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Early transition metal hydride complexes: synthesis and reactivity

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Contents

Abstract

This review describes the synthesis and reactivity studies of early metal (Sc, Y, Ti, Zr, Hf, V, Nb, Ta) hydride compounds that have appeared over the last 10 years. Every attempt has been made to be comprehensive from 1990 to mid-2001. Complexes reported prior to 1990 have not been discussed. It should also be noted that related subjects that have been recently reviewed including the

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organic chemistry applications, polyhydride clusters, silica supported Groups 4 and 5 transition metal hydrides and hydride bridged heterobimetallic complexes have been excluded.

Keywords: Metal hydride complexes; Synthesis; Reactivity

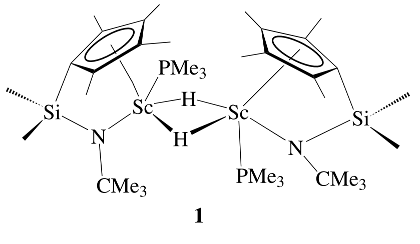
1. Introduction

The ever-expanding vistas in transition metal hydride chemistry prompt continuing interest in this area. Early transition metal hydride derivatives are thought to be responsible for a plethora of organic transformations, catalytic cycles and olefin polymerization intermediates, or deactivation products. For the last 25 years, a number of research groups have focused their activities on the synthesis and application of early metal hydrides. This paper will review the synthetic and reactivity studies of these molecular compounds that have been reported over the last 10 years. Every attempt has been made to be comprehensive from 1990 to mid-2001 for the early metals, specifically Sc, Y, Ti, Zr, Hf, V, Nb, and Ta. Complexes reported prior to 1990 have not been discussed, but references to subsequent reactivity studies have been included. It should be noted that related subjects that have been recently reviewed including the organic chemistry applications of Schwartz's reagent [$Cp_2Zr(H)Cl$] [1–4], polyhydride clusters [5–7], silica supported Groups 4 and 5 transition metal hydrides [8], and hydride bridged heterobimetallic complexes are deemed to be beyond the scope of this review. In these cases, the reader is directed to relevant reviews. In addition, related reviews augment specific aspects of the work described herein [9–11].

2. Scandium

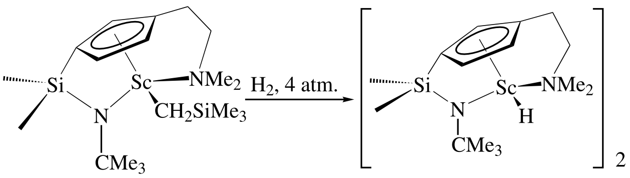
2.1. Mono-CpSc hydride derivatives

Sc-hydrides have received considerably less attention than Groups 4 or 5 metal hydrides. The examples that do exist in the literature, however, are remarkable. The dimeric, constrained geometry scandocene hydride [$(Cp^*SiNR)Sc(PMe_3)(\mu\text{-}H)]_2$ (**1**) was reported by Bercaw and coworkers, in 1990 [12,13]. The Lewis acidity of the metal center as a consequence of its electron deficient nature results in an α-olefin oligomerization catalyst. The polymerization occurs with > 99% 'head-to-tail' coupling, producing linear, atactic polymers. This system stands in contrast to Group 4 catalyst precursors that require an activator to initiate polymerization.



1

An interesting extension of the work above involves a linked amido–cyclopentadienyl ligand system that incorporates an additional pendant amine donor. Piers and coworkers prepared the Sc complex of this ligand via reaction of the ligand precursor with in situ generated $Sc(CH_2SiMe_3)_3$ [14]. Subsequent hydrogenation gave two of four possible diastereomeric μ-dihydride dimers (Scheme 1), one of which, i.e. 1*R*-*trans*-1*S*-[$(C_5H_4(CH_2CH_2NMe_2)$-SiNR)ScH]$_2$ (**2**) was crystallographically characterized. The crystal structure showed a Sc–H bond distance of 2.02(5) Å. This dimer remained, for the most part, intact in solution, with the monomer–dimer equilibrium occurring at a slow rate. The robustness of this dimer was also evidenced by the very slow reaction rates with α-olefins. Bercaw and coworkers noted that dissociation of PMe_3 from **1** occurred prior to olefin insertion. In **2**, dissociation of the pendant amino-arms is disfavored by the chelate effect, presumably accounting for the observed decrease in reactivity.



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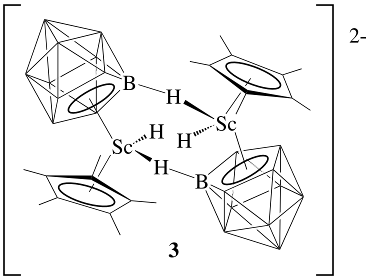
Scheme 1.

In seeking more active Sc catalysts, dicarbolide $[C_2B_9H_{11}]^{2-}$ was introduced as an ancillary ligand in anticipation that the dianionic charge would discourage dimerization of the Sc–H derivative [15]. The species $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)]_2\cdot 3/2(C_6H_5CH_3)$, **3** was generated by hydrogenation of $(Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]Li$ or β-hydrogen elimination resulting from the product of the reaction of $Cp^*(C_2B_9H_{11})Sc(THF)_3$ with *n*-BuLi. Crystallographic data for **3** showed the unexpected formation of dative interactions between the dicarbolide ligands and the electrophilic Sc centers, resulting in a dimeric dianion formulation. This interaction persists even in the presence of strong Lewis bases like PMe_3, thus precluding reactivity with α-olefins.



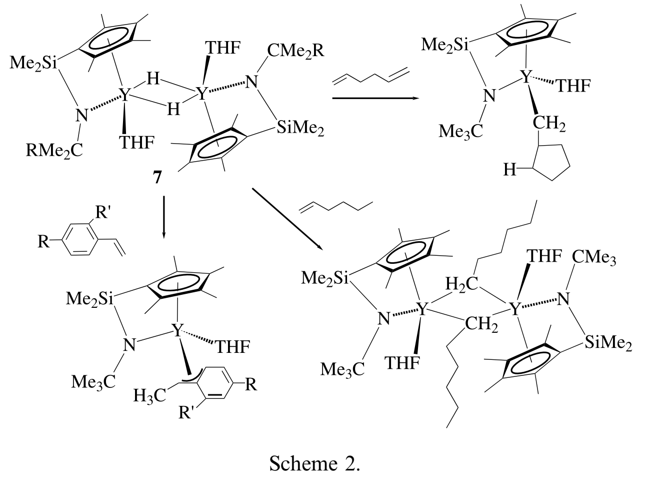
3

Fryzuk has recently described the synthesis of the borohydride derivative CpScCl[N(SiMe$_2$CH$_2$P*i*-Pr$_2$)$_2$] with LiBH$_4$ that yielded the five-coordinate species CpSc(BH$_4$)[N(SiMe$_2$CH$_2$P*i*-Pr$_2$)$_2$]. Subsequent reaction with PMe$_3$ gave the putative hydride, CpScH[N(SiMe$_2$CH$_2$P*i*-Pr$_2$)$_2$] (**4**) which exists in equilibrium in solution greatly favoring the starting scandium borohydride [16].

2.2. Non-CpSc hydride derivatives

Arnold and coworker have prepared dimeric hydride bridged Sc complexes that incorporate the (*N*,*N*′-bis(trimethylsilyl)benzamidinato)-ligands via hydrogenation of the precursor [PhC(NSiMe$_3$)$_2$]$_2$ScCH$_2$SiMe$_3$ [17]. The crystal structure of the dimer [(PhC(NSiMe$_3$)$_2$)$_2$ScH]$_2$ (**5**) showed Sc–H bond distances ranging from 1.87(3) to 2.00(3) Å. Compound **5** reacts with PhCCPh, ethylene or higher olefins to give mono-insertion products of the form, [RC(NSiMe$_3$)$_2$]$_2$-ScC(R)=C(R)H (R = H, alkyl, aryl). At elevated temperature some polymerization of ethylene was observed.

Bercaw and coworkers have also reported a Sc-hydride derivative containing the ancillary ligand, 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) [18]. The formally 12e$^-$ d^0 species CnScMe$_3$, reacts with H$_2$ (4 atm, 80 °C) over several days giving a product of empirical formula CnScH$_3$ (**6**). Although this species was characterized by NMR spectroscopy, a complete interpretation of the data was hampered by the large quadropole moment for ^{45}Sc. The analogous Y chemistry is discussed below.



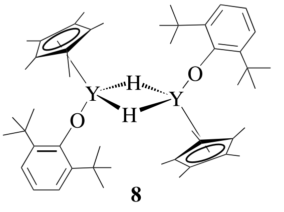
Scheme 2.

3. Yttrium

3.1. Mono-CpY hydride derivatives

‘Constrained geometry’ Y–H systems of the form [Y(C$_5$Me$_4$SiMe$_2$NR)(μ-H)(THF)]$_2$ (**7**), analogous to the Sc systems (Section 2.1), are prepared via hydrogenolysis of Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NR)(CH$_2$SiMe$_3$)(THF) (R = CMe$_3$, CMe$_2$Et) in pentane at 4 atm of H$_2$ pressure. ^{1}H-NMR spectroscopy indicates that the dimer stays intact in solution as evidenced by the characteristic triplet at 5.50 ppm, resulting from Y–H coupling of 29 Hz. When cooled to −40 °C, the NMR evidence suggests a 4:1 mixture of two diastereomers [19]. Compound **7** showed low catalytic activity with ethylene under ambient temperatures (0.08 g mmol^{-1} h^{-1} bar^{-1}) producing linear, highly crystalline polyethylene. Over a period of 12 h at room temperature **7** reacted with 1-hexene or styrene to give mono-insertion products (Scheme 2). No polymerization of 1-hexene was evident, at 60 °C over 5 days. Cyclization of 1,5-hexadiene gave a cyclopentylmethyl complex (Scheme 2).

A Cp–Y aryloxide hydride species was prepared via hydrogenation of [(C$_5$Me$_5$)Y(O-2,6-C$_6$H$_3$*t*-Bu$_2$){CH-(SiMe$_3$)$_2$}]. The dimeric hydride [(C$_5$Me$_5$)Y(O-2,6-C$_6$H$_3$*t*-Bu$_2$)(μ-H)]$_2$ (**8**) reacted irreversibly and regiospecifically with terminal olefins to give bridging hydride, bridging alkyl species. These new μ-alkyl species polymerized ethylene, and were reported to be single-component catalysts for the polymerization of α-olefins and non-conjugated dienes. The hydride also reacted with terminal alkynes to form mono-insertion products [20,21].



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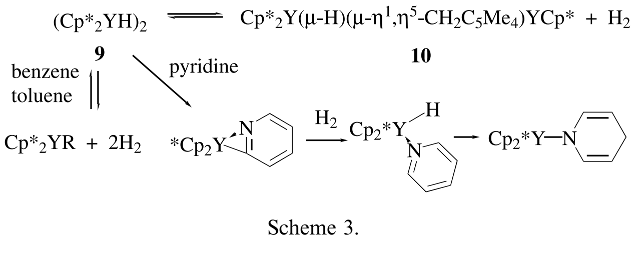


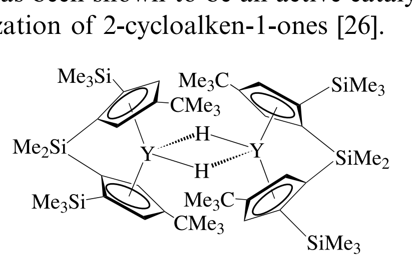
Scheme 3.

3.2. Yittrocene hydride derivatives

Using similar synthetic strategies to those described above, the 14 electron (Cp$^*_2$YH)$_2$ (**9**) was generated in situ via hydrogenation of Cp$^*_2$YCH(SiMe$_3$)$_2$ [22]. Compound **9** could also be synthesized via reaction of (Cp$^*_2$Y(μ − Me))$_2$ with PhMeSiH$_2$ [23]. The resulting hydride species is reactive, resulting in two competing C–H activation pathways. In *n*-octane, or cyclohexane, thermolysis of **9** yields Cp$^*_2$Y(μ − H)(μ − η^1, η^5 − CH$_2$C$_5$Me$_4$)YCp* (**10**), the direct result of C–H activation of one of the Cp* methyl groups (Scheme 3). With benzene or toluene as solvent, metalation of the solvent occurred, as evidenced by rapid H/D scrambling in deuterated solvent at room temperature. This pathway is in competition with the Cp* metalation, but rapid removal of the H$_2$ formed allowed isolation of the kinetic product. Reactions of **9** with substituted arenes, PhX (X = OMe, SMe, NMe$_2$, CH$_2$NMe$_2$, PMe$_2$, PPh$_2$ = CH$_2$, F, Cl, Br) results in metalation of the arene ring *ortho* to the heteroatom. This is consistent with the strong preference for attack on sp^2 hybridized C–H bonds over sp^3 C–H as well as the *ortho*-directing effect of the heteroatom substituents.

The *ortho*-metallation of pyridine via reaction with **9** gave Cp$^*_2$Y(2 − pyridyl) [24]. In deuterobenzene this complex is thought to be in equilibrium with Cp$^*_2$YPh, as evidenced by H/D scrambling between the pyridyl ligand and solvent (Scheme 3). Under 1 atm of H$_2$, Cp$^*_2$Y(2 − pyridyl) reacted over a period of 3 days giving the 1,4-hydride addition product Cp$^*_2$Y(NC$_5$H$_6$). The first step in this reaction is presumably the product of hydrogenolysis of the Y–C bond, leading to a pyridine stabilized Cp$^*_2$YH, which then rearranges to the 1,4 addition product.

An early report of Y–H systems described the first iso-specific, single component Ziegler–Natta polymerization catalyst [rac-Me$_2$Si(2-SiMe$_3$-4-CMe$_3$C$_5$H$_2$)$_2$Y(μ-H)]$_2$ (**11**) for olefin polymerization [25]. Compound **11** was dimeric in solution and almost unreactive toward PMe$_3$, however it reacted with propylene, 1-butene, 1-pentene, and 1-hexene, over a period of days to form modest molecular weight polymers. Subsequently, compound **9** has been shown to be an active catalyst for the oligomerization of 2-cycloalken-1-ones [26].



11

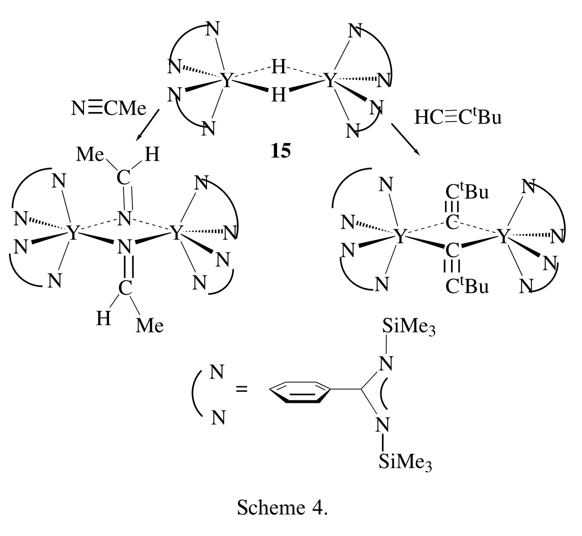
Complexes containing a linked bis(cyclopentadienyl) ligand have been designed to coordinate to Y to afford a single enantiomeric *C*2-symmetric ansa-metallocene of the form (C$_5$H$_3$-2-SiMe$_3$-4-CMe$_3$)$_2$Si(OC$_{10}$H$_6$C$_{10}$H$_6$O)-YCl(THF) [27]. Treatment of rac-(C$_5$H$_3$-2-SiMe$_3$-4-CMe$_3$)$_2$Si(OC$_{10}$H$_6$C$_{10}$H$_6$O)YCH(SiMe$_3$)$_2$ with H$_2$ yields a kinetic mixture of both heterochiral and homochiral dimers (e.g. (*R*,*S*),(*S*,*R*)-{(C$_5$H$_3$-2-SiMe$_3$-4-CMe$_3$)$_2$Si-(OC$_{10}$H$_6$C$_{10}$H$_6$O)Y(μ-H)}$_2$ (**12**) and (*R*,*S*)(*R*,*S*)-{(C$_5$H$_3$-2-SiMe$_3$-4-CMe$_3$)$_2$Si(OC$_{10}$H$_6$C$_{10}$H$_6$O)Y(μ-H)}$_2$ (**13**), respectively. Over several hours this mixture undergoes conversion to the pure homochiral dimers. As anticipated, hydrogenolysis of enantiopure precursors affords directly only enantiopure homochiral dimers. The hydride complex, generated in situ, polymerizes 1-pentene to give highly isotactic poly-1-pentene.

The related compound [(2,4,7-trimethylindenyl)$_2$Y(μ-H)]$_2$ (**14**) has been prepared in a similar manner and shown to be a catalyst for regio- and stereoselective homodimerization of a range of α-olefins as well as head-to-head codimerization of styrene with other olefins [28].

3.3. Non-CpY hydride derivatives

Attempts to prepare the Y analog of the Sc complex CnMH$_3$, (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) from the reaction of CnYMe$_3$ and H$_2$ resulted in decomposition, yielding methane, free Cn ligand and a grey precipitate thought to be YH$_3$ [18].

