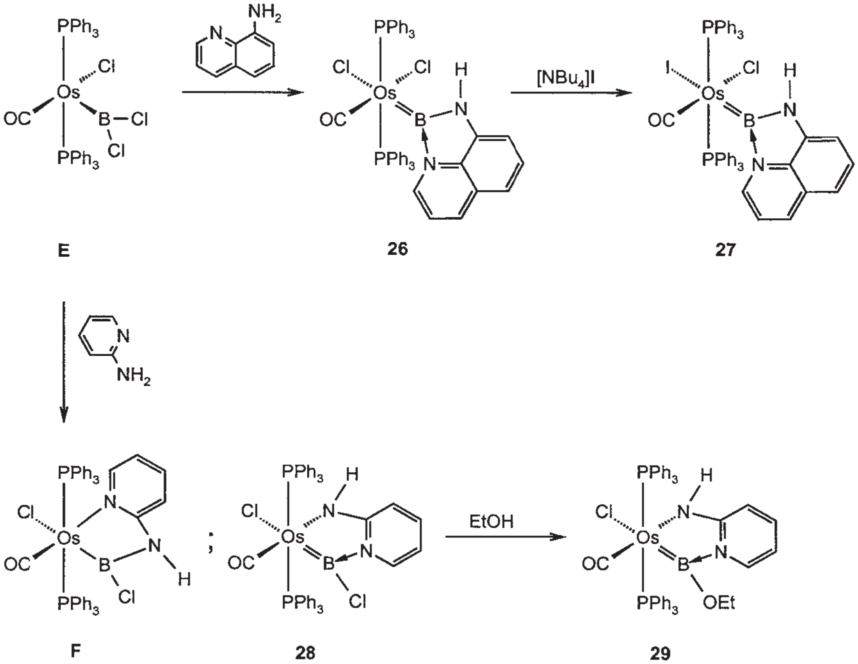


FIG. 7. Formation and reactivity of base-stabilized terminal borylene complexes of osmium.

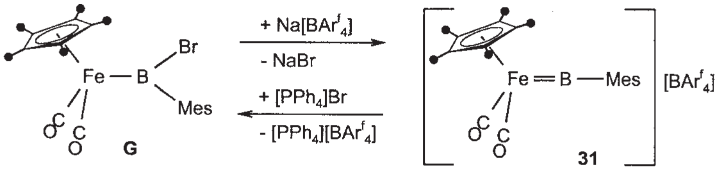
difficulties and restrictions with respect to suitable starting materials that are associated with the synthesis of terminal borylene complexes via salt elimination reactions one might envisage a corresponding strategy employing boryl complexes as precursors for the generation of borylene complexes as a useful alternative. Although boryl complexes with suitable functionalities such as $[(\eta^5\text{-}C_5H_4Me)(OC)_2(H)Mn\text{–}B(Cl)E(SiMe_3)]$ (E = Si, Ge)[146] are well known, all attempts to obtain neutral borylene complexes with elimination of HCl failed.[99–101]

Roper, however, succeeded in converting the osmium boryl complex $[Cl_2BOsCl(CO)(PPh_3)_2]$ (E) into the terminal borylene complex $[Os(=BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$[147] (**26**) upon reaction with 8-aminoquinoline according to Fig. 7. Compound **26** is noteworthy as it represents the first example of a base stabilized terminal borylene complex of the type $[L_xM=B(L)\text{–}R]$ (IVa, Fig. 1).

Subsequent treatment of **26** with $[Bu_4N]I$ yielded the borylene complex $[Os(=BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**27**), in which the chloro ligand *trans* to the boron atom was replaced by iodine, thus giving evidence for the *trans*-influence of the borylene ligand.[147] Interestingly, the same boryl complex $[Cl_2BOsCl(CO)(PPh_3)_2]$ (**E**) gives upon reaction with

2-aminopyridine a mixture of the tethered boryl complex **F** and the base stabilized chloroborylene complex $[Os\{=BCl(NHC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**28**). Treatment of this mixture with ethanol converted **28** into its ethoxyborylene derivative $[Os\{=BOEt(NHC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**29**), which could thus be separated from the accompanying boryl complex and fully characterized (Fig. 7).[148] A corresponding reaction of **E** with 2-(methylamino)pyridine yielded selectively the base stabilized borylene complex $[Os\{=BCl(NMeC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**30**), which was also fully characterised in solution.[148]

Very recently, Aldridge reported on an interesting cationic borylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2{=}BMes][BAr^f_4]$ (**31**; $Ar^f = C_6H_3(CF_3)_2\text{-}3,5$), which was obtained according to Eq. (10) from the corresponding mesitylboryl complex **G** by abstraction of Br and precipitation of sparingly soluble NaBr.[149]

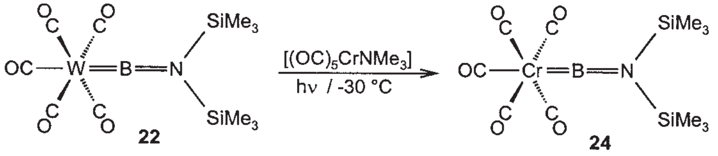


(10)

The borylene complex **31** turned out to be highly reactive and readily regenerates its precursor G upon reaction with $[PPh_4]Br$.

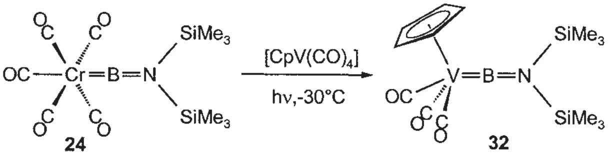
3. By Borylene Transfer

The obvious need for an alternative and more general synthetic access to terminal borylene complexes initiated our studies on the potential use of complexes of the type $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (**22**, M = W; **24**, M = Cr) as a source for the aminoborylene $B{=}N(SiMe_3)_2$. Recently, we reported on the first photochemically induced intermetal borylene transfer according to Eq. (11).[98]



(11)

Although this reaction represents only an alternative synthesis for the chromium species **24** it was conducted as an initial experiment since the expected product was known to be stable under the chosen conditions. Monitoring the progress of the transfer by ^{11}B-NMR spectroscopy proved that the borylene transfer was quantitative after 12 h at −30 °C in toluene and no boron containing byproducts were detected. A corresponding experiment with $[Cr(CO)_6]$, however, provided the chromium borylene complex **24** only in moderate yield, obviously due to the poor solubility of the hexacarbonyl at lower temperatures. Similarly, $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ (**32**), the first half-sandwich complex with a terminal borylene ligand, was obtained from **24** and $[(\eta^5\text{-}C_5H_5)V(CO)_4]$ according to Eq. (12) upon irradiation.[150] The formation of the vanadium complex **32** in particular emphasises the significance of the photochemically induced intermetal borylene transfer, since all attempts to obtain this product by salt elimination reactions from $Na_2[(\eta^5\text{-}C_5H_5)V(CO)_3]$ and $Hal_2B{=}N(SiMe_3)_2$ have failed.[99–101]



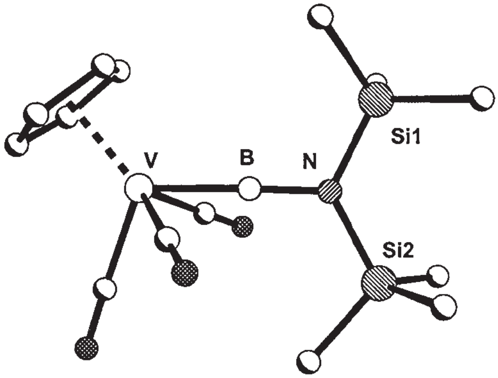
(12)

It should be noted that in 1973, Timms had already recognized borylene complexes to be a potentially useful source of borylenes in cases where gaseous species (i.e., haloborylenes being obtained *via* high temperature synthesis) cannot be used.[3] Future investigations may likely show that borylene complexes have a synthetic applicability as a unique source for B–R species in condensed phase far beyond the intermetal transfer reactions discussed here.

B. *Spectroscopic and Structural Aspects*

In solution, the common and most characteristic spectroscopic feature of all terminal borylene complexes with coordinatively unsaturated, i.e., two coordinate boron atoms, are the ^{11}B-NMR resonances, which are significantly deshielded with respect to those of corresponding amino- and silylboryl complexes of the type $[L_xM{-}B(X)NR_2]$[53–56] and $[L_xM{-}B(X)SiR_3]$.[146]

The aminoborylene complexes **22**, **23**, **24**, and **32** exhibit ^{11}B-NMR shifts in the range from $\delta = 87$ to 93 (Table I), thus resembling those of corresponding bridged borylene complexes with π-donating ligands at boron (*vide supra*). The silylborylene complex $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**25**) is characterized by a strikingly deshielded ^{11}B-NMR resonance at δ 204.3, and hence, greatly extends the known dispersion of the ^{11}B nucleus for classical boranes. Similarly low-field shifted resonances were reported only for metal clusters comprising interstitial boron atoms, e.g., *cis*- and *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$ ($\delta = 211$ and 205).[151,152] The observed significant



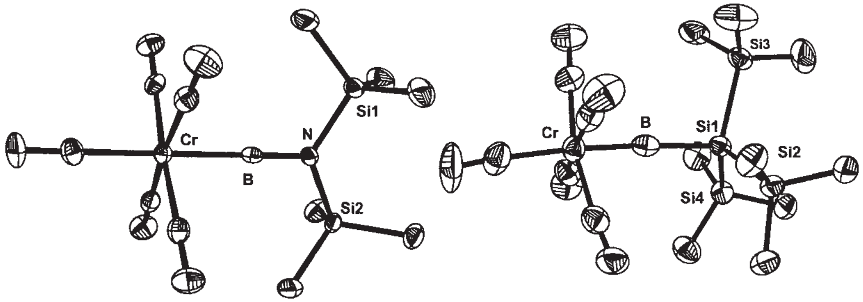
32

FIG. 8. Structure of **32** in the crystal.

difference between **24** and **25** could be expected for terminal borylene complexes in which the boron center is not part of a boron-ligand π-system[70] if one compares the bridged amino- and alkylborylene complexes of the type $[(\mu\text{-BR})\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ ($R = NMe_2$, $\delta\ ^{11}B = 103$; $R = t$Bu, $\delta\ ^{11}B = 170$) (*vide supra*). Due to the higher coordination numbers of the boron centers, $[(OC)_4Fe{-}B(\eta^5\text{-}C_5Me_5)]$ (**21**),[122] $[Os({=}BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**27**),[147] and $[Os\{{=}BOEt(NHC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**29**)[148] display much more shielded ^{11}B-NMR resonances at $\delta = -35.3$, 51.7, and 52.1, respectively, the former being characteristic for apical boron atoms in such *nido*-carboranes.

Crystal structure data are available for the following terminal borylene complexes: $[(OC)_4Fe{-}B(\eta^5\text{-}C_5Me_5)]$ (**21**), $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**22**), $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**24**), $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**25**), $[Os({=}BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**27**), $[Os\{{=}BOEt(NHC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**29**),[148] $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2{=}BMes][BAr^f_4]$ (**31**; $Ar^f{=}C_6H_3(CF_3)_2\text{-}3,5$)[149] and $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ (**32**) (Figs. 8, 9, and 12, Table I).

The metal–boron distances for the aminoborylene complexes **22**, **24**, and **32** range from 197.1 to 215.1 pm, which together with further spectroscopic and structural data suggest a strong boron–to-metal σ-donation and a weaker metal-to-boron π-backbonding. For aminoborylene complexes of first row transition metals this situation was predicted on the basis of *ab initio* calculations.[117] The cationic complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2{=}BMes][BAr^f_4]$ (**31**; $Ar^f = C_6H_3(CF_3)_2\text{-}3,5$) shows an orientation of the mesitylborylene ligand in the crystal that allows for π-donation from the metal center and the mesityl ring into the two vacant perpendicular



24 **25**

FIG. 9. Structure of **24** and **25** in the crystal.

p-orbitals at boron. The iron–boron distance of 179.2(8) pm is shorter than any transition metal–boron linkage previously reported and consistent with a Fe–B double bond.[149] In contrast, for the complex [(OC)$_4$Fe–B(η^5-C$_5$Me$_5$)] (**21**),[122] which exhibits a six-coordinate borylene ligand in axial position, a significantly longer iron–boron distance of 201.0 ppm was reported, which indicates a corresponding single bond. The base-stabilized borylene complexes **27** and **29** are characterized by osmium–boron distances of 205.5 and 206.6(5) pm, thus being longer than an expected double bond. Corresponding findings were made for related base-stabilized silylene complexes.[141,143,153]

The decisive influence of the boron–bound ligand R on the metal–boron linkage in terminal borylene complexes [L$_x$M = B–R] was already demonstrated to some extent by the aforementioned differences in the ^{11}B-NMR shifts. In the solid state, this influence becomes even more evident if one compares the results of the X-ray structure analyses of [(OC)$_5$Cr=B=N(SiMe$_3$)$_2$] (**24**) and [(OC)$_5$Cr=B–Si(SiMe$_3$)$_3$] (**25**) (Fig. 9).

In both molecules, the Cr(CO)$_4$ moieties exhibit approximate C_{4v} symmetry and the central Cr–B–E-fragment (E = N, Si) adopts a linear arrangement. The Cr–B distance in **25** was found to be 187.8 pm, and thus, 12 pm shorter than in the amino counterpart **24**. Obviously, the electron deficiency of the boron center in the silylborylene complex demands an enhanced Cr–B π-backbonding. Further evidence for an increased backbonding in **25** stems from the umbrella effect observed for the equatorial CO-ligands and the pronounced *trans*-influence the B–Si(SiMe$_3$)$_3$ ligand has on the axial CO-ligand manifested by a longer OC–M bond. Unlike in the aforementioned methyleneboranes (Me$_3$Si)$_2$C=B–R, there is no spectroscopic, structural, or computational evidence for the presence of non-classical B–Si–Si three-center, two-electron bonds (hyperconjugation) in the case of **25**, which is known to relieve electron deficiency at such coordinatively and electronically unsaturated boron centers.[127–131]

The question of the nature of the metal–boron bond in terminal borylene complexes was addressed by many theoretical studies in the recent years,[117,132–135,154–156] and, in particular, the selected examples $[(OC)_5W{=}B{=}N(SiH_3)_2]$ (**33**) and $[(OC)_4Fe–B(\eta^5\text{-}C_5H_5)]$ (**30**) were investigated as model compounds for the aforementioned complexes **21** and **22**. It was concluded that borylene ligands (BR) in general have both good σ-donor and π-acceptor properties, but because of the electrophilicity of the boron center, terminal borylene complexes should only be stable with sterically protecting and electron-releasing substituents at the boron atom, for example, $N(SiMe_3)_2$ or $\eta^5\text{-}C_5Me_5$.[117] The metal–borylene orbital interactions resemble those of isoelectronic carbonyl complexes i.e., ligand to metal σ-donation and metal to ligand π-backbonding into the degenerate LUMO of the borylene (Fig. 10). DFT calculations of valence orbital energies of potential ligands AB (N_2, CO, BF, and related borylenes) revealed that the BF HOMO is higher and the LUMO lower in energy with respect to the corresponding frontier orbitals of CO. Hence, BF is a better σ-donor and a better π-acceptor than CO. As a consequence, fluoroborylene complexes were calculated to be thermodynamically more stable than carbonyl complexes with respect to homolytic dissociation of the metal element bond.[117]

The nature of the transition metal–boron bond in $[L_xM{=}B–R]$ is obviously strongly influenced by the boron bonded substituent R. Descriptions based on calculations range from an almost purely

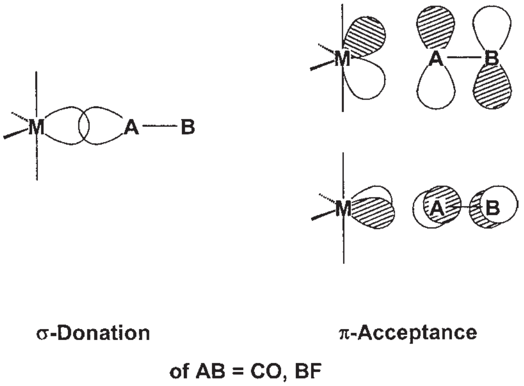
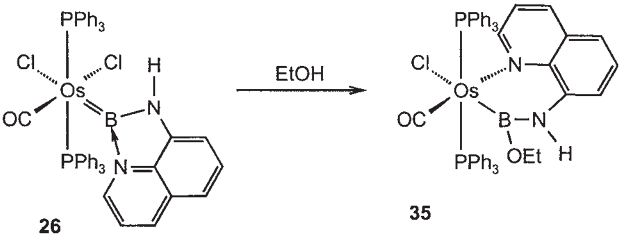


FIG. 10. Schematic orbital interactions in carbonyl and fluoroborylene complexes.

RB → TM σ-bonded model when R is a good π-donor up to a strong TM → BR π-back donation when R is a weaker π-donor.[132–134] However, the most recent studies made the point that the sum of the covalent interactions gives a bond order less than unity, and argued the case for a mainly ionic transition metal–boron bond.[133–135]

C. *Reactivity*

As already indicated, the chemistry of terminal borylene complexes is as yet almost unexplored. In addition to the photochemically induced borylene transfer, which was already discussed in Chapter 3.2, studies of the reactivity of terminal borylene complexes are restricted to two recent reports by Roper.[147,148] The base-stabilized borylene complex [Os(=BNHC$_9$H$_6$N)Cl$_2$(CO)(PPh$_3$)$_2$] (**26**) undergoes a reaction with ethanol to yield the ethoxy(amino)boryl complex [Os{B(OEt)NHC$_9$H$_6$N}Cl(CO)(PPh$_3$)$_2$] (**35**) according to Eq. (13) with a 1,2-shift of the quinoline nitrogen atom from the boron to the osmium center. The alcoholysis of **26** indicates that even the boron atom in base-stabilized borylene complexes displays some electrophilic character—a fact already predicted by a theoretical study.[117]



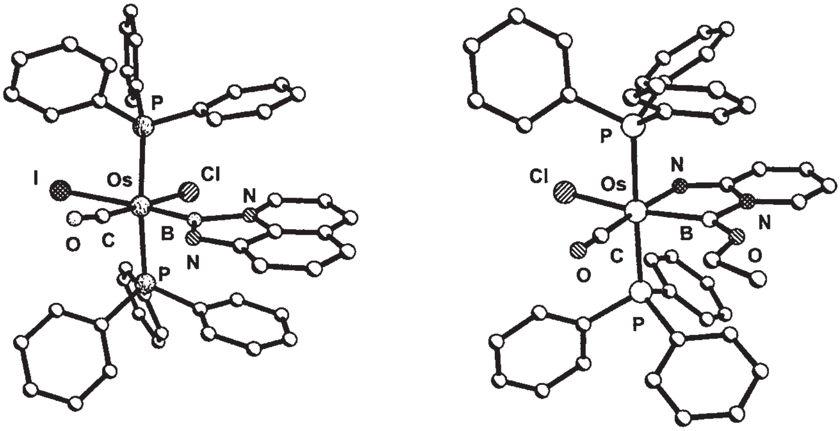
(13)

The reactivity of the boron and transition metal center in the base-stabilised borylene complex [Os{=BCl(NMeC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**30**) was subject to a recent study, especially with respect to substitution of the chloride ligands.[148] The treatment of complex **30** with Na[BH$_4$] furnished the osmium hydride species [Os{=BCl(NMeC$_5$H$_4$N)}H(CO)(PPh$_3$)$_2$] (**36**) (Fig. 11) with selective substitution of the osmium bound chloride. Ethanolysis, however, occurred selectively at the B–Cl site, yielding the ethoxy borylene complex [Os{=BOEt(NMeC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**37**) (Fig. 11).

Reaction of complex **30** with Ag[SbF$_6$] in the presence of MeCN and ethanol yielded the cationic borylene complex [Os{=BOEt(NMeC$_5$H$_4$N)}MeCN(CO)(PPh$_3$)$_2$][SbF$_6$] (**38**) with abstraction of the osmium bound

36 **37**

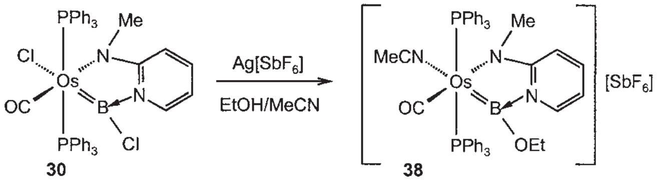
FIG. 11. Derivatives of $[\mathrm{Os}\{=\mathrm{BCl}(\mathrm{NMeC_5H_4N})\}\mathrm{Cl}(\mathrm{CO})(\mathrm{PPh_3})_2]$ (**30**) obtained by selective Os–Cl exchange (right) and selective B–Cl exchange (left).



27 **29**

FIG. 12. Structure of **27** and **29** in the crystal.

chloride and ethanolysis of the B–Cl moiety [Eq. (14)]. All complexes were fully characterized in solution and in the solid state.



(14)

A detailed comparison of the spectroscopic and structural parameters of the base stabilized borylene complexes **30**, **36**, **37**, and **38** with those of tethered boryl complexes such as **F** established their close structural relationship and led the authors to the statement that a formal distinction between those species is somewhat artificial. Their reactivity, however, can differ significantly, as the selective alcoholysis of the chloroborylene complex **28** in the presence of the chloroboryl species **F** (see Fig. 9) proved.

IV

CONCLUSION AND OUTLOOK

Since the first report on the structurally authentic borylene complex $[\mu\text{-B(NMe}_2)\{(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_2\}_2]$ (**1**) in 1995, the chemistry of these compounds has developed to some greater extent. There is now a variety of different synthetic methods at hand, which provide access to a selection of coordination environments for borylene ligands. Some of those methods, e.g., the cleavage of diboranes(4) appear to be quite specific and restricted to the systems discussed. Other routes such as salt elimination, conversion of boryl complexes, or the borylene transfer seem to have a much higher potential for broader application. Nevertheless, syntheses of borylene complexes are still an experimental challenge, which can be judged from the still rather small amount of unequivocally characterized examples in contrast with related complexes exhibiting transition metal–main group element linkages. A reason for that is certainly the fact that hypovalent borylenes B–R are not available as precursors for a direct synthesis of corresponding complexes—a route which is of course feasible in the case of elementdiyls of gallium, indium, silicon, and others. This non-availability of free borylenes, however, could make borylene complexes a rewarding target as a source for those species. The potential to transfer the borylene moiety has already been demonstrated, at least between different transition metals.

Many experimental and theoretical studies have now contributed to the understanding of the classical metal–boron linkage in borylene complexes. Future work could probably envisage possible applications of those species, especially if one considers their close relationship to carbonyl or carbene complexes and their potential in stoichiometric or catalytic reactions.

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Recent Chemistry of the Diboron Compounds

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I

INTRODUCTION

Boron-containing compounds with a boron–boron single bond are important intermediates in structural complexity between simple monoboron derivatives and the polyhedral electron-deficient compounds of the element. The properties of diboron compounds, particularly the simple derivatives of the B_2X_4 type, have attracted the attention of many laboratories around the world since Stock's initial discovery of B_2Cl_4 nearly 80 years ago.[1] These boron-containing compounds provide the simplest examples of catenation in boron chemistry and offer suitable systems to study properties of the covalent B–B bond and the characteristic chemistry of compounds containing this linkage. Studies on the organic and inorganic chemistry of the B–B compounds have been reviewed.[2–7]

Two aspects of the boron chemistry of this class of compounds are particularly relevant: First, synthesis and properties of organodiboron derivatives, and, indeed, even authentic synthetic failure in this area, are of interest in comparison with the rich organic chemistry of monoboron derivatives. Second, the chemistry of subvalent boron compounds and their

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interactions with organic and organometallic systems can lead to novel reactions that make organoboron derivatives accessible.

This chapter will concentrate primarily on features of the chemistry of diboron compounds of particular interest from the organometallic point of view. While our limited scope does not permit a comprehensive review of all aspects of diboron chemistry, we will initially survey some general features of the subject, with emphasis on unique synthetic aspects and on properties particularly characteristic of compounds containing a simple electron-pair bond between boron atoms. Previously, we published several review articles provided some aspects on boron chemistry,[8–16] and including natural boron-containing compounds.[17,18]

II

PREPARATION OF DIBORON COMPOUNDS AND THEIR PROPERTIES

A. *Formation of B–B Bond*

Synthesis of diboron compounds may involve either reductive coupling reactions of monoboron derivatives to form the boron–boron bond,[19] or reactions of compounds possessing preformed B_2 fragments.[20]

The earliest synthesis of characterized diboron compounds was the preparation of B_2Cl_4 by Stock,[1] using an electric discharge between zinc electrodes immersed in liquid BCl_3. Many discharge procedures have been reported for the synthesis of B_2Cl_4.[21–26] Structures of some halogenated diboranes, **1**, **2**, and **3** are shown in Fig. 1. Diborane(6) **3** (or diboron hexahydride) has been reviewed.[27–31]

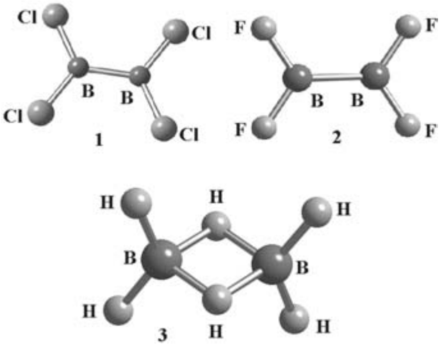


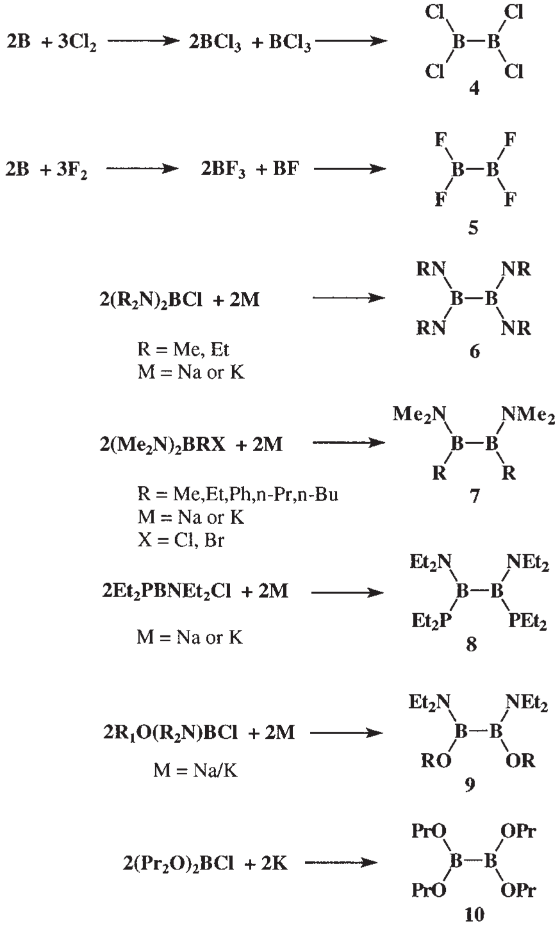
FIG. 1

B. *Synthesis, Structure, and Properties of Some Halogenated Diboranes*

The first formation of B_2Br_4 and B_2I_4 from the trihalides by discharge methods has also been reported,[32,33] but these boron halides are rarely used in synthesis. Attempts to prepare B_2F_4 from BF_3 in a discharge between mercury electrodes were unsuccessful.[34] Conventional chemical reduction of boron trihalides with active metals, metal borides, hydrogen plus metal, or other reducing agents is not a satisfactory route to the tetra(halo)diboranes.[2,22] Synthesis of B_2Cl_4 has been reported by Timms, who condensed BCl_3 at −196 °C with copper atoms produced by vaporization of the metal,[35] or via a high-temperature approach to the formation of B–B bonds by the insertion of BF (formed at 2000 °C from boron and BF_3) into the B–F bond.[36] Formation of tetra(methoxy)- and tetra(ethoxy)diborane(4) from the corresponding dialkoxychloroboranes and sodium was reported by Wiberg and Ruschmann,[37] although later workers were unable to reproduce the synthesis of the ethoxy derivative.[38] Boron reacts vigorously with Cl_2 and F_2 to form BCl_3 and BF_3, respectively. When BCl_3 and BF_3 reacted with boron halides gives compounds **4** and **5** (Scheme 1). Synthesis of other diboron derivatives **6–10** have also been reported (Scheme 1).[38–50]

Diborane compounds with common structure **11** (Scheme 2) have been synthesized.[46,49] The synthesis of a series of bis(catecholato)diborane(4) compounds **12–16**, $B_2[1,2\text{-}O_2C_6H_4]_2$ **12**, $B_2[1,2\text{-}O_2C_6H_3Me\text{-}4]_2$ **13**, $B_2[1,2\text{-}O_2C_6H_2Me_2\text{-}3,5]_2$ **14**, $B_2[1,2\text{-}O_2C_6H_3\text{-}t\text{Bu-}4]_2$ **15**, and $B_2[1,2\text{-}O_2C_6H_2t\text{Bu}_2\text{-}3,5]_2$ **16** (Scheme 2) have been recently reported.[51] The above compounds have been made by reaction of 1% sodium/mercury amalgam with the corresponding halocatecholboranes, which are cleanly formed from the reaction of BCl_3 or BBr_3 and catechol. Combining these two steps in one pot, $B_2[1,2\text{-}O_2C_6H_3t\text{Bu-}4)]_2$ was prepared from BCl_3 and 4-*tert*-butylcatechol, and $B_2[1,2\text{-}O_2C_6H_2t\text{Bu}_2\text{-}3,5]_2$ was prepared from 3,5-di-*tert*-butylcatechol and BBr_3 on a multigram scale. Bis(pinacolato)diborane(4) was not formed from reaction of chloropinacolborane and Na/Hg, but it was obtained by *in situ* addition of pinacol to either $B_2[1,2\text{-}O_2C_6H_3t\text{Bu-}4)]_2$ or $B_2[1,2\text{-}O_2C_6H_2t\text{Bu}_2\text{-}3,5]_2$.

