Coordination Chemistry Reviews, 99 (1990) 137–212
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPLEXES OF GROUPS 3, 4, THE LANTHANIDES AND THE ACTINIDES CONTAINING NEUTRAL PHOSPHORUS DONOR LIGANDS

MICHAEL D. FRYZUK *, T.S. HADDAD and DAVID J. BERG

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Y6 (Canada)

(Received 31 May 1989)

CONTENTS

---

* Author to whom correspondence should be addressed.

0010-8545/90/$26.25

ABBREVIATIONS

2 · 2 · 2	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
acac	acetylacetonate anion $[CH_3C(O)CHC(O)CH_3]^-$
arphos	$Ph_2AsCH_2CH_2PPh_2$
bipy	2,2′-bipyridyl
Bu	butyl
CHT	cycloheptatrienyl cation $(\eta^7\text{-}C_7H_7)^+$
CMAS	^{13}C magic angle spinning NMR
COND	conductance
COT	cyclooctatetraene
Cp	cyclopentadienyl anion $(\eta^5\text{-}C_5H_5)^-$
Cp*	pentamethylcyclopentadienyl anion $(\eta^5\text{-}C_5Me_5)^-$
Cp′	monomethylcyclopentadienyl anion $(\eta^5\text{-}C_5H_4Me)^-$
CV	cyclic voltammetry
Cy	cyclohexyl
dbpe	1,2-bis(dibutylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
depbz	1,2-bis(diethylphosphino)benzene
dippe	1,2-bis(diisopropylphosphino)ethane
dmCh	6,6-dimethylcyclohexadienyl anion $(\eta^5\text{-}C_6H_5Me_2)^-$
DME	dimethoxyethane
dmope	1,2-bis(dimethoxyphosphino)ethane
dmpbz	1,2-bis(dimethylphosphino)benzene
dmpcp	*trans*-1,2-bis(dimethylphosphino)cyclopentane
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,2-bis(dimethylphosphino)methane
DPM	$Bu^tCOCH_2COBu^t$
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
ESR	electron spin resonance
EVANS	Evans' method of magnetic susceptibility
HMPA	hexamethylphosphoramide
Ind	indenyl anion $(\eta^5\text{-}C_9H_7)^-$
IR	infrared
MS	mass spectrometry
MW	molecular weight
NEUT	neutron diffraction
NMR(nucleus)	nuclear magnetic resonance
Np	neopentyl
o-dppy	*ortho*-(diphenylphosphino)pyridine
pd	pentadienyl anion $(\eta^5\text{-}C_5H_7)^-$

POWDIFF	X-ray powder diffraction
SUSC	magnetic susceptibility
THF	tetrahydrofuran
TPP	tetraphenylporphyrinate dianion
trimpsi	*t*-butyltris((dimethylphosphino)methyl)silane ($Bu^tSi(CH_2PMe_2)_3$)
trmpe	1,1,1-tris(dimethylphosphinomethyl)ethane ($MeC(CH_2PMe_2)_3$)
UVVIS	ultraviolet–visible spectroscopy
VT	variable temperature
XRAY	X-ray diffraction

A. INTRODUCTION

Coordination compounds that contain neutral phosphorus donors now pervade the periodic table. Early coordination chemistry (before the 1960s) was based mainly on amine and oxygen donors such as NH_3, ethylenediamine ($H_2NCH_2CH_2NH_2$), H_2O and acetylacetonate ($CH_3COCHCOCH_3$), but in the last 30 years phosphorus-based ligands, eg. PPh_3, PMe_3 and dppe ($Ph_2PCH_2CH_2PPh_2$), have become the donors of choice [1]. Many transition-metal-based catalysts utilize phosphines as ancillary ligands [2] and this has helped fuel research in the basic coordination chemistry of phosphorus compounds. In addition, from a spectroscopic point of view, phosphorus-31 is an easily detectable (100% natural abundance), spin 1/2 nucleus and provides an invaluable characterization tool [3] in this area.

However, there are parts of the periodic table for which neutral, phosphorus-based donors are still rare or even unknown. Of relevance to this review are complexes of the early transition elements, in particular groups 3 and 4 and the lanthanides and actinides; here one finds that phosphorus donors are not all that common, at least by comparison with complexes of the rest of the transition series. A good indication of this comes from a 1977 review [4] which lists a handful of titanium phosphine complexes, but no derivatives of zirconium or hafnium. Similarly, for group 3 and the lanthanides and actinides, no phosphine complexes were available. A monograph [5] published in 1979 also has few examples of phosphine complexes for these elements. More recent treatments [6], however, do have additional examples of such phosphine-containing species, although the numbers are incomplete and only up to 1984. In this review, we have attempted to collect all the data up to the end of 1988 for complexes of groups 3 and 4, the lanthanides and the actinides that contain phosphorus donor ligands. What one finds is that the 1980s have seen a renaissance of the use of phosphine donors for the early *d* elements (groups 3 and 4) and the *f* elements (lanthanides and actinides). Part of the reason for the recent surge of results was simply the recognition that phosphorus donors for these elements were not that common.

B. SCOPE OF THE REVIEW

All complexes of the groups 3 and 4, the lanthanides and the actinides containing neutral phosphorus donors are included. These particular metals are related in that they are all very electropositive and very oxophilic [7]. Indeed, this last point is based on observations that donors most often found for the early metals, the lanthanides and the actinides seem to be oxygen and nitrogen based [8].

Neutral phosphorus donors are defined as primary (PH_2R), secondary (PHR_2) or tertiary phosphines (PR_3), including complexes of phosphine, PH_3. Also reviewed are complexes of PF_3 and phosphites, $P(OR)_3$. Specifically excluded are phosphido derivatives, PR_2^-. Throughout this work, the generic term phosphine is used to describe all the donors mentioned above, simply for convenience. In the tables, the nature of the donor is given explicitly.

Why are there relatively few phosphine ligands of the early *d* and the *f* elements? Most arguments are based on mismatching of donors and acceptors. It is fairly well accepted that phosphines are "soft" ligands [9] while the elements in question are in fact "hard" acids [10]. While there is merit in this idea, it is flawed in one important respect, and that is that while these elements may not prefer to bind phosphorus-based donors, given no other option, phosphine complexes should be attainable. It would appear to be a matter of selecting the correct ligand and the appropriate solvent and ensuring that "hard" ligands are not present in excess. If backbonding is important in these complexes, then it also stands to reason that high-oxidation-state electron-deficient metal centers will be less likely to form stable phosphine complexes. Indeed, many of the phosphine complexes discussed here are reactive in that the phosphine ligands are very labile, which in certain circumstances may be desirable.

The organization of this manuscript is by group. Examination of complexes of group 4 is first, followed by group 3, the lanthanides and lastly, the actinides. For group 4, the elements are discussed individually according to formal oxidation states. For group 3 and the *f* elements, the few examples are presented chronologically.

Because we have chosen to base part of the organization of this review on formal oxidation states, a few words on how delineations were made are in order. Most of the assignments on charge of particular ligands follow that of Collman et al. [11]; in particular, dienes, alkynes and alkenes are considered as neutral donors, as are carbenes. For the early metals, these are not necessarily realistic, particularly for diene complexes, which can be considered as metallocyclopentene derivatives [12], and also for alkynes, for which the metallocyclopropene resonance form [13] is important. In addition, the alkylidene (CR_2^{2-}) formalism is often used instead of the above neutral carbene donor with the early metals. Nonetheless, this oxidation state formalism follows other treatments [14] and does provide a consistent approach to these complexes.

C. BONDING OF PHOSPHORUS DONORS

The simplest picture for the bonding of a neutral phosphorus donor is donation of the available lone pair at phosphorus into a suitably available empty orbital on the metal of interest to generate a covalent bond: $M \leftarrow :PR_3$. Such a treatment considers the phosphine simply as a donor and the availability of the lone pair on, or the basicity [15] of, the phosphorus is the overriding feature. However, there is clear evidence that phosphorus ligands can act as π acceptors with backbonding of electron density from filled π orbitals on the metal to empty orbitals on the phosphorus [16]. Debate has raged about the nature of the empty orbitals on the phosphorus ligand. Textbooks abound with pictures of the overlap of filled metal *d* orbitals overlapping with an appropriate empty 3*d* orbital on phosphorus to generate the necessary synergistic bonding common to π-acceptor ligands. Yet there are studies [17] which rebut the use of the 3*d* orbitals on phosphorus and suggest that 3*p* orbitals, after rehybridization, are more likely. Another possibility suggests that the acceptor orbital may be a σ^* type originating from the phosphorus substituents [18]. Such a proposal seems reasonable particularly for ligands such as PF_3 and phosphites such as $P(OPh)_3$, but does not seem tenable for alkylated phosphines, PR_3. In fact, for those very basic phosphines such as PBu_3 and PCy_3, there is evidence that these ligands are best described as both σ and π donors [19] with little or no π-acceptor capability.

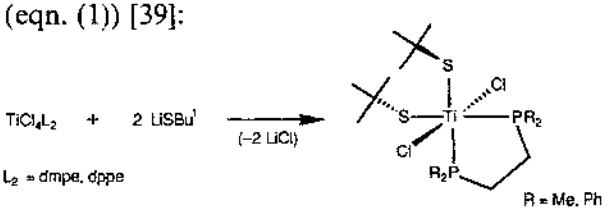
Much of the above discussion on bonding of phosphorus ligands is based on calculations and data on middle and late metal phosphine complexes. For the early metals which are electron deficient particularly in their high oxidation states, π acidity of phosphines has not been addressed. This may be due to the lack of relevant examples, and part of the goal of this review is to remedy this by collecting the known phosphine complexes of these elements into one review.

D. GROUP 4: TITANIUM, ZIRCONIUM AND HAFNIUM

(i) Titanium(IV)

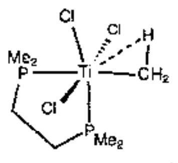
Phosphine adducts of $TiCl_4$ constitute the largest class of tetravalent titanium phosphine derivatives. Most phosphines [20–27] (L = PH_3, PH_2Me, $PHMe_2$, PMe_3, PMe_2Ph, PPh_3, $PEtPh_2$, PEt_3, PBu_3, PCy_3) form both mono, $TiCl_4L$, and bis(ligand) complexes, $TiCl_4L_2$, simply by mixing the reactants in the appropriate stoichiometry. Similarly, $P(OBu)_3$ forms the mono and bis adducts $TiCl_4\{P(OBu)_3\}$ and $TiCl_4\{P(OBu)_3\}_2$ [28]. Chelating bidentate phosphines [22–24,27,29–31] (L_2 = dppm, dmpe, depe, dbpe, dppe, dmpbz and depbz) form 1 : 1 complexes of considerable stability. In addition, dppe is reported to complex to titanium with Ti : dppe ratios of 0.33, 1.5 and 2 [25]; the structures of these latter molecules are unknown but it seems probable that they contain bridging dppe units in a polymeric array. There are also $^{31}P\{^1H\}$NMR spectral data to suggest that PBu_3 and PEt_3 form species of the formula $\{TiCl_4\}_2PR_3$ in solution [26,28]. Presumably, these complexes contain bridging chlorides in a dimeric structure. Most of these $TiCl_4L$- and $TiCl_4L_2$-type complexes have been characterized primarily by IR spectroscopy and elemental analyses, although in a few cases molecular weight determination and NMR spectroscopy have also been employed. No crystallographic data have been reported as yet for any of these derivatives.