Benzamidinate Y–H complexes have been reported. Although several conventional synthetic routes failed, the hydride derivatives were ultimately prepared by analogy to the Sc species via hydrogenolysis of (PhC(NSiMe$_3$)$_2$)$_2$YCH(SiMe$_3$)$_2$ [29,30]. The resulting hydride species was confirmed crystallographically to be a dimer [(PhC(NSiMe$_3$)$_2$)$_2$Y(μ-H)]$_2$ (**15**), with Y–H distances that range from 2.11(3) to 2.19(3) Å. This compound is sparingly soluble in benzene, insoluble in aliphatic solvents, and thermally stable for several days

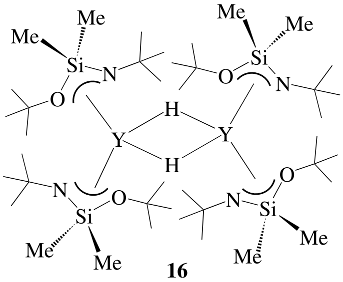


Scheme 4.

at 100 °C in benzene-d_6. No H/D exchange between the Y–H and solvent occurred, in contrast with the yttrocene–hydride chemistry. This was thought to result from the increased ionic character of the bis(benzamidinato)yttrium system.

Compound **15** does not react with stoichiometric amounts of THF in benzene, but a neat THF solution of **15** yields ethane and ethylene, within hours. The Y byproduct of this THF degradation was reported to be an enolate derivative, based on the ^{1}H-NMR data. Compound **15** polymerized ethylene under rather forcing conditions (65 °C, 4 atm), with low activity [30]. Stoichiometric reactions of alkynes with **15** gave the dimeric species $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}CCR)\}_2$, while the catalytic dimerization of 1-alkynes was found to be very slow, with the rate strongly dependent on the steric bulk of the alkyne substituents (Scheme 4). Alkyne-dimerization occurred in a head-to-tail fashion for phenylacetylene and *tert*-butylacetylene but was head-to-head with trimethylsilylacetylene. Acetonitrile also reacted with **15** to give the unstable insertion product $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N{=}C(H)Me)]_2$. Reaction of **15** with pyridine, gave the 1,2-insertion product $[PhC(NSiMe_3)_2]_2YNC_5H_6$, analogous to the Sc case, however thermal isomerization to the 1,4-addition product did not occur in this case [30].

An alkoxysilylamido variation of the bis(benzamidinato) ligand system has been employed by Teuben and coworkers [31] to generate $[(Me_3COSiMe_2(NCMe_3))Y(\mu\text{-}H)]_2$ (**16**) in low yield. This dimeric complex was unstable although it was spectroscopically characterized in THF. Attempts to prepare the hydride in solvents other than THF were unsuccessful, giving only the product of ligand redistribution, i.e. $(Me_3COSi\,Me_2(NCMe_3))_3Y$.



16

4. Titanium

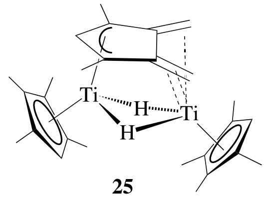
4.1. Mono-CpTi hydride derivatives

Monocyclopentadienyl–titanium hydrides have not received much attention. However, Okuda et al. have recently described the species $(C_5Me_4SiMe_2N(CHMePh)TiCl(\mu\text{-}H_3BH)$. The triple bridging nature of the borohydride fragment in this chiral complex was proposed on the basis of NMR and preliminary structural data [32].

4.2. Titanocene hydride derivatives

A number of reports of dimeric CpTi hydride complexes have involved the reduction of titanocenes. Among the species produced in this manner are: $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2][(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2$ (**17**) [33], $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_2Me_3)_2][(\eta^5\text{-}C_5H_2Me_3)Ti(\mu\text{-}H)]_2$ (**18**) [34], $[\mu\text{-}\eta^3{:}\eta^4\text{-}(C_5HMe_2(CH_2)_2][(\eta^5\text{-}C_5HMe_4)Ti(\mu\text{-}H)]_2$ (**19**), $[\mu\text{-}\eta^3{:}\eta^4\text{-}(C_5Me_4(CH_2)_2][(\eta^5\text{-}C_5Me_5)Ti(\mu\text{-}H)]_2$ (**20**) [35]. In fact, the structure of the Ti(II) species $[Cp^*_2Ti]$ has been shown to be in equilibrium with hydride the derivative $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4CH_2)TiH$ (**21**) [36,37]. Bulky substituents on the Cp rings have allowed the isolation of monomeric Ti(III) hydrides. The first structurally characterized monomeric $Cp_2Ti(III)$ species $(Me_4PhC_5)_2TiH$ (**22**) was reported by Teuben and coworkers [38] while Andersen and coworkers have also shown that the Ti(III) species Cp^*_2TiH (**23**) reacts with BuLi to produce the anionic dihydride species $[Cp^*_2TiH_2]^-$ (**24**) [39]. Reaction of **24** with H_2O affords the dimeric oxo-anion $[Cp^*_2TiOLi(THF)]_2$.

Reduction of $(C_5HMe_4)_2TiCl_2$ with $LiAlH_4$, resulted in the formation of the unusual, formally Ti(III)–Ti(II) dimeric dihydride species **25** [35]. The crystal structure of **25** revealed inequivalent Ti centers, each π-bonded to portions of one μ-η^4:η^3-1,4-dimethyl-2,3-dimethylene-cyclopentenyl ligand with Ti–H distances of 1.79(3) and 1.82(3) Å.

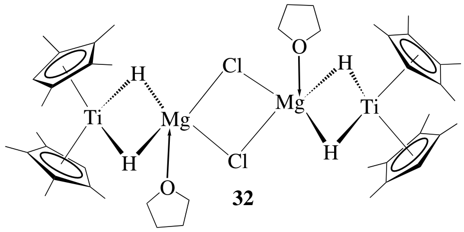


25

Sizov et al. [40] have shown that the reactions of $Cp_2Ti(\mu\text{-}H_2)AlH_2\cdot Et_2O$ (**26**) with protic reagents affords the complexes $\{Cp_2Ti(\mu\text{-}H_2)AlH[\mu\text{-}N(C_2H_4)_2O]\}_2$ (**27**), $[Cp_2Ti(\mu\text{-}H_2)AlH(\mu\text{-}OC_2H_4OMe)]_2$ (**28**) and $(Cp_2Ti(\mu\text{-}H_2)AlH)_2O$ (**29**). Complex **28** converts to the hexanuclear compound $[Cp_2Ti(\mu\text{-}H)_2Al]_2(\mu\text{-}OC_2H_4OMe)[(\eta^1\text{-}\eta^5\text{-}C_5H_4)TiCp(\mu\text{-}H)]_2$ (**29**). The complexes $[Cp_2Ti(\mu\text{-}H_2)AlH(NEt_2)]_2$ (**30**) and $[Cp_2Ti(\mu\text{-}H_2)AlH(OEt)]_2$ (**31**) act as catalysts for the hydrogenation of hex-1-ene [40].

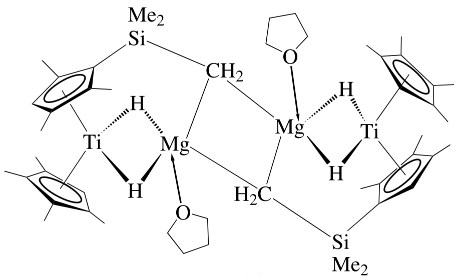
Reduction of $(C_5HMe_4)_2TiCl_2$ with Mg under H_2 gave $[(\eta^5\text{-}C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(THF)(\mu\text{-}Cl)]_2$ (**32**) [41]. The related species $[(\eta^5\text{-}C_5HMe_4)_2Ti(\mu\text{-}H)_2]_2Mg$ (**33**) was also isolated and structurally characterized from this reaction. Solutions of the reaction mixture were found to catalyze the head-to-tail dimerization of *tert*-

butylacetylene.



32

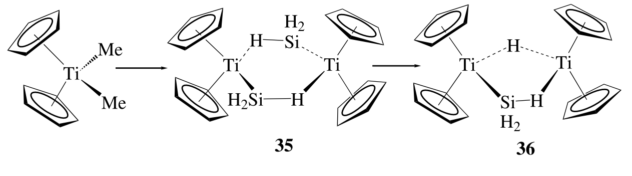
Similar reduction of $[C_5Me_4(SiMe_3)]_2TiCl_2$ gave a paramagnetic product [41] formulated as $\{[\eta^5\text{-}C_5Me_4\text{-}SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})](\eta^5\text{-}C_5Me_5)Ti(\mu\text{-}H_2)Mg(THF)\}_2$ (**34**). The mechanism of formation remains unclear although it has been suggested that the hydrides may arise from activation of the solvent.



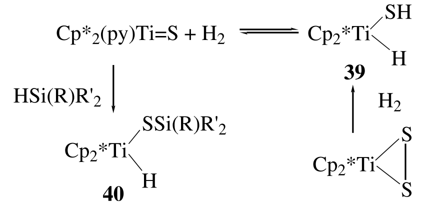
34

Another approach to the formation of new compounds that contain Ti–H bonds has been the reaction of CpTi-dimethyl species with silanes. This chemistry is employed to hydrosilate alkenes, alkynes, ketones carbonyls, imines and pyridines [11,42]. Harrod has recented reviewed much of this chemistry [11]. The species $(MeO)_3SiH$ undergoes substituent redistribution to generate SiH_4. Reaction of Cp_2TiMe_2 with $(MeO)_3SiH$ yielded a Ti(III) dimer, originally thought to be $[Cp_2Ti(\mu\text{-}SiH_2)]_2$ [43] but subsequently shown to be $[Cp_2Ti(\mu\text{-}HSiH_2)]_2$ (**35**) with bridging SiH_3 units [44]. This complex was stable at room temperature for only a few hours, decomposing slowly to give $[Cp_2Ti(\mu\text{-}HSiH_2)(\mu\text{-}H)TiCp_2]$ (**36**) (Scheme 5). This latter species could also be synthesized directly from the reaction of with Cp_2TiMe_2 and SiH_4. Carrying out the reaction in the presence of PMe_3 gave $Cp_2TiSiH_3(PMe_3)$ [45], whereas the analogous reaction of Cp_2TiMe_2 and $PhSiH_3$ in the presence of $PHCy_2$ afforded the hydrido-bridged dimmer $[Cp_2Ti]_2(\mu\text{-}H)(\mu\text{-}PCy_2)$ (**37**) [46].

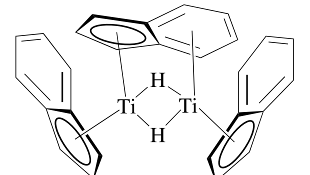
In this vein, the reaction of $(Indenyl)_2TiMe_2$ with phenyl silane gave the mixed valent Ti(III)–Ti(II) species **38** [47]. The crystal structure of **38** showed two enantiomorphs. The formation of **38** is thought to proceed through a mixed valent Ti(IV)–Ti(III) species analogous to **35** [48].



Scheme 5.



Scheme 6.

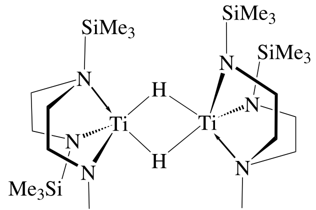


38

The terminal sulfido complex $Cp_2^*Ti(S)(pyridine)$ reported by Sweeney et al. [49] undergoes reversible reaction with H_2 generating $Cp_2TiH(SH)$ (**39**) in solution. Alternatively, **39** was synthesized via the addition of H_2S or $Cp_2^*TiS_2$ to $Cp_2^*TiH_2$ or by reaction of H_2 and $Cp_2^*Ti(S_2)$ (Scheme 6). Silanes also add to $Cp_2^*Ti(S)(pyridine)$ to give new hydrides of the formulation $Cp_2^*TiH(SSiRR'_2)$ (**40**). The crystal structure of $Cp_2^*TiH(SSiHEt_2)$ was reported (Scheme 6).

4.3. Non-CpTi hydride derivatives

Synthesis of $\{TiH[(Me_3SiNCH_2CH_2)_2NSiMe_3]\}_2$ (**41**) was easily achieved by hydrogenolysis of the precursor $Ti(CH(SiMe_3)_2)[(Me_3SiNCH_2CH_2)_2NSiMe_3]$. This complex was the first fully characterized example of a non-Cp based Ti(III) hydride. The Ti–H bond lengths of 1.77(3) and 1.88(3) Å, respectively, are comparable to other Ti(III) hydride complexes [50].



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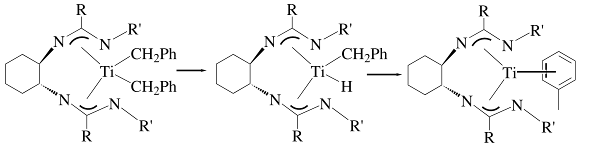
Arnold and coworker have described the reaction of



Scheme 7.

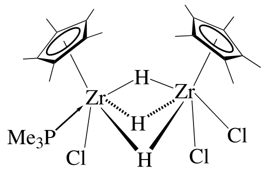
the chelating bis-amidinate Ti complex [(C$_6$H$_{10}$(NC-(C$_6$H$_4$Me)NPh)$_2$)Ti(CH$_2$Ph)$_2$] with H$_2$, effecting elimination of toluene, to give a proposed hydride intermediate which undergoes a σ–π rearrangement of the remaining benzyl ligand, affording a Ti(II)-η^6-toluene product. Although isolation of the hydride intermediate was not possible, deuteration experiments support the proposed reaction pathway (Scheme 7) [51].

5. Zirconium

5.1. Mono-CpZr hydride derivatives

Gambarotta and coworkers have reported the synthesis of a Zr(II)-hydride species CpZr(dmpe)$_2$H (**42**), from the reaction of CpZr(dmpe)$_2$Cl with LiHBEt$_3$ [52]. Analogous reactions with other reagents such as LiAlH$_4$, NaH$_2$Al(OCH$_2$CH$_2$OCH$_3$)$_2$ or Red-Al, or hydrogenolysis of the analogous Zr-methyl derivative gave only complicated mixtures. The analogous hydride CpZr(dmpe)(η^4-butadiene)H (**43**) was prepared from a reaction of CpZr(dmpe)(η^4-butadiene)Cl with Red-Al.

Hydrogenolysis of the 14 electron Cp*Zr[(CH$_2$)$_3$-NMe$_2$]Cl$_2$ gave a trimetallic compound formulated as [Zr$_3$Cp$_3^*$(μ – H)$_4$(μ – Cl)$_2$Cl$_3$] (**44**) [53] based on the crystal structure of the analogous Hf derivative [54]. Compound **44** reacts with PMe$_3$ to give the dimetallic Cp$_2^*$Zr$_2$μ – (H)$_3$Cl$_3$(PMe$_3$) (**45**).



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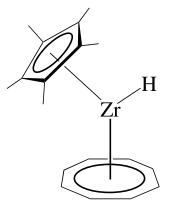
The cyclooctatetraene derivative [Zr(η^8-C$_8$H$_8$)(η^5-C$_5$Me$_5$)Cl] reacts with *n*-PrMgCl to give the somewhat unexpected zirconium hydride monomer [Zr(η^8-C$_8$H$_8$)(η^5-C$_5$Me$_5$)H] (**46**) [55]. While this species did not catalyze the polymerization of olefins even at 100 atm of ethylene, it did react with butadiene to give the mono-insertion product [Zr(η^8-C$_8$H$_8$)(η^5-C$_5$Me$_5$)-(CH$_2$CH=CHMe)].



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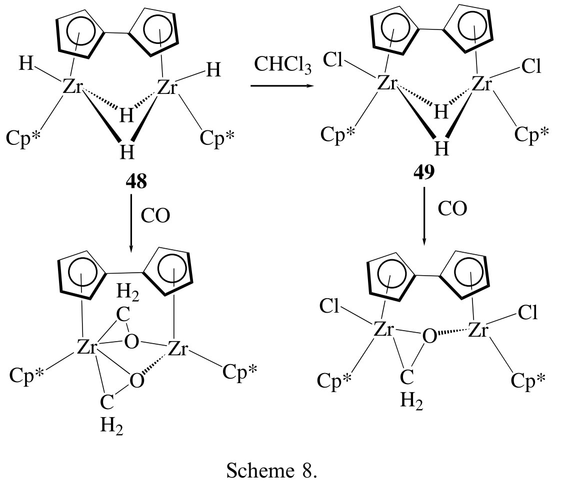


Scheme 8.

5.2. Zirconocene hydride derivatives

Barron and coworkers have described the reaction of Cp$_2$ZrMe$_2$ with the Al species [HAl(η^3-N*t*-Bu)]$_4$ provides dimeric species [Cp$_2$Zr(μ^2-H)Me]$_2$ (**47**). This species decomposes above 60 °C [56].

The Zr$_2$-hydride derivative, [(C$_{10}$H$_8$)][Cp*ZrH(μ^2-H)]$_2$ (**48**), is obtained from the hydrogenolysis of (C$_{10}$H$_8$)[Cp*ZrMe$_2$]$_2$. NMR experiments indicated hydride exchange between bridging and terminal sites. The reactivity of **48** (Scheme 8) revealed that reaction with CHCl$_3$ results in the replacement of two hydride ligands with chlorides affording [(C$_{10}$H$_8$)[Cp*Zr(μ-H)Cl]$_2$ (**49**) and CH$_2$Cl$_2$. Compound **49** is thermally stable to 110 °C, but photochemically eliminates H$_2$ yielding a dinuclear Zr(III) chloro-bridged complex. Both **48** and **49** insert CO, to give bridging formaldehyde derivatives (Scheme 8) [57].

Mixed CpCp*Zr hydride derivatives have been reported by Tilley and coworkers [58]. Hydrogenolysis of either CpCp*ZrCl(EPh$_3$) (E = Si, Ge) or the methyl analogs gave the corresponding hydride chloride CpCp*ZrHCl (**50**), or dihydride CpCp*ZrH$_2$ (**51**) species, respectively.