Reaction of sodium naphthalide with B_2Cl_4 at room temperature was reported to give a liquid product with a suggested structure, **17**. The compound **17** reacts with four equivalents of $(CH_3)_3N$ to form an adduct which decomposes above 100 °C to give the bis(trimethylamine) adduct of B_2Cl_4 and an unstable product that is thought to be **18** (Scheme 3). It was reported that the trimethylamine complex of tetra(methyl)diborane(4) was obtained from the reduction of bromodimethylborane with sodium or silver in trimethylamine.[52]

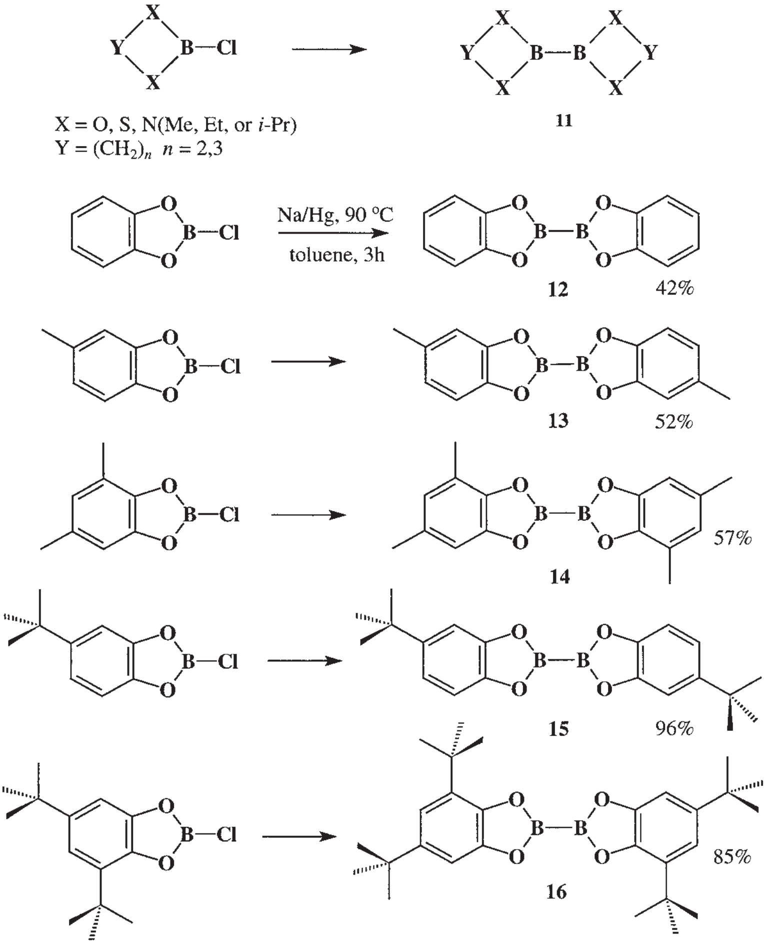


SCHEME 1

Fisch *et al.* reported the synthesis of a 1,2,4,5-tetraborinane heterocyclic compound **19** which was stabilized by dimethylamino groups (Scheme 4) and showed a *nido*-structure (Fig. 2).[53]

Several transamination reactions of $B_2(NMe_2)_4$ **20** with secondary amines have led to mixed tetra(amino)diborane(4) compounds $B_2(NMe_2)_{4-n}(NR_2)_n$ **24–26** (Scheme 5), and $B_2(NC_5H_{10})_4$ **23** has been characterized by an X-ray structure analysis which reveals the presence of a rather long B–B bond (Fig. 3).

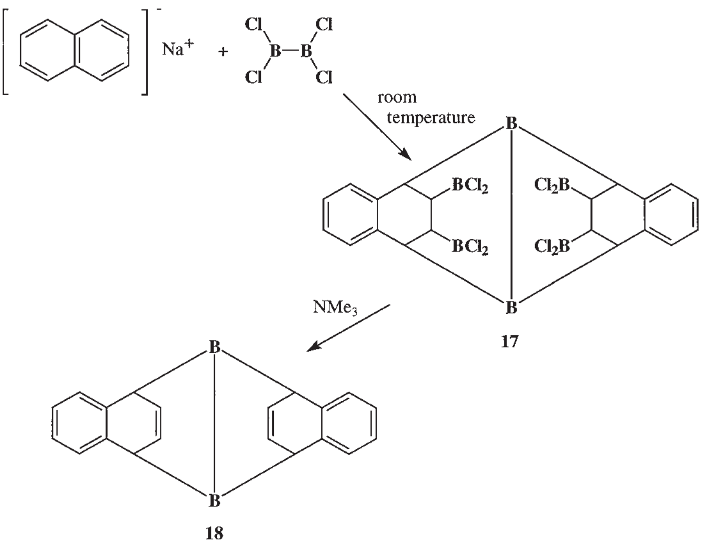
However, tetra(amino)diboranes(4) of type $R_2N(Me_2N)B–B(NMe_2)NR_2$ are more readily accessible from $LiNR_2$ and $B_2(NMe_2)_2Cl_2$. Similarly,



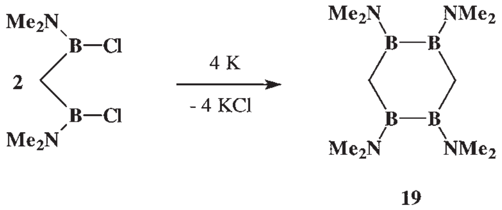
Scheme 2

amination of $B_2(NMe_2)_2Cl_2$ with *N,N′*-dimethylethylenediamine gives B[bis(dimethylamino)-boryl]-*N,N′*-dimethyl-1,3,2-diazaborolidine **29**, while reactions with Li(Me)N–CH_2–CH_2–N(Me)Li also give 2,3-bis(dimethylamino)-1,4-dimethyl-1,2,3,4-diazadiborinane **30** as the kinetically controlled product. Diborane(4) dihalides $B_2(NMe_2)_2X_2$ (X = Cl, Br) **20a** react only in a 1:1 ratio with TMP–B = N–CMe_3 leading to **28** (molecular structure shown in Fig. 4) and **29** (Scheme 6).[54]

Heterocyclic organodiboron compounds **31** and **32** have been obtained by transamination of dialkylbis(dialkylamino)diborane(4) derivatives with *o*-diamines (Scheme 7),[49] and reaction of $B_2[NMe_2]_2(n\text{-}C_4H_9)_2$ with



SCHEME 3



SCHEME 4

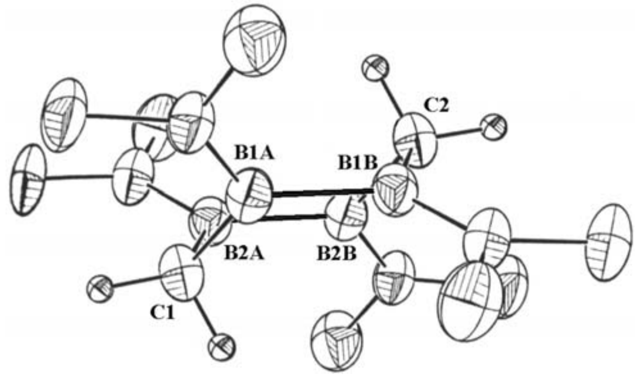
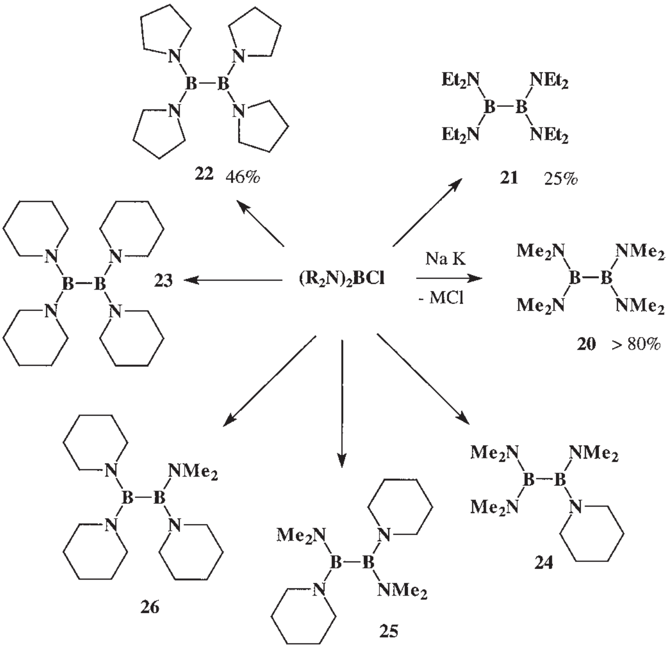


FIG. 2. Crystal structure of novel 1,2,4,5-tetraborinane **19**, B–B bond length have a 1.711 Å. Adapted by authors.



SCHEME 5

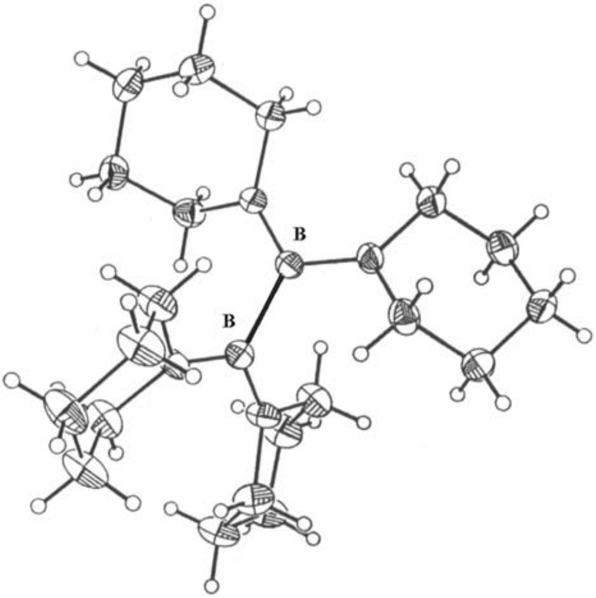


FIG. 3. Molecular structure of **23** with 1.439 Å B–B bond length.

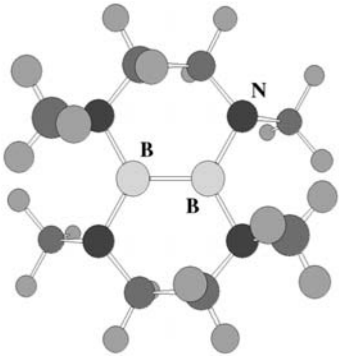
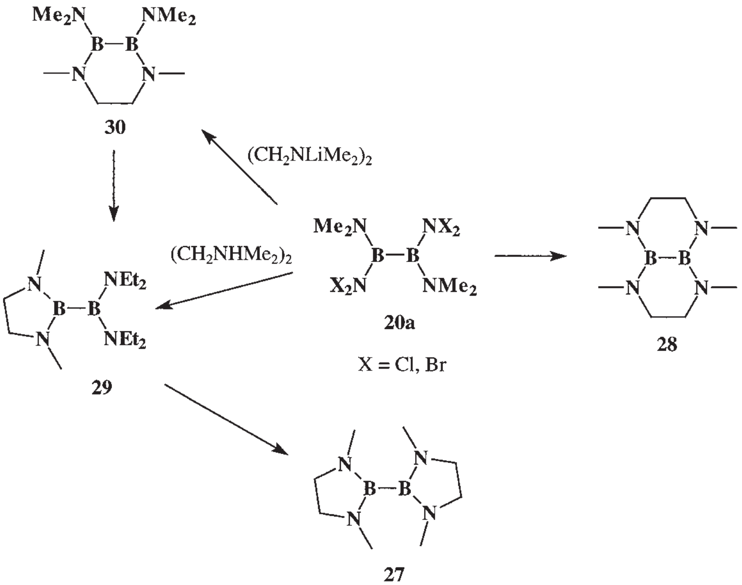


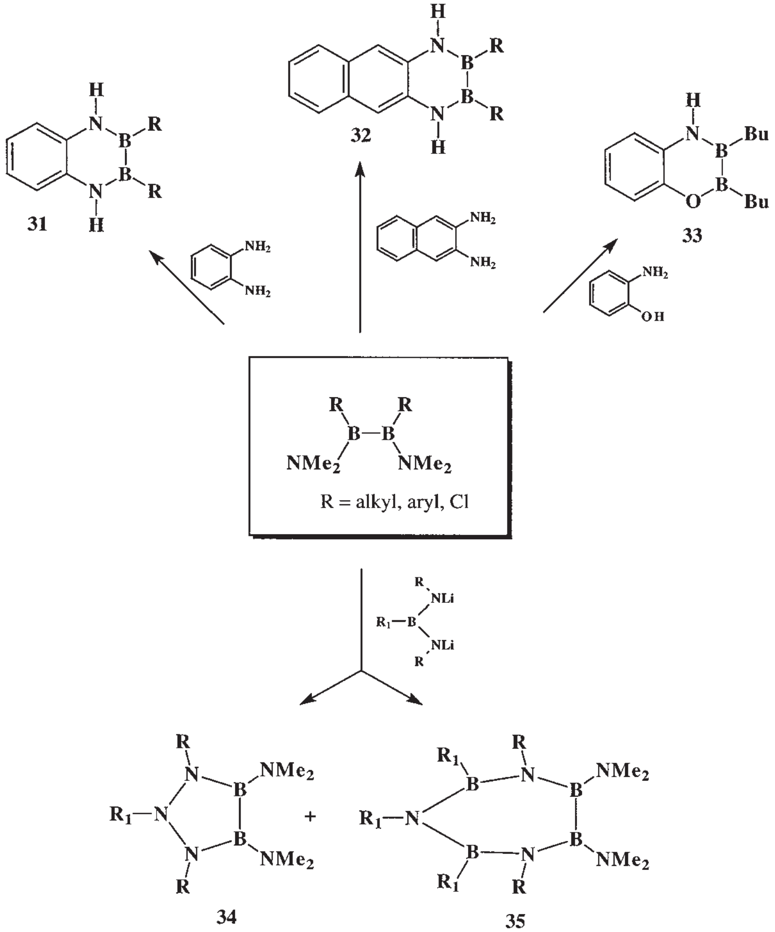
FIG. 4. Molecular structure of heterocyclic compound **28**. Adapted by authors.



SCHEME 6

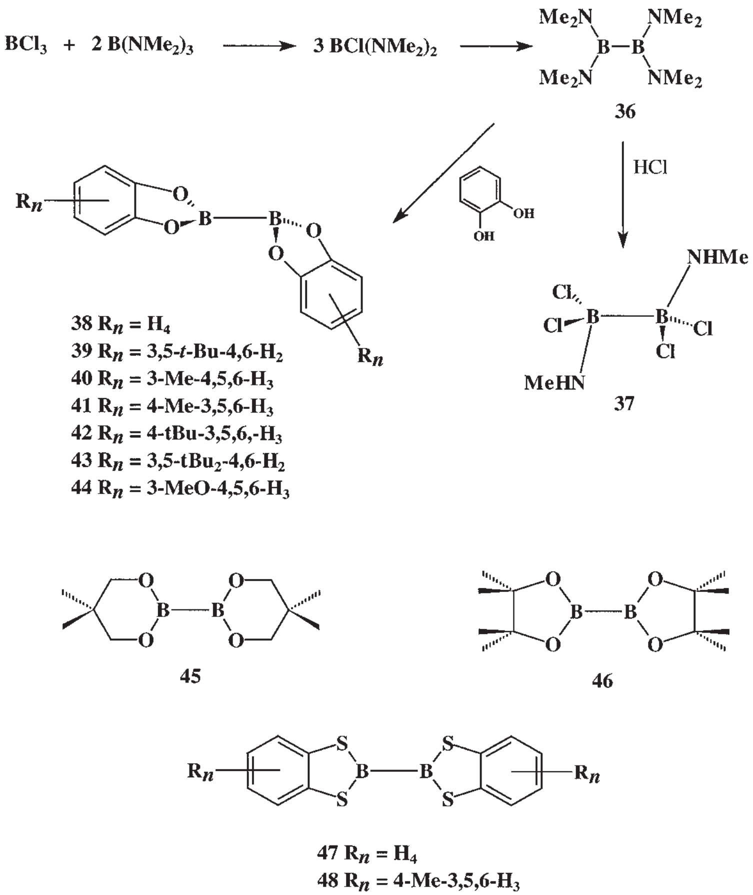
o-aminophenol gave an unstable heterocycle **33**. Organoboron heterocycles **34** and **35** containing the boron–boron bond have been prepared by the reaction of *N*-Lithio derivatives of alkylbis(alkylamino)boranes with l,2-dichloro-l,2-bis(dimethyl-amino)diborane(4).[55]

The synthesis and characterization of a series of bis(catecholato)diborane(4) compounds, $B_2(1,2\text{-}O_2C_6H_4)_2$ **38**, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ **40**, $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$ **41**, $B_2(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)_2$ **42**, $B_2(1,2\text{-}O_2\text{-}3,5\text{-}t\text{Bu}_2C_6H_2)_2$



SCHEME 7

43, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)_2$ **44**, bis(dithiocatecholato)diborane(4) compounds, $B_2(1,2\text{-}S_2C_6H_4)_2$ **47**, $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ **48**, and tetra(alkoxy) diborane(4) compounds, $B_2(OCH_2CMe_2CH_2O)_2$ **45** and $B_2(OCMe_2CMe_2O)_2$ **46** from $B_2(NMe_2)_4$ **36** was described (Scheme 8). Compound **36** was synthesized by reductive coupling of $BCl(NMe_2)_2$, which in turn is prepared from reaction of BCl_3 with $B(NMe_2)_3$ in a 1:2 stoichiometry. Also $[B_2Cl_4\text{–}(NHMe_2)_2]$ **37** which formed from addition of HCl to **36** prior to complete reaction with diols, and the salt, $[NH_2Me_2]\text{–}[B(1,2\text{-}O_2C_6H_4)_2]$, which arises from addition of catechol to $B(NMe_2)_3$ were characterized. Thus, any



36

37

38 $R_n = H_4$
39 R_n = 3,5-*t*-Bu-4,6-H_2
40 R_n = 3-Me-4,5,6-H_3
41 R_n = 4-Me-3,5,6-H_3
42 R_n = 4-tBu-3,5,6,-H_3
43 R_n = 3,5-tBu_2-4,6-H_2
44 R_n = 3-MeO-4,5,6-H_3

45

46

47 $R_n = H_4$
48 R_n = 4-Me-3,5,6-H_3

SCHEME 8

$B(NMe_2)_3$ impurity present after the preparation of **36** needs to be removed by distillation prior to reaction with alcohols.[56]

The X-ray structures of bis(catecholato), bis(dithiocatecholato), and tetra(alkoxy)diborane(4) compounds $B_2(1,2\text{-}O_2C_6H_4)_2$, $B_2(1,2\text{-}O_2\text{-}4\text{-}t\text{BuC}_6H_3)_2$, $B_2(1,2\text{-}O_2\text{-}3,5\text{-}t\text{Bu}_2C_6H_2)_2$, $B_2(1,2\text{-}S_2C_6H_4)_2$, $B_2(1,2\text{-}S_2\text{-}4\text{-MeC}_6H_3)_2$, and $B_2(OCH_2CMe_2CH_2O)_2$ have been described. In the solid state, all the compounds adopt planar structures for the B_2O_4 or B_2S_4 units (Fig. 5).

A series of mixed tetra(amino)diborane(4) compounds bearing pyrrolyl, indolyl, and carbazolyl substituents besides dimethylamino groups has been prepared and subjected to reduction with elemental lithium in the

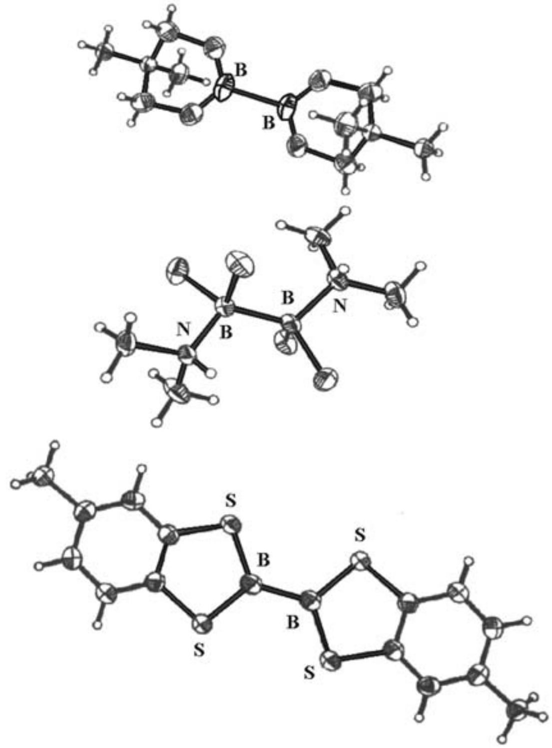
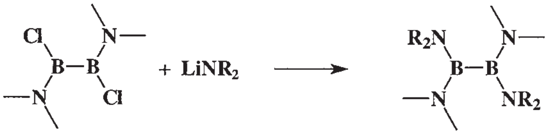


FIG. 5. Molecular structures of some diborane compounds. Structure of $B_2(1,2\text{-}O_2\text{-}3\text{-}Me_2C_6H_3)_2$ **45**, B–B bond length was determined as 1.315 Å; and structure of $B_2(1,2\text{-}O_2\text{-}3,5\text{-}t\mathrm{Bu}_2C_6H_2)_2(NHMe_2)_2$, B–B bond length was found as 1.788 Å; Structure of $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ **48**, B–B length was determined as 1.737 Å. Adapted by authors.



49 NR_2 = pyrrolyl
50 NR_2 = indolyl

SCHEME 9

presence of diethyl ether.[60] Tetra(amino)diborates(2-) are formed, which feature a boron–boron double bond (Scheme 9). The new diborates are isoelectronic with tetra(amino)ethylenes and are expected to be electron-transfer reagents.[57] X-ray crystal structures for **49** and **50** were studied and are depicted in Fig. 6.

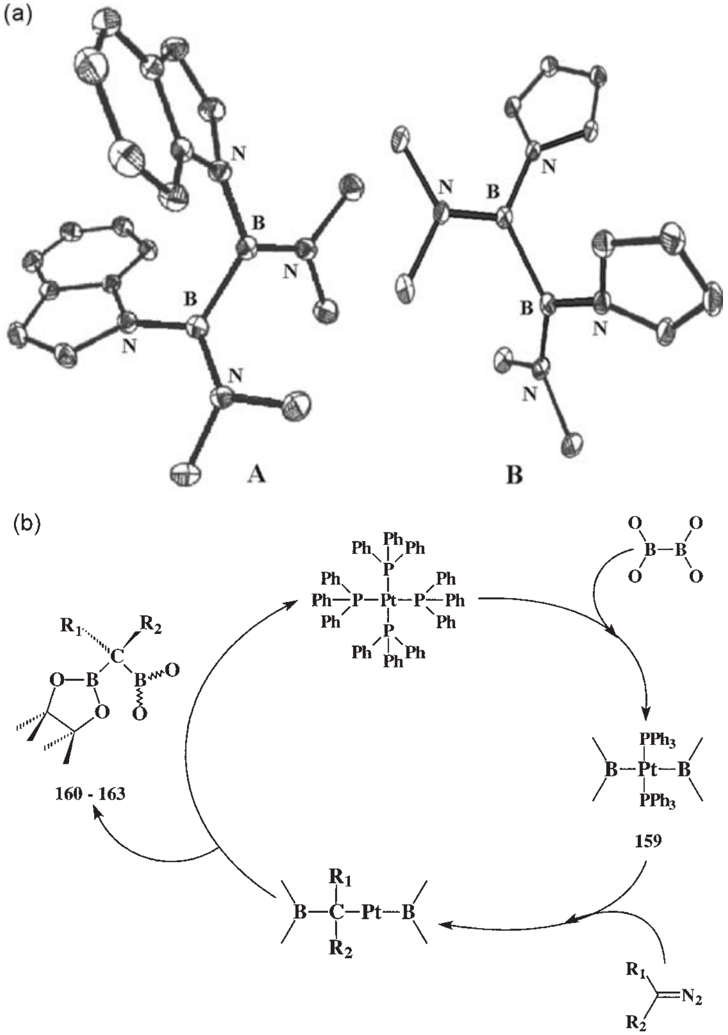
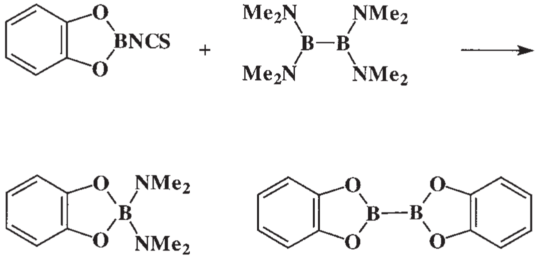


FIG. 6. (a) Molecular structures of **49** (B) and **50** (A) with B–B bonds 1.723 (B) and 1.718 (A) Å. Adapted by authors. (b) The proposed catalytic cycle for formation of bisdiborane B–C–B from B–B compounds.

Tetra(dimethylamino)diborane(4) was treated with *o*-phenylene isothiocyanato-boronate, to give an interesting reaction which involve not only disproportionation but also cleavage of the B–B bond giving compounds **51** and **52**. In addition a third product, 2-(1,3,2-benzodioxaborolo)-1,3,2-benzodioxaborole **12**, was isolated and compared with those previously reported elsewhere[58] (Scheme 10).



51 + **12**

$Me_2NB(NCS)_2$

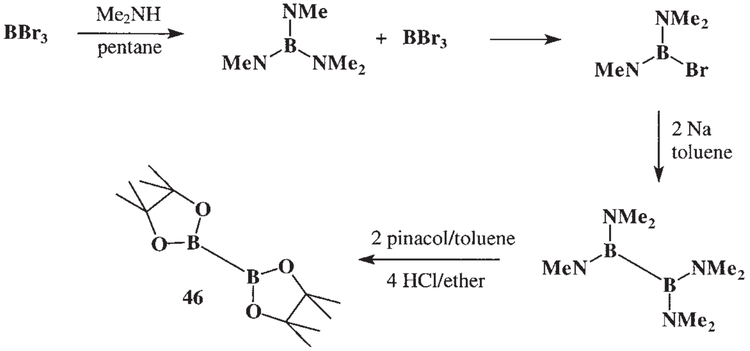
52

Scheme 10

The first synthesis of bis(pinacolato)diboron(4) **46** was reported more than 20 years ago by the practical procedure described below.[59]

A 2 L, three-necked flask fitted with a mechanical stirrer, dropping funnel, and a reflux condenser connected to a nitrogen source and a bubbler is flushed with nitrogen. To the flask, 53.7 g (0.271 mol) of tetra(dimethylamino)diborane(4) and 510 mL of toluene are added, and then a solution of 64.4 g (0.545 mol) of pinacol in 340 mL of toluene is added. The flask is immersed in an ice-water bath and a 5.4 M ethereal solution of hydrogen chloride (203 mL, 1.10 mol) is added dropwise for 2 h. As soon as the addition is started, a white precipitate of dimethylamine hydrochloride appears. The slurry is stirred at room temperature for an additional 4 h. The precipitate is removed by suction filtration, and the filtrate is concentrated on a rotary evaporator to give a white solid. The solid is dissolved in ca. 700 mL of pentane and the remaining solid is again removed by filtration. The filtrate is washed three times with 500 mL of water and dried over anhydrous $MgSO_4$. The drying agent is removed by filtration and the filtrate is concentrated to ca. 150 mL. The flask is heated to dissolve the resulting precipitate, allowed to cool to room temperature, and then thoroughly chilled in a freezer (−30 °C). The first crop is collected by filtration and washed twice with 30 mL of cold pentane. The mother liquor is again concentrated to give another crop of crystals. The procedure is repeated two additional times. The combined crystals are dried under reduced pressure (0.1 mm) for 16 h at room temperature to give 54.3 g (79%) of **46** as colorless plates, mp 138 °C[59] (Scheme 11).

Structural changes as a function of the torsional angle about the B–B bond angle have been studied for the diborane tetrahalides $X_2B–BX_2$



SCHEME 11

(X = F, Cl, Br) by *ab initio* calculations (Table I).[59] The perpendicular structure with D_2d symmetry was predicted to be the most stable conformation when the double-zeta basis 6-31G* set was used in the calculations. A triple-zeta basis set augmented with diffuse functions and polarization functions of the type 6-311 + G* showed that the planar D_2h conformation is the most stable conformation for B_2F_4 which is in agreement with experimental results. Inclusion of correlation through the MP2 level of theory affects mostly the B–F bond length, and only to a small degree the barrier height. For intermediate states with one X–B–B–X torsional angle constrained to lie between 0 and 90° a pyramidal arrangement around the boron atoms is predicted with an overall symmetry of C2, and with two unequal B–X bond distances and two unequal B–B–X bond angles. Vibrational frequencies have been calculated and compared with experimental assignments.[59]

III

REACTIONS OF DIBORON COMPOUNDS

A. *Reactions with Acetylenes and Alkynes*

In 1993, Ishiyama *et al.*[60] reported the synthesis of isomerically pure *cis*-1,2-bis(boryl)alkenes **53a–57a** from their corresponding alkynes **53–57** (Scheme 12)[60,61] via platinum complexes. The solvents did not play an important role in the reaction, but a comparison of the reaction rates at 50 °C revealed that the addition was apparently accelerated in polar

TABLE I

STRUCTURAL PARAMETERS FOR DIBORON B_2X_4 ($X = F, Cl, Br$)[a]

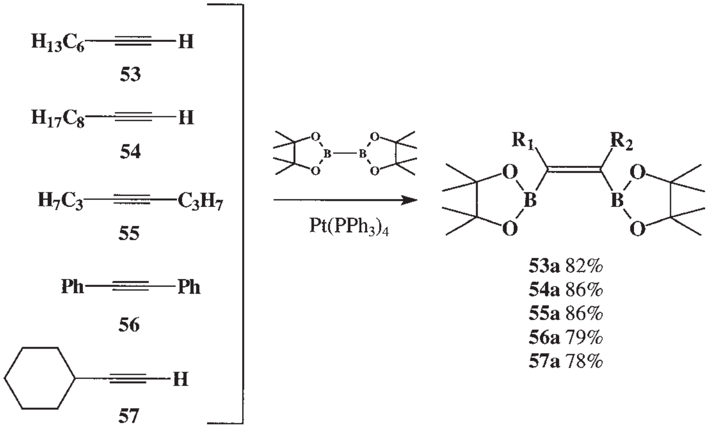
	φ (X1–B2–B3–X4)						
Parameter	0 (D_2h)	15	30	45	60	75	90 (D_2d)
B_2F_4							
r (B–B)	1.73440	1.73404	1.7306	1.73168	1.73026	1.72918	1.72877
r (B2–F1)	1.30783	1.30798	1.30838	1.30891	1.30943	1.30979	1.30993
r (B2–F6)	1.30783	1.30798	1.30838	1.30892	1.30944	1.30979	1.30993
L (B–B–F1)	121.381	121.390	121.417	121.457	121.495	121.528	121.565
L (B–B–F6)	121.381	121.401	121.450	121.507	121.558	121.528	121.565
φ (F1–B2–B3–F5)	180.0	164.95	149.88	134.82	119.79	104.86	90.00
φ (F6–B2–B3–F5)	0.00	15.11	30.24	45.37	60.41	75.28	90.00
E[b]	0.283	0.272	0.236	0.174	0.095	0.027	0.00
B_2Cl_4							
r (B–B)	1.74125	1.73857	1.73176	1.72349	1.71606	1.71105	1.70931
r (B2–C11)	1.74971	1.74978	1.75011	1.75066	1.75131	1.75185	1.75205
r (B2–Cl6)	1.74971	1.74977	1.75056	1.75122	1.75171	1.75196	1.75205
L (B–B–Cl1)	120.695	120.679	120.601	120.449	120.272	120.166	120.218
L (B–BCl6)	120.695	120.616	120.471	120.370	120.337	120.312	120.218
φ (Cl1–B2–B3–Cl5)	180.0	163.86	148.24	133.18	118.53	104.16	90.00
φ (Cl6–B2–B3–Cl5)	0.00	17.28	33.52	48.54	62.94	76.69	90.00
E	2.898	2.664	2.064	1.315	0.630	0.163	0.00
B_2Br_2							
r (B–B)	1.73896	1.73521	1.72564	1.71422	1.70422	1.69757	1.69525
r (B2–Br1)	1.90645	1.90657	1.90685	1.90733	1.90798	1.90859	1.9883
r (B2–Br6)	1.90645	1.90690	1.90786	1.90862	1.90893	1.90889	1.9883
L (B–B–Br1)	120.716	120.697	120.599	120.348	119.984	119.692	119.689
L (B–B–Br6)	120.716	120.555	120.200	119.912	119.808	119.791	119.689
φ (Br1–B2–B3–Br5)	180.0	163.32	147.21	132.02	117.58	103.62	90.00
φ (Br6–B2–B3–Br5)	0.00	18.36	35.58	50.95	64.83	77.75	90.00
E	4.412	4.087	3.212	2.075	1.005	0.262	0.00

[a] Bond distances in angstrom and bond angels in degrees.