The closely related titanium(IV) complexes $Ti(R)X_3$ and TiR_2X_2, where R is an alkyl [32–36,40,42], aryl [34], alkoxy [27,41,42] or alkylthiolate [39] group and X = Cl or Br, also form phosphine adducts of the type $Ti(R)X_3L_n$ ($n = 1$ or 2) and $TiR_2X_2L_2$. Of these adducts, only $Ti(SBu^t)_nCl_2L_2$ (L_2 = dmpe, dppe) was prepared by metathesis of the corresponding $TiCl_4L_2$ (eqn. (1)) [39]:

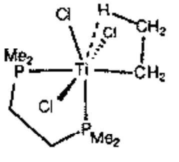


(1)

The remainder were prepared by addition of the phosphine to the appropriate starting material, $Ti(R)Cl_3$ or TiR_2Cl_2. The X-ray crystal structures of $Ti(R)Cl_3$(dmpe) (R = Me and Et) [35,36,40] have been determined and are schematically shown below:



Ti–C–H = 93.5(2)°



Ti–C–C = 86.3(6)°

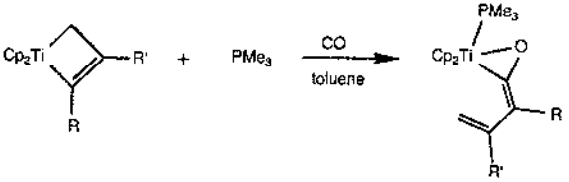
These structures are of considerable interest since they represent the first crystallographically characterized examples of secondary bonding between an electropositive metal and the hydrogen atoms of an alkyl moiety, now more commonly referred to as an agostic interaction. A neutron diffraction study [40] was carried out on the methyl derivative, which confirmed the existence of the agostic interaction. Ab initio molecular orbital calculations [37,38] have also been performed; use of the model compounds $TiMe(PH_3)_2X_2Y$ ($X = H, Cl$; $Y = H, Cl$) and $TiEt(PH_3)_2X_2H$ ($X = H, F, Cl, CF_3$) gave results which suggest that direct overlap occurs between a filled C–H σ bonding orbital of the alkyl group and an empty d_{xy} orbital. These calculations indicate that the strength of the agostic interaction depends critically upon the identity of the ancillary ligands X and Y and on the P–Ti–P bond angle. Electron-withdrawing groups such as Cl lower the energy of the Ti d_{xy} orbital, promoting donation from the C–H σ bond, thereby increasing distortion of the alkyl group. Reduction of the P–Ti–P angle results in extension of the LUMO towards the alkyl moiety which increases the agostic interaction. The optimized geometries obtained from the molecular orbital calculations are in good agreement with the X-ray data.

The remaining titanium(IV) phosphine complexes contain cyclopentadienyl or indenyl ligands. The preparation of $CpTiCl_3(dmpe)$ [43] was recently reported (eqn. (2)):

(2)

The crystal structure of this complex reveals a pseudooctahedral geometry where the Cp ligand and one phosphorus donor occupy the axial sites. Mono and bis(PMe_2Ph) adducts of $CpTiCl_3$ have been characterized in solution by ^1H NMR spectroscopy [42].

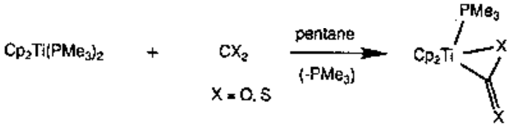
The soluble phosphine-stabilized titanium ketene complex $Cp_2Ti(\eta^2\text{-}OCCH_2)(PMe_2Ph)$ was prepared by phosphine addition to oligomeric $[Cp_2Ti(OCCH_2)]_x$ [44]. More recently, several vinylketene complexes [45] were isolated by addition of CO to a titanacyclobutene in the presence of PMe_3 (eqn. (3)):



(3)

These complexes have been fully characterized in solution and in the solid state for $R = Ph$ and $R' = SiMe_3$.

The related η^2-CX_2 ($X = O$, S) compounds have been isolated in high yield from the reaction of $Cp_2Ti(PMe_3)_2$ with CO_2 and CS_2 [46] (eqn. (4)):



(4)

Interestingly, the corresponding reaction between $Cp_2Zr(PMe_3)_2$ and CO_2 produces polymeric $[Cp_2ZrO]_x$, free CO and PMe_3 [46]. One explanation for this difference in reactivity might be the smaller size of the titanium atom compared with the zirconium atom, which creates unfavorable steric interactions between Cp groups in adjacent Cp_2MO units in the latter derivatives, destabilizing the polymeric product relative to the η^2-CX_2 (presumed) intermediate.

A number of cationic titanium(IV) phosphine complexes of the type $[Cp_2TiMe(L)]^+BPh_4^-$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PBu_3; eqn. (5)) and $[Ind_2TiMe(L)]^+BPh_4^-$ ($Ind = \eta^5$-C_9H_7; $L = PMe_3$, $PMePh_2$) have been recently prepared [47]:

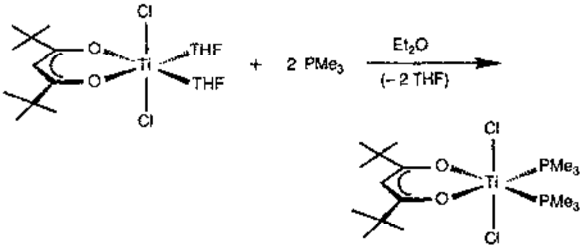
$$Cp_2TiMeCl + L + NaBPh_4 \xrightarrow[(-NaCl)]{THF} [Cp_2TiMe(L)]^+BPh_4^- \tag{5}$$

The idea that phosphines are poorer donors to titanium(IV) than oxygen donors such as THF clearly does not hold here since even a relatively bulky phosphine such as PBu_3 competes effectively with a large excess of THF. The related acyl complex $[Cp_2Ti(COMe)PMe_2Ph]^+BPh_4^-$ has been prepared by phosphine displacement of acetonitrile [47], further demonstrating the willingness of titanium(IV) to accept phosphines as ligands. The cationic chloride species $[Cp_2TiCl(PMe_2Ph)]^+$ is believed to be generated in the electrochemical oxidation of $Cp_2TiCl(PMe_2Ph)$ [48], but no attempt has been made to isolate this compound as a salt.

(ii) Titanium(III)

The phosphine adducts, $TiCl_3L_2$, have been prepared by refluxing the trichloride, $TiCl_3$, with two equivalents of L [49,50] ($L = PH_2Me$, $PHMe_2$, PMe_3, PEt_3, PBu_3, PPr^i_3, PCy_3) or one equivalent of depe [22] in toluene. These $TiCl_3L_2$ complexes have been characterized by UVVIS spectroscopy and in some cases by elemental analysis. Since these complexes are paramagnetic, NMR spectral information was generally not obtained. Tris(phosphine) adducts, $TiCl_3L_3$ ($L = PCy_3$, PPr^i_3, PBu_3) are reported to form at low temperature (− 78 °C) but phosphine dissociation occurs at higher temperatures until room temperature where the bis(phosphine) complex is the predominant species [50]. Solution molecular weight and ESR data support the formation of a monomeric five-coordinate structure for the PEt_3 derivative $TiCl_3(PEt_3)_2$ [49]. IR studies indicate that this complex forms the carbonyl adduct $TiCl_3(PEt_3)_2CO$ at high pressure (800 psi) [51]. The tridentate ligand trimpsi has been used to prepare $TiCl_3$(trimpsi)(THF) by reaction with $TiCl_3(THF)_3$ [52].

A number of titanium(III) diketonate complexes [53,54] have been prepared (eqn. (6)):



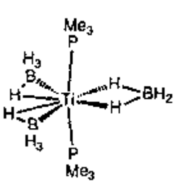
(6)

A structure with phosphine ligands *trans* to the diketonate oxygen atoms were proposed for $TiCl_2(DPM)(PMe_3)_2$ on the basis of equivalent phosphorus-31 nuclei by ESR and a similarity between the electronic spectrum of this complex and $TiCl_2$(DPM)(bipy) [54]. Metathesis with MeLi has been used to prepare the dimethyl derivative $TiMe_2(DPM)(PMe_3)_2$ [54].

The blue titanium(III) borohydride complexes $Ti(BH_4)_3L_2$ ($L = PMe_3$, PEt_3, PMe_2Ph, $P(OMe)_3$; L_2 = dmpe) have been reported [55,56] (eqn. (7)):

$$Ti(BH_4)_3(OEt_2) + 2PR_3 \xrightarrow{Et_2O} Ti(BH_4)_3(PR_3)_2 \qquad (7)$$

Paramagnetic NMR data were obtained for all these complexes although it was not possible to observe the borohydride protons. ESR spectra were also observable for these complexes. From IR analysis, the bonding mode of the BH_4 units was not obvious, so a crystallographic study was undertaken. The structure [56] of $Ti(BH_4)_3(PMe_3)_2$ is shown below:



Two of the three BH_4 ligands are bonded in an unusual B–H side-on arrangement while the third is η^2 with two bridging hydrides.

The reactivity of $Ti(BH_4)_3(PMe_3)_2$ has been investigated in some detail [56]. Prolonged heating in solution results in loss of $H_3B \cdot PMe_3$. Ethylene is polymerized by this complex at 60 °C but this eventually leads to decomposition, presumably through loss of $H_3B \cdot PMe_3$. It is interesting to note that when the chelating diphosphine dmpe is employed, a blue polymer of composition $[Ti(BH_4)_3(dmpe)]_x$ is obtained [56]. Apparently the preference for *trans* phosphorus donor ligation is so pronounced that dmpe is forced to adopt a bridging mode of coordination.