Substituted Cp ligands were employed by Choukroun and coworker to isolate dimeric Zr hydride compounds [59]. For example, reaction of (C$_5$H$_4$R)$_2$ZrCl$_2$ (R = SiMe$_3$, CMe$_3$) with either LiAlH(OCMe$_3$)$_3$ or Red-Al, resulted in the formation of the dihydride dimers [(C$_5$H$_4$R)$_2$Zr(μ-H)H]$_2$ **52** and **53**, respectively. NMR data showed bridging and terminal hydrides. Compound **52** could be reduced chemically or electrochemical, to yield an anionic Zr(III) dihydride complex **54**. This species catalyzes the hydrogenation of 1,5- or 1,3-cyclooctadiene to cyclooctene.

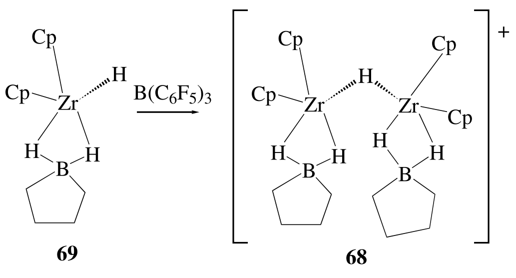
Very recently, Bercaw and coworkers reported the synthesis of a series of new substituted zirconocene hydrides [60]. These compounds were prepared by hydrogenolysis of the corresponding dimethyl species under relatively mild conditions (1 atm H$_2$, 25 °C). The molecularity of these hydride species was dependent on the substituents on the Cp rings. Monomeric compounds were found for sterically crowded systems; $Cp^*(\eta^5-C_5HMe_4)ZrH_2$ (**55**), $Cp^*\{\eta^5-C_5H_3-1,3-(CMe_3)_2\}ZrH_2$ (**56**) and $\{\eta^5-C_5H_3-1,3-(CMe_3)_2\}_2ZrH_2$ (**57**). In contrast, dimeric products were obtained for less sterically crowded systems such as $[\{\eta^5-C_5H_3-1,3-(CHMe_2)_2\}_2ZrH_2]_2$ (**58**), $[Cp^*(\eta^5-C_5H_4CMe_3)ZrH_2]_2$ (**59**) and $[Cp^*(THI)ZrH_2]_2$ (**60**) (THI = η^5-tetrahydroindenyl). An equilibrium mixture of monomer and dimer exist for $(\eta^5-C_5HMe_4)_2ZrH_2$ (**61**) and $[Cp^*\{\eta^5-C_5H_3-1,3-(CHMe_2)_2\}ZrH_2]_2$ (**62**). Monomeric species showed a single downfield hydride resonance ($\delta \approx 7-8$ ppm), whereas the dimeric dihydrides exhibit separate resonances for bridging ($\delta \approx 1--1$ ppm) and terminal hydrides ($\delta \approx 4-5$ ppm). These shift ranges hold true for most other zirconocene hydrides.

Choukroun et al. have shown that the dimeric complex **53** undergoes a pseudo-reversible reduction at $E_{1/2} = -1.9$ V. Electrolysis in an EPR spectrometer reveals the formation of the dihydride monomer radical anion $[(C_5H_4R)_2Zr(\mu-H)H]_2$ (**63**) [61].

The cationic zirconocene hydride species $[(C_5H_4Me)_2ZrH(THF)]^+$ (**64**) is formed by hydrogenolysis of the corresponding precursor methyl-cation. This species reacts slowly to ring open THF affording $[(C_5H_4Me)_2Zr(OBu)(THF)]^+$. It also reacts with D_2 to yield deuterium exchange with the hydride and the β-sites on the Cp-rings, ultimately affording $[(C_5D_2H_2Me)_2ZrD(THF)]^+$. These reactions are proposed to proceed by a conventional σ-bond metathesis process and via a methylcyclopentadiene intermediate, respectively [62].

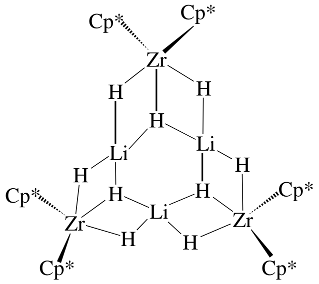
The binuclear hydrido complexes $[(C_5H_4SiMe_3)_4Zr_2H_3][B(C_6F_4R)_4]$ (R = F (**65**), Si*i*-Pr$_3$ (**66**)), was prepared by reaction of $[CPh_3][B(C_6F_4R)_4]$ with **52**. These compounds are active initiators for the polymerization of isobutene and isobutene–isoprene copolymers. A second species formed in this reaction was structurally characterized as the trinuclear hydride $[[(C_5H_4SiMe_3)([(C_5H_4SiMe_3)_5(\eta^1-\eta^5-C_5H_3-SiMe_3)Zr_3H_4]^+[B(C_6F_4SiPri_3)_4]^-$ (**67**) [63].

Shore and coworkers have reported the formation of the dimeric cationic species $[(\mu-H)\{Cp_2Zr(\mu-H)_2BC_4H_8\}_2][HB(C_6F_5)_3]$ (**68**) from the reaction of $Cp_2ZrH\{(\mu-H)_2BC_4H_8$ (**69**) [64] with $B(C_6F_5)_3$ (Scheme 9) while the hydride bridge remains intact in benzene, in ether the species $[Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$ was isolated [65].



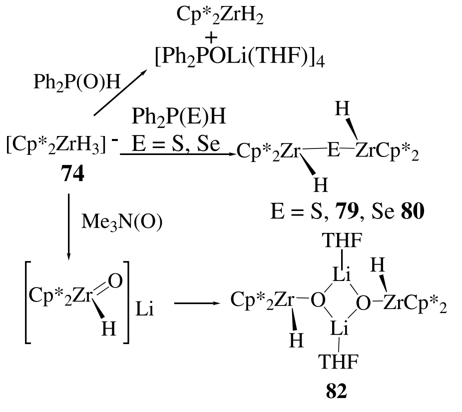
Scheme 9.

Stephan and coworker have reported an anionic Zr(IV) trihydride derivative. The initial synthesis of this complex involved the rather capricious reaction of $Cp^*_2ZCl_2$ with excess KH, to form the new anionic species $[Cp^*_2ZrH_3K(THF)_2]_2$ (**70**) [66]. An alternative synthesis involved treatment of the known species $Cp^*_2ZrH_2$ (**71**) [67,68] with LiH, or KH. A third approach involved the addition of three equivalents *n*-BuLi to $Cp^*_2ZrCl_2$ under an atmosphere of H_2. This formed the anion directly, as the LiCl adduct. A final, and best synthetic method involved addition of $LiAlH_4$ to $Cp^*_2ZrCl_2$, to form the intermediate product $[Cp^*_2ZrH(\mu-H_2AlH_2)]_2$ (**72**) quantitatively. Raston and coworkers subsequently reported the related Zr–Al hydride species $[Cp_2ZrH(\mu-H)_2AlH_2(L)]$ (L = quinuclidine (**73**) or NMe_3 (**74**)) [69], while others have reported the related hydride-bridged Zr–arylAl species [70]. Subsequent addition of *n*-BuLi to **72** resulted in attack of the Al center and transfer of the hydrides to Zr giving clean conversion to the trihydride product, $[Cp^*_2ZrH_3Li]_3$ (**75**) [71].



75

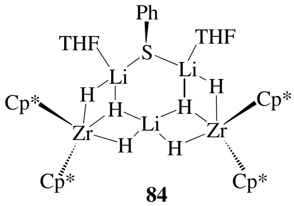
Reactivity studies of **70** and **75** demonstrated their ability to effect the oligomerization of primary phosphines [71–73]. In the dehydrocoupling of RPH_2 to P_5R_5, intermediates are thought to be the anionic Zr–phosphinidene, –diphosphinato and –triphosphinato



Scheme 10.

hydride derivatives, $[Cp^*_2ZrH(PR)]^-$ (**76**), $[Cp^*_2ZrH(PR)_2]^-$ (**77**) and $[Cp^*_2ZrH(PR)_3]^-$ (**78**). Using sterically demanding substituents an analog of **76** was crystallographically characterized [74].

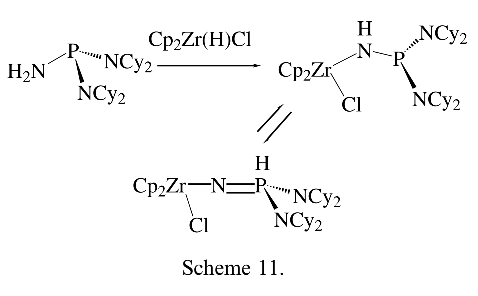
Reaction of $Ph_2PH(E)$ (E = S, Se) with **75** gave the bimetallic species $\{[Cp^*_2ZrH]_2(\mu\text{-}E)\}$ (E = S (**79**), Se (**80**)). The mechanism of these reactions was proposed to involve the formation of the intermediate anion $[Cp^*_2ZrH_2(EPPh_2)]^-$ (**81**), followed by loss of $HPPh_2$, dimerization and loss of Li_2E. The analogous reaction with $Ph_2PH(O)$ resulted simply in deprotonation of the phosphine oxide affording the tetrameric species $[Ph_2POLi(THF)]_4$. In contrast, reaction of **75** with Me_3NO gave the oxo-hydride species $[Cp^*_2ZrH\{OLi(THF)\}]_2$ (**82**) (Scheme 10) [75]. Related reactions of **75** with 2,6-diisopropylphenol, gave the monohydride derivative $Cp^*_2ZrH(OC_6H_32,6\text{-}i\text{-}Pr_2)$ (**83**), while the aniline and *o*-methoxyaniline gave the corresponding diamido-complexes $Cp^*_2Zr(NHR)_2$. In contrast, reaction of **75** with thiophenol afforded the hydride-bridged species $[(Cp^*_2ZrH_3)(LiTHF)]_2(LiSPh)$ (**84**) [76]. In related chemistry, reactions of the metallocene dihydrides $(t\text{-}BuC_5H_4)_2M(SH)_2$ (M = Zr, Hf) have been used to prepare bis-sulfide bridged dimers $(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)_2M(RC_5H_4)_2$ (R = H, *t*-Bu) [77].



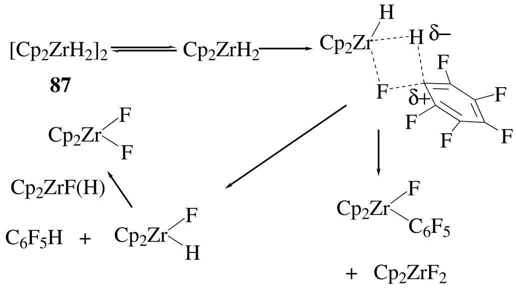
84

In related chemistry, Niecke and coworkers [78] have reported that the the reaction of $[P(NCy_2)_2(NH_2)]$ with Cp_2ZrHCl (**85**) yields the two tautomers of $Cp_2ZrCl(NPH(NCy_2)_2)$ (Scheme 11).

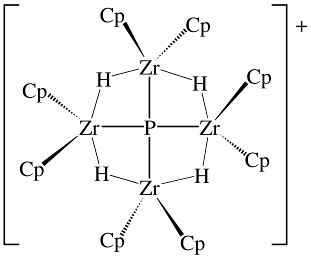
Driess et al. [79] have recently described the reaction of **85** with $[\{(Me_2N)_3P\}_2P^+BPh_4]$ in the presence of triethylamine. This yielded the remarkable planar phosphonium cation $[P\{Zr(H)Cp_2\}_4]^+BPh_4^-$ (**86**). This species is the first 'anti-van't Hoff-Le Bel' planar tetracoordinated phosphonium cation. Stabilization of this unusual geometry was attributed to the electropositive nature of the organometallic ligands, and the hydride bridges.



Scheme 11.



Scheme 12.



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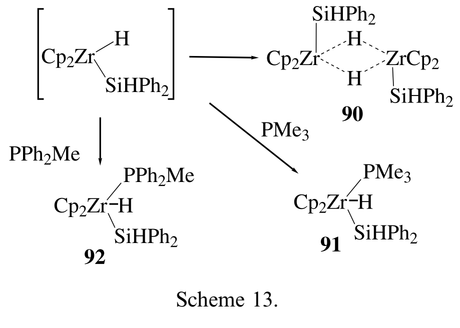
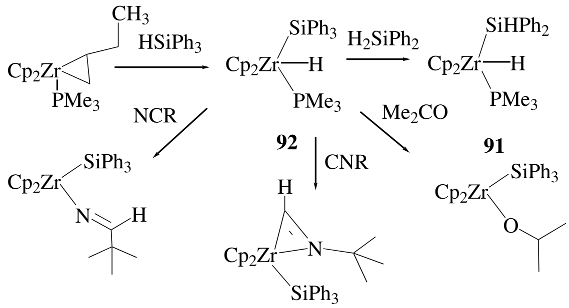
Jones and coworkers have recently reported the use of $(Cp_2ZrH_2)_2$ (**87**) in C–F bond cleavage [80]. The thermal reaction of **87** with C_6F_6 yields C–F activation and formation of $Cp_2Zr(C_6F_5)F$. The proposed mechanisms are thought to follow coordination of fluorine to the Zr center, leading to either reductive elimination of H_2 followed by oxidative addition of C_6F_6, or a concerted σ-bond metathesis reaction, to give C_6F_5H, and Cp_2ZrHF, which conproportionates to give Cp_2ZrF_2 and Cp_2ZrH_2 (Scheme 12) The related species Cp_3ZrH (**88**) was also reported to induce C–F bond activation of C_6F_6, yielding CpH, $Cp_2Zr(C_6F_5)F$, C_6F_5H, Cp_2ZrF_2 Cp_4Zr, and Cp_3ZrF [81].

In 1986, Harrod and coworkers discovered catalytic dehydrocoupling reactions of $RSiH_3$ by Cp_2ZrMe_2 [48]. In the related stoichiometric reactions, the bimetallic complexes $[Cp_2Zr(SiH_2R)(\mu\text{-}H)_2RHZrCp_2]$ (**89**) were obtained [82,83]. Similarly, $Cp_2Zr(n\text{-}Bu)_2$ was shown to catalyze the hydrosilation of alkenes [84]. A mechanism involving several Zr-hydride intermediates has been proposed and several derivatives including $[Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2]_2$ (**90**) and $[Cp_2ZrH(SiHPh_2)(L)]$ (L = PMe_3 (**91**), Ph_2PMe (**92**)) have been characterized. (Scheme 13). The phosphine stabilized monomers were



Scheme 13.



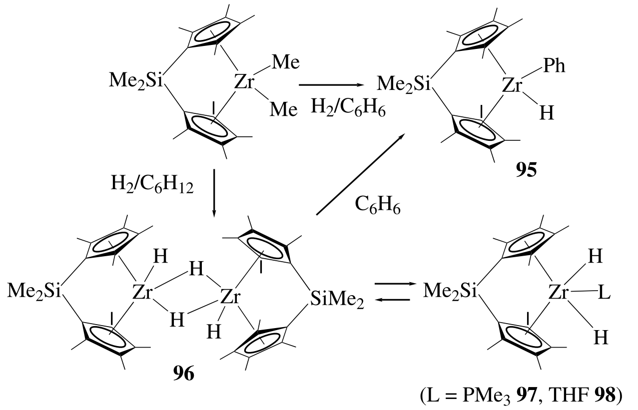
Scheme 14.

found to react with 1-octene to give the product of hydrosilation.

A closely related set of reactions has been reported by Buchwald and coworkers [85]. Addition of Ph$_3$SiH to solutions of the in situ generated Cp$_2$Zr(CH$_2$CHEt)(PMe$_3$) resulted in formation of [Cp$_2$Zr(H)(SiPh$_3$)(PMe$_3$)] (**93**). This species reacts with Ph$_2$SiH$_2$ to effect σ-bond metathesis, forming a mixture of isomers of **91**. Unsaturated organic substrates such as nitriles, ketones and isocyanates were found to insert into the Zr–H bond (Scheme 14). In contrast, reaction with acetylenes resulted in elimination of silane and the formation of a zirconocycle. The related silylamido complex Cp$_2$ZrH(N*t*-BuSiMe$_2$H) (**94**) is one of a number of compounds that had been previously shown to exhibit agostic β-Si–H interactions [86].

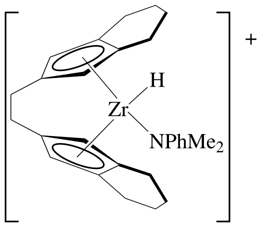
5.3. *Ansa-zirconocene hydride derivatives*

A substantial amount of research probing the 'ansa-effect' has been carried out by Parkin and coworkers [87]. These studies outline the subtle difference between the ansa-zirconocene [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrX$_2$ species and traditional metallocenes. Attempts to prepare the ansa-zirconocene analog of Cp$^*_2$ZrH$_2$ lead instead to C–H bond activation of benzene and formation of [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh(H) (**95**) (Scheme 15) [87]. Performing the reaction in cyclohexane gave the dihydride bridged dimer, [[Me$_2$Si(C$_5$Me$_4$)$_2$]ZrH(μ-H)]$_2$ (**96**). This species readily reacts with benzene to form **95** and could be converted to the monomeric derivatives [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrH$_2$(L) (PMe$_3$ (**97**), THF (**98**)) by upon addition of a donor ligand. Compound **96** also reacts with (CH$_2$=CH)$_2$Mg for the isolation of the first structurally characterized zirconocene ethylene-hydride complex {[Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(η^2-C$_2$H$_4$)H]$_2$Mg (**99**) [88]. This species could also be formed by the reaction of the [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrBr$_2$ with excess ethyl Grignard. Compound **99** can be considered a model for intermediates in catalytic olefin hydrogenation processes [89], and polymerization [90,91]. The unique reactivity observed with these ansa-systems was ascribed to the increased electrophilicity of the metal center.