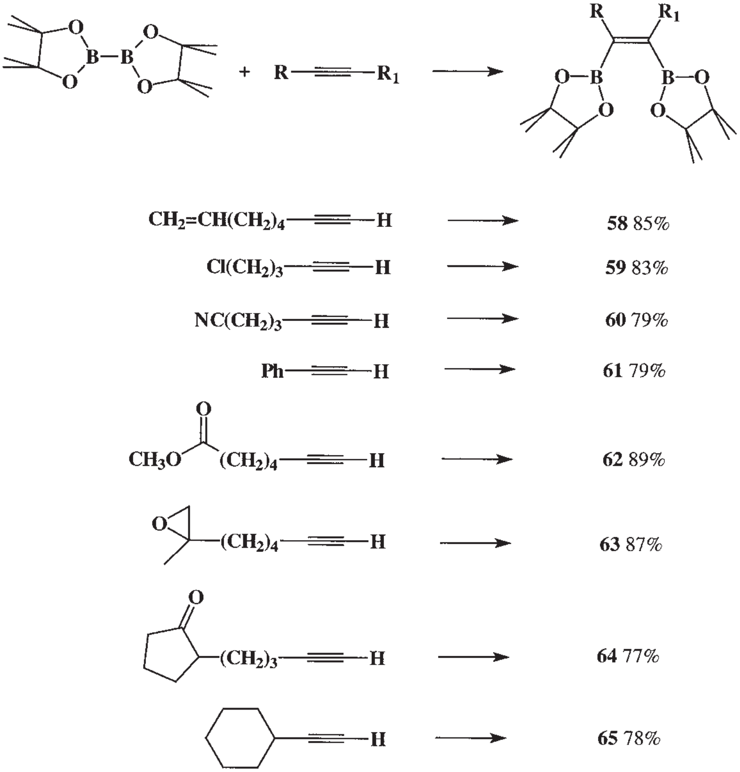
[b] Relative energies in kcal mol^{-1}.

solvents: e.g., $DMF > CH_3CN > THF >$ toluene. Synthesis of *trans*-1-organo-1-alkenyl-boronates was reported when palladium(0) was used as catalyst.[62]

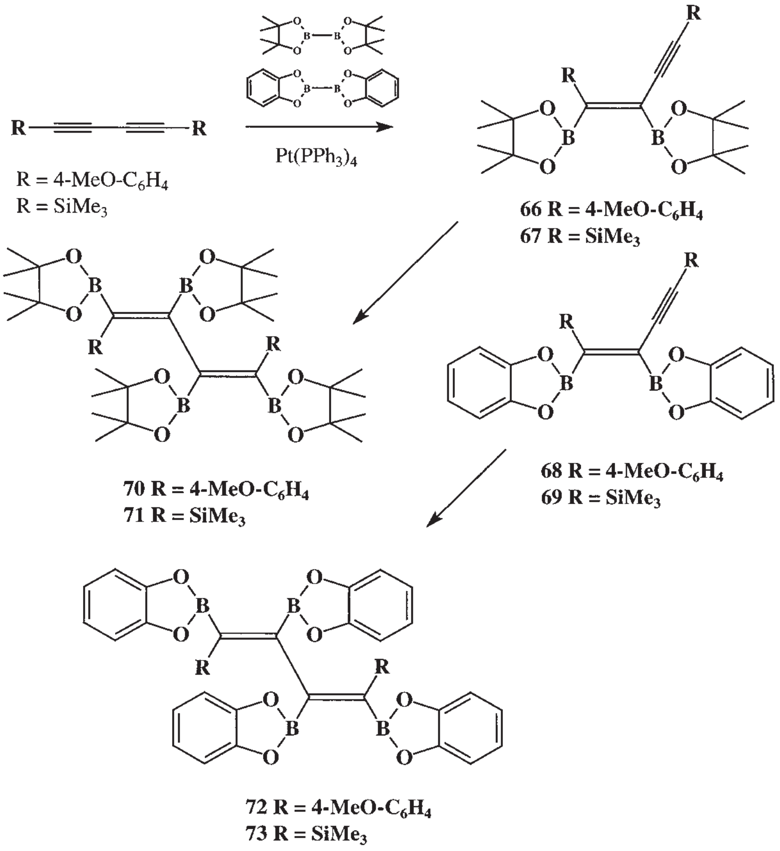
The same reaction produced different alkenes **58–65**[63] (Scheme 13). These reactions were not catalyzed by rhodium(I) or palladium(0). Tetra(methoxo)- and bis(pinacolato)diboron(4) added to both terminal and internal alkynes in the presence of a catalytic amount of $Pt(PPh_3)_4$ to provide stereo defined pinacolato *cis*-bis(boryl)alkenes **58–65** in excellent yields. Because reagents and reaction conditions were sufficiently mild,



SCHEME 12



SCHEME 13



Scheme 14

the procedure was readily extended to various functionalized alkynes (Scheme 13).[63]

The borates react with chlorodialkylboranes in a sterically selective manner, forming *cis*-1,2-bis(dialkylboryl)alkenes in good yields, the protonolysis of which with water or alcohols produces *cis*-olefins.[64] Formation of B–C=C–B compounds **66–73** has been demonstrated with the use of 1,3-diynes via platinum(II) complexes.[68] The addition of (pin)B–B(pin) and (cat)B–B(cat) to $4\text{-MeOC}_6H_4C{\equiv}CC{\equiv}CC_6H_4\text{–4–OMe}$ and $SiMe_3C{\equiv}CC{\equiv}CSiMe_3$ proceeded smoothly to give the novel tetra(boronate ester) compounds **66–73** respectively, (Scheme 14). An important step in the catalyzed diboration of alkynes appears to be the dissociation of phosphine from the $[(PPh_3)_nPt(\eta\text{-alkyne})]$ complexes, giving rise to a mono(phosphine)Pt intermediate which serves as the active catalyst in these systems.[64,65]

B. *Reactions with Dienes and Alkenes*

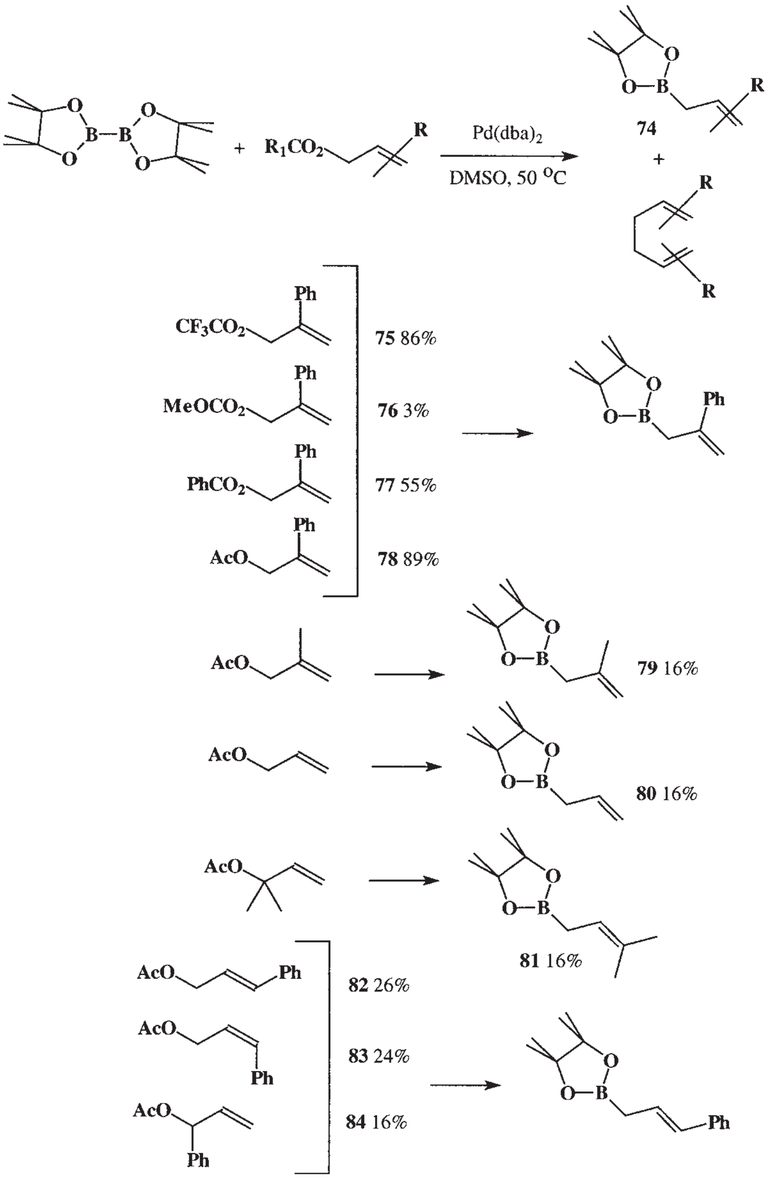
The cross-coupling reaction of bis(pinacolato)diborane(4) [$(Me_4C_2O_2)B–B(O_2C_2Me_4)$] with allyl acetates provided the pinacol esters of allylboronic acids with common structure **74** with regio- and *E*-stereoselectively in high yields as **75–84** have been reported (Scheme 15). The reaction was efficiently catalyzed by $Pd(dba)_2$ in DMSO at 50 °C.[66]

Bis(pinacolato)diborane(4) selectively adds to terminal alkenes and cyclic alkenes having internal strain to provide bis(boryl)alkanes in 76–86% yields **85–89** in the presence of a catalytic amount of $Pt(dba)_2$ at 50 °C[67] (Scheme 16). It is interesting to mention that $Pt(dba)_2$ directed 1,2-addition to certain conjugated dienes, whereas 1,4-addition through a π-allyl-platinum(II) intermediate is an energetically more favorable process. The 1,4-addition to penta-1,3-diene at 80 °C with $Pt(PPh_3)_4$ gives **90**, but the same reaction with $Pt(dba)_2$ selectively produced the 1,2-addition product **91** at room temperature (Scheme 16).

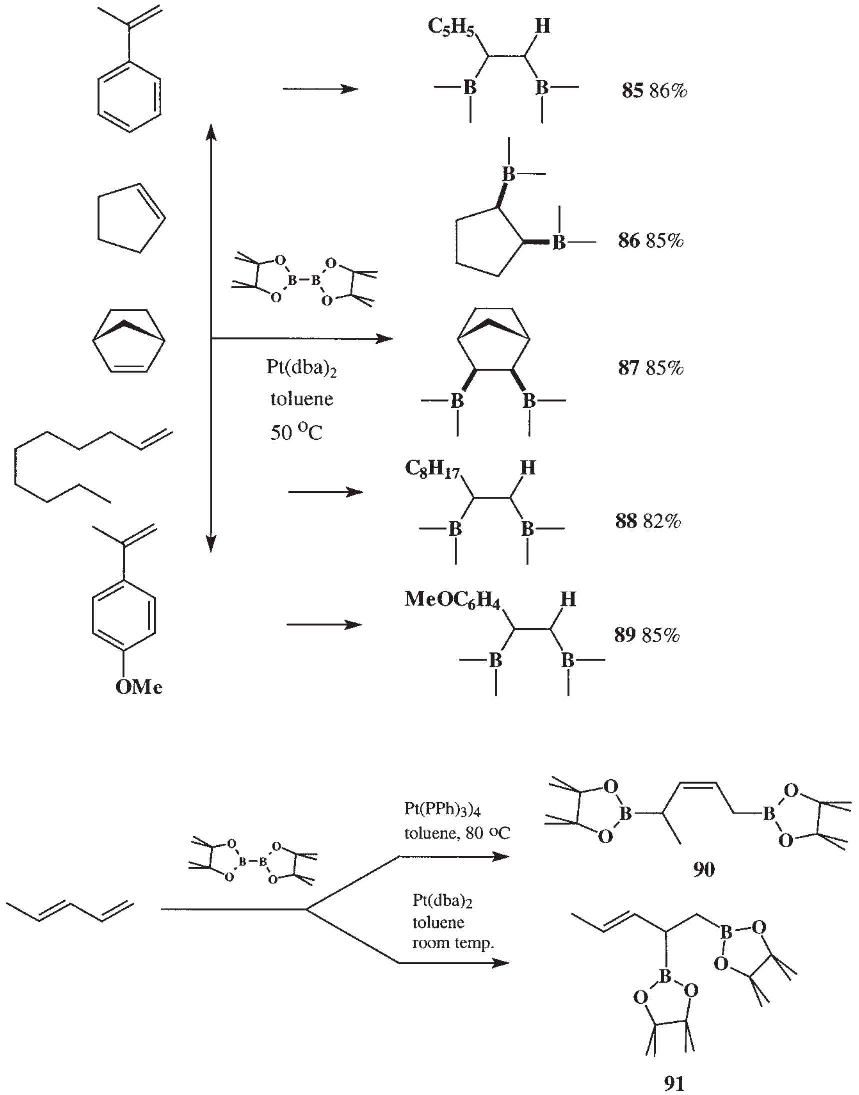
Commercially available $Pt(cod)Cl_2$, catalyzes the diboration of terminal alkenes, vinylarenes, and alkynes using B_2cat_2 to give compounds **92–96** in excellent yields (Scheme 17).[68] The first metal-catalyzed diboration of aldimines to form *R*-amino boronate esters was also obtained when $Pt(cod)Cl_2$ was used.

Bis(alkoxy)diborane(4) was selectively added to alka-1,3-dienes in the presence of a catalytic amount of platinum(0) complexes[69] (Scheme 18).

Initial studies involving phosphine-containing bis(boryl)platinum compounds indicated no activity for the diboration of alkenes.[70] Subsequently however, Smith and co-workers demonstrated an immediate reaction between $[Pt(nbe)_3]$ (nbe = norbornene) and B_2cat_2 (Scheme 19), providing the norbornene diboration product **99** in 88% yield.[71] In this case, oxidative addition of B_2cat_2, followed by insertion of norbornene into the Pt–B bond is a likely mechanism although there is no experimental data to support this. Theoretical studies of Pt–boron compound indicated that insertion of ethylene into the Pt–B bonds in $[Pt(PH_3)\{B(OH)_2\}_2]$ was less favorable energetically compared to the reaction involving acetylene.[72] The substitution of a π-bound ligand for a phosphine ligand should result in an overall reduction of the activation barrier to insertion of alkenes by destabilizing the bis(boryl)platinum complex prior to the insertion step.


O
B—B
+
R₁CO₂
R
Pd(dba)₂
DMSO, 50 °C
74
+
R
R
Ph
CF₃CO₂
75 86%
MeOCO₂
76 3%
PhCO₂
77 55%
AcO
78 89%
79 16%
80 16%
81 16%
82 26%
83 24%
84 16%
O—B
Ph

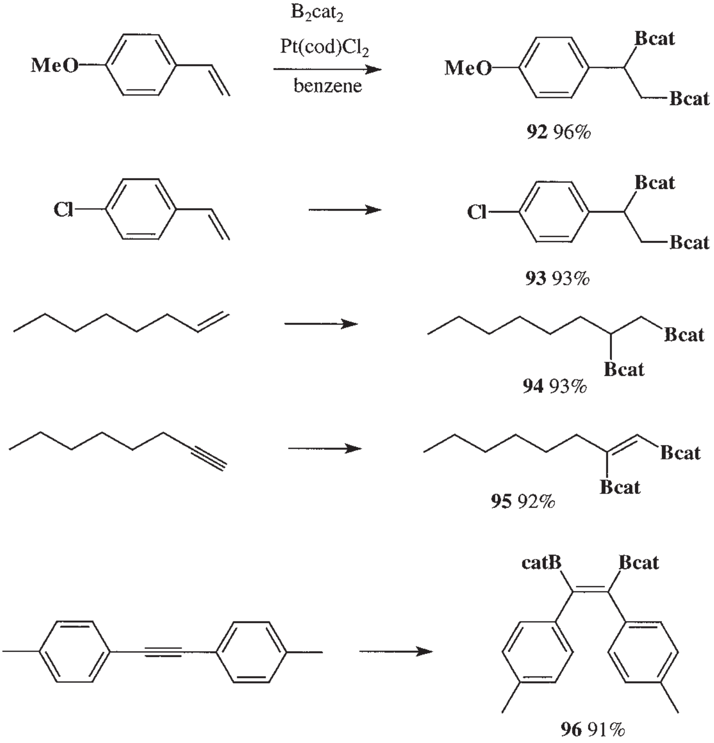
SCHEME 15



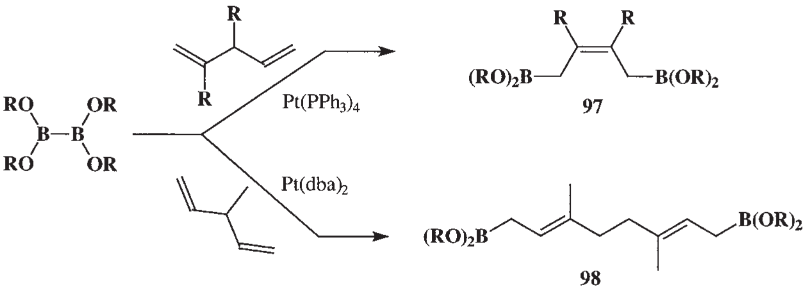
Scheme 16

C. *Reactions with Allenes*

Addition of bis(pinacolato)diborane(4) [$(Me_4C_2O_2)B–B(O_2C_2Me_4)$] to various allenes in the presence of $Pt(PPh_3)_4$ at 80 °C or $Pt(dba)_2/(c\text{-}Hex)_3P$ at 50 °C gives compounds **100–113** in excellent yields. The addition to internal

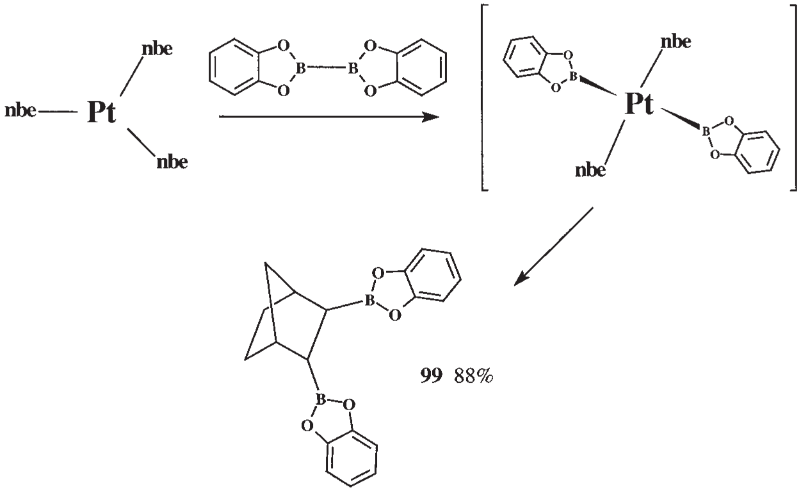


SCHEME 17



SCHEME 18

double bond was predominant for monosubstituted allenes, whereas the terminal diboration products were regioselectively obtained when a sterically bulky phosphine ligand of (c-Hex)$_3$P and 1,1-disubstituted allenes were used[73] (Scheme 20).



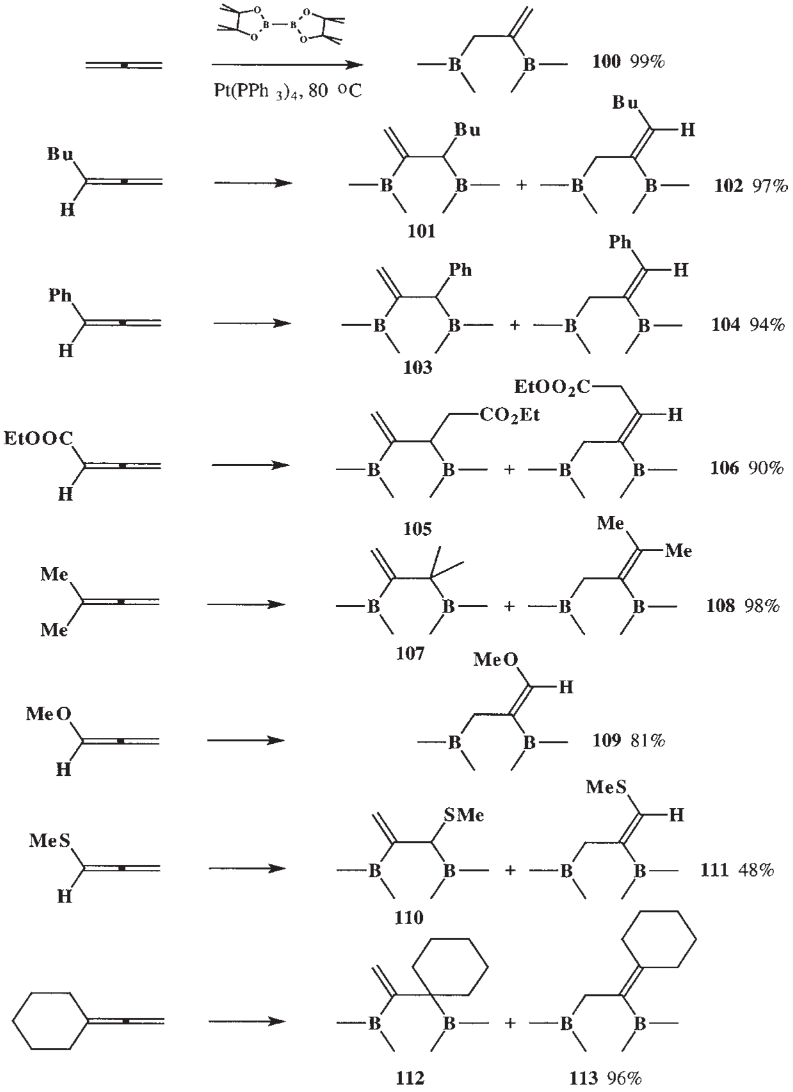
SCHEME 19

Highly regio- and stereoselective acylboration of allenes **114a–e** catalyzed by palladium complexes has been demonstrated by Cheng *et al.*,[74] as the efficient route to a new class of 2-acylallylboronates **115–134** (Scheme 21).

A new efficient route for the synthesis of bis(diboranes) catalyzed by palladium complexes is diboration of allenes (Scheme 22).[75] The stereochemistry of these bisboronic products was studied and the *Z*-isomer was also identified as the major product (93–95%).

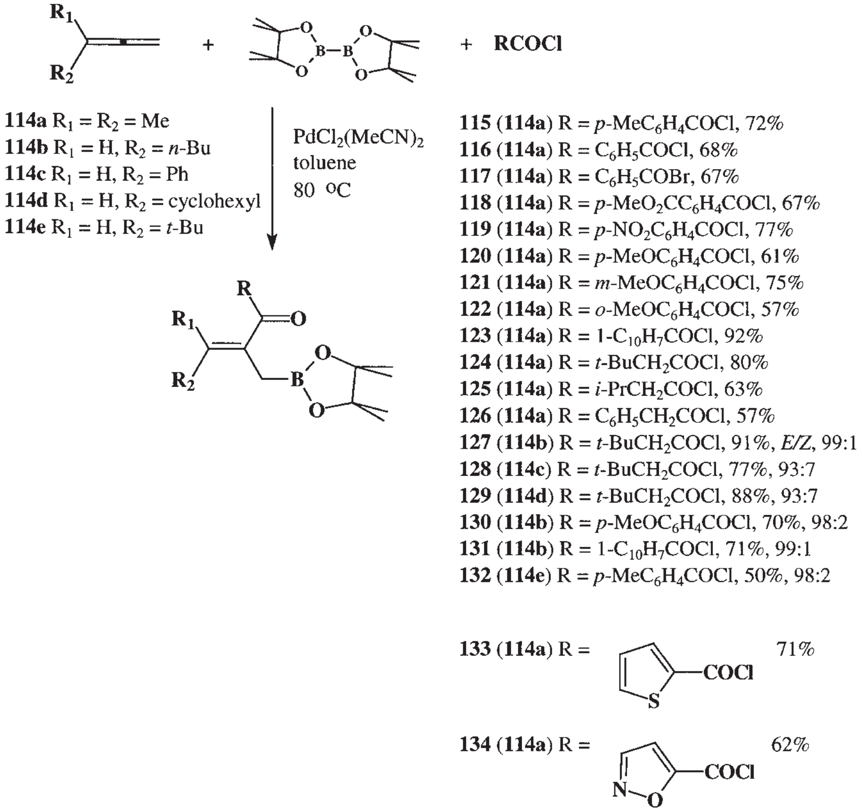
D. *Synthesis of Bisdiboron from Diboron Compounds*

Bisdiborane derivatives are an important class of compounds in boron chemistry. The addition of diboranes ($X_2B–BX_2$) to unsaturated hydrocarbons, first discovered by Schlesinger in 1954,[76] is an attractive and straightforward method to introduce two boryl units into organic molecules.[2,42,52,77–79] Diborane itself, B_2H_4, is stable only when complexed by Lewis base ligands such as amines or phosphines. Although the tetrahalides, B_2X_4 ($X = F$, Cl, Br, I), have a reasonably well-established chemistry, they suffer from low thermal stability (with the exception of B_2F_4) and preparative difficulties. Tetraorganodiborane compounds, B_2R_4, are stable only when substituted with sterically demanding R groups such as *t*-Bu, CH_2-*t*-Bu, and mesityl. The most stable derivatives are those in which good π-donor groups are present such as amido (NR_2)



SCHEME 20

or alkoxy (OR).[42,79] More recently, as part of the interest in the oxidative addition chemistry of the B–B bond and metal-catalyzed diborations of alkenes[67,80–82] and alkynes[63,71,83–86] synthesis of stable, crystalline bis(pinacolato) and bis(catecholato)diborane(4) derivatives have been reported.[9,87,88]



114a $R_1 = R_2 = Me$
114b $R_1 = H, R_2 = n\text{-}Bu$
114c $R_1 = H, R_2 = Ph$
114d $R_1 = H, R_2 =$ cyclohexyl
114e $R_1 = H, R_2 = t\text{-}Bu$

115 (**114a**) R = $p\text{-}MeC_6H_4COCl$, 72%
116 (**114a**) R = C_6H_5COCl, 68%
117 (**114a**) R = C_6H_5COBr, 67%
118 (**114a**) R = $p\text{-}MeO_2CC_6H_4COCl$, 67%
119 (**114a**) R = $p\text{-}NO_2C_6H_4COCl$, 77%
120 (**114a**) R = $p\text{-}MeOC_6H_4COCl$, 61%
121 (**114a**) R = $m\text{-}MeOC_6H_4COCl$, 75%
122 (**114a**) R = $o\text{-}MeOC_6H_4COCl$, 57%
123 (**114a**) R = $1\text{-}C_{10}H_7COCl$, 92%
124 (**114a**) R = $t\text{-}BuCH_2COCl$, 80%
125 (**114a**) R = $i\text{-}PrCH_2COCl$, 63%
126 (**114a**) R = $C_6H_5CH_2COCl$, 57%
127 (**114b**) R = $t\text{-}BuCH_2COCl$, 91%, *E/Z*, 99:1
128 (**114c**) R = $t\text{-}BuCH_2COCl$, 77%, 93:7
129 (**114d**) R = $t\text{-}BuCH_2COCl$, 88%, 93:7
130 (**114b**) R = $p\text{-}MeOC_6H_4COCl$, 70%, 98:2
131 (**114b**) R = $1\text{-}C_{10}H_7COCl$, 71%, 99:1
132 (**114e**) R = $p\text{-}MeC_6H_4COCl$, 50%, 98:2

133 (**114a**) R = 71%

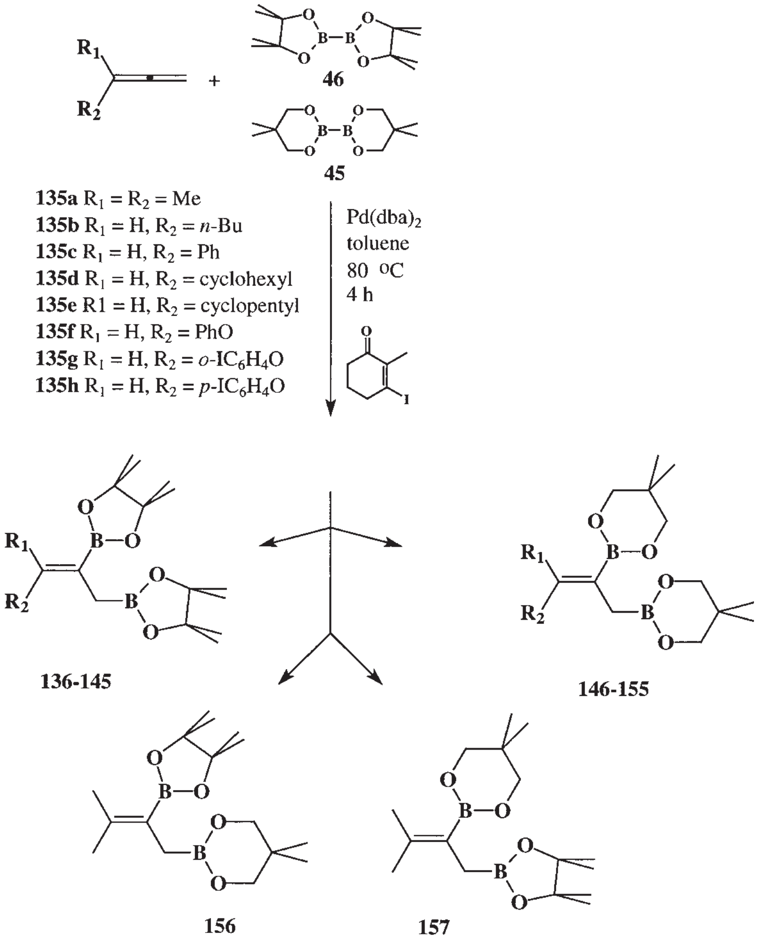
134 (**114a**) R = 62%

SCHEME 21

The development of new strategies in organic synthesis with a minimum of chemical steps is becoming more and more important for the efficient assembly of complex molecular structures.[10,89] The combination of multiple reactions in a single operation represents a particular efficient approach. Among these strategies,[90] geminated organobismetallic derivatives (1,1-bis anions) are becoming more and more useful.[91] During the past decades considerable efforts have been made to find new routes for the preparation of geminated sp^2 organobismetallic derivatives and for their selective reactions with several electrophiles.[91,92]

1. Formation of B–C–B Compounds

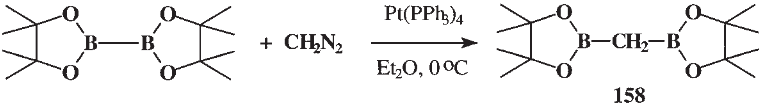
Bisdiborane, B–C–B, compounds are usually prepared by double hydroboration of terminal alkynes with dialkylboranes.[93–95] They are



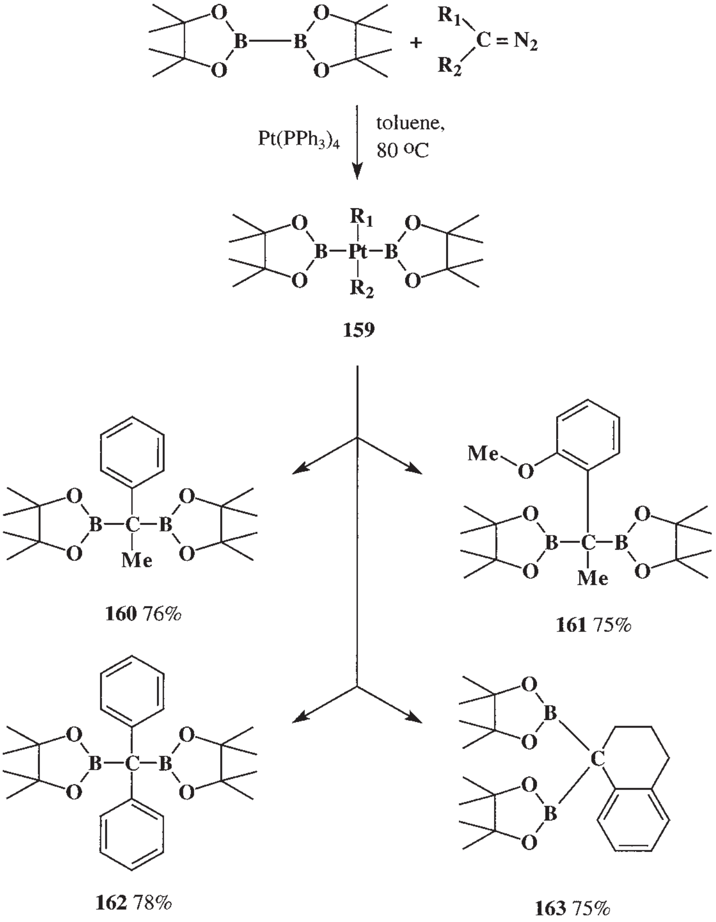
Scheme 22

interesting precursors to *gem*-bimetallics such as BCLi [96–99] and BCMgX.[100] Recently, we reported that the parent compound (pinacolato)$_2$BCH$_2$B, **158**, can be prepared in high yield by reaction of bis(pinacolato)diborane(4) with diazomethane (Scheme 23).[101] This reaction gave good results and were not described before.