Several titanium(III) phosphine complexes have been prepared by either phosphine-induced cleavage of binuclear species or reduction of a titanium(IV) precursor (eqns. (8)–(11)):

$$[Cp_2TiH]_2 + 2PPh_3 \xrightarrow[-30\,°C]{THF} 2Cp_2TiH(PPh_3) \tag{8}$$

$$[Cp_2TiCl]_2 + 2PR_3 \xrightarrow{C_6H_6} 2Cp_2TiCl(PR_3) \tag{9}$$

$$PR_3 = PMe_3,\ PMe_2Ph,\ PMePh_2$$

$$Cp_2TiCl_2 + PMe_3 \xrightarrow[THF]{Mg/HgCl_2} Cp_2TiCl(PMe_3) \tag{10}$$

$$Cp_2TiCl_2 + 2PMe_2SiMe_3 \xrightarrow{C_6H_6} Cp_2TiCl(PMe_2SiMe_3) + Me_3SiCl + Me_2PPMe_2 \tag{11}$$

The hydride complexes [57,58] have only been characterized by ESR spectroscopy but the chloride derivatives [59–63] have been isolated and the crystal structures of the PMe_3 [62] and $PMe_2(SiMe_3)$ [63] adducts have been determined. The use of bulkier bidentate phosphines, such as dppe [59] and arphos [60], results in the formation of the binuclear complexes $[Cp_2TiCl]_2(\mu\text{-}Ph_2ECH_2CH_2PPh_2)$ (E = P or As). The structure of the arphos complex (E = As, eqn. (12))

$$Cp_2TiCl_2 + Ph_2PCH_2CH_2AsPh_2 \xrightarrow[diglyme]{Mn/KOBu^t} [Cp_2TiCl]_2(\mu\text{-}Ph_2PCH_2CH_2AsPh_2) \tag{12}$$

has been confirmed by X-ray crystallography although disorder of the phosphorus and the arsenic atoms prevented an accurate determination of the Ti–P bond length.

Cleavage of the monocyclopentadienyl complex, $[CpTiCl_2]_x$, with phosphines results in the formation of the isolable monomeric complexes $CpTiCl_2L_2$ [64] (L = PMe_2Ph, $PMePh_2$; L_2 = dmpe, dppe). The PMe_3 analogue $CpTiCl_2(PMe_3)_2$ [65] has been prepared by reduction of $CpTiCl_3$ with magnesium metal in the presence of excess PMe_3. The X-ray structure of this complex is best described as a four-legged piano stool [65]; the Ti–P bond length of 2.599(2) Å is identical with that in $Cp_2TiCl(PMe_3)$ [62]. Monophosphine adducts $CpTiCl_2(PR_3)$ ($R = Pr^i$, Ph) have also been reported to form by photo-induced dissociation of the Cp radical from Cp_2TiCl_2 in the presence of added phosphine [66] (eqn. (13)):

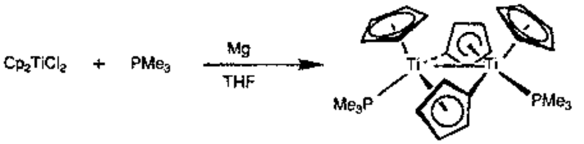
$$Cp_2TiCl_2 + PR_3 \xrightarrow[\text{toluene}]{h\nu} CpTiCl_2(PR_3) + Cp^{\cdot} \qquad (13)$$

$R = Pr^i$, Ph

These adducts have only been characterized in situ by ESR spectroscopy.

Several titanium(III) phosphine complexes have been generated in situ by electrochemical oxidation or reduction. ESR has been used to identify most of these species. The electrochemical reduction of Cp_2TiX_2 in the presence of PMe_2Ph reportedly gives $[Cp_2TiX_2(PMe_2Ph)]^-$ [67] ($a(^{31}P) = 22$ G for X = Cl and Br). Similarly, the presence of $[Cp_2Ti(PMe_2Ph)_2]^+$ has been suggested to account for the presence of a 0.5 e^- oxidation wave for the oxidation of $Cp_2TiCl(PMe_2Ph)$ [48]. The electrochemical reduction of $Cp_2Ti(CH_2PPh_2)_2$, which contains uncoordinated phosphorus atoms, results in the loss of a cyclopentadienide anion and formation of $CpTi(\eta^2\text{-}CH_2PPh_2)_2$ [68]. The phosphorus atoms are now coordinated as shown by ESR spectroscopy ($a(^{31}P) = 9.8$ G).

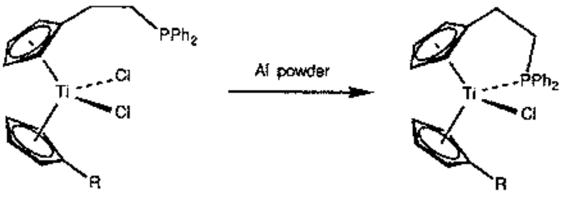
The chemical reduction of Cp_2TiCl_2 with magnesium metal in the presence of one equivalent of PMe_3 leads to the formation of a binuclear $\eta^1 : \eta^5\text{-}C_5H_4$ bridged complex [69,70] (eqn. (14)):



(14)

Interestingly, this complex is diamagnetic and complete NMR characterization has been reported. This diamagnetism suggests the presence of a direct Ti–Ti bond or spin pairing through the bridging ligands (superexchange). No fluxional behavior was observed for this compound in the ^1H and $^{13}C\{^1H\}$ NMR spectra.

Finally, reduction of $(C_5H_4R)\{C_5H_4(CH_2CH_2PPh_2)\}TiCl_2$ ($R = H$ or $CH_2CH_2PPh_2$) with aluminum powder results in the formation of a titanium(III) complex as shown in eqn. (15) [71]; a dimeric formulation is also possible, having a bridging $C_5H_4(CH_2CH_2PPh_2)$ group:



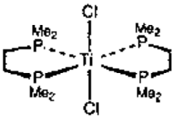
(15)

$R = H, CH_2CH_2PPh_2$

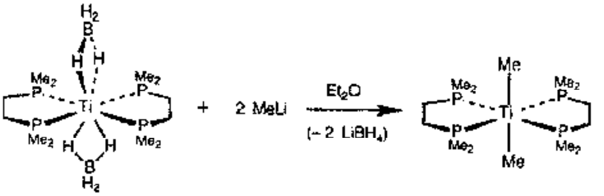
The ESR spectrum clearly shows that only one phosphorus atom is coordinated to the titanium center in these compounds.

(iii) Titanium(II)

Titanium tetrachloride has been reduced with magnesium metal in the presence of dmpe to produce $TiCl_2(dmpe)_2$ [72]:



This red–black paramagnetic species has been characterized by magnetic susceptibility ($\mu = 2.9$ BM, Evans' method), ^1H NMR spectroscopy and X-ray crystallography and has proven to be a versatile starting material for the preparation of other titanium(II) phosphine complexes. The reaction of $TiCl_2(dmpe)_2$ with $LiBH_4$ produces $Ti(BH_4)_2(dmpe)_2$ [73]. Metathesis of this borohydride complex with MeLi cleanly generates $TiMe_2(dmpe)_2$ (eqn. (16)):



(16)

Surprisingly, the dimethyl derivative is diamagnetic (low spin d^2) both in solution and in the solid. Both X-ray and neutron diffraction studies [73] have been carried out on this complex and there is no evidence for agostic interactions in the solid phase. However, solution data (^1H and ^{13}C NMR spectroscopy) are typical of compounds with agostic interactions. $TiMe_2(dmpe)_2$ reportedly polymerizes ethylene under ambient conditions [73]. Attempts to prepare $TiMe_2(dmpe)_2$ directly from $TiCl_2(dmpe)_2$ by reaction with MeLi or Me_2Mg lead to a material with the composition $TiMe_{1.3}Cl_{0.7}(dmpe)_2$ [72]; the X-ray crystal structure of this material showed disorder between the methyl and the chloride ligands and was indicative of the presence of $TiMe_2(dmpe)_2$, $Ti(Me)Cl(dmpe)_2$ and $TiCl_2(dmpe)_2$ in the crystal.

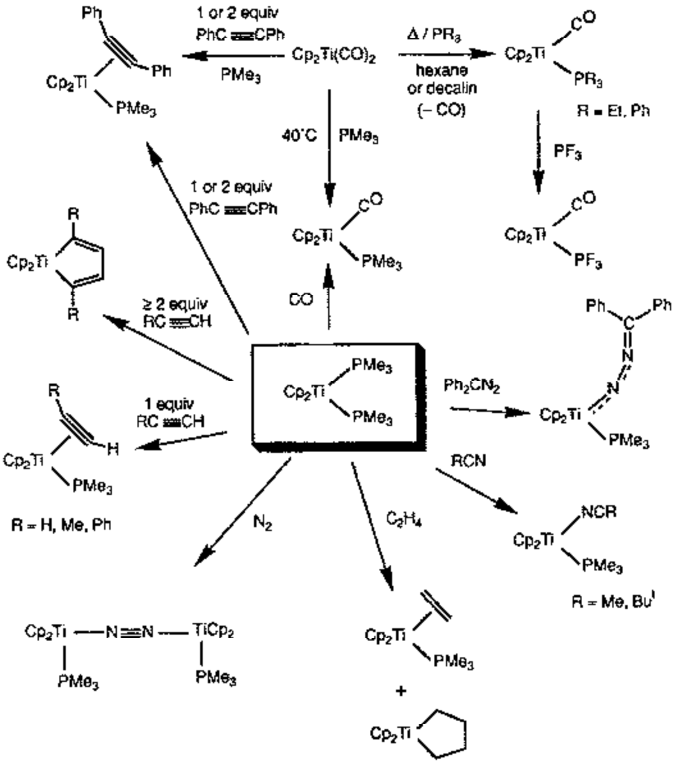
Phosphines and phosphites have been used extensively to stabilize the titanocene fragment, $(\eta^5\text{-}C_5H_5)_2Ti$ (Cp_2Ti). Coordination of two phosphine ligands results in stable, isolable 18-electron complexes of the general formula Cp_2TiL_2. The derivatives containing PMe_3 [70,81], $P(OMe)_3$ [74]

and dmpe [75] have been prepared by the reduction of titanium(IV) halide precursors while the PF_3 complex, $Cp_2Ti(PF_3)_2$ [76], has been prepared by photochemical ligand substitution of $Cp_2Ti(CO)_2$. All these complexes are diamagnetic (low spin d^2) by NMR spectroscopy and highly coloured: L = PMe_3, black; L = $P(OMe)_3$, red; L = PF_3, yellow; L_2 = dmpe, orange–black. The solid state structures of a number of derivatives of general formula Cp'_2TiL_2 ($Cp' = C_5H_5$, L = PMe_3 [70] and PF_3 [76]; $Cp' = C_5H_4Me$, L_2 = dmpe [75]) have been carried out. All show a pseudotetrahedral geometry about titanium with the phosphine ligands lying in the equatorial plane between the two Cp′ rings. The Ti–P bond distances are very similar for the PMe_3 and dmpe derivatives (2.526 Å and 2.534 Å respectively), but the corresponding bond length of 2.345 Å for the PF_3 derivative is nearly 0.2 Å shorter. This has been attributed to the ability of the empty *d* orbitals on the PF_3 ligand to engage in π backbonding with the filled *d* orbital on the titanium(II) center [76]. As discussed in Section C above, the empty orbital on PF_3 is better described as being of σ^* origin.