Scheme 15.

A salt metathesis reaction of rac-(EBTHI)ZrCl$_2$ (**106**) [EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)] with NaEt$_3$BH, yielded the dihydride dimer [(EBTHI)ZrH(μ-H)]$_2$ (**100**) [92]. Subsequent reaction with [PhMe$_2$NH][Co(C$_2$B$_9$H$_{11}$)$_2$] afforded the monomeric cationic hydride complex [(EBTHI)ZrH(NPhMe$_2$)]$^+$ (**101**). The enantiomerically pure cation effected catalytic asymmetric hydrogenation of olefins, reducing 2-phenyl-1-butene under 100 atm of H$_2$, leading to an enantiomeric excess of only 23% [92].



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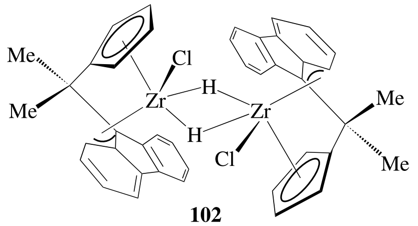
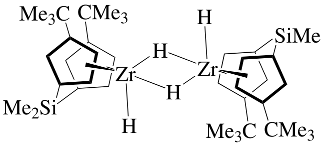
Analogous reaction of the related unsymmetrical ansa-zirconocene (Me$_2$C(η^5-C$_5$H$_4$)(η^5-Flu)ZrCl$_2$ (Flu = fluorenyl) and Li(Et$_3$BH), gave the hydrido–chloro species [Me$_2$C(C$_5$H$_4$)(Flu)ZrCl(μ-H)]$_2$ (**102**) [93]. In this compound the fluorenyl ligand adopts an unprecedented η^3-bonding mode.



102

Bercaw and coworkers [94] have also reported singly and doubly bridged ansa-zirconocene dihydride complexes prepared via hydrogenation of the precursor dimethyl complexes. Hydrogenation of {*meso*-Me$_2$Si(η^5-C$_5$H$_3$-3-CMe$_3$)$_2$}ZrMe$_2$ affords the isomeric dimeric dihydrides [{*meso*-Me$_2$Si(η^5-C$_5$H$_3$-3-CMe$_3$)$_2$}ZrH]$_2$(μ^2-H)$_2$ (**103**). The racemo isomer of Me$_2$Si(η^5-C$_5$H$_2$-2-

$SiMe_3$-4-$CMe_3)_2ZrMe_2$ reacts with H_2, affording the first monomeric ansa-zirconocene dihydride, $Me_2Si(\eta^5$-C_5H_2-2-$SiMe_3$-4-$CMe_3)_2ZrH_2$ (**104**). The doubly $[SiMe_2]$-bridged Zr di-Me complex $\{(Me_2Si)_2(\eta^5$-$C_5H_3)_2\}ZrMe_2$ undergoes hydrogenation under forcing conditions, to give a mixed trimeric species $[\{(Me_2Si)_2(\eta^5$-$C_5H_3)_2\}Zr]_3(\mu^3$-$H)_2(\mu^2$-$H)_3$ (**105**). The substituted doubly bridged zirconocene dihydrides $[\{(Me_2Si)_2(\eta^5$-C_5H-3,5-$(CHMe_2)_2)(\eta^5$-C_5H_2-4-$CHMeEt)\}ZrH]_2(\mu^2$-$H)_2$ (**106**) and $[(Me_2Si)_2(\eta^5$-C_5H-2,4-$(CHMe_2)_2)(\eta^5$-C_5H_2-4-$CHMe_2)ZrH]_2(\mu^2$-$H)_2$ (**107**) were also prepared and are shown to be robust dimers in solution.



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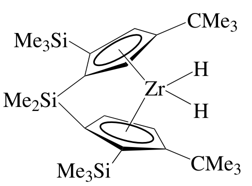

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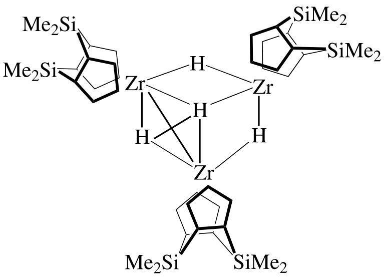
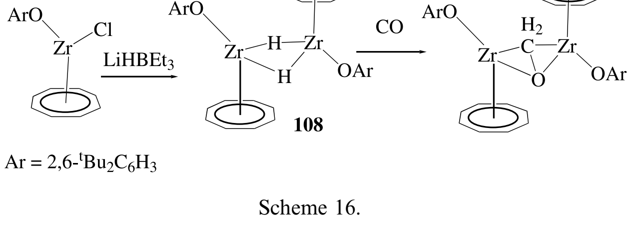


105

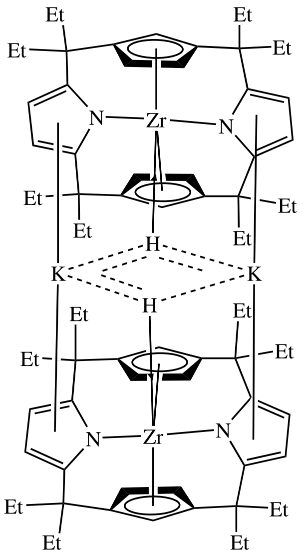
5.4. Non-Cp based Zr hydride derivatives

The species $Zr(\eta^8$-$C_8H_8)(O$-2,6-t-$Bu_2C_6H_3)Cl$ reacts with $LiHBEt_3$ affording the bridging hydride dimer $[\{Zr(\eta^8$-$C_8H_8)(O$-$Ar)\}_2(\mu$-$H)_2]$ (**108**) [95]. This formally 14 electron species reacts with CO to produce a formaldehyde complex (Scheme 16).

Nitrogen based ligand systems have been explored as well. For example, the cationic Zr-benziminidate derivative $[cis$-p-$CH_3C_6H_4C(NSiMe_3)_2)_2Zr(H)]^+$ (**109**) was found to be the active species in the catalytic isomerization of olefins [96]. The hydride was formed following insertion of the olefin into a Zr–methyl bond, with subsequent β-hydrogen elimination. *meso*-Octaethylporphyrinogen Zr-hydride derivatives $[\{(\eta^5:\eta^1:\eta^5:\eta^1$-$OEP)Zr(KH)]_2$ (**110**) and $[\{(\eta^5:\eta^1:\eta^5:\eta^1$-$OEP)Zr\}_4\{KH\}_8\cdot THF)_{10}]$ (**111**) are derived from reaction of $[(\eta^5:\eta^1:\eta^5:\eta^1$-$OEP)Zr(THF)$ with KH. The latter species contains a chain of Zr–H_2K units with both μ_2- and μ_3-hydrides [97].



Scheme 16.



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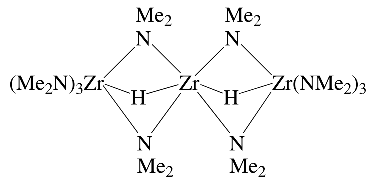
The unusual Zr_3-hydride species, $[(Me_2N)_3Zr(\mu$-$H)(\mu$-$NMe_2)_2]_2Zr$ (**112**) has recently been reported by Wu and coworkers [98]. It was obtained from the reaction of $Zr(NMe_2)_4$ with less than one equivalent of the silanes H_3SiPh, H_2SiPh_2, $H_2SiMePh$, or $HSi(NMe_2)Ph_2$. In contrast, reaction of $(Me_3Si)_3SiZr(NMe_2)_3$ and silane established an equilibrium involving the Zr-hydride species $[(Me_2N)_2ZrH(Si(SiMe_3)_3]$ (**113**).



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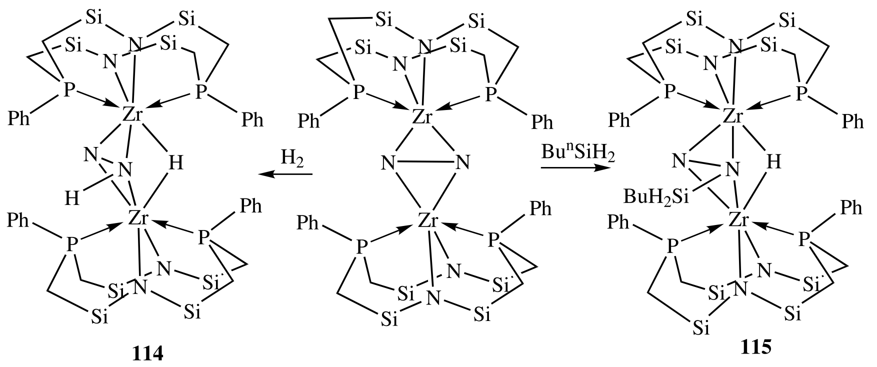
Fryzuk et al. have described the remarkable reaction of their dimeric $[(N_2P_2)Zr]_2(\mu$-$N_2)$ complex ($N_2P_2 = [PhP(CH_2SiMe_2N)]_2$) with H_2 or silane to give $((N_2P_2)Zr)_2(\mu$-$H)(\mu$-$NNH)$ (**114**) and $[(N_2P_2)Zr]_2(\mu$-$HN_2SiBuH_2)(\mu$-$H)$ (**115**) (Scheme 17) [99]. A recent neutron diffraction study and DFT calculations have confirmed the structure of **114** and shown that the reactions with H_2 and silane are exothermic while the corresponding reaction with CH_4 is endothermic [100].



Scheme 17.

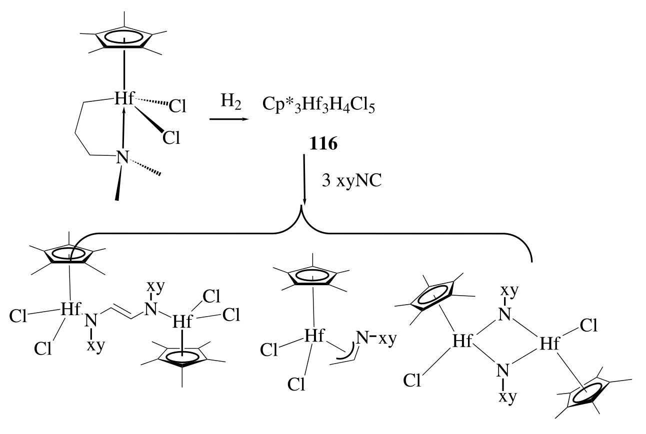
6. Hafnium

6.1. Mono-CpHf hydride derivatives

As briefly mentioned above, Teuben and coworkers have developed the systems containing alkyl tethered amino ligands [54]. Hydrogenolysis of the monoalkyl Hf species Cp*Hf{$(CH_2)_2NMe_2$}Cl_2 resulted in the formation of a polyhydride complex $Cp^*_3Hf_3(\mu-H)_4(\mu-Cl)_2Cl_3$ (**116**). This trinuclear species reacts with 2,6-xylylisocyanide to give a mixture of three products including a μ-enediamide complex [Cp*HfCl$_2$]$_2$[μ-xylNCH=CHNxyl] (xyl = 2,6-dimethylphenyl), an imido complex [Cp*Hf(μ-Nxyl)Cl]$_2$ and an azaallyl species, Cp*Hf(η^3-CH$_2$CHNxyl)Cl$_2$ (Scheme 18).

6.2. Hafnocene hydride derivatives

The first monomeric hafnium hydride, $Cp^*_2HfH_2$ (**117**) [101,102], was reported in 1985 by Bercaw and coworkers. This species was subsequently discovered to react with α,ω-dienes to give mononuclear and binuclear derivatives $Cp^*_2Hf((CH_2)_3CHCH_3)$ and $[Cp^*_2(H)Hf(\mu-CH_2)_nHf(H)Cp^*_2]$ ($n = 4–7$) (**118**). The corresponding reaction with one equivalent of allene gave the allyl hydride derivative (**119**), whereas in a 2:1 ratio, the mixture of products included $[Cp^*_2(H)Hf(CH_2)_3-Hf(H)Cp^*_2]$ (**120**). In a similar fashion, acetylene reacted with **117** to yield the stable species $[Cp^*_2(H)HfCH{=}CH_2]$ (**121**). No further reaction was observed with excess **117** (Scheme 19). Subsequent reactivity studies of **118** found that it behaved similarly to that previously reported for $Cp^*_2Hf(R)H$ [101,103]. For example, reaction of **118** with H_2 gave the respective alkane and **117**. Water reacted with these species to liberate the alkane and a mixture of $Cp^*_2Hf(OH)_2$ and $Cp^*_2Hf(H)(OH)$ (**122**). Several products were formed on reaction with ethylene or CO, but no polymerization of ethylene was evident. Tilley and coworkers have described related chemistry of the species CpCp*HfH(Si(SiMe$_3$)$_3$) (**123**) which loses silane in reactions with ethylene or acetylene giving the corresponding hafnocycles [104].

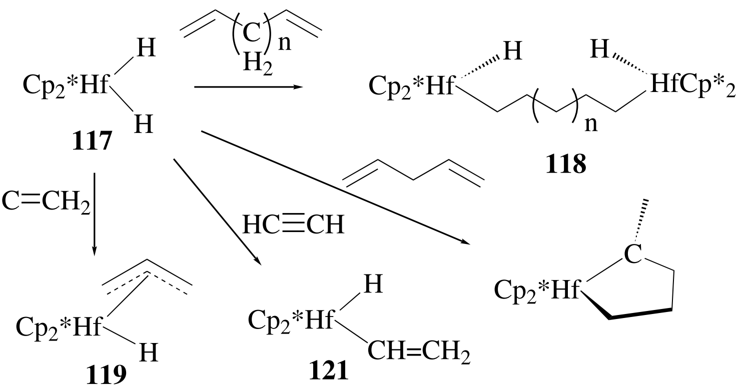


Scheme 18.

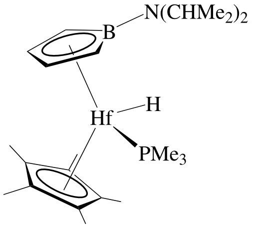
In a study developing synthetic routes to Hf–chalcogenide complexes, Gautheron and coworkers [105] have reported the reaction of a hafnocene hydride complex [(η^5-*t*-BuC$_5$H$_4$)$_2$Hf(H)(μ-H)]$_2$ (**124**) [106] with elemental Se or Te to give the dimers [(η^5-*t*-BuC$_5$H$_4$)$_2$Hf(μ-E)]$_2$. The analogous reaction with S_8, showed evidence of initial insertion into the Hf–H bond, to give (η^5-*t*-BuC$_5$H$_4$)$_2$Hf(SH)$_2$. This species reacts further with **124** to yield [(η^5-*t*-BuC$_5$H$_4$)$_2$Hf(S)]$_2$.

Primary and secondary phosphines react with **117** with extrusion of H_2 to give the phosphido derivsative $Cp^*_2Hf(H)(PRR')$ [R = R′ = Ph (**125**), R = H, R′ = Ph (**126**), R = H, R′ = Cy (**127**)]. Subsequent reactions with H_2, CO, and C_2H_4 gave PHPh$_2$ and **117**, $Cp^*_2Hf(CO)_2$ and the metallacyclopentane $Cp^*_2Hf(C_4H_8)$, respectively. However, CO_2 reacts to form $Cp^*_2Hf(H)(Ph_2PCO_2)$ (**128**). A second equivalent of CO_2 inserts into the Hf–H bond to give $Cp^*_2Hf(HCO_2)(Ph_2PCO_2)$ [107].

Use of an aminoborole ligand as a cyclopentadienyl analog has allowed the isolation of [Cp*{η^5-C$_4$H$_4$BN(CHMe$_2$)$_2$}Hf(H)(PMe$_3$)] (**129**) via the hydrogenolysis of the parent allylic complex [Cp*{η^5-C$_4$H$_4$BN(CHMe$_2$)$_2$}Hf(η^3-C$_3$H$_5$)(PMe$_3$)] [108].



Scheme 19.



129

6.3. *Non-Cp based Hf hydride derivatives*

In an manner analogous to the Zr chemistry the species, $[(Me_2N)_3Hf(\mu\text{-}H)(\mu\text{-}NMe_2)]_2Hf$ (**130**) has recently been reported by Wu and coworkers [109]. Reactions of this species with silanes have been probed.

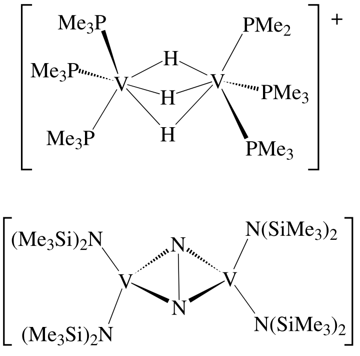
7. Vanadium

7.1. *Mono-CpV hydride derivatives*

Poliakoff and coworkers have reported a non-classical $V{-}H_2$ complex. Photolysis of $[CpV(CO)_4]$ under an atmosphere of H_2 in either *n*-heptane or liquid Xe led to the formation of $[CpV(CO)_3(\eta^2\text{-}H_2)]$ (**131**). The product was characterized by IR spectroscopy, revealing a weak band at 2642 cm^{-1}, which was assigned to the H–H stretch [110].