Novel Cl-bridged bisboronate derivatives **160–163** have been recently reported by insertion of diazoalkanes into bis(pinacolato)diborane(4) by Abu Ali *et al.*[102] (Scheme 24) and the proposed catalytic cycle is shown in Figs. 6 and 7.



SCHEME 23



SCHEME 24

Synthesis of diboron compound **164** via bisdiboranes has been demonstrated by Wrackmeyer and Kehr.[103] Organoboration of tetra(alkynyl)stannanes leads to the spiro-cyclic compound in high yield, which reacts with $MeBBr_2$, *i*-$PrBBr_2$, and $PhBCl_2$ in dichloromethane between −78

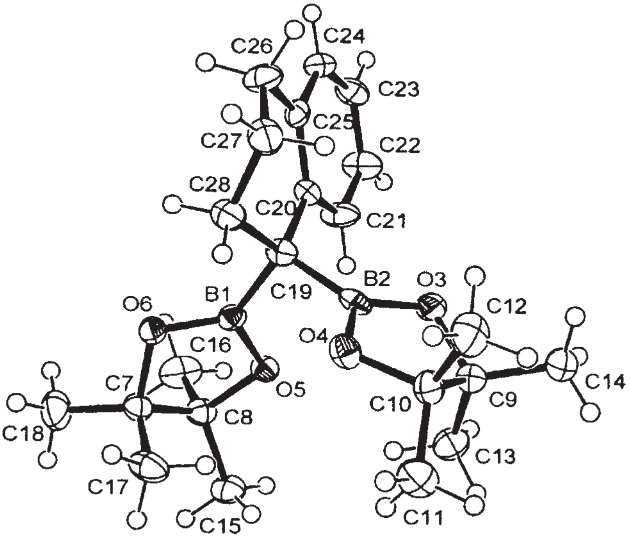
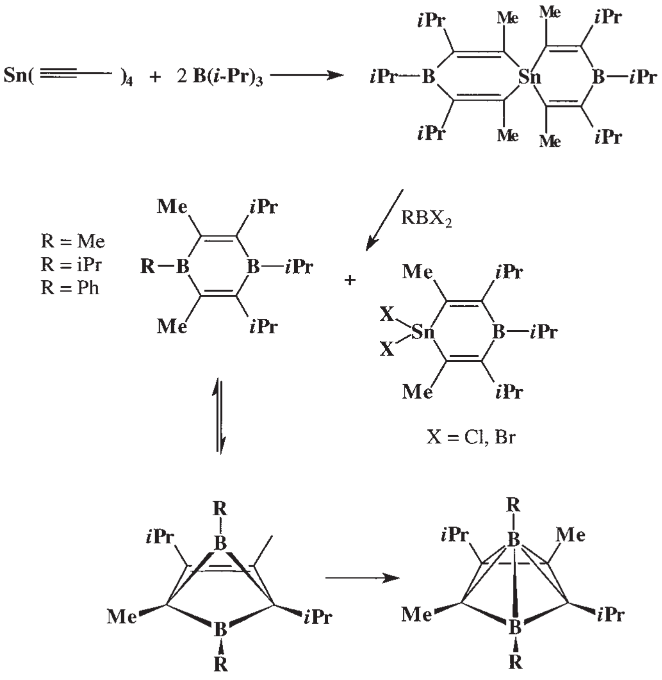


FIG. 7. The proposed view of the geminal organoboron compound **163**, showing the atom-numbering scheme.

and +25 °C to give B–C=C–B compounds and diboron compound **164** (Scheme 25).

The conversion product tetra(carbahexa)borane **167** (molecular structure shown in Fig. 8) can be obtained from diborane **165** (Scheme 26) via a 2,5-diborabicyclo-[2,1,1]-hexane **166** and its structure have been reported by Enders *et al.*[104] Synthesis of carbaboron compounds has also been reviewed previously.[105,106]

A novel and efficient method for *gem*-dimetalation of carbenoids has been reported by Shimizu *et al.*[107] Treatment of alkylidene-type lithium carbenoids with interelement compounds such as silylborane or diborane to generate the corresponding borate complex, followed by warming to room temperature, induced migration of the silyl or boryl group from a negatively charged boron atom to the carbenoid carbon to afford 1-boryl-1-silyl-1-alkenes or 1,1-diboryl-1-alkenes in good yields. Carbon–carbon bond forming transformations of the *gem*-dimetalated compounds mediated by boron or silicon was also described. *gem*-Diborylation of alkylidene-type carbenoids with diboranes has been demonstrated. Thus, commercially available diboranes A–D were used in the reactions (Scheme 27). Bis(pinacolato)diborane(4) A and optically active bis((+)-pinanediolato)-diborane(4) B reacted with **168** to give *gem*-diborylated compounds **169**, **169a**, and **169b** in high yields. In contrast, reaction with



164

SCHEME 25

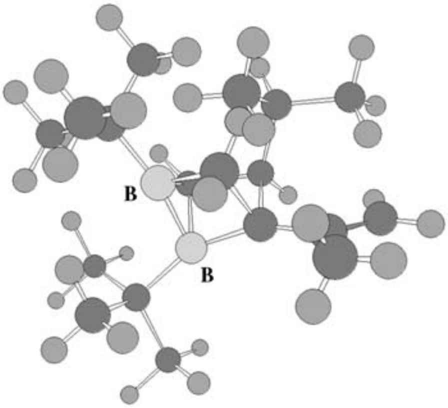
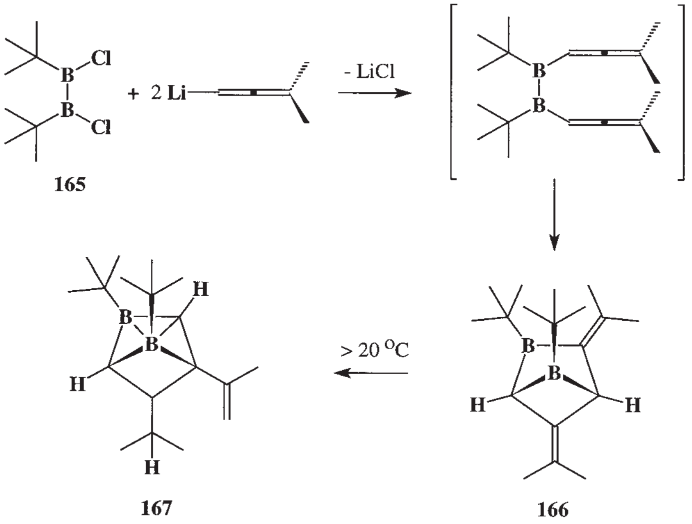
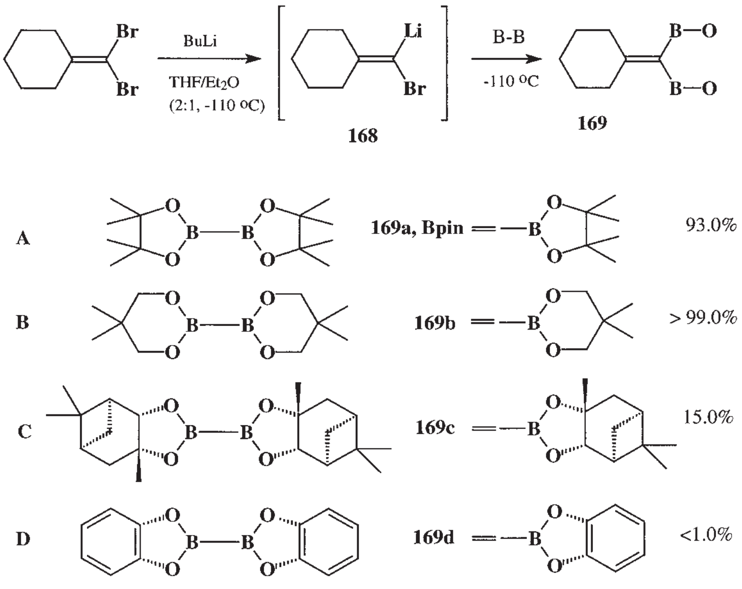


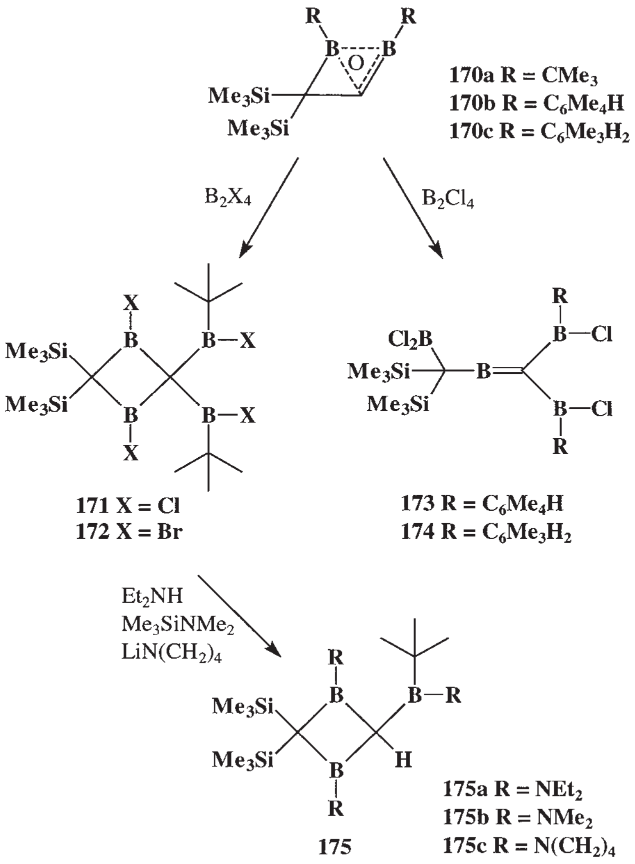
FIG. 8. Molecular structure of compound **167**.



SCHEME 26



SCHEME 27

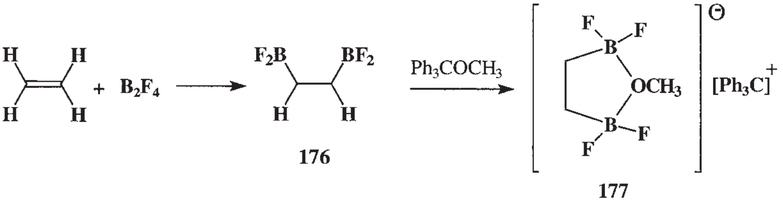


Scheme 28

bis(neopentanediolato)diborane(4) C resulted in low yield of **169c** probably due to its low solubility under the reaction conditions, while no detectable amount of the desired diborylated compound was obtained when bis(catecholato)diborane(4) D was used.

Reaction of the boriranyllideneboranes **170a–c** with tetrahalodiboranes(4) leads to two types of products **171**, **172** and **173**, **174**, respectively, (Scheme 28).[101,108] Compounds **170a–c** were first prepared by Berndt *et al.* more then 20 years ago.[109] Treatment of **171** with four equivalents of dimethylaminotrimethylsilane gave **175a–c**.

Interaction of tetra(fluoro)diborane with ethylene gives B–C–C–B compounds belonging to the bidentate Lewis acid.[110–112] The reactions



SCHEME 29

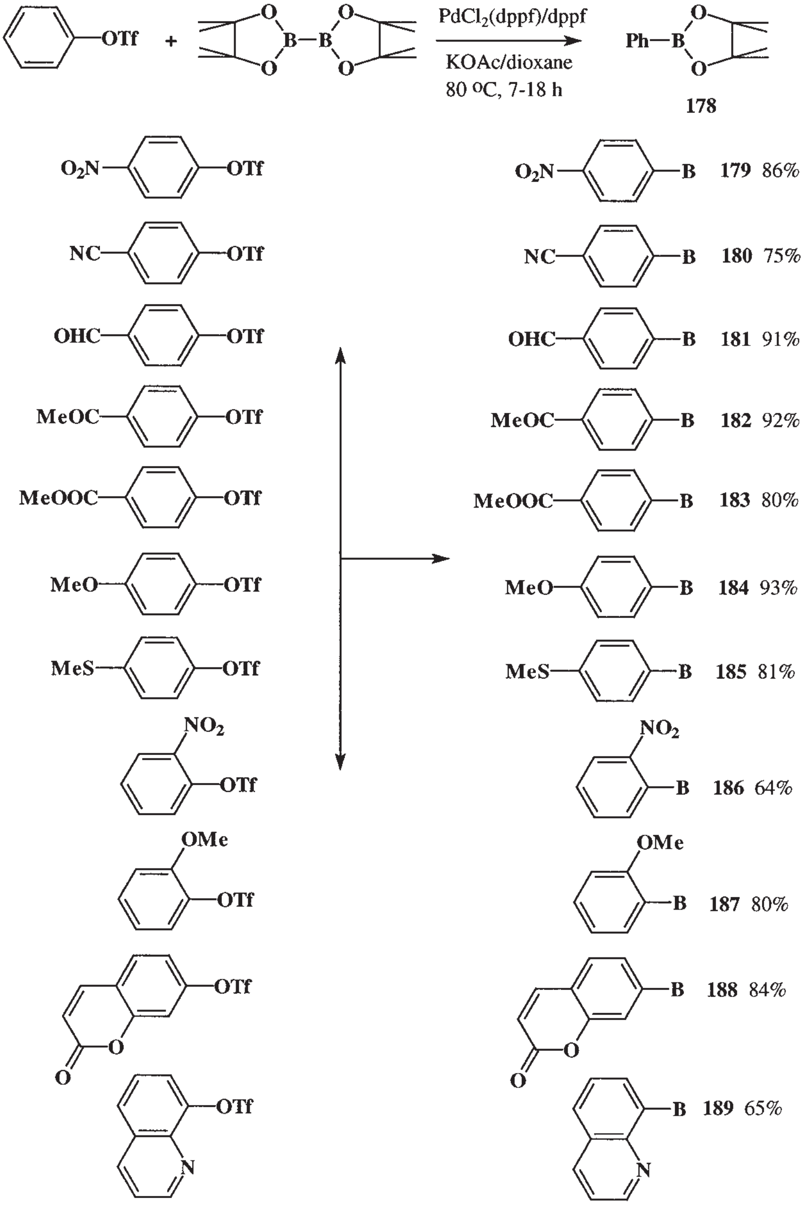
of a bidentate version of the quintessential boron-based Lewis acid (BF_3) with simple Lewis bases and anions have been investigated. Thus, $F_2BCH_2CH_2BF_2$ **176** was prepared by mixing ethylene and B_2F_4 at low temperature (Scheme 29).[113] To obtain diboryl derivative **177** with strongly Lewis acidic boron centers a weakly basic reagent such as Ph_3COMe was required.

E. *Synthesis of Arylboronates*

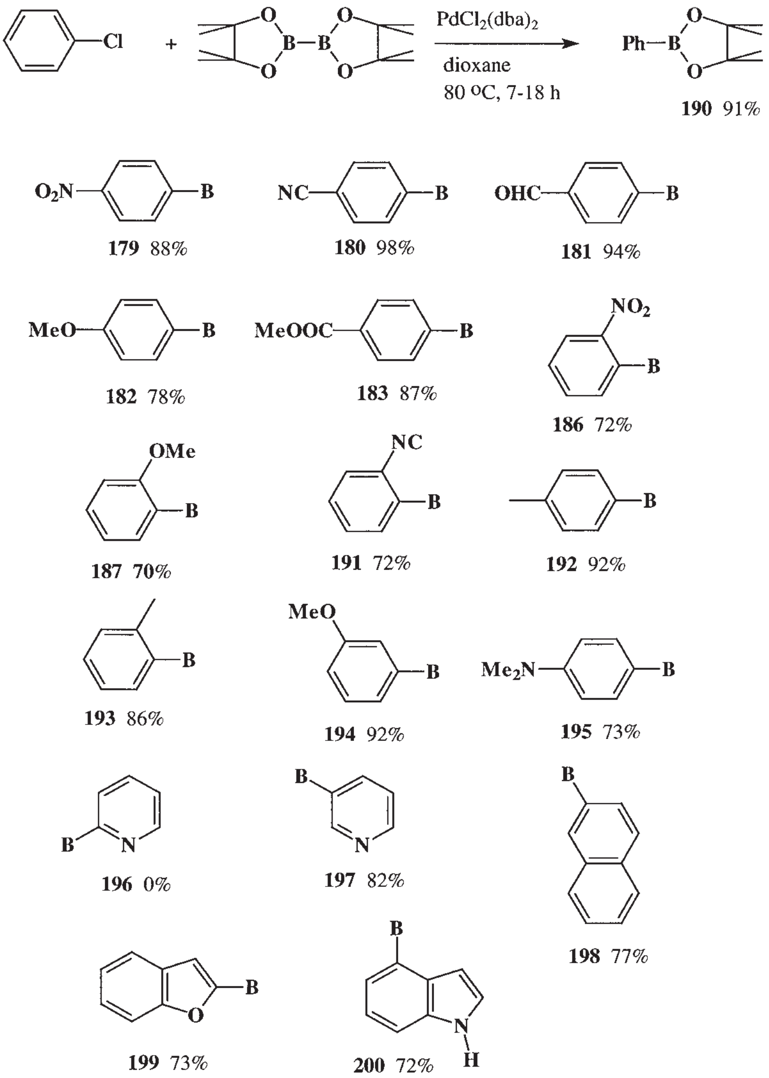
Synthesis of arylboronates via the palladium(0)-catalyzed cross-coupling reaction of tetra(alkoxy)diboranes with aryl triflates has been reported.[114] The cross-coupling reaction of $(RO)_2B–B(OR)_2$ (OR = methoxy and pinacolato) with aryl triflates to give arylboronates **178**–**189** was carried out at 80 °C in the presence of $PdCl_2$(dppf) (3 mol%), and KOAc (three equivalents) in dioxane. The reaction was generalized to various functional groups such as nitro, cyano, ester, and carbonyl groups (Scheme 30).

Synthesis of pinacol arylboronates **190**–**200** via cross-coupling reaction of bis(pinacolato)diborane(4) with chloroarenes catalyzed by palladium(0)-tricyclohexyl-phosphine complexes has been demonstrated by Ishiyama *et al.* (Scheme 31).[115]

2-Pyridylboronic esters **201** were generated by cross-coupling of 2-bromopyridines with bis(pinacolato)diborane(4) in the presence of a base and palladium catalyst. The boronic esters reacted *in situ* with unreacted 2-bromopyridines to afford high yields of 2,2′-bipyridines as homocoupled products. Depending upon the reaction conditions, varying amounts of protodeboronated products were also observed.[116] Masuda and co-workers successfully prepared an uncharacterized poly(pyridine) **203** in 88% yield by reacting 2,6-dibromopyridine with **46** in the presence of NaOH and a palladium catalyst in DMF.[117] This polymeric product was produced by homocoupling of dibromide and likely went through


OTf
PdCl2(dppf)/dppf
KOAc/dioxane
80 °C, 7-18 h
Ph—B
178
O2N
NC
OHC
MeOC
MeOOC
MeO
MeS
NO2
OMe
N
B
179 86%
180 75%
181 91%
182 92%
183 80%
184 93%
185 81%
186 64%
187 80%
188 84%
189 65%

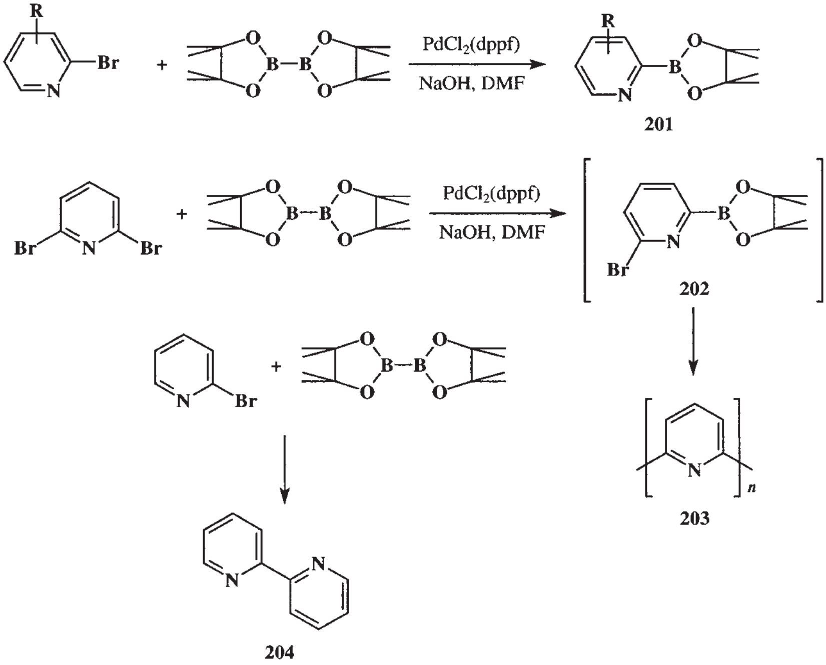
SCHEME 30



Scheme 31

a 2-pyridyl-boronic ester intermediate **202** (Scheme 32). Under these conditions 2-bromopyridine and bis(pinacolato)diborane(4) reacted to give bipyridine **204** in 78% yield.

High yield synthesis of biphenylboronates **205** and also **206** have been demonstrated.[118] The directed *ortho*-lithiation for the synthesis of

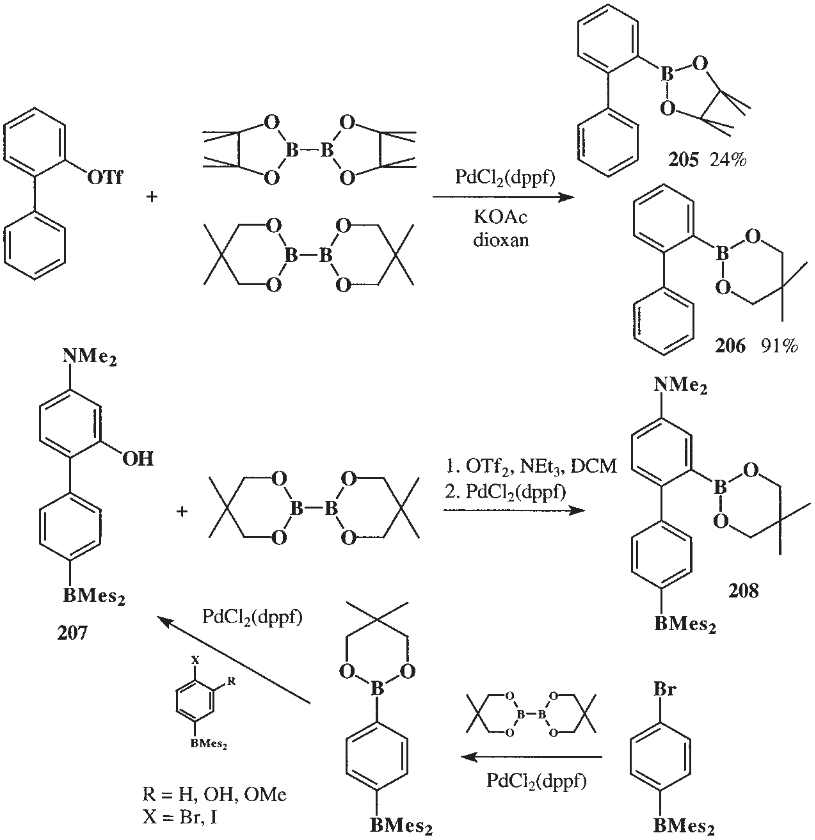


SCHEME 32

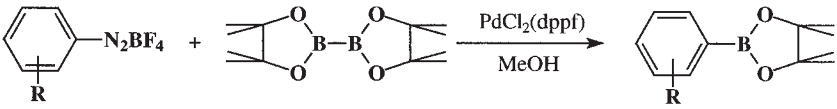
borylated biaryls as an extension to the synthesis of (2-dialkylaminophenyl)-diarylboranes was published.[119] Reactions on 2-dimethylaminobiphenyl **207** gave a mixture of both possible lithiation products; therefore, a symmetrical terphenyl was introduced to give *N,N*-dimethyl-2-(*o*-dimesitylborylphenyl)-5-phenylanilin **208** as the sole product (Scheme 33).