A purple diamagnetic PPh_3 adduct of titanocene, $[Cp_2Ti(PPh_3)]_2$, has been reported [77]. This compound was isolated from the reaction of the titanocene dimer with PPh_3 and by ligand-induced reduction of $[Cp_2TiH]_2$. Only elemental analyses were obtained but reactivity studies seem to support this formulation. For example, addition of THF results in the formation of $Cp_2Ti(PPh_3)THF$, and addition of CO generates the known $Cp_2Ti(CO)_2$. Apparently PPh_3 is simply too large to allow coordination of more than one phosphine to the metal center. The structure of $[Cp_2Ti(PPh_3)]_2$ is unknown.

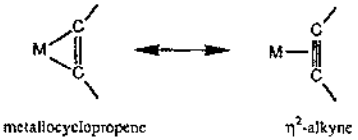
Bis(phosphine) titanocene complexes have proven to be versatile starting materials in the synthesis of other titanium(II) phosphine complexes. Their rich chemistry is primarily due to the high lability of the coordinated phosphines which allows facile substitution by other donor ligands. Thus $Cp_2Ti(PMe_3)_2$ [71] (Scheme 1) reacts readily with CO to produce $Cp_2Ti(PMe_3)CO$. Complexes of the formula $Cp_2Ti(L)CO$ can also be prepared by thermal [76,78–80] or photochemical [62] substitution of PR_3 for CO in the dicarbonyl $Cp_2Ti(CO)_2$. A kinetic study [80] of the thermal substitution reaction of $Cp_2Ti(CO)_2$ with PR_3 in decalin is consistent with an S_N1-type process rather than an S_N2 mechanism as found for the corresponding zirconium and hafnium derivatives (vide infra). The difference in mechanism was attributed to the smaller size of titanium as compared with zirconium and hafnium. The structures of $Cp_2Ti(L)CO$ (L = PMe_3 [62] and PEt_3 [74]) have been reported (Table 1).

A phosphine ligand of $Cp_2Ti(PMe_3)_2$ is readily replaced by acetylenes to give $Cp_2Ti(PMe_3)(RC{\equiv}CR')$ [81–83] (Scheme 1). These complexes are all diamagnetic and show $C{\equiv}C$ stretching frequencies in the range 1590–1740



Scheme 1.

cm^{-1}. Thus it appears that these complexes are more realistically formulated as metallocyclopropenes rather than as η^2-alkyne complexes:



Unfortunately, no structural studies have as yet been reported to confirm this proposal. The diphenylacetylene complex has also been prepared from $Cp_2Ti(CO)_2$, PhC≡CPh and PMe_3 [84–86]. The smaller acetylenes, RC≡CH (R = H, Me, Ph), will displace the remaining phosphine of $Cp_2Ti(PMe_3)$(RC≡CH) to produce a metallocyclopentadiene [81] (Scheme 1). Diphenylacetylene does not react with $Cp_2Ti(PMe_3)$(PhC≡CPh) presumably because of steric crowding [84]. The mixed-ring complex, CpCp*Ti(PhC≡CPh)(PMe_3) [85,86], readily loses PMe_3 under vacuum, indicating that the coordination environment around the metal is very crowded.

The reaction chemistry of $Cp_2Ti(PMe_3)$(HC≡CH) has been studied in some detail [87,90]. Stoichiometric reaction of this complex with alcohols results in protonation of the alkyne unit to form a titanium(IV) vinyl–alkoxide species, $Cp_2Ti(CH{=}CH_2)(OR)$, while reaction with one equivalent of H_2O gives a binuclear vinyl-bridged μ-oxo complex, $[Cp_2Ti(CH{=}CH_2)]_2(\mu\text{-}O)$. Reaction of $Cp_2Ti(PMe_3)(HC{\equiv}CH)$ with organic substrates leads to insertion or coupling to form a metallocyclopentene unit. Taken together, these reactions provide good evidence for the metallocyclopropene formulation and also demonstrate the lability of coordinated monodentate phosphines such as PMe_3.

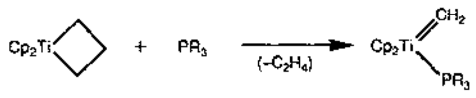
Ethylene has been reported to be catalytically dimerized by $Cp_2Ti(PMe_3)_2$ at room temperature [81]. NMR spectroscopic studies at −50 °C indicate the presence of $Cp_2Ti(PMe_3)(H_2C{=}CH_2)$ and the known metallocyclopentane $Cp_2Ti(C_4H_8)$, but no further details have been reported.

The lability of the PMe_3 ligands in $Cp_2Ti(PMe_3)_2$ is further illustrated by the isolation of the dinitrogen-bridged complex $[Cp_2Ti(PMe_3)]_2(\mu\text{-}N_2)$ from pentane solutions of $Cp_2Ti(PMe_3)_2$ under N_2 [88]. The crystal structure of this dimer shows a nearly linear $N{\equiv}N$ bridge having an N–N distance of 1.191(8) Å; this is longer than that in free N_2 (1.0976 Å) but not as long as a typical $N{=}N$ double bond (1.24 Å). The Ti–P bond distances of 2.538(2) and 2.525(2) Å are nearly identical with those of $Cp_2Ti(PMe_3)_2$. The complex $[Cp_2Ti(PMe_3)]_2(\mu\text{-}N_2)$ slowly decomposes in benzene over a period of a few days to give the known binuclear complex $[CpTi(PMe_3)]_2(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)_2$ [69].

Diphenyldiazomethane reacts rapidly with $Cp_2Ti(PMe_3)_2$ at room temperature to form $Cp_2Ti(PMe_3)(N_2CPh_2)$ [89] (Scheme 1). The structure of this complex shows that the Ph_2CN_2 moiety is coordinated in an end-on fashion through the nitrogen. Again the Ti–P distance of 2.534(3) Å is essentially identical with that observed in $Cp_2Ti(PMe_3)_2$. The remaining PMe_3 of $Cp_2Ti(PMe_3)(N_2CPh_2)$ is not readily lost.

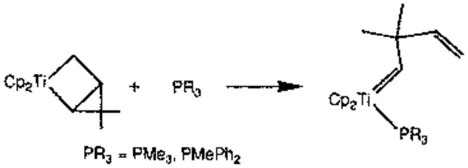
Nitriles readily displace one or both PMe_3 ligands from $Cp_2Ti(PMe_3)_2$ (Scheme 1). Addition of $RC{\equiv}N$ ($R = Me, Bu^t$) rapidly produces the complexes $Cp_2Ti(PMe_3)(N{\equiv}CR)$ [70]. Reaction with excess $MeC{\equiv}N$ or phthalodinitrile results in replacement of both PMe_3 groups with nitriles. No crystallographic data for these latter complexes have yet been obtained.

Phosphine-stabilized carbene complexes, $Cp_2Ti{=}CH_2(L)$ ($L = PMe_3, PMe_2Ph$) [91,92] and $Cp_2Ti{=}CHCMe_2CH{=}CH_2(L)$ ($L = PMe_3, PMe_2Ph$ and $PMePh_2$) [93,94] have been obtained by the phosphine-induced rearrangement of the appropriate metallocyclobutane (eqns. (17) and (18))



(17)

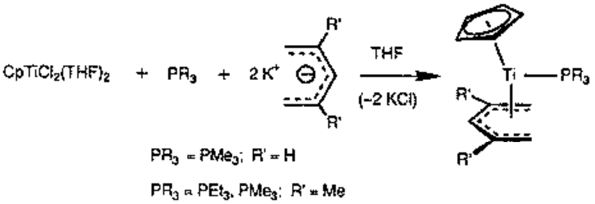
$PR_3 = PMe_3, PMe_2Ph, PEt_3$



(18)

and by cleavage of the binuclear carbene species $[Cp_2Ti]_2(\mu\text{-}CH_2)_2$ with PMe_3. No solid state structural data have been reported as yet.

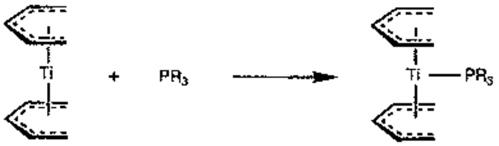
A number of titanium(II) complexes incorporating pentadienyls (pd) as ligands are known. The mixed cyclopentadienyl–pentadienyl complexes CpTi(pd)L (pd = 2,4-dimethylpentadienyl, L = PMe_3 or PEt_3; pd = pentadienyl, L = PEt_3) [95] have been prepared from $CpTiCl_2(THF)$ and the corresponding potassium pentadienyl in the presence of added phosphine (eqn. (19)):



(19)

Interestingly, only complexes containing one phosphine are isolated even with relatively small monodentate phosphines such as PMe_3; presumably this is due to the larger steric requirements of the pentadienyl group as compared with a cyclopentadienyl ligand. The crystal structure of CpTi(2,4-Me_2pd)PEt_3 has been determined [95].

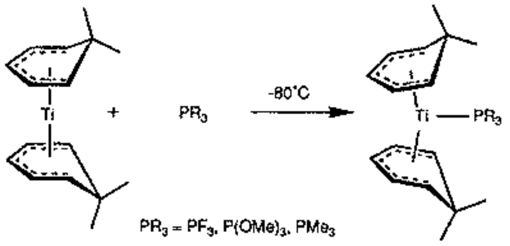
The bis(pentadienyl) complexes $Ti(pd)_2L$ (L = PMe_3, PEt_3, PMe_2Ph) [96] have been prepared by magnesium reduction of $TiCl_4(THF)_2$ in the presence of the potassium 2,4-dimethylpentadienide salt and phosphine or directly by addition of phosphine to $Ti(pd)_2$ (eqn. (20)):



(20)

In both cases, only monophosphine adducts are again isolated. The use of bulkier phosphine ligands results in dissociation in solution. The equilibrium constant for dissociation was determined by NMR spectroscopy and the order of binding was found to be $PF_3 > PMe_3 > PMe_2Ph > P(OMe)_3 > PEt_3$ [96]. This ordering has been attributed primarily to increasing steric bulk of the phosphine. Despite the lability of the coordinated phosphine in solution, molecular ions were observed in the mass spectrum of most of these complexes.