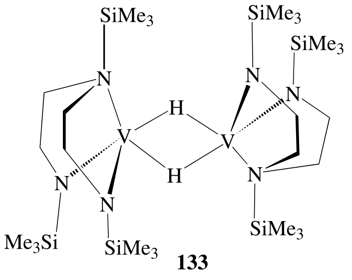
7.2. *Non-CpV hydride derivatives*

A structurally characterized V-hydride species, $[\{(Me_3P)_3V\}_2(\mu\text{-}H)_3][\{[(Me_3Si)_2N]_2V\}_2(\mu\text{-}N)_2]$ (**132**) was synthesized via hydrogenation of an amide-stabilized vanadacyclobutane [111]. This paramagnetic species was shown to have three hydrides by microanalytical data, and the liberation of three equivalents of H_2 upon degradation with HCl.



132

The complex $[\{V(N\{N''\}_2)Cl\}_2]$ containing the related chelating silylamino(disilylamido) ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]$ ($[N(N'')_2]$) reacts with KC_8 under H_2 to give the bridging hydride dimer $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ (**133**). The structure of this paramagnetic species was confirmed by X-ray diffraction [112].



133

8. Niobium

8.1. *Mono-CpNb hydride derivatives*

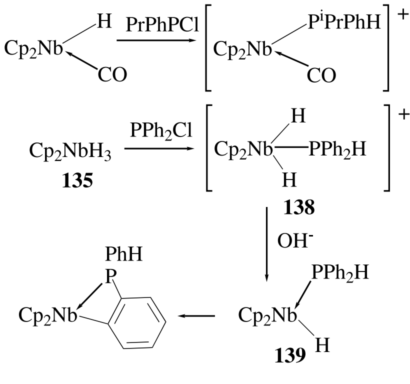
The photolysis of $CpNb(CO)_4$ with H_2 establishes an equilibrium between a classical Nb(III) dihydride $CpNb(CO)_3(H)_2$ (**134**) and a non-classical Nb(I) dihydrogen complex $CpNb(CO)_3(H_2)$ [113].

8.2. Niobocene hydride derivatives [10]

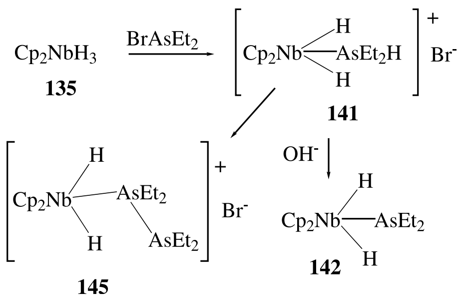
The reaction of Cp_2NbH_3 (**135**) with simple alkynes to form alkyne hydrido complexes $Cp_2NbH(RC{\equiv}CR')$ (**136**) has been known for some time [114,115]. In an application of such compounds, Herberich and Mayer [116] reacted **136** with alkynes and synthesized the novel carbenoid complex [$Cp_2Nb(C(R)C(R)C(R)CHR$]. Yasuda et al. have also reported similar systems [117].

In 1982, Foust et al. published the synthesis of a Nb(III) hydride: $Cp_2Nb(H)CO$ (**137**) [118]. Ten years later, this compound was reacted with PPh(*i*-Pr)Cl to form the ionic product [$Cp_2Nb(CO)$(P*i*-PrPhH)]Cl in high yield [119]. Subsequent treatment of this salt with NaOH gave the phosphido species [$Cp_2Nb(CO)$P(*i*-Pr)Ph)]. Nikonov et al. have used this general reaction mode quite extensively to form a multitude of main-group-niobocene derivatives. For example, in early work, [120] it was found that reaction of **135** with $ClPPh_2$ gave the ionic product [$Cp_2NbH_2(PHPh_2)$]Cl (**138**) quantitatively. This complex formally has two protons with differing acidities (Nb–H and P–H). Reaction of **138** with NaOH led to deprotonation of Nb giving the Nb(III) hydride–phosphine adduct [$Cp_2NbH(PHPh_2)$] (**139**). This species was also obtained directly from the reaction of Cp_2NbH_2Li (**140**) with PPh_2Cl. Compound **138** was unstable, losing H_2, to form the *ortho*-metalated product $Cp_2Nb(C_6H_4PPhH)$ (Scheme 20).

An analogous study targeted the first arsenic substituted niobocene [121]. Et_2AsBr inserts easily into the Nb–H bond of **135** to give the ionic compound [$Cp_2NbH_2(HAsEt_2)$]Br (**141**). Subsequent deprotonation of **141** with $NaN(SiMe_3)_2$, gave the monoarsenido complex $Cp_2NbH_2(AsEt_2)$ (**142**). In a similar manner, the first NbSb derivative, [$Cp_2NbH_2SbPh_2$] (**143**) [122] and [$Cp_2NbH_2PbMe_3$] (**144**) [123] were prepared. The difference in reactivity between **138** and **141** was ascribed to the lower As–H bond energy compared to that of the P–H bond. Excess Et_2AsBr lead to nucleophilic substitution at As affording [$Cp_2NbH_2(AsEt_2AsEt_2)$]Br (**145**) (Scheme 21). In related chemistry, Stephan and coworkers have shown that reactions of **135** or $\{\eta^5\text{-}C_5H_4SiMe_3\}_2NbH_3$ (**146**) with $PhPH_2$ affords $Cp_2'NbH[(PR)_2]$ (**147**) [124].



Scheme 20.



Scheme 21.

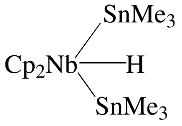
The heterobimetallic species [$\{(C_5H_3(SiMe_3)_2)_2NbH_3\}_2M$][$PF_6$] (M = Cu (**148**), Ag (**149**), Au (**150**)) have also been prepared via the reaction of **135** with [$MPPh_3$][PF_6] [125]. NMR studies are consistent with two bridging hydride ligands between the disparate metals centers [126,127].

This general reaction scheme was also applied to other Group 5 derivatives [128]. Niobocene silyl hydride derivatives have been prepared by oxidative addition of SiH to coordinatively unsaturated niobocene centers [129–133]. For example, **146** undergoes thermal loss of H_2 and oxidative addition of silane to give [$\{\eta^5\text{-}C_5H_4SiMe_3\}_2NbH_2(SiR_3)$] (**151**).[134] Spectroscopic data suggest the presence of only one isomer, in which the silyl group is central between the two hydrido ligands.

The analog of complex **138** was obtained by Otero and coworkers [135] from the initial formation of the phosphonium salt [$(\eta^5\text{-}C_5H_4SiMe_3)_2NbH_2(PHPh_2)$]Cl (**152**) by reaction with PPh_2Cl, followed by deprotonation with NaOH. PPh_2Cl also reacts with [$(\eta^5\text{-}C_5H_4SiMe_3)_2NbH(L)$] (L = CN(xylyl) (**153**), CO (**154**), xylyl = 2,6-dimethylphenyl (**155**))rsqb; to give the analogous salts. Protonation of **152** with CF_3CO_2H gave dihydrogen complex [$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(\eta^2\text{-}H_2)(L)$]$CF_3CO_2$ (L = $PHPh_2$ (**153**), [135] CNR (**154**) [136]). This complex transforms to the transoid dihydrides [$(\eta^5\text{-}C_5H_4SiMe_3)_2NbH_2(PHPh_2)$]$CF_3CO_2$ (**155**) upon warming. Complex **152** also undergoes insertion of CS_2 or CO_2 to generate the species [$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(PHPh_2)(\eta^1\text{-}E\text{–}E(E)CH)$] which rapidly loses phosphine to give [$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(\eta^1\text{-}E\text{-}E(E)CH)$] (E = S, O).

Otero and coworkers [137] have also shown that **153**–**155** reacts with $B(C_6F_5)_3$ or BF_3 to give zwitterionic compounds of the form [$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)(\mu\text{-}HBX_3)$] (X = C_6F_5, F) (L = CN(xylyl) (**156**), CO (**157**), xylyl = 2,6-dimethylphenyl (**158**));. Excess ligand results in the displacement of the bridging borohydride yielding the corresponding salts. The species **146** reacts in acetone with $B(C_6F_5)_3$ to effect hydride transfer and loss of H_2 forming the $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb][(Me_2CHO)B(C_6F_5)_3]$.

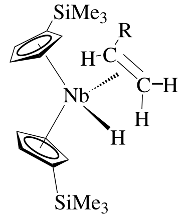
Otero and coworkers have successfully expanded on the above reaction system to include the oxidative addition of Ph_3GeH and Ph_3SnH isolating the series of complexes: $[\{\eta^5\text{-}C_5H_4SiMe_3\}_2Nb(H)_2(EPh_3)]$ (E = Si (**159**), Ge (**160**), Sn (**161**)). Only **159** was found to react with CO, and $CN(2,6\text{-}Me_2C_6H_3)$ with reductive elimination of $HSiPh_3$ forming $[\{\eta^5\text{-}C_5H_4SiMe_3\}_2Nb(H)(CO)]$ (**162**) and $[\{\eta^5\text{-}C_5H_4SiMe_3\}Nb(H)\{CN(2,6\text{-}Me_2C_6H_3)\}]$ (**163**), respectively [138]. Similarly, only **159** underwent hydrogenolysis to give Cp_2NbH_3, suggesting that, Nb–Si is the weakest of the three Nb–E bonds. Finally, **159** reacted with either $HGePh_3$ or $HSnPh_3$ to give **160** and **161**, respectively. Similar reaction of alkyl- or aryltin halide (X_nSnR_{4-n}, $n = 1, 2$) and Cp_2NbH_3 gave $[Cp_2NbH_2(SnX_{3-n}R_n)]$ (R = Me, Ph, Et; $n = 2, 3$; X = Cl, Br). These compounds were also formed via reaction of the analogous silyl-derivative with the Sn halides. Interestingly, the compounds $Cp_2NbH(SiR_3)_2$ do not undergo reaction with organotin halides. However, reaction of Me_3SnNMe_2 with **135** yields $[Cp_2NbH(SnMe_3)_2]$ (**164**). A recent neutron diffraction study of the bis(silyl) complex $Cp_2NbH(SiMe_2Cl)_2$ (**165**) confirmed the central position of the hydride ligand in the plane bisecting the niobocene moiety [139].



164

In a related report [140], activated alkynes were found to react with **135** to give olefin-hydride niobocene complexes $Cp_2NbH(\eta^2\text{-}RHCCH_2)$ (**166**). These remarkable reactions are thought to occur via initial stereospecific *trans*-insertion, followed by intramolecular rearrangement. Similarly, activated alkynes react with complexes of the form $[\{\eta^5\text{-}C_5H_4SiMe_3\}_2NbH(CNR)]$ via *cis*-insertion into the Nb–H bond to give (*E*)-alkenyl products. Interestingly, the analogous reactions with $[\{\eta^5\text{-}C_5H_4SiMe_3\}_2NbHCO]$ (**167**) gave a mixture of both (*E*) and (*Z*) isomers under kinetic control [140].

Otero's group has prepared the *exo* and *endo* isomers $[\{\eta^5\text{-}C_5H_4SiMe_3\}_2Nb(H)(\eta^2\text{-}PhCH{=}CH_2)]$ (**168**) from the reaction of the corresponding Nb–H species and styrene. In contrast, formation of **168** by metathesis of $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$ with $PhCH_2CH_2MgBr$, afforded only the *endo* isomer [141]. In a similar fashion, alkylation of $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$ with an other Grignard reagents gave intermediates that also underwent β-hydride elimination to give a series of olefin-hydride complexes [142]. These complexes react with CO, CO_2 or CS_2 to give $Cp'_2NbR(L)$ (L = CO, CO_2, CS_2), respectively [143].

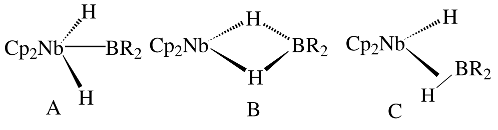


168

The complexes $(C_5H_3RR')_2NbH_3$ (R = R′ = H (**134**), $SiMe_3$ (**169**), R = H, R′ = $SiMe_3$ (**145**)) were prepared by reaction of $(C_5H_3RR')_2NbCl_2$ with Red-Al, followed by hydrogenolysis. These species show temperature dependent H–H coupling constants in the NMR spectra [130,144]. The quantum mechanical nature of this phenomenon is thought to be due to exchange coupling between two hydrides. These observations have been interpreted in terms of the interconversion of Nb-dihydride and Nb-dihydrogen species.

Thermal reactions of the species **145** with a variety of mercapto-, hydroxy-, amino-pyridine, or pyrimidines have been reported by Otero and coworkers [145]. These result in a series of Nb thiolate-, oxo-, amido-pyridine, and -pyrimidine derivatives. These reactions are thought to proceed through initial loss of H_2 from the parent **145**, generating a highly reactive 16-e mono-hydride species.

Green and coworkers have recently reported ansa-niobocene-borohydrides of the form ansa-$(C_5H_3(t\text{-}Bu)CH_2)_2Nb(\mu^2\text{-}H_2BH_2)$ (**170**) that adopt conventional binding borohydride structures [146]. In contrast, Hartwig and Gala [147] have studied reactions of **134** with HBR_2 (R = $O_2C_6H_4$, C_8H_{14}) that proceed via loss of H_2 yielding $[Cp_2Nb(\mu^2\text{-}H_2BR_2)]$ (**171**). Three depictions of the bonding in the $Nb(\mu^2\text{-}H_2BR_2)$ moiety have been proposed (Scheme 22). With catechol borane and 9-BBN the structures were described in terms of structures A–C, respectively. Related complexes $Cp^*_2Nb(H_2B\text{–}(O_2C_6H_4))$ (**172**) were prepared from $Cp^*_2NbH\text{–}(CH_2CHR)$ (**173**). Mechanisms for the catalysis of hydroboration of olefins by **172** have been proposed to involve Nb hydride intermediates [148].



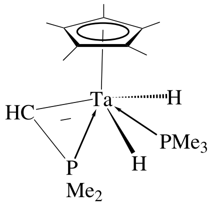
Scheme 22.

9. Tantalum

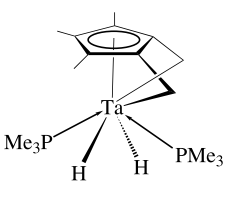
9.1. Mono-CpTa hydride derivatives

The photochemical reaction of $CpTa(CO)_4$ with H_2 gave the classical dihydride complex $[CpTa(CO)_3H_2]$ (**174**) [113]. This stands in contrast to the non-classical Nb analog.

The complex formulated as $Cp^*Ta(PMe_3)_2$ exists as a set of two cyclometallated dihydride species, $Cp^*TaH_2(PMe_3)(CHPMe_2)$ (**175**) and $(C_5Me_3(CH_2)_2)$-$TaH_2(PMe_3)_2$ (**176**), which do not readily interconvert. The reactivity of **175** has been explored [149]. Reaction with phosphines forms an equilibrium of the phosphine adducts. Reaction with the chelating phosphine bis(dimethylphosphinoethane) resulted in initial replacement of a PMe_3 ligand followed by chelation and hydrogen migration from the Ta–H to the metalated phosphine yielding $Cp^*TaH_2(Me_2PCH_2CH_2PMe_2)(CH_2PMe_2)$ (**176**). In contrast, reaction of **175** with CO results in the double hydrogen migration affording a mixture of *cis*- and *trans*-$Cp^*Ta(CO)_2(PMe_3)_2$ and $Cp^*Ta(CO)_3PMe_3$. Reaction with H_2 quantitatively converts **175** into the previously reported species $[Cp^*Ta(PMe_3)_2H_4]$ (**178**) [150]. In a similar manner, **175** reacts with MeX (X = Br, I, Cl) to form the mono- and dihalo-complexes $[Cp^*Ta(PMe_3)(H)(X)(\eta^2\text{-}CHPMe_2)]$ (**179**) and $[Cp^*Ta(X_2)(\eta^2\text{-}CHPMe_2)]$.



175



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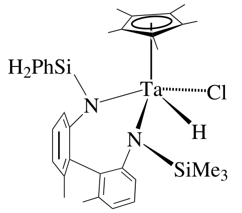
Tilley and coworkers have reported a number of compounds based on the Cp*Ta fragment that includes an additional imido–amido ligand [151]. The species $Cp^*Ta(NC_6H_3Me(C_6H_3MeNSiMe_3))Cl$ reacts with $PhSiH_3$ to effect SiH addition across the Ta=N bond yielding $Cp^*TaH(PhH_2SiNC_6H_3Me(C_6H_3MeNSiMe_3)Cl$ (**180**) and $Cp^*Ta(PhH_2SiNC_6H_3Me(C_6H_3MeNSiPhH_2))Cl_2$ (**181**). This species did not react with D_2 but underwent loss of the trimethylsilyl group from the ligand, to reform an imido–amido species. The related imido-species $Cp^*(2,6\text{-}i\text{-}Pr_2C_6H_3N)Ta(Si(SiMe_3)_3)H$ (**182**) [152] also reacts with $PhSiH_3$ to form a mixture of products including the dihydride dimer $[Cp^*(2,6\text{-}i\text{-}Pr_2C_6H_3N)TaH(\mu\text{-}H)]_2$ (**183**), the paramagnetic compound $[Cp^*_2(2,6\text{-i-}Pr_2C_6H_3N)Ta_2H_2(\mu\text{-}(2,6\text{-i-}Pr_2C_6H_3)NSiHPh)]$ (**184**) and the diamagnetic species $[Cp^*_2Ta_2H_2(\mu\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)NSiHPh)_2]$ (**185**) [153]. Compound **182** also reacts with CO to initially form the adduct $[Cp^*(2,6\text{-}i\text{-}Pr_2C_6H_3N)Ta(Si(SiMe_3)_3)H(CO)$ (**186**) which is transformed to the six-membered tantalacycle $[Cp^*(2,6\text{-}i\text{-}Pr_2C_6H_3N)Ta(CH_2SiMe_2Si(SiMe_3)_2CH_2O)$ (**187**).