A new synthetic approach to fluorescent 4-amino-4′-boryl biaryls by a boronate selective Suzuki-coupling of *p*-(dimesitylboryl)phenylboronates with haloarenes under the employed reaction conditions has been reported. The triarylboryl unity is not attacked whereas non-sterically hindered triarylboranes like tri-1-naphthylborane gave coupling products in good yields **207**.[120]

The first synthesis of arylboronic esters **209**–**215** via the coupling of bis(pinacolato)diborane(4) with easily prepared aryldiazonium tetrafluoroborate salts was reported. The palladium-catalyzed borylation reaction proceeds efficiently under mild reaction conditions in the absence of a base to afford various functionalized arylboronic esters in moderate to high yields (Scheme 34).[121]

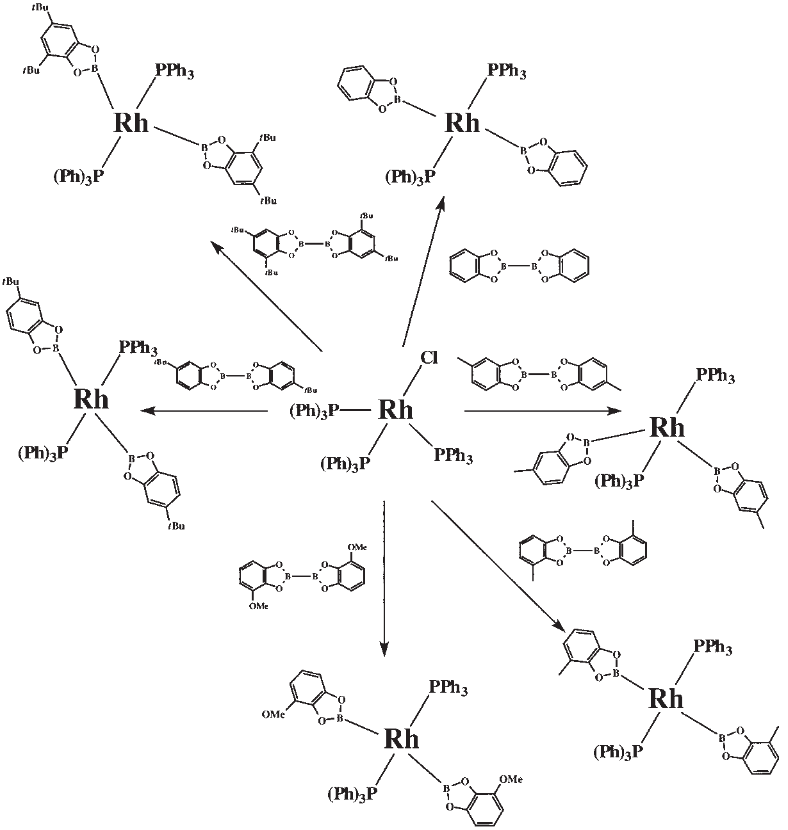


SCHEME 33



201 96%
209 R = 4-Br, 80%
210 R = 4-Me, 87%
211 R = 4-I, 58%
212 R = 4-COOMe, 81%
213 R = 4-OMe, 51%
214 R = 4-NO$_2$, 61%,
215 R = 4-Br, 2-Me-, 42%

SCHEME 34

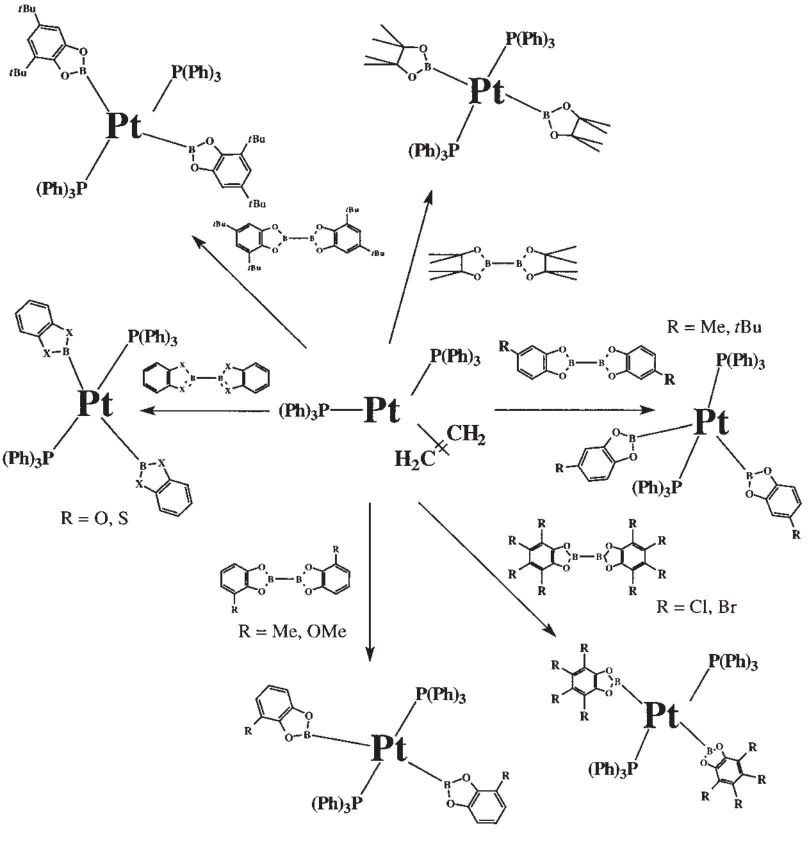


SCHEME 35

F. *Synthesis and Reactions of Diborametal Complexes*

The use of diborane(4) compounds to form metal bisboryl compounds has received considerable attention in recent years, since such compounds can be added catalytically to certain organic functional groups resulting in the formation of two carbon–boron bonds. The reaction of [RhCl(PPh$_3$)$_3$] with HBcat affords a rhodium bisboryl complex. However, reaction of [RhCl(PPh$_3$)$_3$] with B$_2$cat$_2$ gives the Rh(III)-bisboryl compound directly. This method of preparation has proven to be useful for the synthesis of a wide range of Rh-bisboryl compounds (Scheme 35).[122]

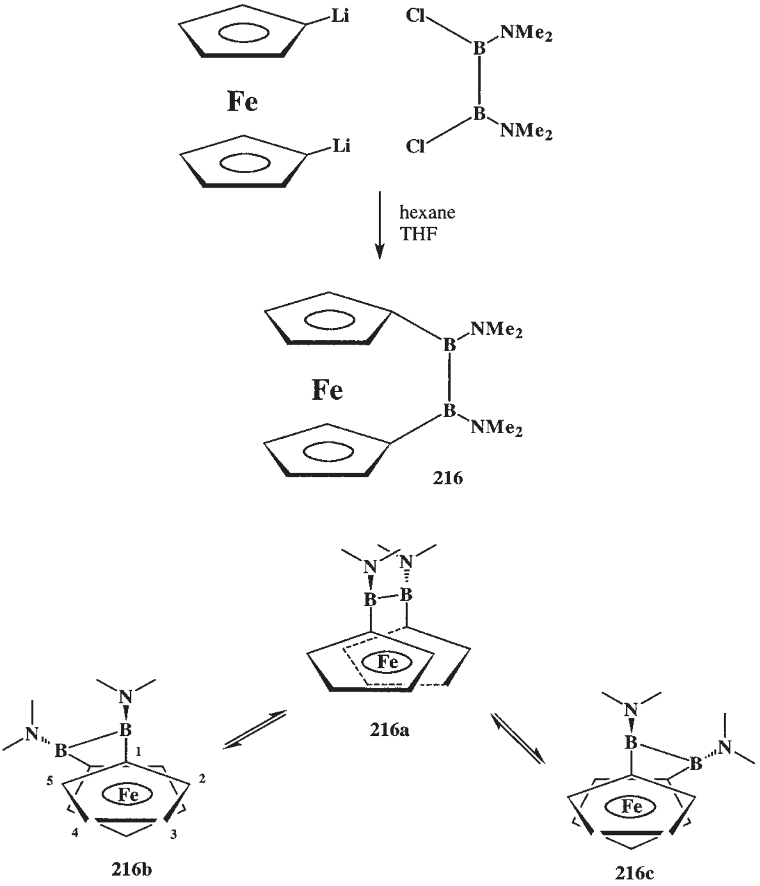
Recently, the structures of several bisboryl platinum compounds have been reported by Miyaura *et al.*[123] The formation of *cis*-[Pt(PPh$_3$)$_2$(Bpin)$_2$] presumably formed by dissociation of two equivalents of PPh$_3$ from [Pt(PPh$_3$)$_4$] followed by oxidative addition of B$_2$pin$_2$ although the precise



SCHEME 36

mechanism has not been established. Recently, the same authors have described the structure of this compound.[63] In addition, Iverson and Smith[124] also reported that $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ reacted with B_2cat_2 via the dissociation of ethylene. Dissociation of ethylene from $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ gives rise to highly reactive intermediates for oxidative addition. In fact, $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ reacts with a wide range of diborane(4) compounds, which include both aryl- and alkyloxydiborane(4) compounds as well as $B_2(1,2\text{-}S_2C_6H_4)_2$ [B_2thiocat$_2$], as shown in Scheme 36.[65,125] Nöth has also reported the synthesis of *cis*-$[Pt(PPh_3)_2\{B(OMe)_2\}_2]$ resulting from the oxidative addition of $B_2(OMe)_4$ which is the sole example of a non-chelating tetra(alkoxy)diborane(4) derivative involving a $[Pt(PPh_3)_2]$ center.[126]

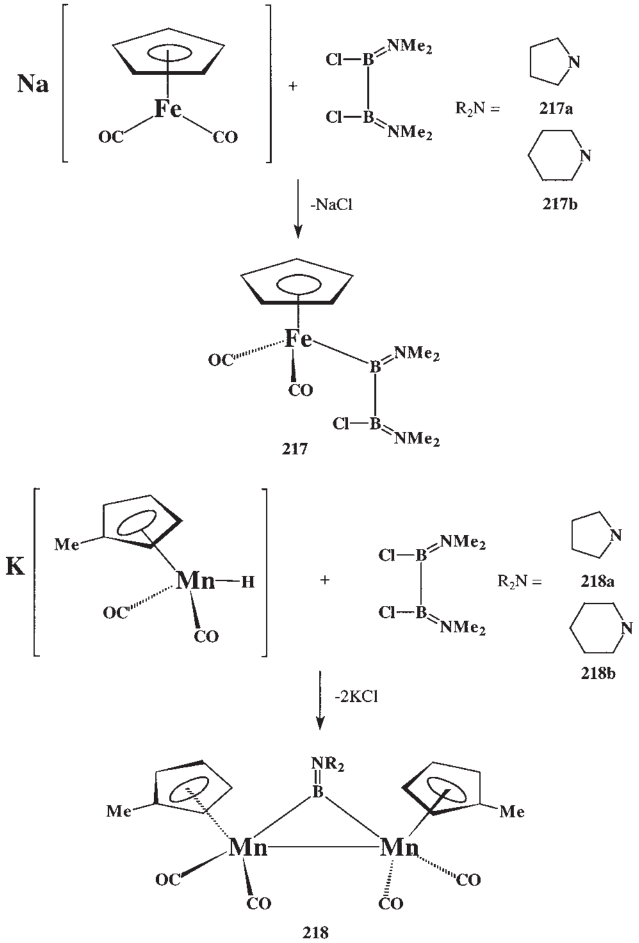
1,2-Bis(dimethylamino)-1,2-dibora-[2]-ferroceneophane **216** was synthesized by the reaction of 1,1′-dilithioferrocene with 1,2-dichloro-bis(dimethylamino)-diborane(4).[127] Conformation of **216(a–c)** has been studied.



SCHEME 37

The staggered conformation causes non-equivalence of 2- and 5-, and 3- and 4-positions at low temperature was shown in Scheme 37.

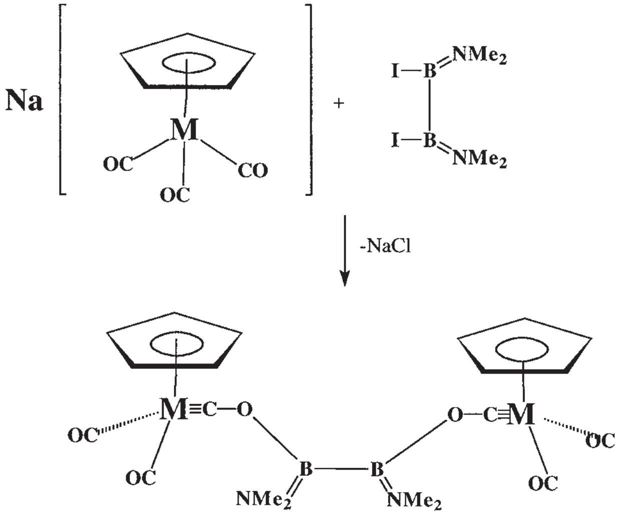
The 1,2-diaminodichlorodiboranes(4) and $B_2(NC_5H_{10})_2Cl_2$ served as starting materials for the syntheses of the iron diborane(4)yl complexes $[Cl(R_2N)B–B(NR_2)Fe(C_5H_5)(CO)_2]$ (**217a**, $NR_2{=}NC_4H_8$, brown, and **217b**, $NR_2{=}NC_5H_{10}$, red colors, in 22 and 10% yields, respectively). Upon reaction with the anionic manganese hydride complex $K[(C_5H_4Me)MnH(CO)_2]$, the bridged borylene complexes $[\{(C_5H_4Me)Mn(CO)_2\}_2BNR_2]$ (**218a**, $NR_2{=}NC_4H_8$; **218b**, $NR_2{=}NC_5H_{10}$, both obtained as dark red crystalline solids in 48 and 40% yields, respectively) were obtained with cleavage of the B–B bond, hydrogen migration from manganese to boron, and formation of the corresponding diboranes(6) $(H_2BNR_2)_2$ (Scheme 38).[128]



SCHEME 38

Reaction of the diborane(4) $B_2(NMe_2)_2I_2$ with two equivalents of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ ($M = Mo$, W, Cr) yielded the dinuclear boryloxycarbyne complexes $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}_2\text{–}B_2(NMe_2)_2]$ (**219**, $M = Mo$; **220**, $M = W$; **221**, $M = Cr$), which were fully characterized in solution by multinuclear NMR techniques (Scheme 39).[129]

Direct borylation of hydrocarbons catalyzed by a transition metal complex has been extensively studied by several groups and has become an economical, efficient, elegant, and environmentally benign protocol for the synthesis of a variety of organoboron compounds. The Rh-, Ir-, Re-, and Pd-catalyzed C-/H borylation of alkanes, arenes, and benzylic positions



219 **M = Mo**
220 **M = W**
221 **M = Cr**

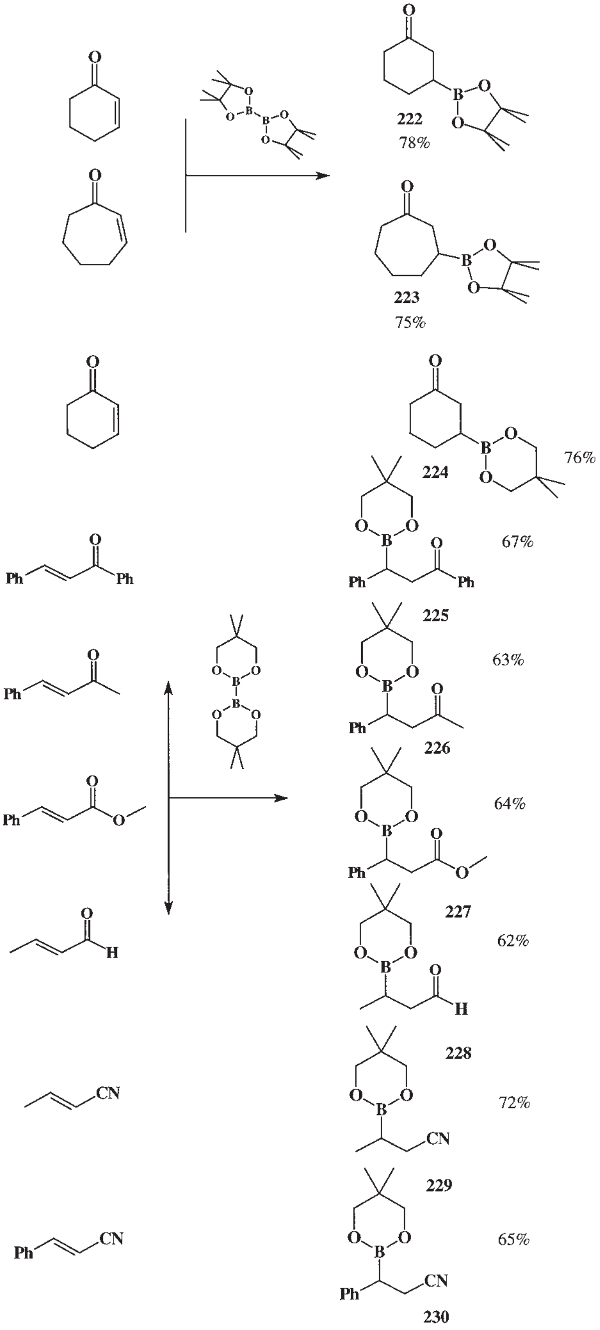
SCHEME 39

of alkylarenes by bis(pinacolato)diborane(4) or pinacolborane providing alkyl-, aryl-, heteroaryl-, and benzylboron compounds have recently been partly reviewed.[130]

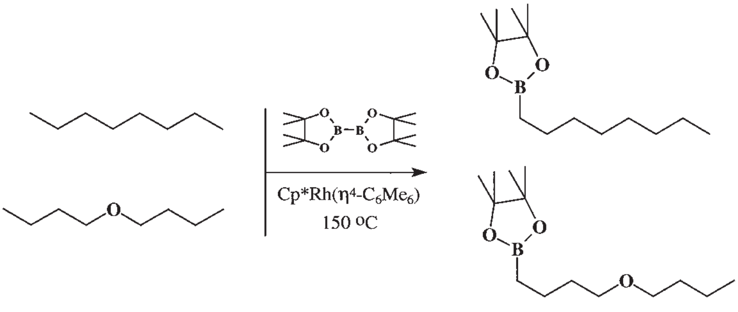
Rhodium-catalyzed 1,4-addition reactions of bis(pinacolato)diborane(4) and bis(neopentyl glycolato)diboron to α,β-unsaturated ketones give the corresponding boron derivatives **222**, **223**, and **224–230** (Scheme 40).[131] This is the first reported example in which a rhodium catalyst was used in addition reaction of diboron reagents to α,β-unsaturated electron deficient alkenes.

Alkanes regiospecifically reacted at the terminal carbon with pinB–Bpin at 150 °C. In the presence of Cp*Rh(η^4-C_6Me_6) (4.0–6.0 mol%), one equivalent of pinB–Bpin afforded almost two equivalents of 1-borylalkanes, thus indicating participation of pinBH in the catalytic cycle. Indeed, pinBH in *n*-octane gave pinacol *n*-octylboronate in 65% yield (Scheme 41).[132]

The C–H coupling of aromatic heterocycles with bis(pinacolato)diborane(4) was carried out in octane at 80–100 °C in the presence of a half equivalent [IrCl(COD)]$_2$-(4,4′-di-*tert*-butyl-2,2′-bipyridine) catalyst (3 mol%). The reactions of five-membered substrates such as thiophene, furan, pyrrole, and their benzo-fused derivatives exclusively produced 2-borylated



SCHEME 40



Scheme 41

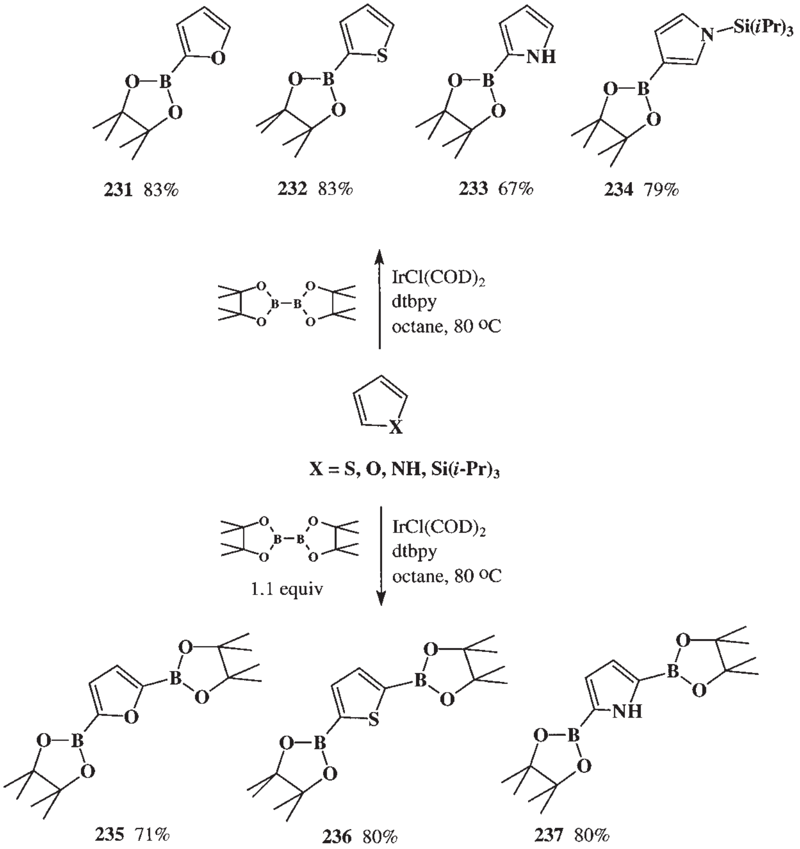
products (Scheme 42), whereas those of six-membered heterocycles including pyridine and quinoline selectively occurred at the 3-position (Scheme 43). Regioselective synthesis of bis(boryl)-heteroaromatics was also achieved by using an almost equimolar amount of substrates and the diborane.[133]

A combination of a Cp*Ir complex and an electron-donating alkylphosphine such as $P(Me)_3$ is effective for aromatic C–H borylation by pinBH, and gave a good Ir-reagent (Scheme 44).[134] Further studies resulted in significant improvement in catalyst efficiency. A maximum turnover number (4500 TON) was achieved at 150 °C when $Ir(\eta^5\text{-}C_9H_7)(COD)$ and a bidentate alkylphosphine such as dmpe(1,2-bis(dimethylphosphino)ethane) were used at 150 °C in a sealed ampule (Scheme 45).[135] The orientation was kinetically determined, thus giving statistical meta/para isomers (ca. 2/1) for monosubstituted arenes. Borylation selectively occurred at the common meta-carbon for 1,3-disubstituted arenes, such as 1,3-dichlorobenzene and methyl 3-chlorobenzoate, since the reaction was more sensitive to steric hindrance than electronic effects of the substituents.

Hartwig and Chen[136] showed that using photochemical activation of $Cp^*Re(CO)_3$ with irradiation from a 450-W medium-pressure mercury lamp in the reaction of bis(pinacolato)diborane(4) in alkane in the presence of $Cp^*Re(CO)_3$ (2.4–5.0 mol%) and CO (2 atm) produced the corresponding alkylboronates. Photochemical reaction of *n*-hexane with $Cp^*Re(CO)_2(Bpin)_2$, prepared from $Cp^*Re(CO)_3$ and pin_2B_2, led to the regiospecific formation of 1-borylpentane in quantitative yield (Scheme 46).

G. *Miscellaneous Reactions*

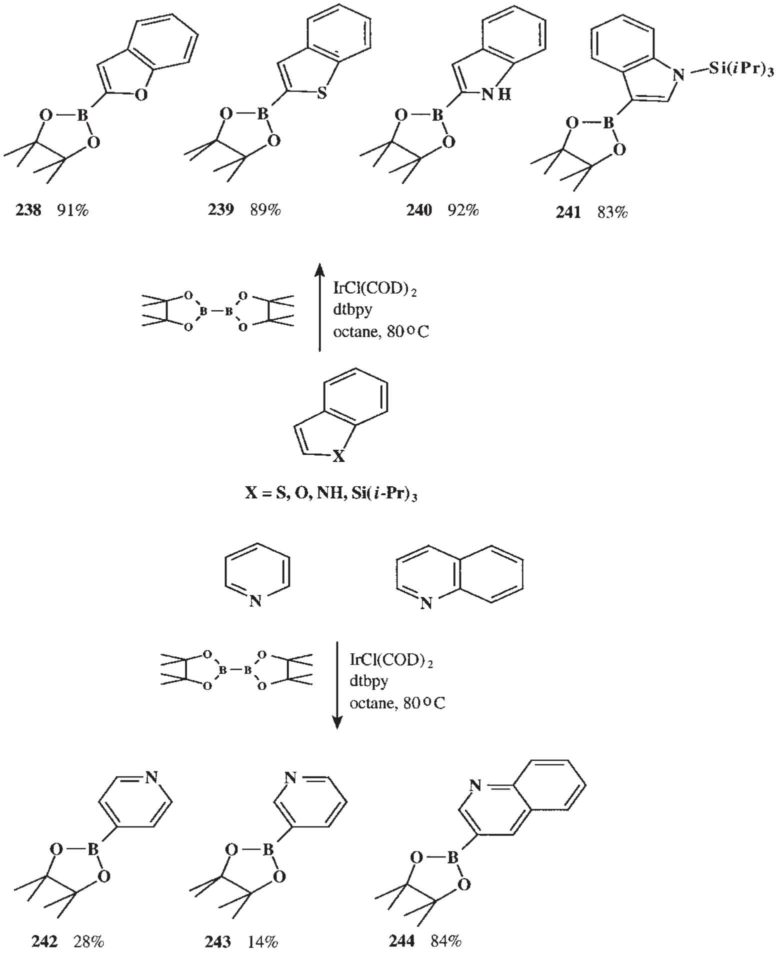
The insertion of CO into the B–B bond of 1,2-bis(diisopropylamino)-2,5-dihydro-1*H*-1,2-diborole **256** and 1,2-bis(diisopropylamino)-3-methylidene-1,2-diborolane **252** leads to the dimeric spiro products 1,7,9,14-tetrakis (diisopropyl-amino)-6,13-dioxa-1,7,9,14-tetraboradispiro[4,2,4,2]tetradeca-2,



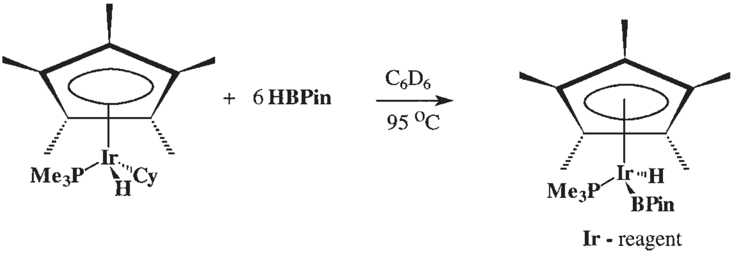
Scheme 42

10-diene **257** and 1,7,9,14-tetrakis(diisopropyl-amino)-bismethylidene-6,13-dioxa-1,7,9,14-tetrabora-dispiro[4,2,4,2]-tetradecane **253**. The reaction of **256** with *tert*-butyl isocyanide and 2,6-dimethylphenyl isocyanide in THF leads to the formation of the monomeric insertion products 1,3-bis(diisopropylamino)-2-*tert*-butylimino-1,3-diboracyclohex-4-ene **258** and 1,3-bis(diisopropylamino)-2-(29,69-dimethylphenylamino)-1,3-di-boracyclohex-4-ene **259**. Treatment of **252** with the isonitriles gives 2-*tert*-butylimino-1,3-bis(diisopropylamino)-4-methylidene-1,3-diboracyclohexane **254** and 1,3-bis(diisopropylamino)-2-(29,69-dimethylphenylamino)-4-methylidene-1,3-dibora-cyclohexane **255** (Scheme 47).[137]

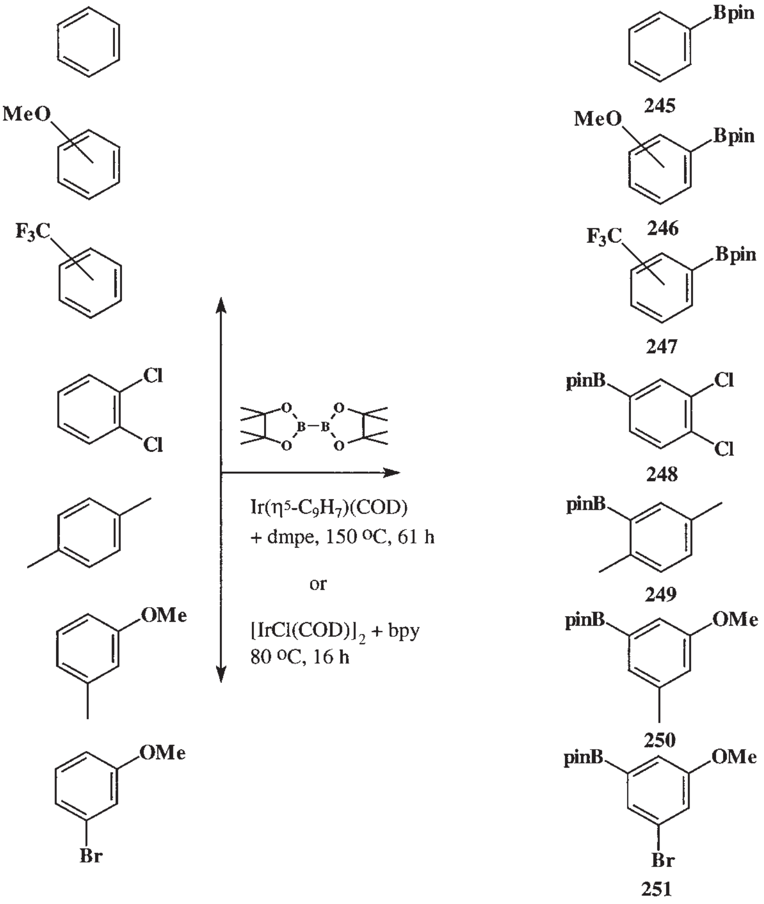
Commercially available Pt(cod)Cl_2 catalyzes the diboration of alkenes, alkynes, and aldimines using bis(catecholato)diborane(4) (cod = 1,5-cyclooctadiene). Catalyzed aldimine diboration provides the first direct



SCHEME 43



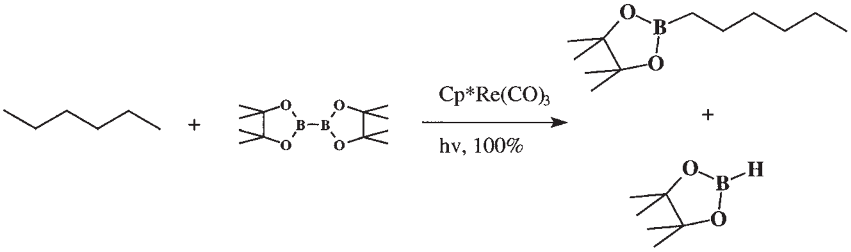
SCHEME 44



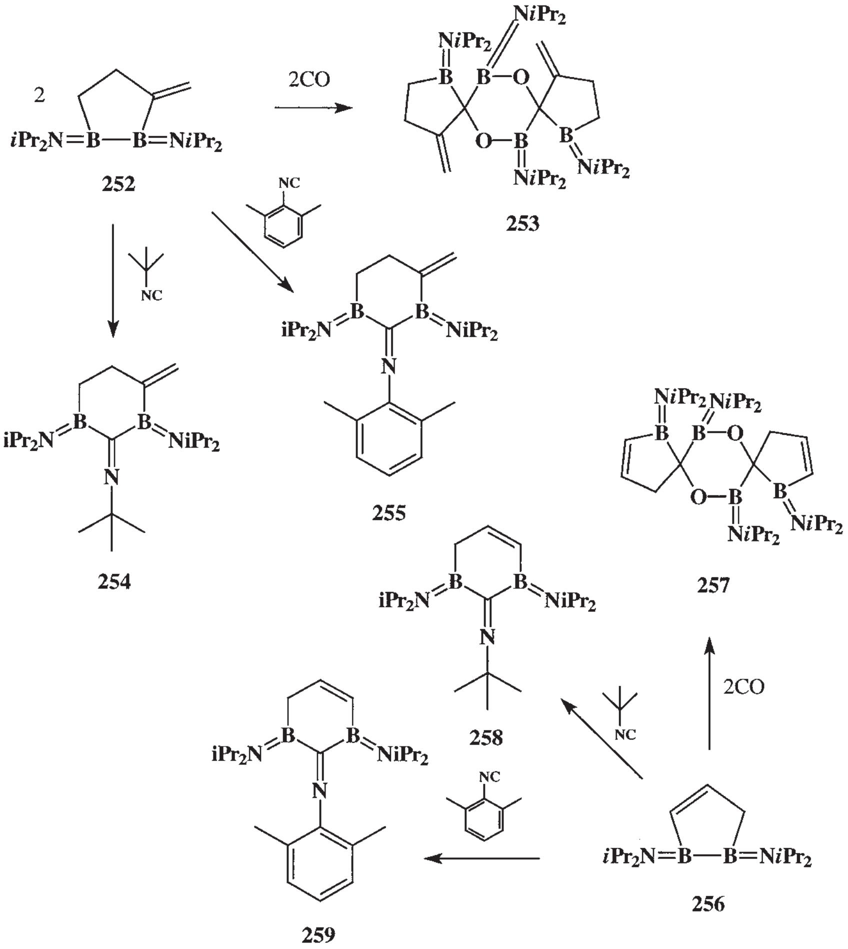
Scheme 45

route to R-aminoboronate esters. The diboration product from *N*-benzylidene-2,6-dimethylaniline was structurally characterized by physico--chemical methods (Scheme 48).[68]

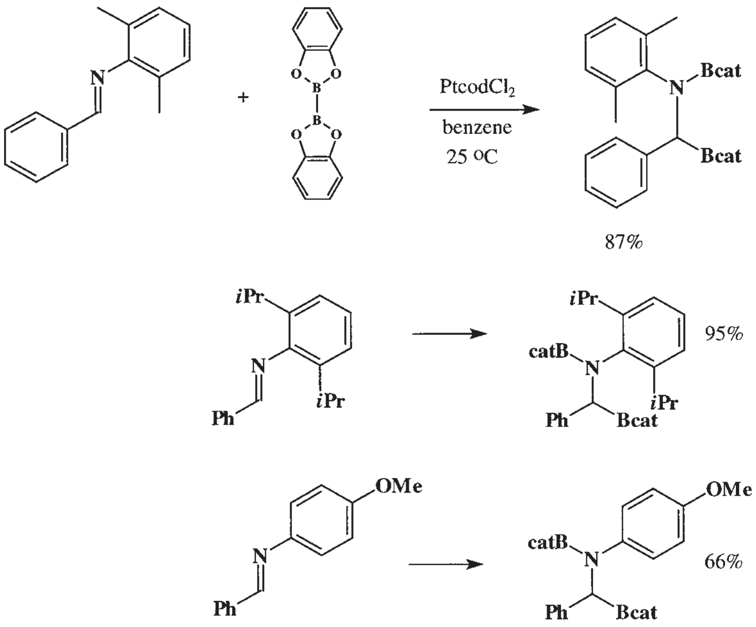
A novel linking strategy has been developed for synthesizing configurationally stable α-amino aldehyde on polymeric supports. Alkylation of L-alanine methyl ester with 9-bromo-9-*p*-bromophenylfluorinene, followed by ester hydrolysis and coupling to isoxazolidine, provided *N*-(9-*p*-bromophenylfluoren-9-yl)-alanine isoxazolidide(5) **260**, which was transformed into its corresponding boronate **261** by a palladium-catalyzed cross-coupling reaction with bis(pinacolato)-diborane(4). Boronate **261**