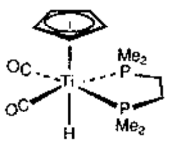
The green bis(cyclohexadienyl) complexes Ti(dmCh)$_2$ form very labile red–brown mono adducts with PMe$_3$, P(OMe)$_3$ and PF$_3$ [97] (eqn. (21)):

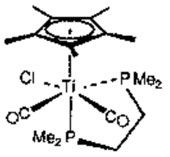


(21)

Only the PF$_3$ complex was stable enough at −78 °C to be characterized by ^{1}H NMR spectroscopy.

Two closely related mono(cyclopentadienyl) titanium(II) phosphine complexes have been reported. CpTi(CO)$_2$H(dmpe) [98] was synthesized by protonation of the titanium(0) species [K(2 · 2 · 2)]$^+$[CpTi(CO)$_2$dmpe]$^-$ with acetic acid. This red–violet hydride has been fully characterized both in solution and in the solid state. In the X-ray crystal structure the Ti–P bond distances of 2.505(2) and 2.520(2) Å are comparable with those in other titanium(II) complexes (see Table 1). Cp*Ti(CO)$_2$Cl(dmpe) [99] was prepared by sodium naphthalenide reduction of Cp*TiCl$_3$ in the presence of dmpe and CO. This complex was only characterized in solution owing to its low stability. The more stable hafnium complex has been structurally characterized and, unlike CpTi(CO)$_2$H(dmpe), one phosphorus end of the dmpe ligand is bonded transoid to the Cp* ring [99]:



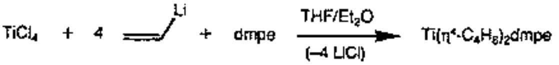


This may be due to the greater bulk of the Cp* ring which forces one end of the chelate out of the cisoid (to the Cp* ring) orientation. The similarity of the solution NMR spectroscopic data of Cp*Ti(CO)$_2$Cl(dmpe) and Cp*Hf(CO)$_2$Cl(dmpe) suggests that these derivatives are isostructural and different from the hydride CpTi(CO)$_2$H(dmpe).

Finally, the existence of the titanium(II) species [Cp$_2$TiX(PMe$_2$Ph)]$^-$ has been postulated in the two-electron reduction of Cp$_2$TiX$_2$ during cyclic voltammetry studies [67]; no further corroborating evidence has been reported.

(iv) Titanium(0)

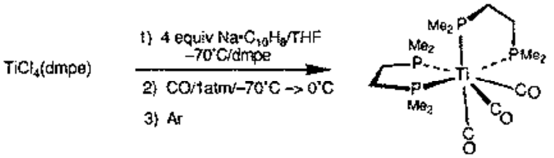
A number of formally titanium(0) phosphine complexes incorporating 1,3-butadiene or carbonyl ligands have been reported. Since the butadiene complexes have been used to prepare the carbonyl complexes, these will be discussed first. All the known titanium(0) diene–phosphine derivatives are of the general formula $Ti(\eta^4\text{-}C_4H_6)_2L$, where L is a chelating bidentate phosphine or phosphinite such as dmpe, depe, dppe, or dmope [100,101]. No complexes incorporating monodentate phosphines have been prepared to date. The synthesis of these compounds is general; "magnesium butadiene" ($[Mg \cdot C_4H_6 \cdot 2THF]_n$) serves as a reducing agent for $TiCl_4(THF)_2$ in the presence of the diphosphine. The dmpe derivative has also been prepared by the reductive coupling of four equivalents of vinyllithium with $TiCl_4$ and dmpe [100] (eqn. (22)):



(22)

Reduction of $TiCl_4$(dmpe) with sodium amalgam (Na/Hg) in the presence of 1,3-butadiene also gives $Ti(\eta^4\text{-}C_4H_6)_2$(dmpe). Although characterization in solution has been accomplished, no solid state structural details have yet been obtained, despite the relative ease of preparation of these complexes. $Ti(\eta^4\text{-}C_4H_6)_2$(dmpe) catalyzes the dimerization and trimerization of ethylene while the dppe complex polymerizes this same substrate [101]. No activity was observed for the dmope derivative.

The dmpe and depe–butadiene complexes react with CO at 0 °C to produce the seven-coordinate derivatives $Ti(CO)_3L_2$ (L = dmpe, depe) [102]. The dmpe complex has also been prepared by the sodium naphthalenide reduction of $TiCl_4$(dmpe) followed by exposure to CO [103] (eqn. (23)):



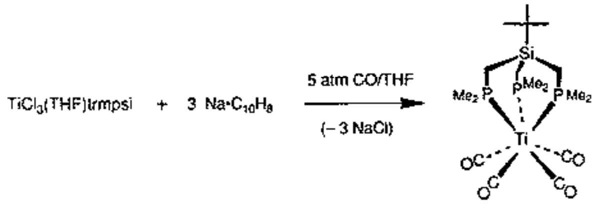
(23)

The crystal structure of $Ti(CO)_3(dmpe)_2$ [104] shows a monocapped octahedral geometry with two axial and two equatorial phosphorus donors. The axial (*trans*) Ti–P distances are significantly shorter than the equatorial (*cis*) lengths (2.567 Å, 2.523 Å vs. 2.637 Å, 2.630 Å respectively). As expected for a seven-coordinate molecule, $Ti(CO)_3(dmpe)_2$ is stereochemically non-rigid in solution. $^{31}P\{^1H\}$ NMR spectroscopy indicates two separate fluxional processes [104]; a low temperature (−60 °C) process exchanges one pair of four inequivalent phosphorus resonances, and concurrent with this, $^{13}C\{^1H\}$ NMR spectroscopy shows that two of the three inequivalent carbonyl resonances undergo exchange. Above $-40\,^\circ C$, all phosphorus and carbonyl resonances are in fast exchange. The lower temperature process has been rationalized in terms of a trigonal twist mechanism. No particular mechanism has been proposed for the high temperature process.

Addition of PF_3 to $Ti(CO)_3(dmpe)_2$ readily displaces one carbonyl to produce $Ti(CO)_2PF_3(dmpe)_2$ [102]. The crystal structure of this compound indicates a capped trigonal prism geometry. Treatment of $Ti(CO)_3(dmpe)_2$ with two equivalents of $BH_3 \cdot THF$ in the presence of CO results in the formation of $Ti(CO)_5dmpe$ [103]. Unfortunately, a large excess of $BH_3 \cdot THF$ does not result in the formation of the binary carbonyl $Ti(CO)_7$. The anionic titanium(0) complexes $Ph_4As^+[Ti(CO)_4(EPh_3)dmpe]^-$ have been isolated by reaction of $Ti(CO)_5dmpe$ with $NaEPh_3$ (E = Ge, Sn) followed by metathesis. As previously mentioned, the anionic complex $[K(2 \cdot 2 \cdot 2)]^+$-$[CpTi(CO)_2dmpe]^-$ [98], prepared by reduction of $Cp_2Ti(CO)_2$ and potassium naphthalenide, followed by work-up with $2 \cdot 2 \cdot 2$, can be protonated to generate the formally titanium(II) hydride $CpTi(CO)_2H(dmpe)$.

The tridentate phosphines, trmpe and trimpsi, have been used to prepare very stable carbonyl complexes of the formula $Ti(CO)_4L$ [52,103,105]. In both cases, alkali metal naphthalenide reduction of a high valent titanium chloride derivative in the presence of CO was used as the synthetic route (eqns. (24) and (25)):

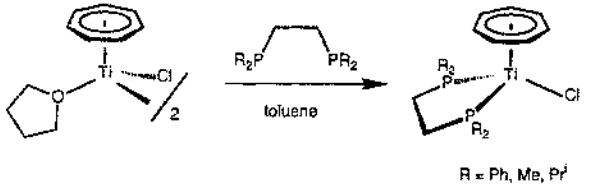
$$TiCl_4(THF)_2 + trmpe + 4\ K{\cdot}C_{10}H_8 \xrightarrow[2)\ CO/1\ atm/-65^\circ C]{1)\ -65^\circ C/DME} Ti(CO)_4trmpe \qquad (24)$$



(25)

The carbonyl stretching frequencies for the trimpsi complex are about 50 cm^{-1} lower than those of the trmpe derivative; this is strong evidence that the silicon in the backbone of the trimpsi ligand does exert some electronic effect in the overall bonding of this complex. The structure of $Ti(CO)_4$-trimpsi [52(a)] has been determined and its geometry is that of a four-legged piano stool. If the reduction is conducted in the absence of CO, the naphthalene adduct $Ti(\eta^6\text{-}C_{10}H_8)$trimpsi can be obtained [52(b)]. This paramagnetic complex reacts immediately with CO to generate the above carbonyl complex, $Ti(CO)_4$trimpsi.

The final class of titanium(0) phosphine complexes are those incorporating the tropylium or cycloheptatrienyl ligand, formally considered as CHT^+. A number of these complexes have been prepared by displacing THF in the formally titanium(0) dimer $[Ti(CHT)Cl(THF)]_2$ with a chelating diphosphine such as dmpe, dppe, dippe or dmpcp, or two equivalents of PMe_3 [106,107] (eqn. (26)):



(26)

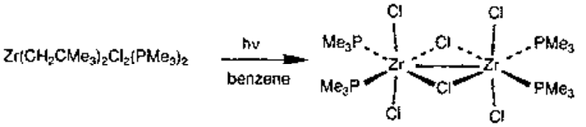
Under vacuum, the $Ti(CHT)Cl(PMe_3)_2$ derivative loses PMe_3 to give $[Ti(CHT)Cl]_2(PMe_3)$. Metathesis of the chloride ligands with Grignard reagents or sodium borohydride yields Ti(CHT)R(dmpe) and $Ti(CHT)BH_4$(dmpcp) respectively. The crystal structure of Ti(CHT)Et(dmpe) [107] has been determined and it clearly shows that the ethyl moiety does not show any agostic interaction with the metal center. This has been explained by the unfavorable location of the potential acceptor orbital on titanium.

(v) Zirconium(IV)

A number of phosphine adducts of zirconium(IV) halides have been prepared by direct addition of the phosphine to the halide in an appropriate solvent. The size of the phosphine seems to dictate the stoichiometry of the adduct obtained. Thus the small chelating phosphine, dmpe, affords $ZrCl_4(dmpe)_2$ [108,109] as a crystalline white solid. Both the observation of a molecular ion in the mass spectrum and the appreciable solubility in hydrocarbon solvents suggest that this complex adopts an eight-coordinate monomeric structure even though no crystallographic studies have been carried out to confirm this. Addition of monodentate phosphines such as PEt_3 and PBu_3 to $ZrCl_4$ forms six-coordinate bis(ligand) complexes $ZrCl_4L_2$ [27,110]. Similarly, the bulkier bidentate phosphine dppe only forms ZrX_4(dppe) (X = Cl, Br). It has been reported that dbpe ($Bu_2PCH_2CH_2PBu_2$) forms a mono(ligand) complex; however, the low solubility of the product obtained seems to suggest that this is not a simple mononuclear species but rather contains bridging dbpe units in a higher nuclearity structure [27].