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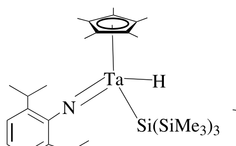
9.2. Tantalocene hydride derivatives [10]

The species of $Cp^*_2TaH_3$ (**188**) [154] has been known for some time [155]. Parahydrogen induced polarization has been employed to examine the mechanism of formation of **188** from the addition of H_2 to the benzyne complex $Cp^*_2Ta(C_6H_4)H$ (**189**). An intermediate dihydride complex, $Cp^*_2Ta(C_6H_5)H_2$ (**190**) has been inferred in this process [156].

A number of reactions of **188** with conjugated dienes have been carried out by Bercaw and coworkers [157]. Reaction with excess allene gave the η^3-allyl tantalocene complex $[Cp^*_2Ta(\eta^3 - C_3H_5)]$ with formation of H_2 and propene. This new allyl complex was stable at room temperature, but at 80 °C underwent rearrangement to give an η^1-propenylidene complex $[Cp^*_2TaH(C{=}CHMe)]$ (**191**). Mechanistic studies on this interconversion inferred a 1-propyne complex intermediate. Reaction of **188** with 1,3-butadiene, under similar conditions, gave an initial product $[Cp^*_2TaH(\eta^2 - CH_2{=}CHCH{=}CH_2)]$ (**192**) which rearranged to $[Cp^*_2TaH(\eta^2 - CH_2{=}C{=}CHMe)]$ (**193**). This compound was synthesized independently via reaction of $Cp^*_2TaCl_2$ with two equivalent of *trans*-crotylMgBr. The reaction of **193** with CO affords only the *cis*-butenyl complex, indicating that **193** was the *exo*-isomer. A third product formed



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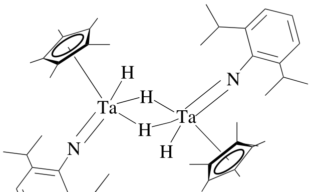

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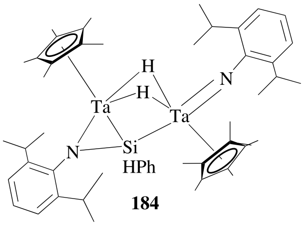

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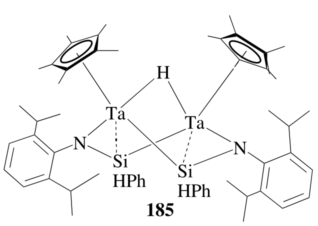

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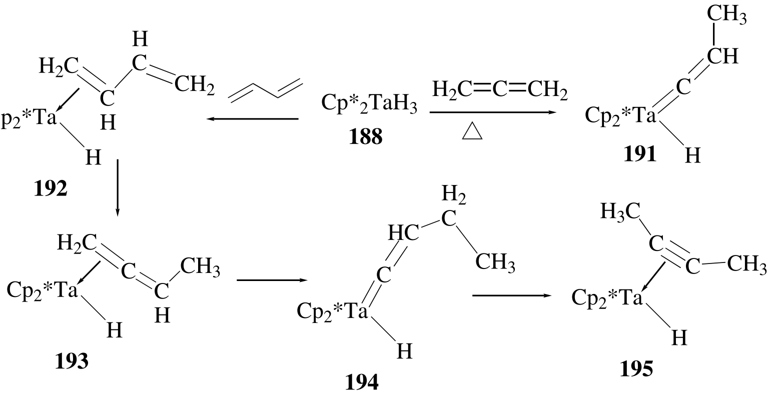
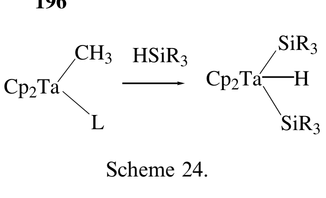


Scheme 23.

in this sequence was the butenylidene complex [Cp$^*_2$TaH(=C=C(H)Et)] (**194**). A final product of the reaction of butadiene with **188** was the but-2-yne complex [Cp$^*_2$Ta(H)(MeC≡CMe)] (**195**). This latter product could also be prepared by reaction of the **188** with but-2-yne (Scheme 23).

Thermal or photochemical reactions of Cp_2TaH_3 (**196**) with hydrosilanes were reported to give complexes of the form [$Cp_2Ta(H)_2(SiR_3)$] [133]. In these cases, the major isomer was the symmetrical structure with the silyl moiety occupying the central position between the two hydride ligands. Excess silanes reacted with $Cp_2TaCH_3(L)$ (L = CO, PMe_3, $CH_2{=}CH_2$) to give the Ta(V)–bis(silyl) complexes [$Cp_2Ta(H)(SiR_3)_2$] (SiR_3 = $SiMeH_2$ (**197**), $SiMe_2H$ (**198**), $SiMe_3$ (**199**), $SiMe_2Cl$ (**200**), $Si(OMe)_3$ (**201**)). These too formed the symmetric isomer but for $Cp_2Ta(H)(SiMeH_2)_2$ (**202**) where both isomers were observed (Scheme 24). In the presence of PMe_3 or CO, these Ta–bis(silyl) complexes were thermolyzed to give the corresponding Ta(III) mono-silyl compounds [$Cp_2Ta(L)(SiR_3)$] (L = PMe_3, CO).

Soon after the report of the niobocene–boryl complexes by Harwig et al. [146] the species [Cp_2TaH_2-$BO_2C_6H_4$] (**203**) [158] was prepared by reaction of chlorocatecholborane with $(Cp_2TaH_2Li)_x$ (**204**) [159]. The related compound Cp$^*_2$$TaH_2BO_2C_2H_4$ (**205**) was prepared in a manner described for the Nb analog [147]. These d^0-boryl complexes exist as a mixture of the *endo*- and *exo*-isomers. A mechanistic study of the reaction of catecholborane with the complexes $Cp_2Ta(CH_2{=}CHR)H$ (**206**) was recently reported. It revealed that reaction of *endo*- and *exo*-[$Cp_2TaH(CH_2{=}CHMe)$] (**207**) with $HB(O_2C_6H_4)$ gave only the *endo*-isomer of **203** and the product of hydroboration *n*-$PrB(O_2C_6H_4)$ [160].



Scheme 24.

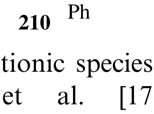
The first tantalocene phosphido derivative was prepared by reaction of Ph_2PCl with **196** yielding [$Cp_2TaH_2(HPPh_2)$]Cl (**208**) [161]. This complex was easily deprotonated to give [$Cp_2TaH_2(PPh_2)$] (**209**). This species reacted with Ph_2PH to give traces of [$Cp_2Ta(HPPh_2)(PPh_2)$], whereas removal of H_2 afforded the diphosphanato complex [$Cp_2TaH(\eta^2\text{-}(PPh)_2$] (**210**) [162,163]. In contrast, reaction of Me_2PCl with **196** led to the formation of [$Cp_2Ta(H)(HPMe_2)$] (**211**). Both **209** and **211** were shown to act as metalloligands, reacting with $M(CO)_4L_2$ (M = Cr, Mo, W) to give μ-phosphido μ-hydrido bimetallic complexes of the form $Cp_2TaH(\mu\text{-}H)(\mu\text{-}PPh_2)M(CO)_4$ (**212**). In related work, the terminal sulfido hydrido species (C_5H_4t-Bu)$_2TaH(S_2)$ (**213**) [164–166] has been used to obtain sulfide-bridged heterobimetallics [167,168].

The diphosphanato complexes [$Cp_2TaH(PR)_2$] (R = Ph (**214**), Cy (**215**)) have also been prepared via thermolysis of **196** with H_2PR [124]. Interestingly, reaction of P_4 with **196** affords the parent species [$Cp_2TaH(PH)_2$] (**216**). Variable temperature and 2D-NMR studies on **216** were consistent with a transoid disposition of the hydrogen atoms on P at low temperature [124].

Bercaw and coworkers [169] have described the synthesis of the species Cp$^*_2$Ta(O)H (**217**), Cp$^*_2$Ta(NH)H (**218**), and Cp$^*_2$Ta(NPh)H (**219**) from Schrock's methylidene species Cp$^*_2$$Ta(CH_2)H$ (**220**) or from Cp$^*_2$Ta(THF)Cl [170]. The related chalcogenide species [$(t\text{-}BuC_5H_4)_2TaH(\eta^2\text{-}Se_2)$] (**221**) and [Cp$^*_2$$Ta(\eta^2Se_2)H$] (**222**) were prepared from (t-$BuC_5H_4)_2TaH_3$ (**223**) or **188** with elemental Se, respectively [171,172]. Performance of this reaction under ambient lighting afforded the complex [Cp$^*_2$Ta(Se)SeH] (**224**). Both tautomers **222** and **224** reacted with MeI, to form Cp$^*_2$Ta(Se)I. Similarly, reaction with PMe_3 gave [Cp$^*_2$Ta(Se)H] (**225**) which reacted with MeI, to give [Cp$^*_2$$TaHI_2$] (**226**). Alkylation of Cp$^*_2$Ta(Se)I with MeLi lead to the formation of the selenoformaldehyde species $[Cp^*_2Ta(\eta^2-SeCH_2)H]$ (**227**). Se abstraction was also effected by the reaction of **221** with $P(OEt)_3$ giving $[(t\text{-}BuC_5H_4)_2Ta(Se)H]$ (**228**). Subsequent reduction of **228** with Na/Hg, followed by hydrolysis gave $[(t\text{-}BuC_5H_4)_2Ta(SeH)H_2$ (**229**). (Scheme 25).

In an analogous manner $[Cp^*_2Ta(\eta^2\text{-}Te)_2H]$ (**230**) was prepared [173]. Reaction with PMe_3 gave $[Cp^*_2Ta(Te)H]$ (**231**). The compound $[Cp^*_2Ta(\eta^2\text{-}TeCH_2)H]$ (**232**) was prepared by reaction of Schrock's alkylidene **220** with Te in the presence of PMe_3. Under thermal conditions, **232** was converted to the more stable telluride–methyl isomer $[Cp^*_2Ta(Te)CH_3]$ [173].

In recent work, Green and coworkers [174] have reported the generation of $Cp_2TaH_2(\eta^1\text{-}HB(C_6F_5)_3)]$ (**233**) by reaction of the parent trihydride complexes with the Lewis acid $B(C_6F_5)_3$. In related recent work protonation of $Cp'_2TaH(CO)$ ($Cp' = C_5H_5$ (**234**), C_5H_4t-Bu (**235**)) by $HBF_4 \cdot Et_2O$ was shown to give $[Cp'_2TaH_2(CO)BF_4]$ ($Cp' = C_5H_5$ (**236**), C_5H_4t-Bu (**237**)) at −78 °C. These compounds exists as two isomers, the minor one being the *trans*-dihydride and the major isomer the dihydrogen complexes $[Cp_2Ta(\eta^2\text{-}H_2)(CO)]BF_4$. VT-NMR studies revealed a large kinetic isotope effect for the classical rotation of H_2. DFT calculations suggest a transition state in which H_2 is only coordinated through σ-donation from the H–H bond. Analogous protonation of $Cp_2TaH_2(SiMe_2Ph)$ (**238**) by $(Et_2O)_2 \cdot H[B(3,5\text{-}C_6H_3(CF_3)_2)_4]$ gives the dinuclear complex $[(Cp_2TaH_2)_2(\mu\text{-}H)][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$ (**239**) [175]. The heterobimetallic complexes $[(C_5H_4t\text{-}Bu)_2TaH_3MPPh_3][PF_6]]$ (M = Cu (**240**), Ag (**241**), Au (**242**)) have been prepared via the reaction of **223** with $[MPPh_3][PF_6]$ [125].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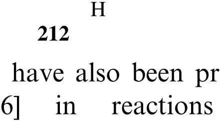
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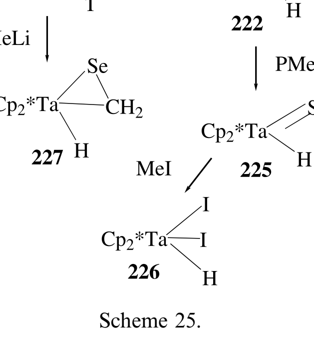
Related cationic species have also been prepared by Sauvageot et al. [176] in reactions of $(t\text{-}BuC_5H_4)_2Ta(H)(OCOCF_3)_2$ (**243**) prepared from the acidolysis of **223** with excess trifluoroacetic acid. Subsequent reaction of **243** with electrophiles (H^+ or CPh_3^+) yielded the cationic species $[(t\text{-}BuC_5H_4)_2Ta(H)_2(L)]^+$ ($L = SMe_2$ (**244**), tetrahydrothiophene (**245**), CN*t*-Bu (**246**), PMe_2Ph (**247**), and CO (**248**)). Alternatively, these cationic species could be prepared by oxidation of **223** by $[Cp_2Fe][PF_6]$ in the presence of a donor. In the case of acetonitrile, oxidation of **223** gave the isomeric azaalkenylidene complexes $[(t\text{-}BuC_5H_4)_2Ta(H)(NCHMe)]PF_6$ (**249**). A cationic heterobimetallic complex $[(t\text{-}BuC_5H_4)_2Ta(H)_2(\mu\text{-}H)Nb\text{-}(CO)Cp_2]PF_6$ (**250**) was also obtained by reaction of $[(t\text{-}BuC_5H_4)_2Ta(H)_2(L)]^+$ with **136**.

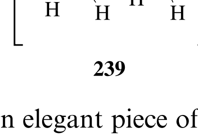

Scheme 25.

Recently, Shin and Parkin [177] have probed the ansa-effect by comparing $(Me_2Si(C_5Me_4)_2)TaH_3$ (**251**) and $(Me_2Si(C_5Me_4)_2)TaH(C_2H_4)$ (**252**) with the Cp^*_2Ta analogs. Kinetic studies showed that the ansa-bridge enhances the rate of both reductive elimination of H_2 and insertion of ethylene into a Ta–H bond.

Analogs of tantalocene species have also been prepared using the borollide ligands. The parent complexes $[Cp^*\{\eta^5\text{-}C_4H_4BN(CHMe_2)_2\}TaMe_2]$ or $[Cp^*\{\eta^5\text{-}C_4H_4BMe\}TaMe_2]$ undergo hydrogenolysis in the presence of PMe_3 to give the air-stable species $[Cp^*\{\eta^5\text{-}C_4H_4BN(CHMe_2)_2\}Ta(PMe_3)(H)_2]$ (**253**) and $[Cp^*\{\eta^5\text{-}C_4H_4BMe\}Ta(PMe_3)(H)_2]$ (**254**), respectively [178,179].

9.3. Non-CpTa hydride derivatives

The penta-hydride species $[TaH_5(dmpe)_2][LiHBEt_3]$ (**255**) was obtained via treatment of $[TaCl_4(dmpe)_2]$ with $Li[HBEt_3]$. The Li is located between the Ta and B atoms and is bonded to the hydride of the triethylborohydride while interacting with two of the Ta–H 2 groups [180].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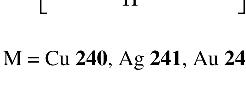
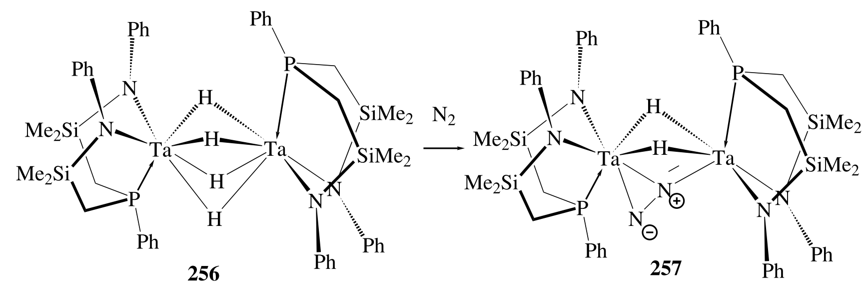

M = Cu **240**, Ag **241**, Au **242**

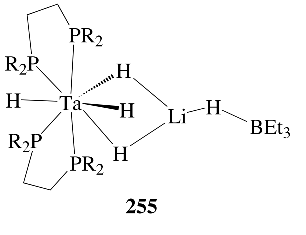
In an elegant piece of work, Fryzuk et al. have shown that the species $[(PhP(CH_2SiMe_2NPh)_2)TaMe_3]$ undergoes hydrogenolysis to produce a purple dinuclear diamagnetic Ta(IV) hydride $[(PhP(CH_2SiMe_2NPh)_2)\text{-}Ta(\mu\text{-}H)_2]_2$ (**256**) [181]. This species, upon exposure to N_2 loses H_2 forming a novel dinitrogen complex $[(PhP(CH_2SiMe_2NPh)_2))TaH]_2((\mu\text{-}\eta^1\text{-}\eta^2\text{-}N_2)$ (**257**) (Scheme 26). Spectroscopic and crystallographic evidence suggest that the N_2 moiety is bound to the two tantalum centers unsymmetrically [182]. The reaction of **257** with propene generates the end-on bound dinitrogen complex $[(PhP(CH_2SiMe_2NPh)_2))TaCH_2CH_2CH_3]_2N_2$



Scheme 26.

while with $PhCH_2Br$ results in the formation of $(PhP(CH_2SiMe_2NPh)_2))Ta(\mu\text{-}\eta^1\text{-}\eta^2\text{-}N_2CH_2Ph)(\mu\text{-}H)_2TaBr(PhP(CH_2SiMe_2NPh)_2))$ (**258**) [183]. Fryzuk et al. have also investigated the parmagnetic species $[(PhP(CH_2SiMe_2NPh)_2)Ta)_2(\mu\text{-}H)_4]^+I$ derived from reaction of **256** with MeI [181].