SCHEME 46



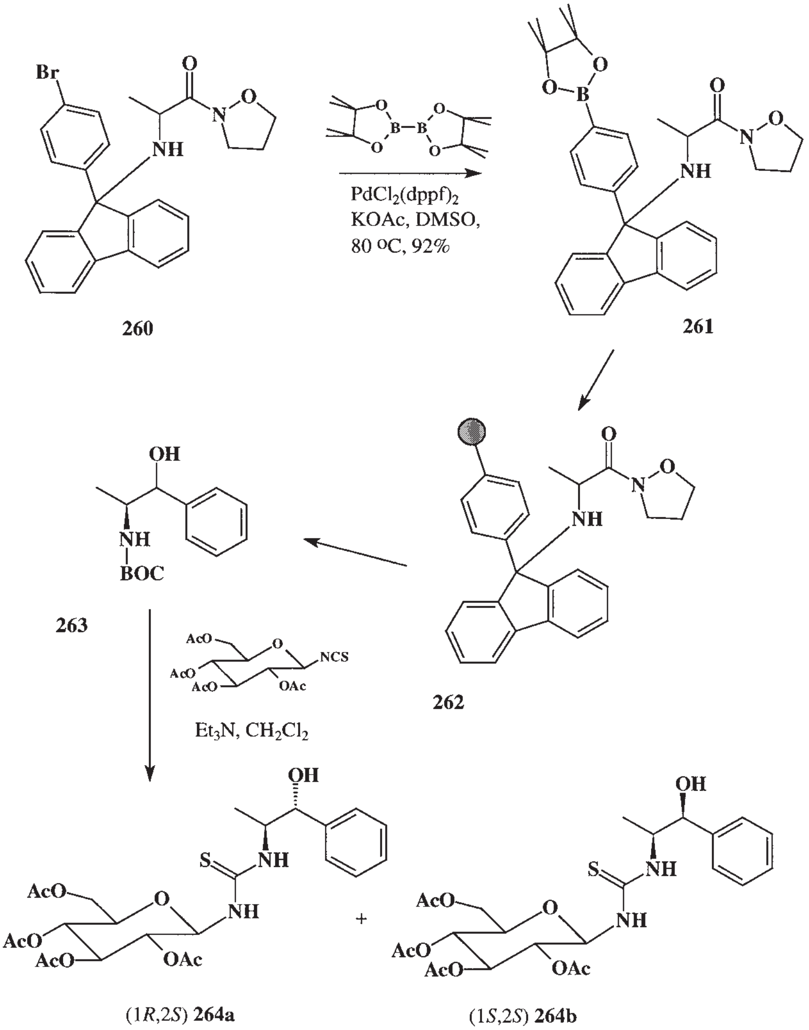
SCHEME 47



SCHEME 48

was anchored to four different polymeric aryl halides in 70–99% yields. Polymer-bound alaninal was then synthesized on non-cross-linked polystyrene by hydride reduction of isoxazolidide **262**. Treatment of alaninal with phenylmagnesium bromide, cleavage of the resulting amino alcohol in a 1:2:2 TFA/CH_2Cl_2/anisole cocktail, and acylation with di-*tert*-butyl dicarbonate furnished *N*-(BOC)norephedrines **263** that were demonstrated to be enantiopure by conversion to diastereomeric thioureas **264a** (99%) and **264b** (1%) (Scheme 49).[138]

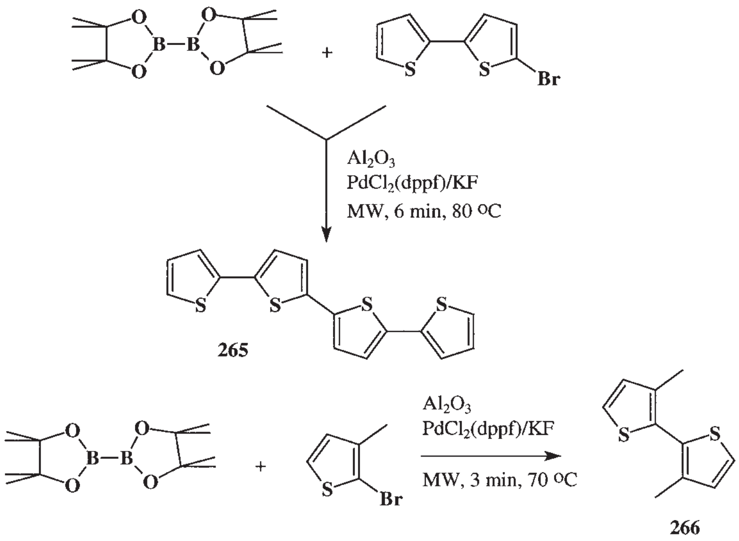
The solvent-free, microwave-assisted coupling of thienyl boronic acids and esters with thienyl bromides, using aluminum oxide as the solid support, served to rapidly check the reaction trends on changing times, temperature, catalyst, and base and easily optimize the experimental conditions to obtain the desired product in fair amounts. This procedure offers a novel, general, and very rapid route to the preparation of soluble thiophene oligomers. Quaterthiophene **265** was obtained in 6 min by reaction of 2-bromo-2,2′-bithiophene with bis(pinacolato)diborane(4) in 65% yield, whereas dithiophene **266** was obtained with 70% yield. The synthesis of new chiral 2,2′-bithiophenes also was reported. The detailed



Scheme 49

analysis of the by-products of some reactions elucidated a few aspects of reaction mechanisms (Scheme 50).[139]

Synthesis of chiral 2,2′-bithiophenes **268** and **269** have been reported.[139] The new methodology for the synthesis of the two enantiomers of bithiophene bearing R(−) and S(+) chiral groups at the terminal positions (compounds **268** and **269**) is presented here and the synthetic pattern is



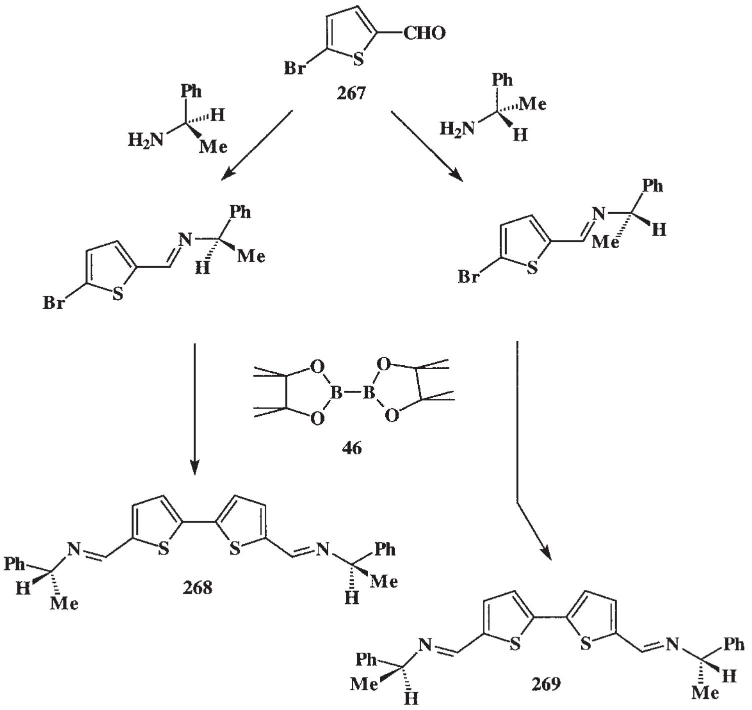
SCHEME 50

shown in Scheme 51. As shown in Scheme 51, the monobrominated monomers were obtained by condensation of commercial 5-bromo-2-thiophene aldehyde with R(−) and S(+) 1-phenylethylamine. Later, they were reacted with bis(pinacolato)diborane(4) using the same experimental conditions employed for the preparation of quaterthiophene **267**. After a few minutes of microwave irradiation, bithiophenes **268** and **269** were recovered in high yield (isolated yield for both compounds >70%).

Free-base porphyrins react with haloboranes to give diborylporphyrins **270**–**272** in which the porphyrin ligands show marked rectangular distortions (Scheme 52).[140]

As for the biaryl ether containing macrocycles, an array of bioactive macrocycles with an endo aryl–aryl bond exist in nature. A new palladium catalyzed reaction has been recently developed in which bis(pinacolato)diborane(4) mediated the process to reach such a structural motif. The reaction consists of a domino process involving a Miyaura's arylboronic ester synthesis and an intramolecular Suzuki-coupling. Synthesis of a bicyclic A–B–O–C ring system of RP-66453 **273**, a neurotensine receptor antagonist, with an *endo* aryl–aryl and an *endo* aryl–aryl ether bond was described (Scheme 53).[141]

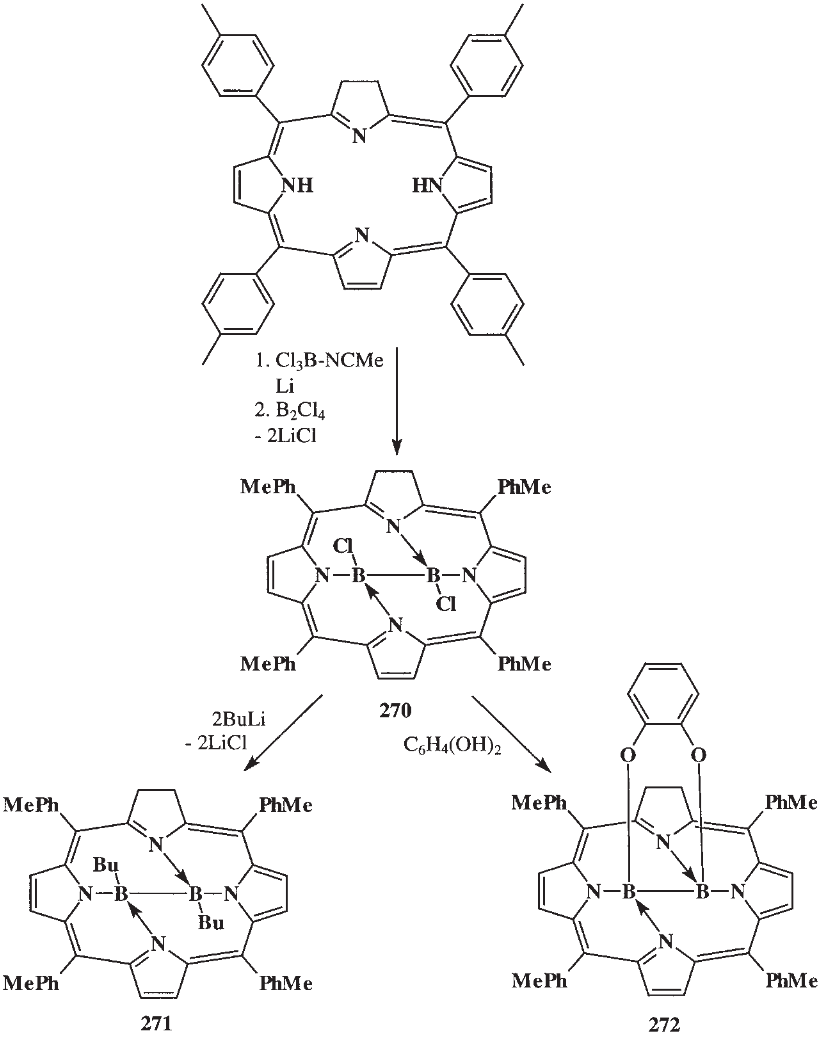
Diborination of α,β-unsaturated ketones has been reported.[142] The diboration of enones with **274** gives 1,4-addition products **275**–**280** in the presence of a platinum(0) catalyst such as $Pt(C_2H_4)(PPh_3)_2$



Scheme 51

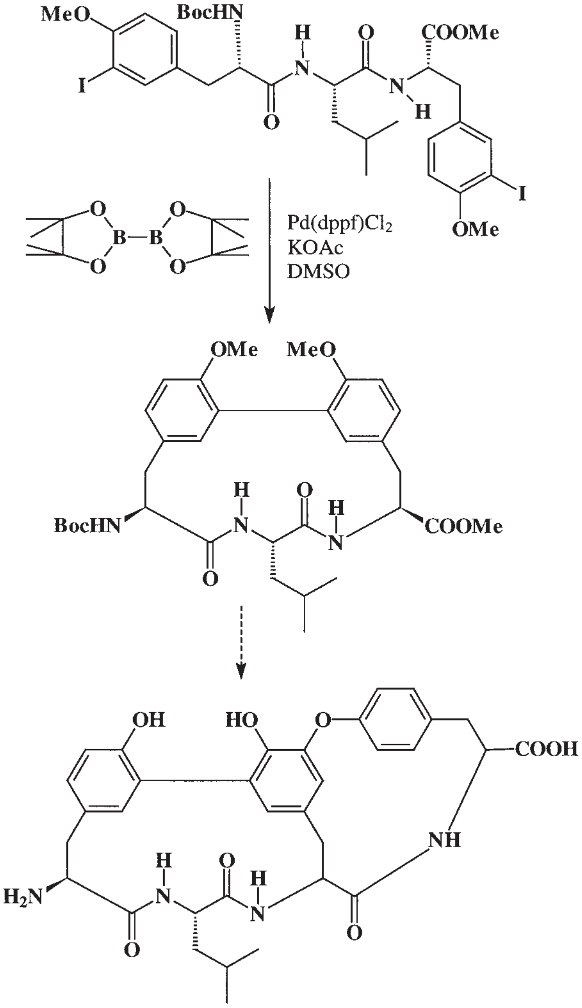
at 80 °C or Pt(dba)$_2$ at room temperature (Scheme 54). The reaction catalyzed by Pt(C$_2$H$_4$)(PPh$_3$)$_2$ affords a single isomer which is assumed to be the *Z*-enolate. The hydrolysis of **275**–**280** with water gives β-borylketones in high yields, the conversion of which is synthetically equivalent to the conjugate 1,4-addition of a boryl anion to enones. The diboration of α,β-unsaturated esters and nitriles affords similar products.[142]

Methylenecyclopropane and its derivatives are of interest as the substrate for the transition metal-catalyzed addition reactions because of their high and unique reactivities originating from the highly strained structure. The platinum catalyzed reaction of bis(pinacolato)diboron(4), **46** proceeds through the proximal bond cleavage of the cyclopropane ring (Scheme 55).[143] The catalytic cycle involving the insertion of methylenecyclopropane into the B–Pt bond of **282**, followed by the rearrangement to a homoallylplatinum(II) species gives a ring-opening product **281**. The selective formation of the *cis*-isomers for bicyclic methylenecyclopropane



Scheme 52

suggests a four-centered cyclic transition state for the ring-opening rearrangement. The results also provide information on the insertion mechanism of **282**, i.e., the addition of the Pt–B bond to terminal alkene gives a primary alkyl-platinum intermediate, the selectivity being similar to that for the silylboration of alkenes.[144]



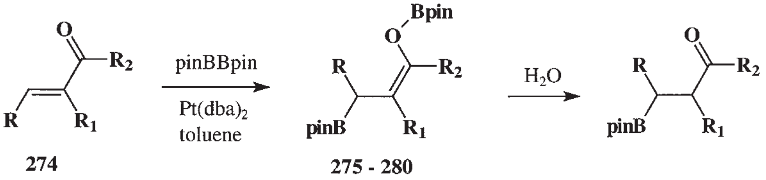
273 RP-66453

SCHEME 53

IV

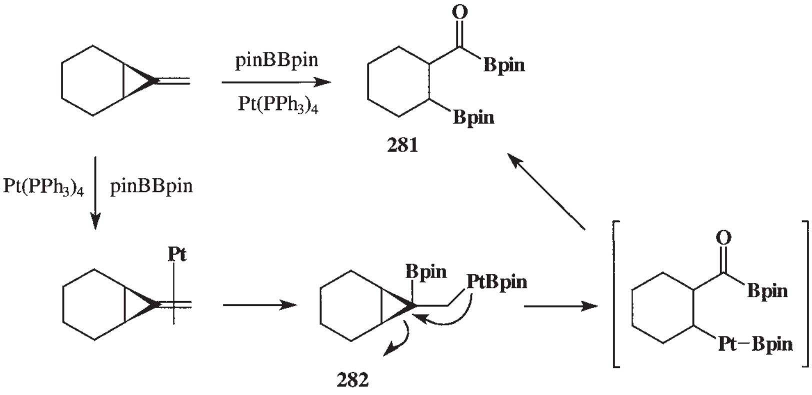
CONCLUDING REMARKS

In the past 20–25 years, the use of transition metal catalysts has opened up many new possibilities in the area of borylation reactions. Catalytic hydroboration with diboranes is an exciting new strategy for



275 $R = Ph, R_1 = H, R_2 = Me$, Yield, > 90%
276 $R = H, R_1 = R_2 = Me$, 64%
277 $R = R_2 = Me, R_1 = H$, 72%
278 $R = R_2 = Ph, R_1 = H$, > 90%
279 2-cyclopentenone, 88%
280 2-cyclohexenone, 61%

SCHEME 54



SCHEME 55

obtaining different chemo-, regio-, and stereoselectivities relative to the uncatalyzed reaction. Diboron derivatives are an important class of compounds that have been utilized as synthetic intermediates, functional molecules, functional polymers, ^{10}B carriers for neutron capture therapy, and biologically active compounds. Traditional methods for their synthesis are based on the alkylation of trialkylborates with organomagnesium or lithium reagents (transmetalation) or uncatalyzed addition of hydroboranes to unsaturated hydrocarbons and have been partly reviewed in this chapter. Although these methods are now most common and convenient for large-scale preparations, the metal-catalyzed reactions are advantageous in terms of efficiency and selectivity of the transformations. Diboration of alkenes and alkynes is one of the most studied of reactions in the synthesis of organoboron compounds and their application to organic synthesis. The addition of diboron tetrahalides B_2X_4 ($X = F$, Cl, Br) to unsaturated hydrocarbons (diboration) is an attractive and straightforward method to introduce boryl groups into organic molecules, but the synthetic use has been severely limited because of the instability and limited availability of the reagents. Although tetra(alkoxo)diboron dramatically enhances the stability of the B–B species at the expense of reactivity for organic nucleophiles, the B–B compounds oxidatively add to low-valent transition metals with the B–B bond cleavage, thus allowing the catalyzed transfer of boron to unsaturated organic substrates. The metal-catalyzed addition of B–B reagents to alkenes or alkynes provides a new class of boron compounds including heterofunctionalized alkyl-, alkenyl-, and allylboronates.

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Palladium Catalyzed Reactions in Ionic Liquids

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I

INTRODUCTION

Ionic liquids have become a focus of increasing interest over the last decade.[1] Some of this interest is due to their possible use as ‘‘greener’’ alternatives to volatile organic solvents (see below). There is, however, also a great deal of fundamental interest in how the unusual solvent environment that they present might affect reactions conducted in them. Recently, there have been a number of excellent ionic liquid reviews concerning their chemical and physical properties,[2] and applications in synthesis and catalysis.[1,3,4] It is remarkable that in 1999 it was possible to

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write a comprehensive review of the use of ionic liquids in synthesis and catalysis, yet by 2003 this required an entire monograph. This review focuses on palladium catalyzed reactions conducted in ionic liquids. This is because, to date, palladium is probably the most widely used metal for catalysis in ionic liquids; an extensive range of reactions has been studied and the chemistry of the palladium center(s) itself in these reactions is proving to be fascinating.

II

WHAT ARE IONIC LIQUIDS?

A. *Characteristics of Ionic Liquids*

Although it is only an arbitrary divide, ionic liquids are generally defined as salts that melt at or below 100 °C to afford liquids composed solely of cations and anions. In some cases the ionic liquids are even free-flowing liquids at room temperature, so-called *ambient temperature ionic liquids*. Other terms such as molten salts or fused salts are also used, particularly in the older literature.

The list of ionic liquids grows daily, but the cations are generally bulky ammonium or phosphonium salts, or hetero aromatics, with low symmetry, weak intermolecular interactions, and low charge densities (Fig. 1). The 1,3-dialkylimidazolium salts* remain the most intensively investigated. Typically, the anions are inorganic and include $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, and $[(CF_3SO_2)_2N]^-$, although, more recently, organic anions (e.g., $[RCO_2]^-$) have also been introduced. The physical and chemical properties of the ionic liquid, including their melting points, are dependent on both the nature of the cation and the anion.

Ionic liquids are attractive as potential solvents for a number of reasons:

- They are generally colorless liquids with relatively low viscosities.
- They exhibit very low vapor pressures under ambient conditions and thus are effectively non-volatile.
- They are good solvents for a broad spectrum of inorganic, organic, and polymeric materials and are immiscible with numerous organic solvents. Thus, applications in process intensification and as non-aqueous polar alternatives in biphasic systems are possible.

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*Note on nomenclature. 1-alkyl-3-methylimidazolium cations will be abbreviated throughout this Chapter as $[C_n\text{mim}]^+$, where *n* is the lenght of the alkyl chain.

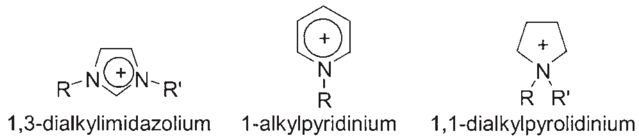


FIG. 1. Some common cations used for ionic liquids.

- Being composed of two parts, there is a synthetic flexibility that is not available for single component molecular solvents.

In addition to these unique properties, they are also readily prepared from commercially available reagents. It is now possible to source ionic liquids commercially from a number of suppliers in a range of different qualities.

The "green" credentials of ionic liquids lay in two of the properties listed above. First, the non-volatile nature of the ionic liquids means that they are more easily contained, recycled and prevented from escaping into the environment than volatile organic solvents. The second is in the flexibility provided by the potential choice of ions. It should be possible to design ionic liquids with ions that are environmentally benign; this would certainly be "green". The other possibility is that it may be possible to design an ionic liquid that makes a synthesis more efficient, or occur at lower temperatures, so reducing waste and energy use.

B. *Quantifying Solvent Properties*

In order to compare the use of ionic liquids with other solvents it is necessary to have some kind of measure of how they interact with solute species. In molecular solvents this occurs through any of dipole–ion$_{\text{solute}}$ dipole–dipole, dipole induced dipole interactions, dispersion interactions, hydrogen bonding, and/or π-interactions. In ionic liquids, interionic and ion$_{\text{solvent}}$–solute interactions are also possible. The question is: does this make any difference?

The usual measurement of the solvent property of a liquid is its polarity as expressed by the dielectric constant. Direct measurement of the dielectric constant is by measuring the capacitance of the medium. This is not possible for a conducting medium and so, dielectric constants are not available for ionic liquids. Amongst the questions that need to be addressed are: how are ionic liquids different/similar to molecular solvents; how are ionic liquids different/similar to other ionic liquids; how can ionic liquids interact with solute species to change their behavior?

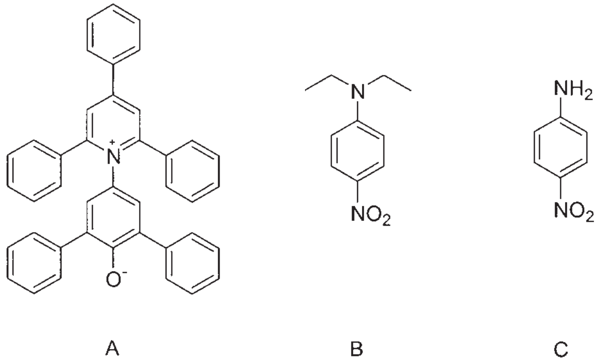


FIG. 2. The dyes used: Reichardt's dye (A), *N,N*-diethyl-4-nitroaniline (B) and 4-nitroaniline (C).

This can be achieved using empirical "polarity" scales.[5–7] These suggest that there is no qualitative difference between ionic liquids and molecular solvents.

The Kamlet and Taft system[8] gives complimentary scales of hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity/polarizability effects (π^*). It should be stressed that these are not fundamental molecular properties. The values can change according to the selection of dye sets or by the precise method used to calculate the values. However the dye sets have been carefully chosen so that general trends within any one set are paralleled in the others. It is in this light that the following should be considered. The α, β, and π^* values, obtained with Reichardt's dye, 4-nitroaniline and *N,N*-diethyl-4-nitroaniline (Fig. 2), for a selection of ionic liquids, and some molecular solvent comparisons, are listed in Table I.[5a]

All of the π^* values (Table I) for the ionic liquids are high in comparison with most non-aqueous molecular solvents and, although differences between the ionic liquids are small, both the cation and the anion can affect the value. π^* is the value that mostly resembles our qualitative notions of "polarity" in the absence of hydrogen bonding effects, so it is no surprise that it is high for ionic liquids. However, when compared to the value for water, there is no way in which the ionic liquids could be thought of as "super polar".

The α values for the ionic liquids are also listed in Table I. The values are largely determined by the nature of the cation, but there is also a smaller anion effect. The values for the $[C_4mim]^+$ are generally moderately high. It has long been known that all three of the imidazolium ring protons are acidic,[9] and it was predicted that hydrogen bonding to solutes would be

TABLE I

KAMLET/TAFT PARAMETERS FOR A SELECTION OF IONIC LIQUIDS AND MOLECULAR SOLVENTS[5a,8]

Solvent	π^*	α	β
$[C_4mim][SbF_6]$	1.039	0.639	0.146
$[C_4mim][BF_4]$	1.047	0.627	0.376
$[C_4mim][PF_6]$	1.032	0.634	0.207
$[C_4mim][TfO]$	1.006	0.625	0.464
$[C_4mim][N(Tf)_2]$	0.984	0.617	0.243
$[C_4mmim][BF_4]$	1.083	0.402	0.363
$[bmpy][N(Tf)_2]$	0.954	0.427	0.252
$[C_4mmim][N(Tf)_2]$	1.010	0.381	0.239
Water	1.33	1.12	0.46
Methanol	0.73	1.05	0.61
Acetonitrile	0.799	0.350	0.370
Acetone	0.704	0.202	0.539
Dichloromethane	0.791	0.042	−0.014
Toluene	0.532	−0.213	0.077
Hexane	−0.12	0.07	0.04

significant in the absence of hydrogen bond accepting anions.[10] The $[C_4mmim]^+$ ionic liquids have the lowest α values, reflecting the loss of the proton on the 2-position of the ring. $[bmpy][Tf_2N]$ has a slightly higher α value than $[C_4mmim][Tf_2N]$. Although not included in the table because a different dye set was used, the N–H hydrogen bond donor $[EtNH_3][NO_3]$ has an even higher value for α (1.10),[11] showing that there is a great deal of opportunity to manipulate this quantity.

β is the hydrogen bond basicity of the solvent and is also listed in Table I. As the conjugate bases of strong acids, the anions of the ionic liquids might be expected to have low β-values in comparison to other solvents. However, although those found in this study are not as high as for acetone, they are comparable to acetonitrile, which is thought of as an electron pair donor solvent.

While polarity measures such as these are now available for ionic liquids and we have some idea of how they compare to other solvents, substantial attempts to use them to explain how the ionic liquids may affect the reactivity of solute species have yet to be published.

There is one scale that is of particular relevance here and that is one that seeks to determine the coordinating ability of the solvent to metal centers.[5,6] The λ_{max} for the lowest energy d → d band of the square planar cation of $[Cu(acac)(tmen)][BPh_4]$ {where acac = pentane-2,3-dione and tmen = N,N,N',N'-tetramethylethylenediamine} Fig. 3 correlates well with solvent

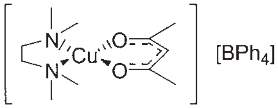


FIG. 3. [Cu(acac)(tmen)][BPh_4].

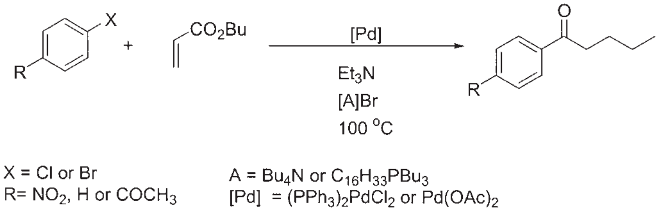
donor numbers[12] and the β values described above. The λ_{max} shift results from the d-orbital splitting of Cu^{2+} as the cationic complex becomes five or six coordinate. The $[BPh_4]^-$ anion was assumed to be completely non-coordinating. Not surprisingly, this value is dominated by the nature of the anion of the ionic liquid, since the cations cannot coordinate to the $[Cu(acac)(tmen)]^+$ complex probe.

It might seem surprising, since the anions that are used to make ionic liquids are usually considered to be non-coordinating, that any great difference between the ionic liquids is seen. The fact that these so-called non-coordinating ions very clearly coordinate to the metal center reveals something about the nature of coordination in an ionic liquid in comparison to a molecular solvent, that can have profound effects in catalytic chemistry. If we consider a cationic metal center that is coordinatively unsaturated with vacant orbitals dissolved in a molecular solvent; the possibilities are: (i) an anion can directly coordinate to the metal center, (ii) the anion and the cation may be well separated in the solvent, with the cation coordinated to molecules of the solvent, or the cation and anion can exist as either an (iii) intimate, or (iv) solvent separated ion-pair. In an ionic liquid there are no molecules available to separate the ions and the cations of the ionic liquid will be repelled by the charge on the metal complex. Hence, in an ionic liquid options (i) and (iii) are the only ones available. The cationic center will effectively always be closely associated with the anions. Since the anions are in the neighborhood and there is no other source of potential electron pairs (until deliberately added as a reagent) and being the solvent and therefore in vast excess, they will coordinate to some extent to the metal center. This idea has been used to explain the reactivity of nickel catalysts in the biphasic oligomerisation reactions in $[PF_6]^-$ ionic liquids.[13]

III

INTRODUCTION TO PALLADIUM CATALYSIS IN IONIC LIQUIDS

Ionic liquids have been used as solvents for palladium catalyzed reactions in attempts to address some of the common problems associated with the use of palladium catalysts. Specifically, these include decomposition



SCHEME 1. The Heck reaction of halogenoarenes with butyl acrylate.

and leaching of expensive catalytic systems, laborious product isolation, low activities and selectivities, poor reagent and catalyst solubilities, and difficulties in catalyst recycling. The ionic liquid is often used to immobilize the palladium catalyst in an ionic phase of a biphasic reaction system, thus bridging the gap between homo- and heterogeneous catalysis. As we will see below, although individual ionic liquids can provide benefits for different reactions, there does not appear to be any such thing as a generalized "ionic liquid effect".