Compounds where an alkyl or aryl group replaces one or more of the halide ligands of ZrX_4L_2 have also been prepared. The only mono(hydrocarbyl) complexes prepared to date are $Zr(Ph)Cl_3(PPh_3)$THF and

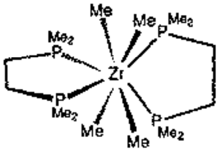
Zr(Ph)Cl$_3$dppe by ligand displacement in Zr(Ph)Cl$_3$L$_x$ (L = CH$_3$CN, x = 2; L = THF, x = 3) with the appropriate phosphine [111]. Schrock and coworkers have prepared ZrNp$_2$X$_2$L$_2$ and ZrBz$_2$Cl$_2$(PMe$_3$)$_2$ by phosphine displacement of coordinated diethyl ether [112]. The neopentyl complexes are thermally sensitive but have been characterized by NMR spectroscopy. Monodentate phosphines such as PMe$_3$ and PMe$_2$Ph undergo rapid exchange with free phosphine on the NMR time scale. In addition, the PMe$_3$ derivative is photosensitive, generating a zirconium(III) dimer [112] (eqn. (27)):

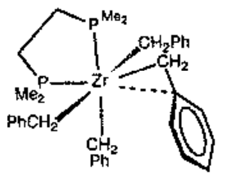


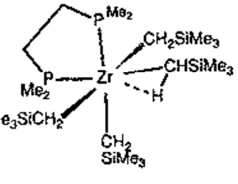
(27)

ZrMe$_2$Cl$_2$(dmpe)$_2$ has been prepared from ZrCl$_4$(dmpe)$_2$ and Me$_2$Mg [114]. The mono(phosphine) complex ZrNp$_3$Cl(PMe$_3$) has been synthesized from ZrNp$_2$Cl$_2$(OEt$_2$)$_2$ and MgNp$_2$ in the presence of PMe$_3$ [112]. Presumably, incorporation of three neopentyl groups prevents coordination of a second phosphine ligand. Indeed, heating ZrNp$_3$Cl(PMe$_3$) to 50 °C in benzene results in rapid ligand redistribution to generate ZrNp$_4$ and ZrNp$_2$Cl$_2$(PMe$_3$)$_2$ [112].

ZrCl$_4$(dmpe)$_2$ can be completely alkylated using alkyl lithium reagents. With methyllithium, ZrMe$_4$(dmpe)$_2$ [113] is obtained in good yield. The X-ray crystal structure shows a dodecahedral ligand arrangement where the phosphorus atoms occupy the A sites and the Me groups the B dodecahedral sites. The average Zr–P bond distance is 2.814(1) Å. Alkylation of ZrCl$_4$(dmpe)$_2$with excess LiCH$_2$SiMe$_3$ produces the six-coordinate complex Zr(CH$_2$SiMe$_3$)$_4$dmpe [113,114]. The crystal structure [114] of this complex shows an agostic interaction between an α-hydrogen of one CH$_2$SiMe$_3$ ligand and the zirconium center. The benzyl analogue, ZrBz$_4$(dmpe), has been prepared by addition of dmpe to ZrBz$_4$ [113]. The structure of this compound shows a strong interaction between the β-carbon and the zirconium center as evidenced by a Zr–C–C(β) angle of only 94.2(4)°, compared with values of 111.1(4)–122.1(4)° for the remaining non-interacting benzyl groups:







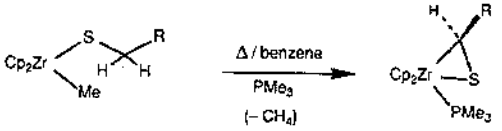
Interestingly, the Zr–P bond distances in $Zr(CH_2SiMe_3)_4$dmpe and $ZrBz_4$(dmpe) are similar to one another (average 2.924 Å and 2.874 Å respectively) but are significantly longer than those found in $ZrMe_4(dmpe)_2$ (average 2.814 Å) [113], despite the fact that the latter represents a higher coordination number. This would suggest that these agostic interactions are of considerable strength since they compete effectively with phosphorus ligation; indeed, all three of these complexes undergo reversible phosphine dissociation according to ^1H NMR spectroscopy. This process can be frozen out for $ZrMe_4(dmpe)_2$, but phosphine exchange is still rapid at −50 °C for $Zr(CH_2SiMe_3)_4$dmpe. No data have been reported for $ZrBz_4$dmpe owing to its low solubility. It is also noteworthy that addition of PMe_3 to $ZrBz_4$ generates only the mono adduct $ZrBz_4(PMe_3)$ [115]. This may be due to an agostic interaction of one or more benzyl groups, which is preventing a second PMe_3 from binding. Not surprisingly, the less basic and more bulky triphenylphosphine ligand causes no shift in the ^1H NMR spectral resonances of $ZrBz_4$, indicating that it does not bind at all to the zirconium center.

Cyclopentadienyl derivatives constitute a large class of the known zirconium(IV) phosphine complexes. $CpZrCl_3(PEt_3)_2$ has been prepared by oxidation of a zirconium(III) phosphine complex with TlCp (eqn. (28))

$$1/2\left[(Et_3P)_2ZrCl_2\right](\mu\text{-}Cl)_2 + TlCp \xrightarrow[(-Tl)]{\text{toluene}} CpZrCl_3(PEt_3)_2 \qquad (28)$$

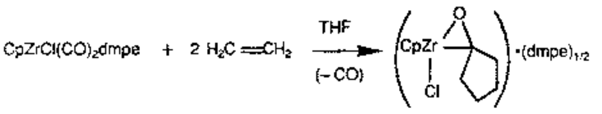
and by direct addition of PEt_3 to $CpZrCl_3$ [116]. The closely related mono(pentamethylcyclopentadienyl) complexes $Cp^*ZrMe_3L_2$ ($L = PMe_3$; $L_2 =$ dmpe) [117] and $Cp^*ZrCl_2Np(PMe_3)$ [112] have been prepared by addition of phosphine to Cp^*ZrMe_3 and Cp^*ZrCl_2Np respectively. The effect of steric crowding is particularly pronounced for these neopentyl complexes since the bis(neopentyl) derivative, $Cp^*ZrClNp_2$, and the tris(neopentyl) complex, Cp^*ZrNp_3, do not form PMe_3 adducts at all [112]. Low temperature addition of PF_3 to the 16-electron complex $Cp_2^*ZrH_2$ gives $Cp_2^*ZrH_2(PF_3)$ [118,119], but this is reported to be unstable and characterization has been limited to solution only. Addition of other phosphorus ligands such as $P(OMe)_3$ and PMe_3 did not result in the formation of adducts [119].

Elimination of methane from $Cp_2Zr(SCH_2R)Me$ and trapping with PMe_3 has been used to prepare $Cp_2Zr(\eta^2\text{-}SCHR)PMe_3$ [120] (eqn. (29)):



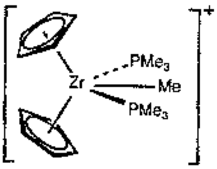
(29)

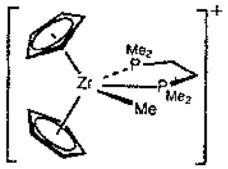
A similar oxygen-containing metallocycle has been isolated by coupling of two equivalents of ethylene with $CpZrCl(CO)_2dmpe$ [121], although the exact structure is not known (eqn. (30)):



(30)

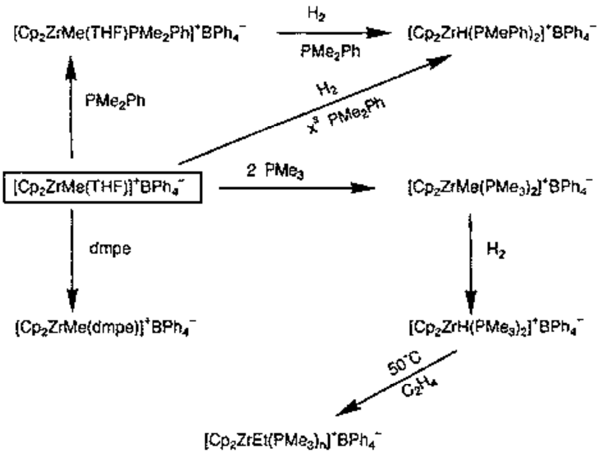
Cationic zirconium(IV) phosphines have recently been prepared [122]. Addition of PMe_3 to $[Cp_2ZrMe(THF)]^+BPh_4^-$ results in replacement of THF with two equivalents of PMe_3 (Scheme 2). Similarly, dmpe reacts to give $[Cp_2ZrMe(dmpe)]^+BPh_4^-$ and the bulkier monodentate phosphine PMe_2Ph forms $[Cp_2ZrMe(THF)PMe_2Ph]^+BPh_4^-$. Both the PMe_3 and the PMe_2Ph derivatives show extensive phosphine dissociation in solution by NMR spectroscopy at room temperature. At low temperatures (−60 °C), however, both PMe_3 ligands of $[Cp_2ZrMe(PMe_3)_2]^+$ BPh_4^- remain coordinated and the appearance of binomial triplets for both the Cp and the methyl resonances in the ^1H NMR spectrum indicates a symmetrical structure. The dmpe complex does not undergo phosphine dissociation at room temperature and the $^{31}P\{^1H\}$ NMR spectrum shows an AB quartet consistent with the expected unsymmetrical structure:





Hydrogenation of $[Cp_2ZrMe(PMe_3)_2]^+BPh_4^-$ produces the corresponding hydride $[Cp_2ZrH(PMe_3)_2]^+BPh_4^-$ (Scheme 2). The ^1H NMR spectrum again indicates a symmetrical structure but in this case phosphine dissociation does not occur at room temperature in this complex. The X-ray crystal structure of this hydride confirms the same symmetrical geometry in the solid state as found for the methyl derivative $[Cp_2ZrMe(PMe_3)_2]^+$ shown above. The Zr–P bond distances of 2.676 and 2.684 Å are 0.1–0.2 Å shorter than those found in other zirconium(IV) phosphine complexes, probably due to the increased electrophilicity of the positively charged Cp_2ZrMe fragment. The short Zr–P distances and small P–Zr–P angle (119.7°) are further evidence of the relatively uncrowded nature of the coordination sphere in this cationic zirconium hydride species.