Some interesting seven coordinate Ta(V) hydride complexes have been reported by Rothwell and coworkers [184]. Hydrogenolysis of $[Ta(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2Cl(CH_2SiMe_3)_2]$ or $[Ta(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(CH_2SiMe_3)_3]$ in the presence of phosphines gave seven-coordinate di- and tri-hydride compounds **259** and **260**, respectively. Hydrogenolysis of the analogous 2,6-diphenylphenoxide complexes led to 2,6-dicyclohexylphenoxide derivative **261**. This observation lead to the development of the catalytic hydrogenation of arene rings in cyclohexane solutions of **259** [185]. In related work Rothwell's group has also shown that $[TaH(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2Cl_2(PMe_2Ph)_2]$ (**262**) reacts with nitriles to give η^2-iminoformyl complexes [186].



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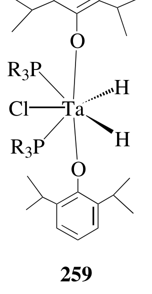

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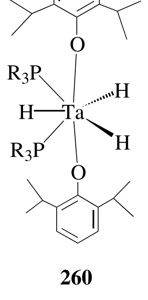

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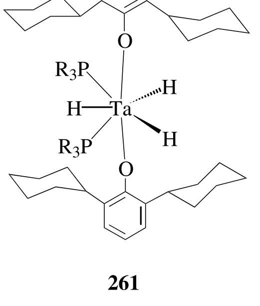

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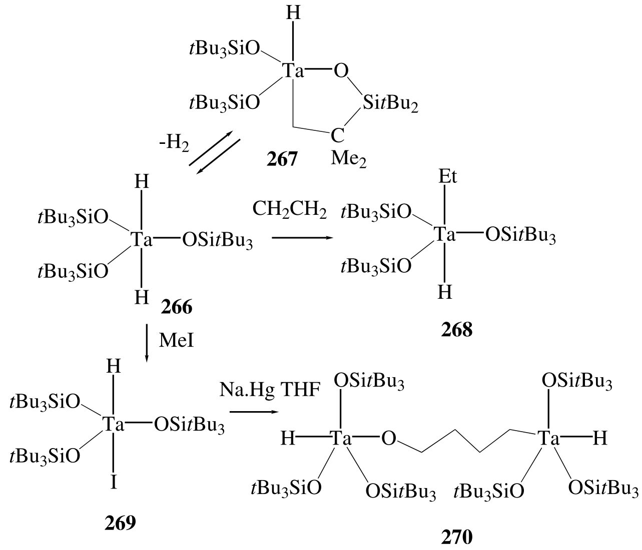
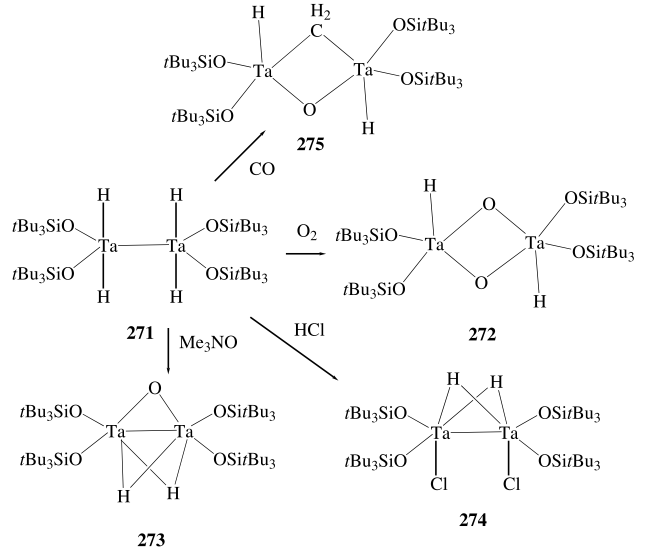
Rothwell and coworkers [187] have also studied the reactions of $[TaH_2(O\text{-}2,6\text{-}Ph_2C_6H_3)_2Cl(PMe_3)_2]$ (**263**), $[TaH_2(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2Cl(PMe_2Ph)_2]$ (**264**) and $[TaH_2(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2Cl(PMePh_2)_2]$ (**265**) with olefins and alkynes. The nature of the products varies with the ancillary aryloxide ligands. Olefin and alkyne complexes of the form $[Ta(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(olefin)Cl(PMe_3)]$ are formed in the reactions of **263**. In contrast, the analogous reactions of **264** result in dehydrogenation yielding $[Ta(OC_6H_3i\text{-}Pr,\ \eta^2\text{-}CMeCH_2)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)Cl(PMe_2Ph)_2]$. Labeling studies showed that both Ta-hydrides are transferred to the olefinic substrate. In the case of **265** reaction with styrene generates the cyclometalated species $[Ta(O\text{-}2,6\text{-}t\text{-}BuC_6H_3t\text{-}CMe_2CH_2)(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)(CH_2CH_2Ph)Cl]$. Related theoretical studies have probed the H–Ta–H angles as a function of the ligand effects in six-coordinate complexes of the form $[TaH_2(OR)_2LL']^+$ [188].

The related dihydride species $(t\text{-}Bu_3SiO)_3TaH_2$ (**266**) was prepared by reduction of $(t\text{-}Bu_3SiO)_3TaCl_2$ under an atmosphere of H_2. Compound **266** undergoes cyclometallation to give $(t\text{-}Bu_3SiO)_2TaH(OSi(t\text{-}Bu_2)CMe_2CH_2)$ (**267**) which is reversed in the presence of H_2. Compound **266** also reacts with ethylene to give the species $(t\text{-}Bu_3SiO)_3TaH(Et)$ (**268**) and with MeI to give $(t\text{-}Bu_3SiO)_3TaHI$ (**269**). The related insertion reactions of $H_2C{=}CHX$ (X = OR; R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, $CH{=}CH_2$, Ph) with **266** afforded $(t\text{-}Bu_3SiO)_3TaHCH_2CH_2X$ which undergo β-X-elimination to give ethylene and $(t\text{-}Bu_3SiO)_3TaHX$ [189]. Complex **266** reacts with Na in THF to give the linked dimer $[(t\text{-}Bu_3SiO)_3Ta(H)]_2(\mu\text{-}OCH_2CH_2CH_2CH_2)$ (**270**) (Scheme 27). This related species $[(t\text{-}Bu_3SiO)_2TaH_2]_2$ (**271**), generated by reduction of $(t\text{-}Bu_3SiO)_2TaCl_3$ under H_2 reacts with O_2 to give the di-oxo bridged species $[(t\text{-}Bu_3SiO)_2Ta(\mu\text{-}O)H]_2$ (**272**) or with Me_3NO to give $[(t\text{-}Bu_3SiO)_2TaH]_2(\mu\text{-}O)(\mu\text{-}H)_2$ (**273**). HCl adds to **271** to give the complex $[(t\text{-}Bu_3SiO)_2TaCl(\mu\text{-}H)]_2$ (**274**). Studies of the reaction of **250** with CO showed the formation of several species including $[(t\text{-}Bu_3SiO)_2TaH]_2(\mu\text{-}O)(\mu\text{-}CH_2)$ (**275**), $[(t\text{-}Bu_3SiO)_4Ta_2H](\mu\text{-}O)(\mu\text{-}CH_2)$ (**276**), and $[(t\text{-}Bu_3SiO)_2Ta]_2(\mu\text{-}O)_2(\mu\text{-}CHCH_3)$ (Scheme 28). The relation of this carbonylation chemistry was discussed in relation to the Fischer–Tropsch process [190].



Scheme 27.



Scheme 28.

10. Summary and outlook

This review has described the advances made in early metal hydride chemistry over the past decade. For the most part, this review has focused on the synthesis and reactivity of these compounds. Early metal hydrides have been shown to be useful in a variety of stoichiometric transformations as well as catalytic processes. This reactivity, though diverse, has still been limited by the solubility of most of the hydride derivatives, owing to their propensity for forming aggregates. As the general trend in organometallic chemistry of the early metals moves away from cyclopentadienyl ligand systems, new monomeric, soluble hydride complexes are anticipated. Such systems offer even richer and more diverse chemistry for the future.

References

[1] S. Gambarotta, Comprehensive Organometallic Chemistry, Vol 4, 543, Pergamon Press, New York, 1995.
[2] E. Fernandez-Megia, Synlett 7 (1999) 1179.
[3] J.-P. Majoral, M. Zablocka, A. Igau, N. Cenac, Chem. Ber. 129 (1996) 879.
[4] M. Kalesse, Acros Org. Acta 1 (1995) 29.
[5] L. Chen, F.A. Cotton, W.A. Wojtczak, Angew. Chem. Int. Ed. 34 (1995) 1877.
[6] L. Chen, F.A. Cotton, W.A. Wojtczak, Inorg. Chem. 36 (1997) 4047.
[7] F.A. Cotton, J. Lu, M. Shang, W.A. Wojtczak, J. Am. Chem. Soc. 116 (1994) 4364.
[8] F. Lefebvre, J.-M. Basset, J. Mol. Catal. Sect. A 146 (1999) 3.
[9] G.S. McGrady, A.J. Downs, Coord. Chem. Rev. 197 (2000) 95.
[10] A. Antinolo, F. Carrillo-Hermosilla, M. Fajardo, J. Fernandez-Baeza, S. Garcia-Yuste, A. Otero, Coord. Chem. Rev. 193–195 (1999) 43.
[11] J.F. Harrod, Coord. Chem. Rev. 206–207 (2000) 493.
[12] P.J. Shapiro, E. Brunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.
[13] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
[14] Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, V.G. Young, Jr., Organometallics 15 (1996) 2720.
[15] G.C. Bazan, W.P. Schaefer, J.E. Bercaw, Organometallics 12 (1993) 2126.
[16] M.D. Fryzuk, G.R. Giesbrecht, S.J. Rettig, Can. J. Chem. 78 (2000) 1003.
[17] J.R. Hagadorn, J. Arnold, Organometallics 15 (1996) 984.
[18] S. Hajela, W.P. Schaefer, J.E. Bercaw, J. Organomet. Chem. 532 (1997) 45.
[19] K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 2238.
[20] C.J. Schaverien, J.H.G. Frijns, H.J. Heeres, J.R. van den Hende, J.H. Teuben, A.L. Spek, Chem. Commun. (1991) 642.
[21] C.J. Schaverien, Organometallics 13 (1994) 69.
[22] M. Booij, B.-J. Deelman, R. Duchateau, D.S. Postma, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 3531.
[23] A.Z. Voskoboynikov, I.N. Parshina, A.K. Shestakova, K.P. Butin, I.P. Beletskaya, L.G. Kuz'mina, J.A.K. Howard, Organometallics 16 (1997) 4041.
[24] B.-J. Deelman, W.M. Stevels, J.H. Teuben, M.T. Lakin, A.L. Spek, Organometallics 13 (1994) 3881.
[25] E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606.
[26] B.-J. Deelman, E.A. Bijpost, J.H. Teuben, Chem. Commun. (1995) 1741.
[27] J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045.
[28] W.P. Kretschmer, S.I. Troyanov, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 284.
[29] K.H. Den Haan, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053.
[30] R. Duchateau, C.T.v. Wee, J.H. Teuben, Organometallics 15 (1996) 2291.
[31] R. Duchateau, T. Tuinstra, E.A.C. Brussee, A. Meetsma, P.T.v. Duijnen, J.H. Teuben, Organometallics 16 (1997) 3511.

[32] J. Okuda, S. Verch, R. Sturmer, T.P. Spaniol, J. Organomet. Chem. 605 (2000) 55.
[33] S.I. Troyanov, H. Antropiusova, K.J. Mach, J. Organomet. Chem. (1992) 49.
[34] V. Varga, K. Mach, M. Polasek, P. Sedmera, J. Hellier, U. Thewalt, S.I. Troyanov, J. Organomet. Chem. (1996) 241.
[35] S.I. Troyanov, K. Mach, V. Varga, Organometallics 12 (1993) 3387.
[36] G.A. Luinstra, J.H. Teuben, J. Am. Chem. Soc. 114 (1992) 3361.
[37] J.E. Bercaw, J. Am. Chem. Soc. 96 (1974) 5087.
[38] J.M. de Wolf, A. Meetsma, J.H. Teuben, Organometallics 14 (1995) 5466.
[39] W.W. Lukens, P.T. Matsunaga, R.A. Andersen, Organometallics 17 (1998) 5240.
[40] A.I. Sizov, T.M. Zvukova, V.K. Bel'sky, B.M. Bulychev, Russ. Chem. Bull. 47 (1998) 1186.
[41] M. Horacek, J. Hiller, U. Thewalt, M. Polasek, K. Mach, Organometallics 16 (1997) 4185.
[42] J.F. Harrod, R. Shu, H.-G. Woo, E. Samuel, Can. J. Chem. 79 (2001) 1075.
[43] G. Henken, E. Weiss, Chem. Ber. Recl. 106 (1973) 1747.
[44] L. Hao, A.-M. Lebuis, J.F. Harrod, E. Samuel, J. Chem. Soc. Chem. Commun. (1997) 2193.
[45] L. Hao, A.-M. Lebuis, J.F. Harrod, J. Chem. Soc. Chem. Commun. (1998) 1089.
[46] S. Xin, H.G. Woo, J.F. Harrod, E. Samuel, A.M. Lebuis, J. Am. Chem. Soc. 119 (1997) 5307.
[47] F. Gauvin, J. Britten, E. Samuel, J.F. Harrod, J. Am. Chem. Soc. 114 (1992) 1489.
[48] C.A. Aitkens, J.F. Harrod, E. Samuel, J. Am. Chem. Soc. 108 (1986) 4059.
[49] Z.K. Sweeney, J.L. Polse, R.G. Bergman, R.A. Anderson, Organometallics 18 (1999) 5502.
[50] J.B. Love, H.C.S. Clark, F.G.N. Cloke, J.C. Green, P.B. Hitchcock, J. Am. Chem. Soc. 121 (1999) 6843.
[51] J.R. Hagadorn, J. Arnold, Angew. Chem. Int. Ed. Engl. 37 (1998) 1729.
[52] Y. Wielstra, S. Gambarotta, A.L. Spek, Organometallics 9 (1990) 572.
[53] J.R. van den Hende, B. Hessen, A. Meetsma, J.H. Teuben, Organometallics 9 (1990) 537.
[54] C. Visser, J.R. van den Hende, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 20 (2001) 1620.
[55] W.J. Highcock, R.M. Mills, J.L. Spencer, P. Woodward, J. Chem. Soc. Dalton Trans. (1986) 821.
[56] C.J. Harlan, S.G. Bott, A.R. Barron, J. Chem. Soc. Dalton Trans. (1997) 637.
[57] C.J. Curtis, R.C. Haltiwanger, Organometallics 10 (1991) 3220.
[58] H.-G. Woo, W.P. Freeman, T.D. Tilley, Organometallics 11 (1992) 2198.
[59] A.-M. Larsonneur, R. Choukroun, Organometallics 12 (1993) 3216.
[60] P.J. Chirik, M.W. Day, J.E. Bercaw, Organometallics 18 (1999) 1873.
[61] R. Choukroun, F. Dahan, A.-M. Larsonneur, E. Samuel, J. Petersen, P. Meunier, C. Sornay, Organometallics 10 (1991) 374.
[62] Z. Guo, P.K. Bradley, R.F. Jordan, Organometallics 11 (1992) 2690.
[63] A.G. Carr, D.M. Dawson, M. Thornton-Pett, M. Bochmann, Organometallics 18 (1999) 2933.
[64] J. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 37 (1998) 496.
[65] F.-C. Liu, J. Liu, E.A. Meyers, S.G. Shore, J. Am. Chem. Soc. 122 (2000) 6106.
[66] M.C. Fermin, D.W. Stephan, J. Am. Chem. Soc. 117 (1995) 12645.
[67] L.E. Schock, T.J. Marks, J. Am. Chem. Soc. 110 (1988) 7701.
[68] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. (1978) 2716.
[69] K. Khan, C.L. Raston, B.W. Skelton, A.H. White, Organometallics 16 (1997) 3252.
[70] R.J. Wehmschulte, P.P. Power, Polyhedron 18 (1999) 1885.
[71] N. Etkin, A.J. Hoskin, D.W. Stephan, J. Am. Chem. Soc. 119 (1997) 11420.
[72] N. Etkin, M.C. Fermin, D.W. Stephan, J. Am. Chem. Soc. 119 (1997) 2954.
[73] A.J. Hoskin, D.W. Stephan, Angew. Chem. Int. Ed. Engl. 40 (2001) 1865.
[74] M.C. Fermin, J. Ho, D.W. Stephan, Organometallics 14 (1995) 4247.
[75] A.J. Hoskin, D.W. Stephan, Organometallics 18 (1999) 2479.
[76] A.J. Hoskin, D.W. Stephan, Organometallics 19 (2000) 2621.
[77] G. Tainturier, M.F., G. Trouve-Bellan, B.J. Gautheron, Organomet. Chem. (1989) 321.
[78] G. Schick, M. Raab, D. Gudat, M. Nieger, E. Niecke, Angew. Chem. Int. Ed. Engl. 37 (1998) 2390.
[79] M. Driess, J. Aust, K. Merz, C. van Wullen, Angew. Chem. Int. Ed. Engl. 38 (1999) 3677.
[80] B.L. Edelbach, A.K.F. Rahman, R.J. Lachicotte, W.D. Jones, Organometallics 18 (1999) 3170.
[81] W.W. Lukens, R.A. Andersen, Organometallics 14 (1995) 3435.
[82] Y. Mu, C. Aitken, B. Cote, J.F. Harrod, Can. J. Chem. 69 (1990) 264.
[83] C.A. Aitken, E. Samuel, J.F. Harrod, Can. J. Chem. 64 (1986) 1677.
[84] T. Takahashi, M. Hasegawa, N. Suzuki, M. Suburi, C.J. Rousset, P.E. Fanwick, E. Negishi, J. Am. Chem. Soc. 113 (1991) 8564.
[85] K.A. Kreutzer, R.A. Fisher, W.M. Davis, E. Spaltenstein, S.L. Buchwald, Organometallics 10 (1991) 4031.
[86] L.J. Procopio, P.J. Carroll, D.H. Berry, J. Am. Chem. Soc. 116 (1994) 177.
[87] H. Lee, P.J. Desrosiers, I. Guzei, A.L. Rheingold, G. Parkin, J. Am. Chem. Soc. 120 (1998) 3255.
[88] H. Lee, T. Hascall, P.J. Desrosiers, G. Parkin, J. Am. Chem. Soc. 120 (1998) 5830.
[89] T. Takahashi, N. Suzuki, M. Kageyama, Y. Nitto, M. Saburi, E. Negishi, Chem. Lett. (1991) 1579.
[90] W.E. Piers, Chem. Eur. J. 4 (1998) 13.
[91] R.H. Grubbs, G.W. Coates, Acc. Chem. Res. 29 (1996) 85.
[92] R.B. Grossman, R.A. Doyle, S.L. Buchwald, Organometallics 10 (1991) 1501.
[93] M. Bochmann, S.J. Lancaster, M.B. Hursthouse, M. Mazid, Organometallics 12 (1993) 4718.
[94] P.J. Chirik, L.M. Henling, J.E. Bercaw, Organometallics 20 (2001) 534.
[95] P. Berno, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Chem. Commun. (1991) 109.
[96] C. Averbuj, M.S. Eisen, J. Am. Chem. Soc. 121 (1999) 8755.
[97] D. Jacoby, S. Isoz, C. Floriani, K. Schenk, A. Chiesi-Villa, C. Rizzoli, Organometallics 14 (1995) 4816.
[98] X. Liu, Z. Wu, Z. Peng, Y.-D. Wu, Z. Xue, J. Am. Chem. Soc. 121 (1999) 5350.
[99] M.D. Fryzuk, J.B. Love, S.J. Rettig, V.G. Young, Science (Washington DC) 275 (1997) 1445.
[100] H. Basch, D.G. Musaev, K. Morokuma, M.D. Fryzuk, J.B. Love, W.W. Seidel, A. Albinati, T.F. Koetzle, W.T. Klooster, S.A. Mason, J. Eckert, J. Am. Chem. Soc. 121 (1999) 523.
[101] D.M. Roddick, M.D. Fryzuk, P.F. Seidler, G.L. Hillhouse, J.E. Bercaw, Organometallics 4 (1985) 97.
[102] J.E. Bercaw, J.R. Moss, Organometallics 11 (1992) 639.
[103] D.M. Roddick, J.E. Bercaw, Chem. Ber. 122 (1989) 1579.
[104] G.L. Casty, C.G. Lugmair, N.S. Radu, T.D. Tilley, J.F. Walzer, D. Zargarian, Organometallics 16 (1997) 8.