IV

HECK REACTIONS

A. *Thermal Heck Reactions*

The Heck reaction has been the most extensively reported catalytic reaction in ionic liquids thus far. It is also an extremely popular reaction to study under other conditions.[14] This is probably due to its industrial significance and the fact that it has a number of well-known attendant problems and that many view it as the quintessential palladium catalyzed reaction. The related cross-couplings have also been well studied (see below).

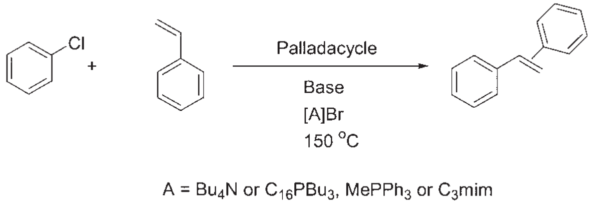
The first palladium catalyzed reaction reported in an ionic liquid, by Kaufmann in 1996, was a Heck reaction.[15] A series of aryl bromides were efficiently coupled with *n*-butyl acrylate in tributylhexadecylphosphonium bromide ($[C_{16}PBu_3]Br$) and tetrabutylammonium bromide ($[NBu_4]Br$) to afford the *trans*-cinnamates in yields of over 90% in some cases (Scheme 1). Product isolation was achieved by distillation from the ionic liquid or by solvent extraction.

$[PdCl_2(PPh_3)_2]$ was used as a palladium source to provide stable yellow homogeneous solutions in both ionic liquids at 70–80 °C without any need to add another ligand. For the reaction of bromobenzene with butyl acrylate it was possible to achieve a $>99\%$ yield in $[C_{16}PBu_3]Br$. No catalyst decomposition was reported, even after complete consumption of the aryl halide. In addition, comparable catalytic activities were achieved for two successive runs following product isolations.

Perhaps more surprisingly, $[Pd(OAc)_2]$ and $PdCl_2$ could be used in just the same way and, since no phosphine was added, constituted a "ligand-free" system. For $[Pd(OAc)_2]$, adding extra acetate, in the form of NaOAc, led to an increase in the rate, but a decrease in selectivity, resulting in the formation of 5% of the *cis*-cinnamate. With $PdCl_2$ catalyst decomposition was evident during the reaction.

Tetraalkylammonium salt additives have previously been reported by Jeffery,[16] for biphasic (organic solvent/water) Heck reactions[17] where it was believed that the salts were acting as phase-transfer catalysts. While one of the positive effects of using the ionic liquid may have been to increase the solubility of the organic starting materials in the catalyst solution, the ability to generate a stable form of the catalyst without the addition of stabilizing ligands suggests that more complex factors are operating.

Kaufmann's article[15] clearly caught the attention of several groups around the world, and a few years later papers on the Heck, and closely related reactions began to appear. In 1999, Herrmann also reported the use of $[NBu_4]Br$ as a solvent for these reactions.[18,19] In his hands, the reaction of bromobenzene with butyl acrylate, using $PdCl_2$ as the palladium source gave an 80% yield of butyl cinnamate at 130 °C. Herrmann also investigated the binuclear palladacycle *trans*-[di(μ-acetato)-*bis*(di-*o*-tolylphosphino)benzyl] dipalladium(II) as the catalyst for Heck reactions of chloroarenes with styrene (Scheme 2). When the ionic liquids $[C_{16}PBu_3]Br$, $[MePPh_3]X$ ($X = Cl$, Br) and $[C_3mim]Br$ were employed, it was found that the yields of reactions were lower. The highest activities and stabilities were afforded by the palladacycle catalysed Heck reactions in $[NBu_4]Br$ with NaOAc as the activating base and when either $[PPh_4]Cl$ or $[SbPh_4]Cl$ were added. This ionic liquid also achieved better activity and stability than previously observed for this catalyst in conventional solvents with salt additives. Repetitive catalytic reactions of bromobenzene with styrene in $[NBu_4]Br$ at 130 °C gave 95–99% yields of stilbene, following successive product



SCHEME 2. Palladacycle catalyzed Heck reactions in ionic liquids.

distillation from six runs. Significant catalyst decomposition was only observed after the fourth run and was attributed to the increased concentration of the accumulated NaBr by-product. When other sources of palladium were used, the presence of phosphine either pre-coordinated to the palladium complex used or as an additive, greatly increased the reactivity of the system.

At about the same time, Seddon reported the Heck reactions of bromo- and iodoarenes in a series of *N*-hexylpyridinium {$[C_6py]^+$} and *N*,*N*′-dialkylimidazolium based liquids with $[PF_6]^-$ and $[BF_4]^-$ anions.[20] The effects of changing the ionic liquid and reaction conditions upon the Heck reaction of iodobenzene with ethyl acrylate were reported using 2 mol% $Pd(OAc)_2$.

The Heck reactivity in *N*-hexylpyridinium based ionic liquids was found to be dependent on the nature of the anion, with the following order of reactivity $Cl^- \gg [BF_4]^- > [PF_6]^-$. In $[C_6py]Cl$, a 98% yield of *trans*-ethyl cinnamate was achieved in 24 h at 40 °C, whereas when the reaction was conducted in $[C_6py][PF_6]$ and $[C_6py][BF_4]$ the reaction temperature had to be raised to 80 °C for 72 h to obtain 42 and 99% yields, respectively. The addition of PPh_3 was found to inhibit the reaction in $[C_6py]Cl$ such that higher temperatures were required to afford comparable yields. Conversely, for the *N*,*N*′-dialkylimidazolium based ionic liquids much higher yields were achieved in $[C_4mim][PF_6]$ with a PPh_3 additive than without. The imidazolium ionic liquids were found to be the least effective solvents in terms of catalyst reactivity without the addition of phosphine, but by far the most effective in combination with phosphine.

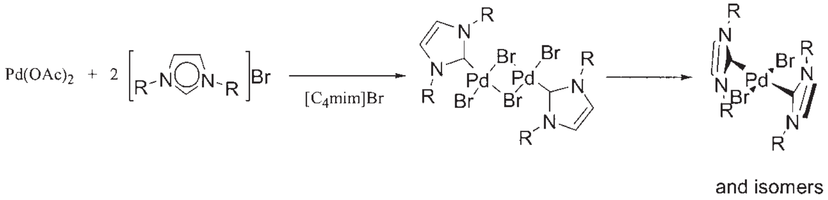
The use of the hydrophobic ionic liquid $[C_4mim][PF_6]$ allowed the reactions to be carried out in a triphasic hexane/$[C_4mim][PF_6]$/water system. Six repetitive catalytic runs, using $Pd(OAc)_2$ as the palladium source and NEt_3 as the base, were reported to give *trans*-ethyl cinnamate in 95–99% yields under these triphasic conditions and no catalyst decomposition was reported. The product was removed into the hexane phase whilst the stoichiometric amounts of $[HNEt_3]I$ generated during each run were removed in the aqueous phase. Thus, where direct comparison could be made, $[NBu_4]Br$ gave higher reactivity, but $[C_4mim][PF_6]$ facilitated easier recycling of the catalyst immobilized in the ionic liquid phase.

The question that therefore arises is why do the ionic liquids prove to be such good solvents for the Heck reaction? Naturally, it is entirely possible that more than one process operates. Furthermore, it should also be emphasized that although these salts are being considered as ionic liquids within the context of this review, they are made up of different ions and there may be different chemistries in different ionic liquids or at phase interfaces.

One possibility is that these media can stabilize certain ionic intermediates or transition states in the reaction mechanism and thereby accelerate the reaction. One indication that this could be contributing to the improved Heck reactions comes from a study of the regioselectivity of the reaction of butyl vinyl ether with aryl halides catalyzed by $Pd(OAc)_2$/DPPP in $[C_4mim][BF_4]$.[21] Here, yields of 87–97% with $>99:1$ $\alpha:\beta$ isomer ratios were found, as compared to 75:25 in DMSO and 46:54 in toluene. This has been attributed an ionic mechanistic pathway such that the ionized $[L_2PdAr]^+ X^-$ is favored by the ionic liquid, as opposed to a neutral pathway involving $[L_2PdArX]$ that would lead to predominantly β arylation. If this is interpreted as being due to the stabilization of the ionic intermediates (and transition states leading to them) with respect to the starting materials as well as the neutral intermediate, there will be a reduction in the activation energy of the reaction and an increase in the reaction rate. This interpretation does not require the generation of any new catalyst species and is consistent with results that are beginning to emerge on the effects of ionic liquids on simple organic reactions.[22]

Another possibility is that the ionic liquids are interacting directly with the organic starting materials in some way. The double bond of the olefin in Heck reactions is usually activated by an electron withdrawing group. It has been demonstrated that in Diels-Alder reactions[23] ionic liquids can act as a Lewis acid and interact with the electron withdrawing substituent to increase the reagent's dienophilicity. However, one would expect this to be strongest for the more hydrogen bond donating imidazolium based ionic liquids than for the tetraalkylammonium ionic liquids; the observed reactivity is, in fact, the reverse of this.

Alternatively, the ionic liquids could be generating an entirely new catalyst *in situ*. The first evidence for this possibility came from the observation that the Heck reaction proceeds more efficiently in $[C_4mim]Br$ than $[C_4mim][BF_4]$.[24] Also, "palladium black" was seen to precipitate during reactions performed in $[C_4mim][BF_4]$. Xiao found that the complexes $[PdBr_2(C_4mimy)_2]$ and $[Pd2(\mu\text{-}Br)_2Br_2(C_4mimy)_2]$ (C_4mimy = 1-butyl-3-methylimidazolylidene) could be isolated from the $[C_4mim]Br$ solution but not from the far less active $[C_4mim][BF_4]$ solution. Often called *N*-heterocyclic carbenes (NHC's), these ligands have been used to prepare catalysts for a wide variety of reactions.[25] Synthesis of $[PdX_2(C_nC_n,imy)_2]$ (X = Br, I) complexes from the imidazolium halide and $Pd(OAc)_2$ is particularly facile.[26] However, when the imidazolium chloride salt is used, the reaction does not proceed at all. This strong anion effect probably explains why the complexes form in $[C_4mim]Br$, but not in $[C_4mim][BF_4]$. When independently prepared $[PdBr_2(C_4mimy)_2]$ was dissolved in $[C_4mim][BF_4]$ the yield of the reaction was the same as that when palladium



SCHEME 3. The formation of [$PdBr_2(C_4mimy)_2$] in [C_4mim][Br_4].

acetate was used. This suggests that, if the [$PdBr_2(C_4mimy)_2$] complex is responsible for the improved yields in [C_4mim]Br, it must rapidly form another species when dissolved in [C_4mim][BF_4] (Scheme 3).

An EXAFS study of palladium acetate dissolved in [C_4mim][BF_4], [C_4mim][PF_6], [C_4py][BF_4], and [C_4py][PF_6] showed that a gradual change to palladium metal occurred.[27] However, the use of [C_6mim]Cl led to the formation of [$PdCl_2(C_6mimy)_2$]. This is entirely consistent with Xiao's observations above.[24] Interestingly, when [C_6mmim]Cl, which has its C-2 position blocked, is used to prevent NHC complex formation, $[PdCl_4]^{2-}$ is formed rather than the metal. This is clearly the result of the relative coordinating strengths of the Cl^- anion in comparison to $[BF_4]^-$ and $[PF_6]^-$. At no time was the palladium acetate itself stable in solution in the ionic liquid. When the experiment was repeated in the presence of PPh_3, [C_6mmim]Cl yielded [$PdCl_2(PPh_3)_2$] while [C_6mim]Cl still gave [$PdCl_2$ $(C_6mimy)_2$]. However, when the $[BF_4]^-$ and $[PF_6]^-$ ionic liquids were studied under these conditions, nanoparticulate palladium (0.8–1.6 nm diameter) was seen. The addition of the Heck reagents did not change the palladium speciation. Unfortunately, [C_6mim]Cl does not give a catalytically active solution for the Heck reaction and no Br^- based ionic liquids were studied. So it remains possible that although [$PdBr_2(C_4mimy)_2$] is formed in [C_4mim]Br, nanoparticles are also formed and that these are responsible for the catalysis with the coordination complex itself being catalytically inactive.[24] However, this is not consistent with Xiao's observation that the [C_4mim]Br gives the most active solution. It is also possible that the inactivity of the chloride ionic liquids arises from the high coordinating ability of the Cl^- ion itself, and is completely unrelated to the formation of NHC complexes. Clearly, although the formation of *N*-heterocyclic carbene complexes in the imidazolium based ionic liquids may be important, it cannot be invoked to explain the effects of tetraalkylammonium salts.

In a series of papers,[28] Calò has taken the approach of using ([$PdI_2(mbth)_2$] (mbth = methylbenzthiazolylidene, Fig. 4) complexes in [NBu_4]Br, with sodium formate as a reducing agent, but without added

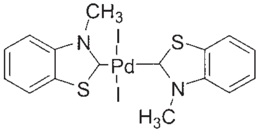


FIG. 4. Bis(methylbenzthiazolylidene)palladium diiodide.

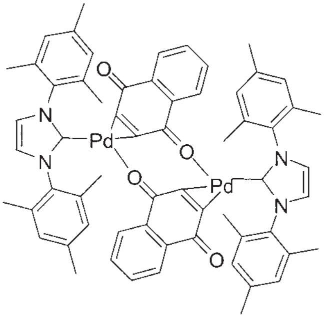


FIG. 5. (1,3-Dimesitylimidazolylidene)(benzoquinone)palladium(0).

phosphine. With this catalyst they found that the reaction of butyl acrylate with bromobenzene could yield 94% of the butyl cinnamate in 10 min. When they attempted to conduct the reactions with non-halide ionic liquids, no reaction was seen. Initially,[28b] they believed that the stabilization of a Pd(0) complex, $[PdBr(mbth)_2]^-$, was giving their high catalytic activities. Later,[28c] they identified palladium nanoparticles of 2–6 nm diameter as the palladium reservoir. They speculated that reaction of the metallic palladium with the aryl halide of the Heck reaction and the anion of the ionic liquid leads to the formation of $[ArPdX_3]^{2-}$, which then goes on to react with the olefin.

A series of palladium(0) mono-imidazolylidene complexes have also been prepared and used for the Heck reaction of aryl chlorides in $[NBu_4]Br$.[29] The authors' report that two of their catalysts, (1,3-dimesitylimidazolylidene)(naphthoquinone)palladium(0) and (1,3-dimesitylimidazolylidene)(benzoquinone)palladium(0) (Fig. 5) remain stable throughout the reaction and will couple even non-activated aryl chlorides in good yields. Clearly, the authors believe that the imidazolylidene complex is responsible for this activity.

Muzart *et al.* used $PdCl_2$ in $[NBu_4]Br$ for the Heck reaction of iodobenzene with various allylic alcohols.[30] The Heck reaction of allylic alcohols can lead to the formation of aryl ketones (α- or β-substituted) as well as the (α- or β-) arylated allylic alcohols. However, these authors did not discuss the regioselectivity of the reaction, since they only identified carbonyl products. Using their $[PdI_2(mbth)_2]$ catalysts in $[NBu_4]Br$ for the reaction of bromoarenes, Calò *et al.* also only identified carbonyl products.[31] When β-substituted allylic alcohols were used the regioselectivity of the reaction was poor. In both of these papers the authors' reported that the recycling of the ionic liquid catalyst solution lead to significant reductions in the yields of the reactions, probably due to the build-up of NaX in the reaction mixture. In both papers the authors attributed the effect of the ionic liquid to the formation of anionic palladium halide complexes, $[PdBr(mbth)_2]^-$ and subsequently $[PdArBr_2(mbth)_2]^-$,[31] or perhaps $[Pd_2Br_6]^{2-}$.[30]

Making comparisons between the work of different groups is extremely difficult. Even in the few cases where the same reagents have been used, different reaction conditions and auxiliary reagents, such as bases, have been employed. It is also impossible to know how much effort was put into optimising the reactions in terms of yields and rates. However, it does seem to be true that under "ligand-free" conditions $[NBu_4]Br$ is the preferred ionic liquid for the Heck reaction and that the palladium is mainly present as nanoparticles.[15,26,28] $[NBu_4]Br$ has the added advantage that it is relatively cheap and easily available. $[NBu_4]Br$ has a melting point of 103 °C and once the product mixture is cooled to room temperature it is solid. This means that the isolation of solid products is complicated by the need to be extracted from the solid mixture. This may not be a trivial problem, especially on an industrial scale. Yields and rates have been found to be much lower in imidazolium based ionic liquids.[26,28] In these ionic liquids the catalyst appears to remain in solution, possibly due to the formation of imidazolylidene complexes and the product mixture similarly remains a solution. However, ease of product separation is not an advantage if the amount of product formed in reasonable time is not viable synthetically. To achieve a more practical system that retains the high reactivities observed in $[NBu_4]Br$, but to have the advantages of a liquid at room temperature, unsymmetrical ammonium salts,[15,19] pyrolidinium, or asymmetric phosphonium salts could be explored. The imidazolium based systems respond far more to the addition of phosphine ligands to the reaction mixture than do the simple ammonium ionic liquids.[15,20]

B. *Ultrasound Assisted Heck Reactions*

The use of ultrasound as a way of supplying energy to a reaction system has been widely studied recently.[32] Ultrasonically assisted (cleaning bath of frequency 50 KHz) Heck reactions of aryl iodides in $[C_4C_4im]Br$ and $[C_4C_4im][BF_4]$ have been reported to exhibit considerably enhanced reaction rates at 30 °C.[33] Using $Pd(OAc)_2$ or $PdCl_2$ as the palladium source and NaOAc as the base, iodobenzene reacted with ethyl acrylate in 1.5 h to give an 87% yield of ethyl cinnamate, with no reaction occurring under silent conditions. A similar reaction in $[C_4mim][BF_4]$ required heating to 90 °C for 24 h to get a 43% conversion,[24] Repetitive catalytic runs were reported without any loss of activity. However, bromo- and chloroarenes were found to be unreactive under these conditions. Investigations into the nature of the catalytic species were also reported, which identified the *in situ* formation of $[PdY_2(C_4C_4imy)_2]$ ($Y = Br^-$, $[BF_4]^-$) as an intermediate enroute to palladium nanoparticles.

The effect of sonication on $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ has recently been reported.[34] As expected for liquids with such a hydrogen bonded network structure, acoustic cavitation clearly occurred. However, decomposition of the ionic liquid was evident, which will severely limit their use as solvents for sonochemical reactions.

C. *Microwave Assisted Heck Reactions*

Another popular form of heating reactions is using microwaves.[35] Rapid microwave assisted Heck reactions have been reported in $[C_4mim][PF_6]$.[36] The reaction of butyl acrylate and bromobenzene using the combination of $PdCl_2$ and $P(o\text{-tolyl})_3$ in $[bmim][PF_6]$ gave an 87% yield of butyl cinnamate in only 20 min. The ionic liquid, in a sealed vessel, was very effectively and quickly brought up to the reaction temperature of 220 °C, so giving the increased rate of reaction in comparison to the lower temperatures used in thermal heating experiments. The negligible vapor pressure of $[C_4mim][PF_6]$ prevented over-pressurisation of the sealed system. The synthesis of β,β-diphenylacrylate was also reported in a 50% yield from the combination of $PdCl_2$ and $2P(o\text{-tolyl})_3$ with Et_3N in $[C_4mim][PF_6]$ at 220 °C (MW) after 45 min by the double Heck reaction of excess bromobenzene with butyl acrylate. As ionic species, ionic liquids absorb microwaves very effectively and rapidly. They have even been used as additives for poorly absorbing non-polar solvents to allow them to be heated by microwaves.[37] Hence, caution should be used when attempting microwave heating of ionic liquids without temperature controlled equipment.

D. *Supported Heterogeneous Palladium Systems*

Heck reactions of iodo- and bromoarenes and ethyl acrylate have been conducted under heterogeneous conditions with Pd/C in $[C_4mim][PF_6]$.[38] Bromobenzene achieved a 40% yield after 12 h at 140 °C. The significant advantage of this method is in product isolation and recovery of the catalyst. Although repetitive runs did show a slow reduction in yields, due to the formation of the [HNEt$_3$]I by-product, the original activity could be restored by water extraction of the [HNEt$_3$]I from the Pd/C suspension in [C$_4$mim][PF$_6$]. ICP analysis of the [C$_4$mim][PF$_6$] reaction mixtures after filtration of the Pd/C revealed only negligible palladium concentrations, showing that the catalysis had occurred on the palladium surface and not from leached homogeneous palladium species.

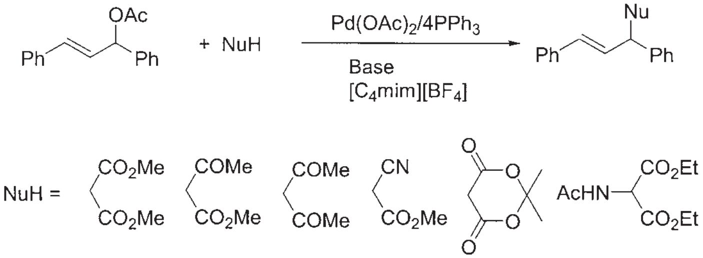
Recently, silica supported catalysts have been reported in heterogeneous ionic liquid mediated Heck reactions.[39] The Heck reaction of iodobenzene with ethyl acrylate was investigated with Pd^{II}/SiO_2, Pd^0/SiO_2 and a $Pd(NH_3)_4Cl_2$ mixture with silica in [C$_4$mim][PF$_6$] at 80 °C. The Pd^{II}/SiO_2 system was the most active with a 66% conversion to ethyl cinnamate with one equivalent of Et_3N after 1 h, although an induction period was reported. When two equivalents of Et_3N were employed a 99% conversion was afforded within 1 h. This was more active than either the 88% conversion achieved in DMF or with the $Pd(OAc)_2/4PPh_3$ system in [C$_4$mim][PF$_6$] at 100 °C. Atomic absorption spectroscopy of the reaction mixture revealed that approximately half of the palladium in the system was dissolved from Pd^{II}/SiO_2 into the [C$_4$mim][PF$_6$]. It appears that the catalysis was performed by the palladium species dissolved in the [C$_4$mim][PF$_6$], since identical conversions were observed from repetitive Heck reactions in the [C$_4$mim][PF$_6$] filtrates.

V

ALLYLATION/TROST–TSUJII REACTIONS

Palladium catalysed Trost–Tsujii coupling reactions were also among the first C–C coupling reactions to be conducted in ionic liquids. Preliminary results by Bellefon in 1999 reported the $Pd(OAc)_2$/TPPTS (TPPTS $P(C_6H_4SO_3Na)_3$) catalyzed reaction of ethyl cinnamyl carbonate with ethyl acetotacetate in a biphasic methylcyclohexane/[C$_4$mim]Cl mixture at 80 °C.[40] A 90% yield of *Z*-ethylcinnamylacetoacetate was reported, compared to 65% under otherwise similar conditions in a biphasic butyronitrile/water system. This significant difference could be attributed, in part, to the formation of cinnamyl alcohol as a by-product in the presence of water. The turnover frequency of the ionic liquid reaction was also very much greater. The use of the TPPTS ligand, although designed to give water soluble complexes, should also give a greater retention of any palladium phosphine complexes by the ionic liquid.

Also in 1999, Xiao reported the $Pd(OAc)_2/PPh_3$ catalyzed allylation of 1,3-diphenylallyl acetate with a wider range of stabilized carbanions in



SCHEME 4. Palladium catalyzed allylation reactions in $[C_4mim][BF_4]$.

$[C_4mim][BF_4]$ under various conditions (Scheme 4).[41] In contrast to Bellefon's results, it was found that a base was required to generate the carbanions. The bases K_2CO_3 and DBU were both found to be effective, but only the latter formed a homogeneous solution. The catalyst system was prepared by heating $Pd(OAc)_2$ (2 mol%) with four equivalents of PPh_3 (8 mol%) in $[C_4mim][BF_4]$ at 80 °C for 20 min. The solvent–catalyst system was then cooled and the reaction was conducted at ambient temperature with the addition of the substrates and the base. Outstanding reactivities were observed. The reaction was later found to be dependent on the nature of the phosphine ligands employed.[42] For instance, strongly electron donating phosphines ligands gave enhanced reactivity relative to PPh_3, while weakly σ-electron donating and strongly π-electron accepting phosphines exhibited a decrease in activity. This strongly suggests that the active catalyst is a palladium phosphine species. Again the use of TPPTS as a ligand prevented catalyst leaching into the product layer during recycling, which had been a problem when using PPh_3.

The enantioselective allylation of (*rac*)-(*E*)-1,3-diphenyl-3-acetoxyprop-1-ene with dimethyl malonate by a series of homochiral palladium(0) ferrocenylphosphine complexes was subsequently reported in $[C_4mim][PF_6]$.[43] A significant enhancement in enantioselectivity was reported in $[C_4mim][PF_6]$, affording a 53% yield with a 68% *ee*, in comparison to THF, which gave a 62% yield with a 40% *ee* under the same conditions. Recycling of the ionic liquid catalyst solution led to a decreased yield, but with retention of enantioselectivity.

VI

CROSS-COUPLING REACTIONS

There is a group of cross coupling reactions that are closely related to the Heck reaction and several of these have been investigated in ionic

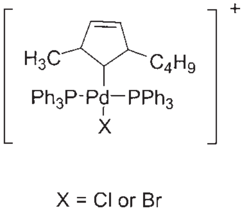


FIG. 6. The phosphine-imidazolylidene palladium complex $[(\text{bmimy})(\text{PPh}_3)_2\text{PdX}]^+$.

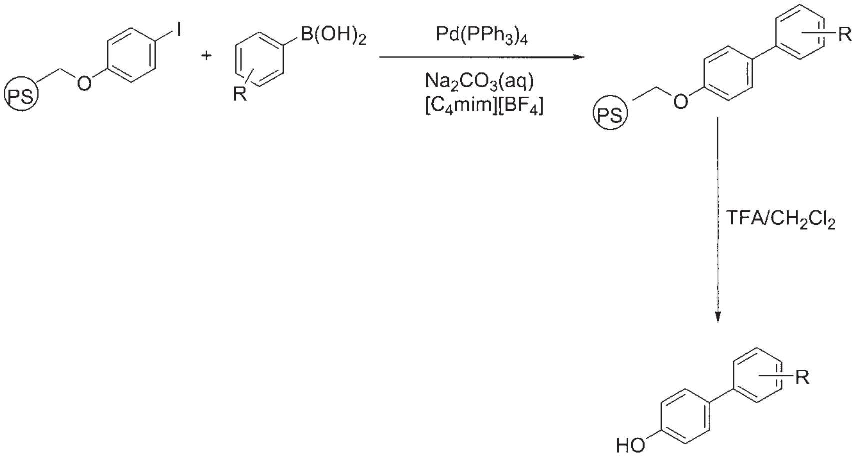
liquids. No one of them has received as much attention as the Heck reaction, but together they are beginning to be a substantial body of work.

A. *The Suzuki Reaction*

The Suzuki reaction,[44] the coupling reaction of a halogenoarene with an arylboronic acid or ester, is probably the most commonly performed of the C–C palladium catalyzed cross coupling reactions and was the first example to be performed in an ionic liquid.[45] It was reported that a stable solution could be formed in $[C_4\text{mim}][BF_4]$ from $Pd(PPh_3)_4$ that catalyzed the reaction of a range of bromo- and iodoarenes with phenylboronic acid, more effectively than under the usual conditions in molecular solvents. However, no activity towards chloroarenes was observed. Subsequent investigation of the reaction conditions and analysis of the catalytically active solutions revealed the presence of a mixed phosphine-imidazolylidene palladium complex (Fig. 6).[46] It is notable that the preparation of the catalyst solution described in Xiao's allylations[41] is very similar to that required for a successful Suzuki reaction and for the synthesis of the $[(\text{bmimy})(\text{PPh}_3)_2\text{PdX}]^+$ ($X = Cl$ or Br) complex in the $[C_4\text{mim}][BF_4]$.

4-Iodophenol, immobilized on a polystyrene-Wang resin, has been treated with a series of arylboronic acids dissolved in $[C_4\text{mim}][BF_4]$ using $Pd(PPh_3)_4$ as the palladium source (Scheme 5).[47] The catalytic system was initiated in a similar manner to that previously reported[45] and the reactions conducted at 110 °C for 2 h. A 1:1 mixture with DMF was required to swell the hydrophobic cross-linked polystyrene resin and when neat $[C_4\text{mim}][BF_4]$ was used no biaryl products were isolated.

The Suzuki reaction has also been reported in $[C_4C_4\text{im}][BF_4]$ using ultrasound as the energy source.[48] Iodo- and bromoarenes coupled efficiently at 30 °C to achieve 82–93% conversions in 20–30 min whereas chloroarenes required 1–1.5 h to obtain 42–52% conversions. This compares to only 25% conversion for the silent reaction at 25 °C. Significant homocoupling of the phenylboronic acid was reported when the reactions were

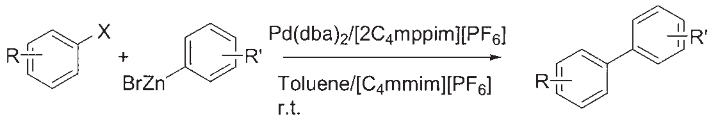


SCHEME 5. Ionic liquid mediated solid-phase Suzuki reaction of immobilized 4-iodophenol.

performed under air, but this could be reduced by using an inert argon atmosphere. Palladium decomposition prevented repetitive catalytic runs, although the ionic liquid could be recycled and used in other reactions.

$[PdX_2(C_4C_4imy)_2]$ was independently prepared and, when used as the source of palladium for the reaction, gave comparable conversions to $Pd(OAc)_2$. Interestingly, when $[PdX_2(C_4C_4imy)_2]$ was used no decomposition or homo-coupling was reported even when the reaction was conducted under air. The $[PdX_2(C_4C_4imy)_2]$ complex was quantitatively recovered and used in three repetitive catalytic runs for the reaction of 4-bromoanisole with phenylboronic acid, with only a slight decrease in activity from 88 to 75% conversion. In contrast to when this complex was used for ultrasound irradiated Heck reactions under similar conditions,[33] TEM revealed no evidence of nanoparticle formation.

Suzuki reactions have also been reported in tetradecyltrihexylphosphonium chloride $\{[C_{14}PHex_3]Cl\}$.[49,50] Aryl iodides coupled with a series of arylboronic acids in a toluene/$[C_{14}PHex_3]Cl$/water mixture affording yields of 86–100% after 1 h at 50 °C using $Pd_2(dba)_3$ as the palladium source. Aryl bromides required addition of PPh_3 to achieve comparable yields after 1–3 h, as did aryl chlorides, which were heated at 70 °C for 30 h. No homo-coupling was reported in any of these reactions. Triphasic conditions of Hexane/$[C_{14}PHex_3]Cl$/water were also investigated in which the catalyst remained immobilized in the central ionic liquid layer. Several repetitive catalytic runs of iodobenzene with phenylboronic acid afforded biphenyl yields of 82–97% by isolation of the hexane phase. The active catalyst was not identified, however no precipitation of palladium was



X = I or Br
R= NO_3, CO_2Me, CO_2Et or *m*-OMe
R' = OMe, Cl or CN

SCHEME 6. Negishi reaction in [C_4mmim][PF_6] with $Pd_2(dba)_3$/[C_4mppim][PF_6].

noted and, of course, in these reactions there is no possibility for the formation of palladium NHC complexes. It is possible that palladium trialkylphosphine complexes have been formed, either from residual phosphine in the ionic liquid from the manufacturing process or from the oxidative addition of phosphonium salts to a palladium(0) complex, which would be expected to show high activities.