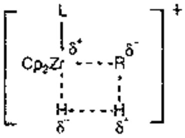
Hydrogenation of $[Cp_2ZrMe(THF)PMe_2Ph]^+BPh_4^-$ in the presence of PMe_2Ph produces $[Cp_2ZrH(PMe_2Ph)_2]^+BPh_4^-$ [122]. Thus coordination of bulkier phosphines is facilitated by the smaller hydride ligand as compared



Scheme 2.

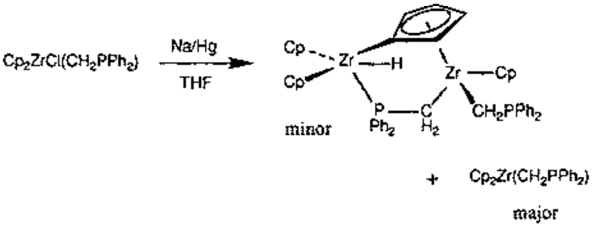
with the methyl group. The phosphine ligands in this hydride complex are not labile, as evidenced by NMR spectroscopy, which also indicates a symmetrical structure for this cation.

The rate of hydrogenation varies considerably, depending upon the identity of the ancillary ligand. It has been found that the smaller phosphines such as PMe_3 and PMe_2Ph greatly enhance the rate of hydrogenolysis of the Zr–Me group compared with that of $[Cp_2ZrMe(THF)]^+BPh_4^-$. Conversely, ligands such as dmpe and CH_3CN, the latter of which forms a bis(ligand) complex, retard the rate of hydrogenolysis. One rationale for this behaviour is provided by assuming that the reaction with dihydrogen involves a four-center four-electron transition state [123], the energy of which depends on the presence of a low lying LUMO on the metal center:



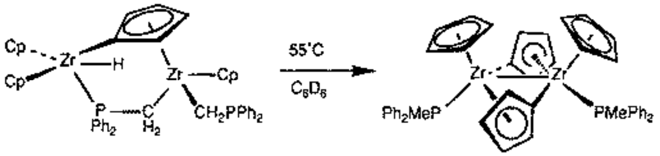
Since THF can function as a π donor, the energy of the LUMO is increased and the transition state for hydrogenation becomes less favorable energetically. Simple alkyl phosphines are generally regarded as only σ donors (however, see discussion in Section A), so provided a vacant site can be generated at the metal center, the rate of hydrogenation should increase. As already mentioned, both the cations $[Cp_2ZrMe(PMe_3)_2]^+$ and $[Cp_2ZrMe(THF)PMe_2Ph]^+$ show considerable phosphine dissociation at room temperature, thus providing the open site and low energy LUMO required for the above transition state. This would also explain why the dmpe and CH_3CN complexes do not undergo hydrogenation since neither ligand dissociates and the vacant site is unavailable. The chemistry of these cationic hydride complexes has not yet been studied extensively but there is a report [112] of the formation of $[\mathrm{Cp_2ZrEt(PMe_3)}_n]^+\mathrm{BPh_4^-}$ from the reaction of the hydride and ethylene at 50 °C. The number of coordinated $\mathrm{PMe_3}$ groups has not yet been established, but ^{1}H NMR spectroscopy seems to indicate a bis(ligand) adduct (Scheme 2). One or two acetonitrile ligands of the zirconium(IV) dication, $[\mathrm{Cp_2Zr(NCCH_3)_3}]^{2+}(\mathrm{BPh_4^-})_2$, are displaced by $\mathrm{PMe_3}$ to produce $[\mathrm{Cp_2Zr(NCCH_3)}_{3-n}(\mathrm{PMe_3})_n]^{2+}(\mathrm{BPh_4^-})_2$ ($n = 0, 1, 2$) [124]. ^{1}H and ^{31}P NMR spectroscopy suggest that there is an equilibrium operative between all possible species in solution.

A binuclear zirconium(IV) phosphine complex has been prepared as the minor product from $\mathrm{Cp_2ZrCl(CH_2PPh_2)}$ by reduction with sodium amalgam [125] (eqn. (31)):



(31)

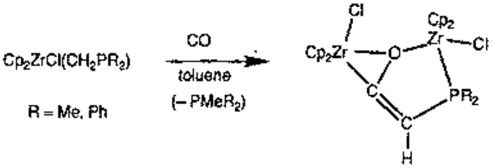
Both free and uncoordinated phosphorus environments are identifiable in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum. Heating to 55 °C results in formation of the zirconium(III) $\eta^1:\eta^5$-$\mathrm{C_5H_4}$ bridged dimer [125] (eqn. (32)):



(32)

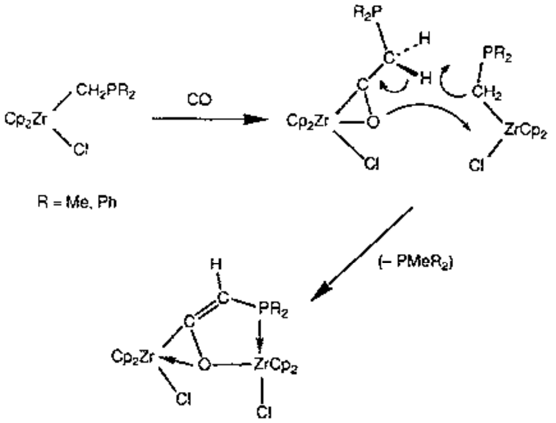
The major product, $\mathrm{Cp_2Zr(\eta^2\text{-}CH_2PPh_2)}$, is described in Section D(vi).

Treating $\mathrm{Cp_2ZrCl(CH_2PR_2)}$ (R = Ph [126], Me [127,128]) with CO results in the insertion of CO into the Zr–C bond and rearrangement to a bridging μ-O–C=CHPR$_2$ unit (eqn. (33)):



(33)

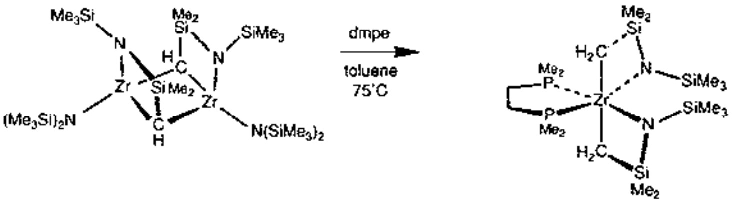
The X-ray structure of this molecule has been determined for both the methyl and the phenyl derivatives and each shows essentially identical geometries and bond lengths. It has been proposed that these complexes form by reaction of an initially formed acyl with a second equivalent of $Cp_2ZrCl(CH_2PR_2)$, followed by hydride transfer and loss of $PMeR_2$ [127] (Scheme 3):



Scheme 3.

Binuclear zirconium(IV) complexes have also been prepared by the addition of $Cp_2Zr(CO)PMe_3$ to $Cp_2^*ZrH_2$ to give the complex $Cp_2Zr(PMe_3)$-$(=CHOZr(H)Cp_2^*)$ [129]. The remaining hydride on the permethyl zirconocene fragment can be replaced by an iodide on treatment with CH_3I. The resulting iodide complex has been crystallographically characterized and the Zr–P distance of 2.693(2) Å is not unusual.

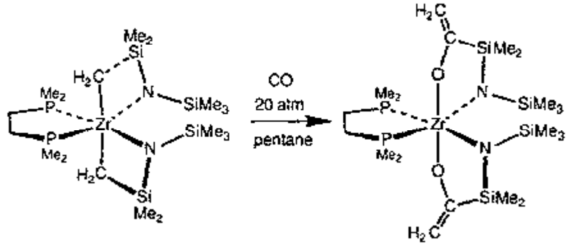
Several zirconium(IV) phosphine complexes containing the amide functionality have been reported by Andersen's group. The metallated disilylamide $Zr[CH_2SiMe_2N(SiMe_3)]_2dmpe$ complex has been synthesized by cleavage of a binuclear metallacyclic bridging carbene (eqn. (34))



(34)

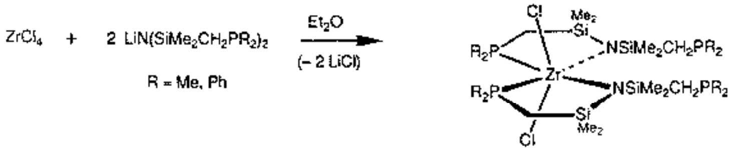
or by direct thermolysis of the bis(trimethylsilylamido) alkyl complexes $ZrR_2[N(SiMe_3)_2]_2$ (R = Me, Et, CH_2SiMe_3) in neat dmpe [130]. The crystal structure of this compound shows a distorted octahedral geometry about zirconium, with Zr–P bond distances of 2.848(1) and 2.855(1) Å that are similar to those in $ZrBz_4(dmpe)$ [113] and $Zr(CH_2SiMe_3)_4dmpe$ [114] (2.874

Å and 2.924 Å respectively). Reaction of $Zr[CH_2SiMe_2N(SiMe_3)]_2dmpe$ with CO at 20 atm gives a zirconium(IV) bis(enolate) complex with the phosphine ligand retained [130] (eqn. (35)):



(35)

Hybrid ligands incorporating both disilylamido and phosphine functionalities have been used to prepare phosphine complexes of zirconium(IV). The reaction of two equivalents of $LiN(SiMe_2CH_2PR_2)_2$ (R = Me, Ph) with $ZrCl_4$ yields the bis(ligand) complexes $ZrCl_2[N(SiMe_2CH_2PR_2)_2]_2$ [131] which have each ligand bound in a bidentate mode with a dangling phosphine arm (eqn. (36)):



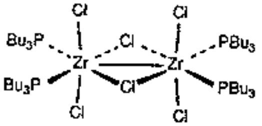
(36)

The X-ray crystal structure of $ZrCl_2[N(SiMe_2CH_2PMe_2)_2]_2$ shows that the distorted octahedral geometry is chiral, and this is supported by the solution ^1H NMR spectral data which show a rigid chiral environment to 60 °C, indicating that dissociation of the phosphine donors is not facile. The remaining chlorides are completely inert to substitution by any nucleophiles including alkyl lithium reagents, Grignards and $LiBH_4$. This is ascribed to steric shielding of these chlorides by the chelated arms of the ancillary ligand to external attack. While the bis(ligand) derivatives are surprisingly unreactive to further functionalization, the mono(ligand) complexes turn out to be very reactive. Reaction of one equivalent of $LiN(SiMe_2CH_2PR_2)_2$ (R = Me, Pr^i, Bu^t) with $ZrCl_4$ in toluene generates $ZrCl_3[N(SiMe_2CH_2PR_2)_2]$ [132] which has the ligand bound in a tridentate mode, and in the meridional configuration. It is noteworthy that the hafnium complex $HfCl_3[N(SiMe_2CH_2PMe_2)_2]$ adopts a facial geometry in the solid state but isomerizes to the meridional form in solution. The higher reactivity of these mono(ligand) derivatives is indicated by the reaction with methyl Grignard reagents. Addition of three equivalents of MeMgCl to $ZrCl_3[N(SiMe_2CH_2PR_2)_2]$ generates $ZrMe_3[N(SiMe_2CH_2PR_2)_2]$; for R = Me, the trimethyl complex was too unstable to be isolated [133].