[105] G. Tainturier, B. Gautheron, M. Fahim, J. Organomet. Chem. 373 (1989) 193.
[106] G. Couturier, G. Tainturier, B. Gautheron, J. Organomet. Chem. 195 (1980) 291.
[107] G.A. Vaughan, G.L. Hillhouse, A.L. Rheingold, Organometallics 8 (1989) 1760.
[108] A. Pastor, A.F. Kiely, L.M. Henling, M.W. Day, J.E. Bercaw, J. Organomet. Chem. 528 (1997) 65.
[109] X. Liu, Z. Wu, H. Cai, Y. Yang, T. Chen, C.E. Vallet, R.A. Zuhr, D.B. Beach, Z.-H. Peng, Y.-D. Wu, T.E. Concolino, A.L. Rheingold, Z. Xue, J. Am. Chem. Soc. 123 (2001) 8011.
[110] M.T. Haward, M.W. George, S.M. Howdle, M. Poliakoff, J. Chem. Soc. Chem. Commun. (1990) 913.
[111] P. Berno, S. Gambarotta, Angew. Chem. Int. Ed. Engl. 34 (1995) 822.
[112] G.P. Clancy, H.C.S. Clark, G.K.B. Clentsmith, F.G.N. Cloke, P.B. Hitchcock, J. Chem. Soc. Dalton Trans. (1999) 3345.
[113] M.T. Haward, M.W. George, P. Hamley, M. Poliakoff, J. Chem. Soc. Chem. Commun. (1991) 1101.
[114] J.A. Labinger, J. Schwartz, J. Am. Chem. Soc. 97 (1975) 1596.
[115] J.A. Labinger (Ed.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon Press, Oxford, UK, 1982.
[116] G.E. Herberich, H. Mayer, Organometallics 9 (1990) 2655.
[117] H. Yasuda, H. Yamamoto, T. Arai, A. Nakamura, J. Chen, Y. Kai, N. Kasal, Organometallics 10 (1991) 4058.
[118] D.F. Foust, R.D. Rogers, M.D. Rausch, J.L. Atwood, J. Am. Chem. Soc. 104 (1982) 5646.
[119] G. Bonnet, M.M. Kubicki, C. Moise, R. Lazzaroni, P. Salvadori, G. Vitulli, Organometallics 11 (1992) 964.
[120] G.I. Nikonov, D.A. Lemenovskii, J. Lorberth, Organometallics 13 (1994) 3127.
[121] G.I. Nikonov, J. Lorberth, K. Harms, D.A. Lemenowski, Inorg. Chem. 34 (1995) 2461.
[122] G.I. Nikonov, L.G. Kuzmina, J.A.K. Howard, Organometallics 16 (1997) 3723.
[123] G.I. Nikonov, E.V. Avtomonov, W. Massa, Chem. Ber. Recl. 130 (1997) 1629.
[124] N. Etkin, M.T. Benson, S. Courtenay, M.J. McGlinchey, A.D. Bain, D.W. Stephan, Organometallics 16 (1997) 3504.
[125] A. Antinolo, F. Carrillo-Hermosilla, B. Chaudret, M. Fajardo, J. Fernandez-Baeza, M. Lanfranchi, H.-H. Limbach, M. Maurer, A. Otero, M.A. Pellinghelli, Inorg. Chem. 35 (1996) 7873.
[126] V.I. Bakhmutov, E.V. Vorontsov, E.V. Bakhmutova, G. Boni, C. Moise, Inorg. Chem. 38 (1999) 1121.
[127] A. Antinolo, F. Carrillo-Hermosilla, B. Chaudret, M. Fajardo, Fernandez-Baeza, M. Lanfranchi, H.-H. Limbach, M. Maurer, A. Otero, M.A. Pellinghelli, Inorg. Chem. 35 (1996) 7873.
[128] G.I. Nikonov, L.G. Kuzmina, J. Lorberth, J.A.K. Howard, Eur. J. Inorg. Chem. (1999) 825.
[129] J.S. Allison, B.J. Aylett, H.M. Colquhoun, J. Organomet. Chem. 112 (1976) 67.
[130] M.D. Curtis, L.G. Bell, W.M. Butler, Organometallics 4 (1985) 701.
[131] D.H. Berry, Q. Jiang, J. Am. Chem. Soc. 109 (1987) 6211.
[132] C. Aitken, J.-P. Barry, F. Gauvin, J.F. Harrod, A. Malek, D. Rousseau, Organometallics 8 (1989) 1732.
[133] Q. Jiang, P.J. Carroll, D.H. Berry, Organometallics 10 (1991) 3648.
[134] A. Antinolo, F. Carrillo, M. Fajardo, A. Otero, M. Lanfranchi, M.A. Pellinghelli, Organometallics 14 (1995) 1518.
[135] A. Antinolo, F. Carrillo-Hermosilla, J. Fernandez-Baeza, S. Garcia-Yuste, A. Otero, J. Sanchez-Prada, E. Villasenor, Eur. J. Inorg. Chem. (2000) 1437.
[136] A. Antinolo, F. Carrillo-Hermosilla, M. Fajardo, S. Garcia-Yuste, A. Otero, S. Camanyes, F. Maseras, M. Moreno, A. Lledos, J.M. Lluch, J. Am. Chem. Soc. 119 (1997) 6107.
[137] A. Antinolo, F. Carrillo-Hermosilla, J. Fernandez-Baeza, S. Garcia-Yuste, A. Otero, J. Sanchez-Prada, E. Villasenor, J. Organomet. Chem. 609 (2000) 123.
[138] A. Antinolo, F. Carrillo-Hermosilla, A. Castel, M. Fajardo, J. Fernandez-Baeza, M. Lanfranchi, A. Otero, M.A. Pellinghelli, G. Rima, J. Satge, E. Villasenor, Organometallics 17 (1998) 1523.
[139] V.I. Bakhmutov, J.A.K. Howard, D.A. Keen, L.G. Kuzmina, M.A. Leech, G.I. Nikonov, E.V. Vorontsov, C.C. Wilson, Dalton (2000) 1631.
[140] A. Antinolo, F. Carrillo-Hermosilla, M. Fajardo, S. Garcia-Yuste, M. Lanfranchi, A. Otero, M.A. Pellinghelli, S. Prashar, E. Villasenor, Organometallics 15 (1996) 5507.
[141] A. Antinolo, F. Carrillo, S. Garcia-Yuste, A. Otero, Organometallics 113 (1994) 2761.
[142] A. Antinolo, F. Carrillo-Hermosilla, I. del Hierro, A. Otero, M. Fajardo, Y. Mugnier, Organometallics 16 (1997) 4161.
[143] A. Antinolo, I. del Hierro, M. Fajardo, S. Garcia-Yuste, A. Otero, O. Blaque, M.M. Kubicki, J.J. Amaudrut, Organometallics 15 (1996) 1966.
[144] A. Antinolo, B. Chaudret, G. Commenges, M. Fajardo, F. Jalon, R.H. Morris, A. Otero, C.T. Schweitzer, J. Chem. Soc. Chem. Commun. (1988) 1210.
[145] A. Antinolo, F. Carrillo-Hermosilla, J. Fernandez-Baeza, A.M. Fernandez de toro, S. Garcia-Yuste, A. Otero, J.C. Perez-Flores, A.M. Rodriguez, Inorg. Chim. Acta 302 (2000) 131.
[146] S.L.J. Conway, L.H. Doerrer, M.L.H. Green, M.A. Leech, Organometallics 19 (2000) 630.
[147] J.F. Hartwig, S.R. De Gala, J. Am. Chem. Soc. 116 (1994) 3661.
[148] D.R. Lantero, D.L. Ward, M.R. Smith, III, J. Am. Chem. Soc. 119 (1997) 9699.
[149] H.M. Anstice, H.H. Fielding, V.C. Gibson, C.E. Housecroft, T.P. Kee, Organometallics 10 (1991) 2183.
[150] J.M. Mayer, J.E. Bercaw, J. Am. Chem. Soc. 104 (1982) 2157.
[151] T.I. Gountchev, T.D. Tilley, J. Am. Chem. Soc. 119 (1997) 12831.
[152] U. Burckhardt, T.D. Tilley, J. Am. Chem. Soc. 121 (1999) 6328.
[153] U. Burckhardt, G.L. Casty, T.D. Tilley, T.K. Woo, U. Rothlisberger, Organometallics 19 (2000) 3830.
[154] V.C. Gibson, W.J. Bruton, J.E. Bercaw, R.D. Sanner, Organometallics 5 (1986) 976.
[155] T.M. Zvukova, A.I. Sizov, Izv. Akad. Nauk. Ser. Khim. (1995) 2050.
[156] S.P. Millar, D.L. Zubris, J.E. Bercaw, R. Eisenberg, J. Am. Chem. Soc. 120 (1998) 5329.
[157] V.C. Gibson, G. Parkin, J.E. Bercaw, Organometallics 10 (1991) 220.
[158] D.R. Lantero, D.H. Motry, D.L. Ward, M.R. Smith, III, J. Am. Chem. Soc. 116 (1994) 10811.
[159] M.J. Bunker, A. De Cain, M.L.H. Green, J.J.E. Moreau, N. Siganporia, J. Chem. Soc. Dalton Trans. (1980) 2155.
[160] D.R. Lantero, S.L. Miller, J.-Y. Cho, D.L. Ward, M.R. Smith, III, Organometallics 18 (1999) 235.
[161] G.I. Nikonov, L.G. Kuzmna, P. Mountford, D.A. Lemenovskii, Organometallics 14 (1995) 3588.
[162] J.-C. Leblanc, C. Moise, J. Organomet. Chem. (1989) C3.
[163] O. Lavastre, G. Bonnet, G. Boni, M.M. Kubicki, C. Moise, J. Organomet. Chem. (1997) 141.
[164] H. Brunner, M.M. Kubicki, J.-C. LeBlanc, C. Moise, F. Volpato, J. Wachter, J. Chem. Soc. Chem. Commun. (1993) 851.
[165] H.-J. Bach, H. Brunner, J. Wachter, M.M. Kubicki, J.-C. Leblanc, C. Moise, F. Volpato, B. Nuber, M.L. Ziegler, Organometallics 11 (1992) 1403.
[166] J.E. Nelson, G. Parkin, J.E. Bercaw, Organometallics 11 (1992) 2181.
[167] H. Brunner, S. Challet, M.M. Kubicki, J.-C. Leblanc, C. Moise, F. Volpato, J. Wachter, Organometallics 14 (1995) 3623.

[168] S. Challet, O. Blacque, G. Gehart, M.M. Kubicki, J.-C. Leblanc, C. Moise, H. Brunner, J. Wachter, New J. Chem. 21 (1997) 903.

[169] G. Parkin, A. van Asselt, D.J. Leahy, L. Whinnery, N.G. Hua, R.W. Quan, L.M. Henling, W.P. Schaefer, B.D. Santarsiero, J.E. Bercaw, Inorg. Chem. 31 (1992) 82.

[170] D.M. Antonelli, W.P. Schaefer, G. Parkin, J.E. Bercaw, J. Organomet. Chem. 462 (1993) 213.

[171] H.J. Shin, G. Parkin, Organometallics 14 (1995) 1104.

[172] H. Brunner, M.M. Kubicki, J.-C. Leblanc, W. Meier, C. Moise, A. Sadorge, B. Stubenhofer, J. Wachter, R. Wanninger, Eur. J. Inorg. Chem. (1999) 843.

[173] H.J. Shin, G. Parkin, Organometallics 13 (1994) 2147.

[174] L.H. Doerrer, A.J. Graham, D. Haussinger, M.L.H. Green, J. Chem. Soc. Dalton Trans. (2000) 813.

[175] S. Sabo-Etienne, V. Rodriguez, B. Donnadieu, B. Chaudret, H. Abou el Makarim, J.-C. Barthelat, S. Ulrich, H.-H. Limbach, C. Moise, New J. Chem. 25 (2001) 55.

[176] P. Sauvageot, A. Sadorge, B. Nuber, M.M. Kubicki, J.-C. Leblanc, C. Moiese, Organometallics 18 (1999) 2133.

[177] J.H. Shin, G. Parkin, J. Chem. Soc. Chem. Commun. (1999) 887.

[178] G.C. Bazan, S.J. Donnelly, G. Rodriguez, J. Am. Chem. Soc. 117 (1995) 2671.

[179] C.K. Sperry, G.C. Bazan, W.D. Cotter, J. Am. Chem. Soc. 121 (1999) 1513.

[180] D.M. Dawson, A. Meetsma, J.B. Roedelof, J.H. Teuben, Inorg. Chim. Acta 259 (1997) 237.

[181] M.D. Fryzuk, S.A. Johnson, S.J. Rettig, Organometallics 19 (2000) 3931.

[182] M.D. Fryzuk, S.A. Johnson, S.J. Rettig, J. Am. Chem. Soc. 120 (1998) 11024.

[183] M.D. Fryzuk, S.A. Johnson, B.O. Patrick, A. Albinati, S.A. Mason, T.F. Koetzle, J. Am. Chem. Soc. 123 (2001) 3960.

[184] B.C. Ankianiec, P.E. Fanwick, I.P. Rothwell, J. Am. Chem. Soc. 113 (1991) 4710.

[185] I.P. Rothwell, J. Chem. Soc. Chem. Commun. (1997) 1331.

[186] J.R. Clark, P.E. Fanwick, I.P. Rothwell, Organometallics 15 (1996) 3232.

[187] D.R. Mulford, J.R. Clark, S.W. Schweiger, P.E. Fanwick, I.P. Rothwell, Organometallics 18 (1999) 4448.

[188] C.A. Bayse, M.B. Hall, Organometallics 17 (1998) 4861.

[189] S.A. Strazisar, P.T. Wolczanski, J. Am. Chem. Soc. 123 (2001) 4728.

[190] R.L. Miller, R. Toreki, R.E. LaPointe, P.T. Wolczanski, G.D. Van Duyne, D.C. Roe, J. Am. Chem. Soc. 115 (1993) 5570.