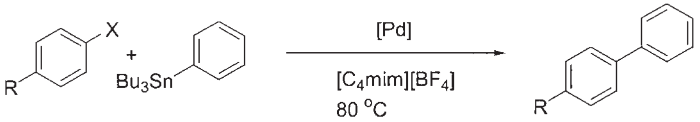
B. *The Negishi Reaction*

When the coupling partner for the halogenoarene is an aryl or benzyl zinc halide the reaction is referred to as the Negishi reaction. Such reactions have been reported in [C_4mmim][PF_6] with the novel 1-butyl-3-methyl-2-diphenylphosphino-imidazolium[51] hexafluorophosphate ([C_4mppim][PF_6]) ionic ligand system with $Pd_2(dba)_3$ (Scheme 6).[52] The [C_4mmim][PF_6] ionic liquid was employed to deliberately prevent the *in situ* formation of 1-butyl-3-methylimidazolylidene, or its palladium complexes, that otherwise could result from [C_4mim][PF_6].

The reactions of a range of aryl, benzylic, and heterocyclic zinc reagents with iodo- and bromoarenes were reported at ambient temperature under biphasic conditions with [C_4mmim][PF_6] and toluene. The biaryl products were readily isolated by decanting the toluene phase, with yields of 70–92% achieved after several minutes. However, attempts to recycle the catalytic ionic liquid solution resulted in significantly decreased activities.

C. *The Stille Reaction*

The reaction of halogenoarenes and halogenoenones with organostannanes is referred to as the Stille reaction,[53] and has been reported using tributylphenyltin and tributylvinyltin in [C_4mim][BF_4] with a [$PdCl_2(PhCN)_2$]/$AsPh_3$/CuI catalytic system (Scheme 7).[54] Although the reaction of 2-iodo-3-methyl-2-cyclohexen-1-one was sluggish in [C_4mim][BF_4] in



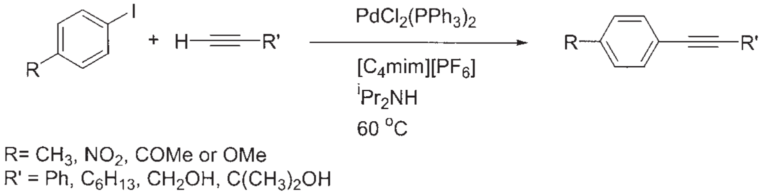
X = I then [Pd] = $PdCl_2(PhCN)_2/2AsPh_3/CuI$
X = Br then [Pd] = $Pd(PPh_3)_4$

SCHEME 7. Ionic liquid mediated Stille reactions.

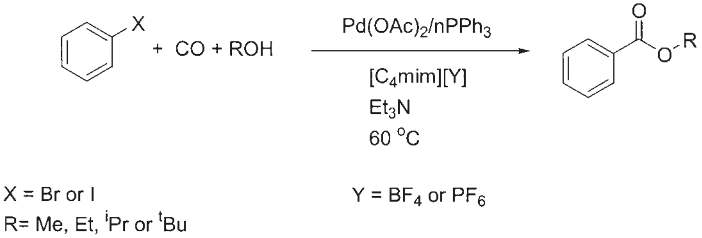
comparison to *N*-methylpyrolidinone, the product was readily extracted with diethyl ether and the catalytic ionic liquid solution could be used for repeat runs with only a slight loss in activity. The $[PdCl_2(PhCN)_2]$ catalytic system was reported to be considerably more active for the Stille coupling of aryl iodides than alternatives ($[Pd(PPh_3)_4]$, $Pd(OAc)_2/P(o\text{-tolyl})_3$, $[Pd_2(dba)_3]/P(t\text{-Bu})_3$), whereas $[Pd(PPh_3)_4]$ was the preferred palladium source for reactions of bromoarenes. The difference in reactivity of the two catalytic systems was, however, not sufficient to overcome the intrinsic activity of aryl halides (i.e., $I > Br$), as illustrated by the absence of chemoselectivity from the reaction of 4-iodobromobenzene. Re-use of the catalyst solutions was reported for both systems with no loss of activity after five runs. The catalyst solutions were reported to be stable even under air for several weeks, but no attempt was made to identify any palladium species in solution.

D. *The Sonogashira Reaction*

The Sonogashira reaction involves the coupling of halogenoarenes with terminal alkyl- or arylacetylenes,[55] and usually requires a copper co-catalyst to enhance the transmetalation of alkynyl nucleophiles. However, the reactions of a series of iodoarenes to make arylacetylenes has been reported in $[C_4mim][PF_6]$ employing $[PdCl_2(PPh_3)_2]$ as the catalyst source without any copper co-catalyst (Scheme 8).[56] This copper-free $[PdCl_2(PPh_3)_2]$ system was successfully re-used for three repetitive runs with only slight loss of activity. Using the reaction of iodobenzene with phenylacetylene as a model reaction, $[PdCl_2(PPh_3)_2]$ was also used in both $[C_4mim][BF_4]$ and $[C_2mim][BF_4]$ with slightly lower yields being obtained in the former. This compares favorably with toluene and THF, which gave appreciably lower yields and DMF, which gave comparable results. In $[C_4mim][PF_6]$, phosphine-free palladium sources, including $Pd(OAc)_2$; $PdCl_2$; $[PdCl_2(NCPh)_2]$; and $[PdCl_2(NCMe)_2]$ gave poorer yields than phosphine containing solutions. Unfortunately, no attempt was made to identify the catalyst in solution.



SCHEME 8. Copper-free Sonogashira reactions in $[C_4mim][PF_6]$.



SCHEME 9. Alkoxycarbonylation reactions in ionic liquids.

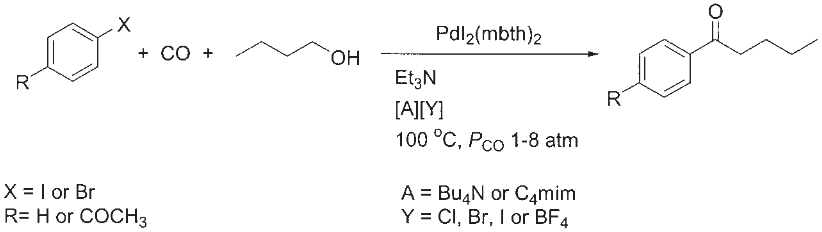
VII

OTHER PALLADIUM CATALYSIS IN IONIC LIQUIDS

A. *Carbonylation of Aryl Halides*

Another useful method of creating an aryl–carbon bond is by the carbonylation of halogenoarenes.[57] The substrate is reacted with a nucleophile, such as an alcohol (alkoxycarbonylation), a primary or secondary amine (aminocarbonylation) or water (hydroxycarbonylation) in the presence of carbon monoxide and a palladium complex. Both alkoxycarbonylation and aminocarbonylation of halogenoarenes using $[Pd(OAc)_2]/4PPh_3$ in $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ have been reported.[58] The reaction of bromobenzene with methanol and CO yielded 82% methylbenzoate in $[C_4mim][BF_4]$, in comparison to 30% when the alcohol itself was used as the solvent. Initially, deposition of palladium metal and deactivation of the catalyst solutions, which prevented efficient recycling, was observed. This was avoided by using 20 equivalents of PPh_3, with respect to the $[Pd(OAc)_2]$, resulting in solutions that could be recycled (Scheme 9).

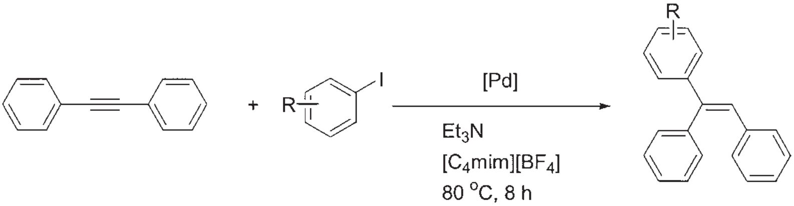
Subsequently, Calò has used his pre-formed $[PdI_2(mbth)_2]$ complex for the carbonylation of halogenoarenes (Scheme 10) in both ionic liquids and



SCHEME 10. Butoxycarbonylation of aryl halides in ionic liquids with $[PdI_2(mbth)_2]$.

molecular solvents.[59] Activated halogenoarenes reacted smoothly in DMA to give excellent yields [90–99%] with an atmospheric pressure of CO at 80–130 °C. However, to achieve similar yields for non-activated bromoarenes and chloroarenes, the reaction had to be performed in the presence of $[NBu_4]Br$ and PPh_3 additives. When the use of ionic liquids as the solvent was explored, a different nucleophile was employed, so no direct comparison of the ionic liquids with DMA, either neat or with added $[NBu_4]Br$, is possible. All that can be said is that the reaction yields for the butoxycarbonylation of 4-bromoacetophenone are higher in $[NBu_4]Br$ (76%) than in the chloride or iodide salts, which each gave approximately the same results (30 and 32%, respectively) and that all of these gave higher yields than imidazolium based ionic liquids, e.g., $[C_4mim]Br$ (16%). It was also demonstrated that $[Pd(OAc)_2]/PPh_3$ was a more effective source of palladium for the reaction than the $[PdI_2(mbth)_2]$ complex on first use, but deactivated rapidly on re-use. On the other hand, the $[PdI_2(mbth)_2]$ solution in $[NBu_4]Br$ is easily recycled without loss of activity, prior to the build-up of the $[HNEt_3]Br$ by-product, which significantly increases the viscosity of the ionic liquid, preventing further use. It was proposed that the mbth ligands remained bound to the palladium and the *in situ* formation of mixed NHC/phosphine complexes was suggested. Several possible roles for the ionic liquids were discussed in this paper, including both acting as a source of bromide to stabilize Pd(0) complexes, or as a binding agent for bromide removal from Pd(II) species.

Another interesting carbonylation that has been carried out in ionic liquids is that of 3-alkyn-1-ols and 1-alkyn-4-ols by $[Pd(OAc)_2]/PyPPh_2$($PyPPh_2$=2-(diphenylphosphino)pyridine) to give *exo*-α-methylene γ- and δ-lactones, respectively.[60] The products were isolated in almost quantitative yields by distillation under reduced pressure or by solvent extraction from the ionic liquid with diethyl ether. However, when recycling of the ionic liquid solution was attempted for the carbonylation of 3-butyn-1-ol the yield fell from 99 to 37% after only two runs.



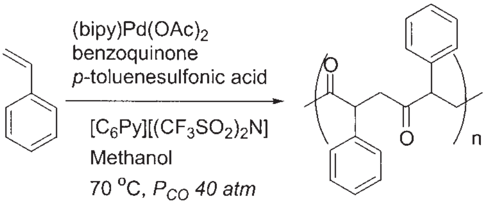
SCHEME 11. Hydroarylations of alkynes in ionic liquids.

B. *Hydroarylation Reactions of Alkynes*

Iodoarenes have also been used for the palladium catalyzed hydroarylation reactions of alkynes in ionic liquids.[61] For instance, the reaction of 4-iodoanisole with diphenylacetylene and Et_3N in $[C_4mim][BF_4]$ at 80 °C afforded an 82% yield of 4-methoxylphenyl-1,2-diphenylethylene after 8 h using $[Pd_2(dba)_3]$ (Scheme 11). However, repetitive catalytic runs resulted in a significant decrease in the yields. This could be prevented by using [(*E*,*E*,*E*)-1,6,11-tris(*p*-toluenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene]palladium(0) as the catalyst, which gave an 89% yield with only a slight loss of activity on recycle.

C. *Alternating Copolymerization of Styrene and CO*

Polyketones formed by the palladium catalyzed alternating copolymerization of styrene and CO have become the subject of a great deal of attention.[62] Almost concurrently, two papers appeared describing this reaction in ionic liquids.[63,64] Seddon *et al.* used $[Pd(bipy)_2][PF_6]$ in a variety of ionic liquids (Scheme 12).[63] The complex was active in methanol [ca. 17.4 kg $(\text{g Pd})^{-1}$], but the product polyketone was contaminated with palladium. In the ionic liquids the activity of the catalyst was dependent on the nature of the anion, decreasing in the order $[N(SO_2CF_3)_2]^- > [PF_6]^- > [BF_4]^-$ for both pyridinium and imidazolium based liquids. Increasingly longer alkyl chain lengths of the pyridinium ionic liquids $[C_nPy][N(SO_2CF_3)_2]$ ($n = 4$–10) were reported to afford higher yields, although palladium leaching was noted for $n = 8$, 10, and 18. However, in $[C_6py][NTf_2]$ no palladium decomposition and/or leaching was detected and repetitive catalytic runs were possible with no loss of activity after four runs. When $[Pd(OAc)_2(bipy)]$ was used as the catalyst,[64] a 10:1 mixture of $[C_6py][NTf_2]$/methanol was needed to observe any reaction. This was believed to be because the methanol reacts with L_nPd^{II} and CO to form $[LPdC(O)OCH_3]^+$, which initiates the copolymerization. Bromide contamination (0.5% w/w) of



SCHEME 12. Alternating copolymerization of styrene and CO in $[C_6py][NTf_2]$.

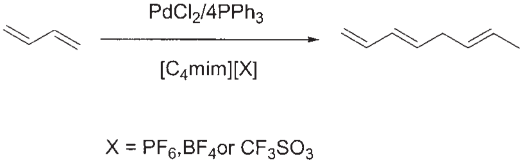
$[C_6py][N(SO_2CF_3)_2]$ was reported to completely stop the copolymerization. Repeated catalytic runs resulted in progressively lower activities on account of palladium precipitation.

D. *Biphasic Olefin Dimerization*

The final way in which C–C σ-bonds have been made by using palladium catalysts in ionic liquids has been by dimerization of olefins. A variety of Pd(II) sources, with four equivalents of PPh_3, in dry $[C_4mim][BF_4]$, $[C_4mim][PF_6]$ or $[C_4mim][OTf]$ selectively dimerize 1,3-butadiene to 1,3,6-octatriene in a biphasic system.[65] The biphasic system allowed easy separation of the product and recycling of the catalyst solution without significant loss of activity. There was very little difference in the activities of $PdCl_2$ in the different ionic liquids, which were all much greater than in THF, or in a mixture of $[C_4mim][BF_4]$ with THF. Decomposition to palladium black was also noted in these latter cases. The nature of the catalyst in solution was not discussed, but clearly the ionic liquid is playing a key role in stabilizing the solution species (Scheme 13).

When water is added to the system in $[C_4mim][BF_4]$, a mixture of the telomeric octa-2,7-dien-1-ol (major product) and 1,3,7-octatriene (minor product) is formed.[66] Although the reaction occurred in its absence, higher activities were achieved by pressurizing the system with CO_2. However, CO_2 had no impact on the selectivity of the reaction. Using $[C_4mim]_2[PdCl_4]$ as the palladium source prevented catalyst decomposition and allowed recycling of the solution. The formation of bis(methylimidazole)palladium dichloride, which was proposed as the true catalyst precursor, was demonstrated under the reaction conditions.

The reaction of butadiene with methanol leads to the formation of the telomers 1-methoxy-2,7-octadiene (*trans*- and *cis*-), 3-methoxy-1,7-octadiene and the dimers 1,3,7-octatriene and 4-vinylcyclohexene (as minor products). Using palladium(II) acetate with either PPh_3 or TPPMS in a biphasic system with ionic liquid leads to an inactive system when $[C_2mim]^+$ and $[C_4mim]^+$

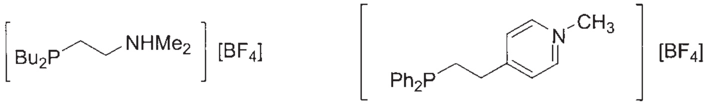


SCHEME 13. The dimerization of 1,3-butadiene to 1,3,6-octatriene in ionic liquids.

salts were used as the ionic liquids, regardless of the anion used, but highly active and selective systems when $[C_4mmim]^+$ salts where employed.[67] The system generated by the $[C_4mmim][Tf_2N]$ ionic liquid and TPPMS was recycled four times, with little loss of activity and no observation of palladium black formation, although in this case heptane was added to give the biphasic system. When $[C_4py][PF_6]$ was used, the system was active, but not very selective for telomerization and the formation of palladium black was observed. Attempts to directly observe the deactivated palladium species in the $[C_2mim]^+$ and $[C_4mim]^+$ salts were unsuccessful. However, the results of a poisoning study suggested that a palladium monoimidazolylidene complex was forming, perhaps similar to that observed by Mathews *et al.*[46]

Telomerization has also been achieved in $[C_4mim][BF_4]$ with 1,3-butadiene and $HNEt_2$,[68] yielding 1-octadienyl amines, in a high E/Z ratio (87:1) and excellent regioselectivity; addition products and diene dimers were also formed. Both mono- and trisulfonated forms of triphenyl phosphine were used as the ligands for the palladium, in an attempt to improve the solubility of the catalyst in the ionic liquid solution and to prevent extraction of the catalyst into the product. Greater sulfonation of the phosphine gave better retention in the ionic liquid phase. The use of TPPTS as the ligand allowed effective recycling of the ionic liquid solution.

Unlike many early transition metal catalysts, palladium allows the use of functionalised olefins. The $[Pd(acac)_2]/PBu_3$ catalyzed dimerization of methylacrylate has recently been reported to afford significant rate enhancements, but similar selectivities, when carried out in $[C_4mim][BF_4]$ rather than when the methylacrylate itself was used as the solvent.[69] Product inhibition effects were, however, reported to limit conversions to ~80%. When the reaction was performed under biphasic toluene/$[C_4mim][BF_4]$ conditions, the catalyst leached from the ionic liquid layer. However, the chelating dibutylphosphinoethylene–dimethylammonium ligand, [Fig. 7(1)], achieved comparably high catalytic activities from four repetitive runs [139–127 TOF] without any decomposition or leaching of the catalyst. The biphasic reaction was also conducted in a continuous flow



1 2

FIG. 7. Ionic liquid soluble phosphine ligands.

reactor. The ammoniumphosphine catalytic system afforded > 4000 TONs after 50 h with > 90% selectivity for dihydrodimethylmuconate, compared to only 500 TONs for the $PtBu_3$ system on account of decomposition. The related diphenylphosphinoethylene pyridinium ligand, [Fig. 7(2)], has been reported in rhodium hydroformylation reactions in ionic liquids to afford similar benefits.[70]

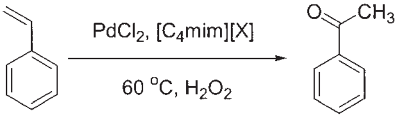
The involvement of *in situ* generated palladium imidazolylidene complexes was dismissed on account of the acidic reaction conditions, the inactivity of preformed complexes in dimerization reactions and the similar rate improvements observed in pyridinium based ionic liquids.[69] The reaction mixture was monophasic and homogeneous without $[C_4mim][BF_4]$ and, therefore, the enhancements could not be accounted by improved solubilities and/or *in situ* extraction affects. The enhancements were, therefore, attributed to the stabilization of the cationic transition state for the reaction and consequently a lowering of the activation barrier of the rate determining step. When $[(dppe)Pd(dba)(N\text{-}PhCH_2N{=}CMe_2)][BPh_4]_2$ was used as the catalyst, the rate of the reaction was increased by the use of $[C_4mim][BF_4]$, but with markedly reduced selectivity for the tail-to-tail dimer, dimethyl (*E*)-hex-2-enedioate, in comparison to the reaction in methylacrylate itself.[71]

E. *Hydrogenation*

As well as forming C–C bonds, palladium can be used to form C–H bonds in hydrogenation reactions. Palladium on carbon, entrapped in a ionic liquid polymer gel $\{[C_4mim][PF_6]$/poly(vinylidene fluoride)-hexafluoropropylene copolymer$\}$ has been used to hydrogenate propene, with conversions reaching 70% in 2 h.[72] Palladium on carbon has also been used as a catalyst for transfer hydrogenation of alkenes, alkynes, and nitro-compounds, using microwave irradiation, with formic acid as the hydrogen source in $[bmim][PF_6]$.[73] Extraction of the ionic liquid with MTBE for most products or with aqueous acid for the water soluble products facilitated simple product isolation. However, there was little other advantage in using the ionic liquids and reactions in propane-1,3-diol afforded similar reactivities, where comparison was made. Also, the reaction was ineffective for the reduction of nitriles to amines.

A more detailed study of the use of palladium on carbon in a variety of ionic liquids in the hydrogenation cinnamaldehyde has recently been reported.[74] The reaction was slower in all of the ionic liquids used than in the best performing molecular solvents (toluene, cyclohexane, and dioxane), and selectivity to hydrocinnamaldehyde (rather than 3-phenylpropanol) was greater in the ionic liquids. It was proposed that a hydrogen bond donation from the cation to the carbonyl oxygen of the substrate was responsible for the changing selectivity but, is this fully borne out by the data? One would expect that if this was the case, the stronger hydrogen bond donating [C_4mim][NTf_2] ionic liquid would give higher selectivities for hydrocinnamaldehyde than the poorer hydrogen bond donating [$N_{6,2,2,2}$][NTf_2] and [$N_{8,8,8,1}$][NTf_2] ionic liquids.[5] This is not the case. However, considering the [C_4mim]$^+$ ionic liquids in isolation, with respect to the effect of the anion, and using the type of analysis used to explain the selectivities of Diels-Alder reactions,[23] suggests that such an interaction may be occurring. This Lewis acid interaction would be expected to enhance the reactivity of the olefin, and the data for the conversion of the cinnamaldehyde in the various ionic liquids do support this. However, this may well be equally attributed to the higher viscosities of the ammonium ionic liquids. In fact, when comparing to the molecular solvents, which have no potentially rate enhancing interactions with the substrate, viscosity and, therefore, mass transfer does seem to be the major determinant of the rate of the reaction. More work will be required to deconvolute the various effects that seem to be occurring here.

[C_4mim][PF_6] has been used as a solvent for the hydrogenation of simple olefins with phenanthroline stabilized palladium nanoparticles.[75] The catalyst system was reported to be highly active for the hydrogenation of cyclohexene and 1-hexene, showing much higher conversions in a given time than in acetic acid. The reaction system could be re-used several times without loss of activity. The phenanthroline was essential to generate a stable catalytically active system and its absence led to slightly reduced activity in the first run which was significantly reduced in the second. Rather conveniently, the hydrogenation of 1,3-cyclohexadiene was selective, occurring more rapidly than the hydrogenation of cyclohexene. Only when the cyclohexadiene was exhausted did the slower hydrogenation of cyclohexene to cyclohexane proceed. Selective hydrogenation of dienes was also observed in the only example of a homogeneous palladium catalyzed hydrogenation in an ionic liquid.[76]



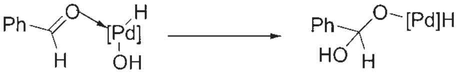
$X = PF_6$ or BF_4

SCHEME 14. The reaction of styrene with H_2O_2 in the presence of ionic liquids.

F. *Oxidation*

Most ionic liquids currently in use are stable to oxidation. Hence, they provide ideal solvents for oxidation processes. The oxidation of alkenes to aldehydes or ketones, the Wacker oxidation, is usually achieved with palladium(II) catalysts and either O_2 or H_2O_2.[77] The reaction of styrene with H_2O_2 to give acetophenone (Scheme 14) has been reported to be catalyzed by $PdCl_2$ in the presence of $[C_4mim][PF_6]$ and $[C_4mim][PF_6]$.[78] The need for only a small excess (1.15 equivalent) of aqueous H_2O_2 was demonstrated, which is a significant increase in H_2O_2 utilization over previously reported methods. It was shown that even a very small amount of ionic liquid could improve the reaction rate significantly. However, given the small amount of ionic liquid used, it is probably more appropriate to consider this reaction as occurring in a reagent/product mixture solution containing the ionic liquids.

Benzyl alcohol has been oxidized (dehydrogenated) in a variety of substituted imidazolium based ionic liquids to benzaldehyde with higher rates than in DMSO.[79] The palladium acetate was used as the catalyst source, with O_2 as the oxidant. In $[C_6mim]Cl$ a homogeneous solution of $[PdCl_4]^{2-}$ was formed, conversion rates were low and dibenzyl ether was produced in addition to benzaldehyde. When $[BF_4]^-$ ionic liquids were used, the palladium acetate precipitated palladium metal under the same reaction conditions and high rates were achieved without the formation of any by-products. The over-oxidation of the benzaldehyde to benzoic acid can be brought about by the presence of water, and water is a product of the dehydrogenation itself, yet benzoic acid was not formed in the $[BF_4]^-$ ionic liquids without the deliberate addition of water. A similar effect was seen in oxidations using perruthenate salts in ionic liquids, where molecular sieves are required in molecular solvents to avoid over-oxidation, but not in $[C_4mim][BF_4]$.[80] These ionic liquids mix well with water and it is certainly present in the solution as the reaction proceeds. Therefore, some explanation of this effect is required. The hydrophilic ionic liquids have very strong interactions with water[81] and it appears that, at least at



SCHEME 15. The insertion of the carbonyl of benzaldehyde into a [Pd]-OH species.

relatively low concentrations, the water preferentially associates with the anions of the ionic liquids and is not available for reaction with the benzaldehyde. If this is the case, and if the reaction mixture is re-used repeatedly or for large amounts of starting material, water will build up until it saturates the sink provided by the ionic liquid and it will then be able to react with the benzaldehyde. Therefore, frequent drying of the solution is necessary.

The dehydrogenation of benzyl alcohol has also been reported in $[Bu_4N]Br$ using $PdCl_2$ as the source of catalyst.[82] However, it yielded *n*-butylbenzoate as the principal product. The reactions were performed at 120 °C and, even though it is possible that the ionic liquid will suppress the vapor pressure of dissolved water, it is probably not present in very large amounts. The reaction was conducted in O_2 free conditions and so it was suggested that the benzoic acid intermediate arises from the insertion of the carbonyl of benzaldehyde into a [Pd]-OH species (Scheme 15). The same reaction system was also used for the oxidation of indan-1-ol to indan-1-one which, as a ketone, cannot over-oxidize to an acid. The reaction was performed with no oxidant, which somewhat begs the question: what is being reduced? The authors propose that H_2 is the other product of the reaction.

VIII

CONCLUSIONS

Clearly, a wide range of palladium catalyzed reactions can be performed in ionic liquids and sometimes real advantages can be derived from doing so. These can include isolating the catalyst to allow recycling, enhancing the reactivity of substrates to improve the process or to generate new catalytic species, either homogeneous or heterogeneous. Which of these occurs, if any, depends on both the ionic liquids used and the reactions being investigated. Even reactions that we superficially think of as being very similar can have very different outcomes even in the same ionic liquid. For example the Heck reaction in $[C_4mim]^+$ ionic liquids appears to proceed heterogeneously with nanoparticulate palladium, whereas in the Suzuki reaction the formation of NHC complexes is strongly implicated.

The formation of NHC complexes is clearly going to be important to the palladium chemistry seen in ionic liquids. The formation of such complexes has been seen to be advantageous (as in the Suzuki reaction) or disadvantageous (as in the telomerization of butadiene with methanol), depending on the particular system being investigated. What is yet to be seen is if the ionic liquid can be manipulated to generate NHC's with particular useful properties.

So far, most of the published results in this area are of the form of simply presenting reactions that occur in the ionic liquid. There has been very little by way of detailed investigation of the catalytic process. It is a testament to how quickly ionic liquids have caught peoples' imaginations that we are in this position and it is a great opportunity for a contribution to the field. It is only through the thorough understanding that is the next step to be taken in this area that we will be able to really make use of these interesting solvents. The development of stoichiometric inorganic and organometallic chemistry in ionic liquids will also be needed to understand the individual steps in catalysis, and they are in their infancy. Again there is a huge potential for interesting work here.

Finally, the author would like to make some general points. When an area of chemistry has such potential for application and becomes fashionable discussion around it often polarizes. That seems very much to be the case with ionic liquids. Ionic liquids are not a panacea for all of the problems of chemical industries, but that equally well does not mean that they are a waste of time. It is just over a decade since the modern generation of ionic liquids were first discovered.[83] This is a remarkably short period of time and it is not surprising that large-scale processes that use these ionic liquids are not yet in place. However, in this short time, huge advances have been made in understanding how they might be useful.

The claim to "greenness" is the most controversial of those surrounding ionic liquids. They have the advantage of being non-volatile and so accidental exposure to them is far less likely than with volatile organic solvents. However, if large volumes of organic solvents are required to extract products from them, or if they need heating to distil products, this is unlikely to be a great advantage. In the end, it is the entire process that will be "green" or not, not just one component of it.

Finally, much of the contention that seems to arise around ionic liquids derives from statements of the kind: "ionic liquids are…". No one would ever consider making the blanket statement: "molecular liquids are…".

Ionic liquids are a group of materials that share the two features of being ionic and liquids. Beyond that, some are acidic, while others basic, some mix with water, others do not, some react violently with water and decompose in the process. In other words, different ionic liquids have different properties and what is true when using one may not be true while using another. I, for one, am thankful of this; it's what makes them so interesting to work with.

IX

ABBREVIATIONS

[bmppim]	1-butyl-3-methyl-2-diphenylphosphino-imidazolium
[bmpy]	1-butyl-1-methylpyrolidinium
[C_{14}PHex$_3$]	tetradecyltrihexylphosphonium
[C_4C_4im]	1,3-dibutylimidazolium
[C_4mim]	1-butyl-3-methylimidazolium
[C_4mmim]	1-butyl-2,3-dimethylimidazolium
[C_6mim]	1-hexyl-3-meythylimidazolium
[C_6mmim]	1-hexyl-2,3-dimethylimidazolium
[C_4py]	*N*-butylpyridinium
[C_6py]	*N*-hexylpyridinium
[C_2mim]	1-ethyl-3-methylimidazolium
[C_3mim]	1-methyl-3-propylimidazolium
[$N_{6,2,2,2}$]	triethylhexylammonium
[$N_{8,8,8,1}$]	trioctylmethylammonium
acac	pentane-2,3-dione
C_4C_4imy	1,3-dibutylimidazolylidene
C_4mimy	1-butyl-3-methylimidazolylidene
C_6mimy	1-hexyl-3-methylimidazolylidene
dba	di(benzylidene)acetone
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
DPPP	1,3-bis(diphenylphosphino)propane
mbth	methylbenzthiazolylidene
MTBE	methyl tertiary butyl ether
OAc	acetate
PyPPh$_2$	2-(diphenylphosphino)pyridine
[NBu$_4$]	tetrabutylammonium
TEM	transmission electron microscopy
Tf	trifluoromethylsulfonyl, SO_2CF_3
tmen	*N,N,N′,N′*-tetramethylethylenediamine
TON	turn over number
TPPMS	triphenylphosphine sulfonate, sodium salt; $PPh_2(C_6H_4SO_3Na)_3$
TPPTS	triphenylphosphine trisulfonate, tri-sodium salt; $P(C_6H_4SO_3Na)_3$

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