A zirconium(IV) diallyl species with the formula $ZrCl_2(\eta^3:\eta^3\text{-}C_8H_{12})(PEt_3)_2$ has been isolated from the reaction of $[ZrCl_3(PEt_3)_2]_2$ with excess 1,3-butadiene [116]; $ZrCl_4(PEt_3)_2$ is also produced. The mechanism of this reaction and the structure of the diallyl derivative are unknown.

(vi) Zirconium(III)

The reduction of $ZrCl_4$ with Na/Hg in the presence of phosphine produces binuclear zirconium(III) complexes of the formula $[L_2ZrCl_2]_2(\mu\text{-}Cl)_2$ [116,134]. The structure of the PBu_3 derivative is shown below:

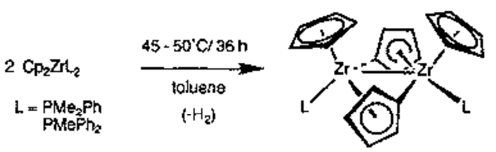


Although the PMe_3 derivative could not be prepared in pure form by this procedure (owing to its low solubility), as already mentioned this complex is formed via photolysis of $ZrNp_2Cl_2(PMe_3)_2$ [112] (see eqn. (27)). Molecular weight studies suggest the occurrence of an equilibrium between the dimer $Zr_2Cl_6L_4$ and the monomer $ZrCl_3L_2$. This is supported by the observation of an ESR signal for the d^1 monomer in the presence of excess phosphine [116]. The structures of the dimeric dppe, PEt_3 and PMe_2Ph complexes have been recently reported and all show similar molecular details in the solid state [134].

Heating $Zr_2Cl_6(PMe_2Ph)_4$ results in the formation of the formally zirconium(II) derivative $Zr_6Cl_{12}(PMe_2Ph)_6$ [135]. The X-ray structure shows a cluster consisting of an octahedral cage of zirconium atoms with edge-bridging chlorides and terminal phosphines. This is the only structurally characterized group 4 phosphine cluster of nuclearity greater than two.

Ethylene and propylene react with the zirconium(III) dimers to generate binuclear complexes with bridging hydrocarbyl ligands [116]. The structure of $[(Et_3P)_2ZrCl_3]_2(\mu\text{-}\eta^2:\eta^2\text{-}CH_2CH_2)$ [136] shows a symmetrically bound C_2H_4 moiety having a planar Zr_2C_2 array with *trans* phosphines perpendicular to this plane. This latter complex also formed when $[(Et_3P)_2ZrCl_2]_2(\mu\text{-}Cl)_2$ was recrystallized from 1,2-dichloroethane [136].

Trivalent zirconium phosphine complexes containing cyclopentadienyl ligands are quite well known although most of these complexes have only been generated in situ and characterized by ESR spectroscopy. The only examples of isolable complexes in this class are the binuclear $\eta^1 : \eta^5$-C_5H_4 bridged species prepared by heating solutions of Cp_2ZrL_2 [137] (eqn. (37))



(37)

or by reduction of Cp_2ZrCl_2 in the presence of PMe_2Ph or $PMePh_2$ [138]. Cryoscopic molecular weights and mass spectral data support a binuclear structure in solution and in the solid state. All these complexes are diamagnetic, indicating either the presence of a Zr–Zr bond or electron pairing through the bridging $\eta^1 : \eta^5$-ligands.

A large number of bis(cyclopentadienyl) zirconium(III) phosphines of the general type $Cp_2ZrX(L)$ ($X = Cl$, Br, H, alkyl, aryl; $L = PR_3$) have been characterized by ESR spectroscopy [68,139–146]. In some cases, both the X and L functionalities are contained in a single bidentate ligand such as CH_2PR_2 [68,144–146] or o-$C_6H_4PPh_2$ [146]. The four main routes to these derivatives are shown in eqns. (38)–(41):

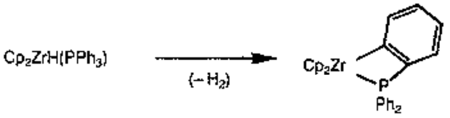
$$Cp_2Zr(PMePh_2)_2 + RX \longrightarrow Cp_2ZrX(PMePh_2) + R^{\bullet} \qquad (38)$$

$R = Bu^n, Bu^s, Bu^t$
$X = Cl, Br$

$$Cp_2ZrR_2 \xrightarrow[L]{h\nu} Cp_2ZrR(L) + R^{\bullet} \qquad (39)$$

$R = H, Me, Bz, CH_2SiMe_3, Ph$

$$Cp_2ZrX_2 \xrightarrow[L]{e^-} Cp_2ZrX(L) + X^- \qquad (40)$$



(41)

The ^{31}P hyperfine coupling constants range from 17 to 29 G but no trend based on structure or bonding is readily apparent. A few examples of mono(cyclopentadienyl) complexes such as $CpZrPh_2(PEt_3)$ [140], $CpZr(\eta^2$-$CH_2PPh_2)_2$ and $CpZr(\eta^2$-$O_2CCH_2PPh_2)_2$ [68] have also been reported by photochemical loss of $Cp^{\bullet}$ or by loss of Cp^- during electrochemical reduction of the corresponding bis(cyclopentadienyl) precursors.

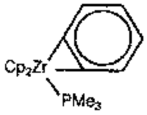
(vii) Zirconium(II)

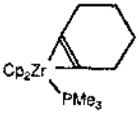
The only known zirconium(II) halide complex with phosphine ligands is the already discussed $Zr_6Cl_{12}(PMe_2Ph)_6$ cluster [135] prepared by thermolysis of the zirconium(III) precursor $Zr_2Cl_6(PMe_2Ph)_4$. Almost all the remaining zirconium(II) complexes contain the cyclopentadienyl ligand. The bis(cyclopentadienyl)zirconium or zirconocene complexes constitute the most important class of zirconium(II) phosphine derivatives. The bis(phosphine) adducts Cp_2ZrL_2 ($L = PMe_3$, $P(OMe)_3$; L_2 = dmpe) are accessible by reduction of zirconocene dichloride (Cp_2ZrCl_2) with either Na/Hg or magnesium in THF [70,74,137]; the sodium amalgam reduction is reported to work best for dmpe [137]. An alternative synthesis of Cp_2ZrL_2 ($L = PMe_2Ph$, $PMePh_2$; L_2 = dmpe, dppe) involves phosphine-induced reductive elimination of methylcyclohexane from $Cp_2ZrH(CH_2C_6H_{11})$ [147]. Those zirconocene derivatives containing monodentate phosphine ligands are reported to be thermally unstable and readily convert to the binuclear zirconium(III) complexes $[CpZr(L)]_2(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)_2$ [137,138,147] discussed previously (see eqn. (36)). Despite this instability, the PMe_3 derivative $Cp_2Zr(PMe_3)_2$ [70] has been structurally characterized and as expected shows the pseudotetrahedral geometry with a Zr–P bond length of 2.64 Å.

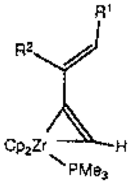
The closely related phosphine or phosphite carbonyls $Cp_2Zr(CO)L$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, PBu_3, $P(OMe)_3$) can be prepared either by thermolysis [62,80,148,150] or photolysis [106,149] of $Cp_2Zr(CO)_2$ in the presence of added phosphine. The kinetics of the thermal substitution process have been examined and it was concluded that this reaction proceeds by an S_N2 mechanism [80]. This is in contrast with the titanium analogues where an S_N1 mechanism was implicated. Presumably, the greater size of zirconium(II) compared with titanium(II) facilitates expansion of the coordination sphere to accommodate the incoming ligand. Interestingly, addition of CO to the corresponding Cp_2ZrL_2 derivatives generally results in the formation of $Cp_2Zr(CO)_2$ as the main product. Only $Cp_2Zr(CO)(PMePh_2)$ has been prepared by this procedure [137,138].

Complexes containing an alkyne unit have been described. Acetylene reacts with $Cp_2Zr(PMe_3)_2$ to give $Cp_2Zr(HC{\equiv}CH)(PMe_3)$ [83]. The C≡C stretching frequency of 1597 cm^{-1} implies that this complex should be formulated as having a metallocyclopropene structure rather than one with a π,η^2-alkyne unit. The diphenylacetylene complex $Cp_2Zr(PhC{\equiv}CPh)(PMe_3)$ [151] was also prepared by addition of PhC≡CPh to $Cp_2Zr(PMe_3)_2$ generated in situ. Almost simultaneously, the 1-hexyne complex $Cp_2Zr(HC{\equiv}C\text{-}C_4H_9)(PMe_3)$ was reported, prepared via elimination of CH_4 from $Cp_2Zr(CH{=}CHC_4H_9)Me$ and trapping with PMe_3 [152]. The X-ray crystal structures of these complexes show the C–C bond lengths to be 1.286(5) Å

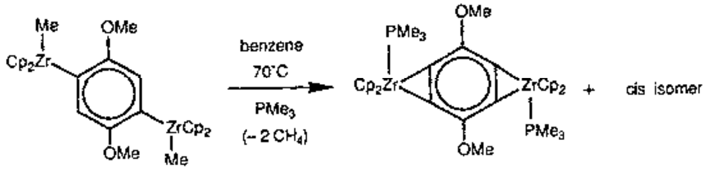
(1-hexyne) and 1.36 Å (diphenylacetylene), which are intermediate between a carbon–carbon double and triple bond. The elimination of methane or benzene from alkenyl or diaryl complexes, followed by trapping with PMe_3, is an apparently general procedure for the preparation of strained cycloalkyne [153], benzyne [154] and enyne [155] derivatives:







Indeed, the extension to binuclear benzdiyne complexes has recently been reported [156]. From the thermolysis of the *para*-phenylene-bridged complex, $[Cp_2ZrMe]_2(\mu\text{-p-}C_6H_4)$, a mixture of four inseparable isomers with the formula $[Cp_2Zr(PMe_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_2)$ was obtained. However, blocking two sites on the benzene ring with methoxy substituents only allows formation of the 1,4-benzdiyne complexes $[Cp_2Zr(PMe_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}1,4\text{-}C_6(OMe)_2)$ (eqn. (42)):

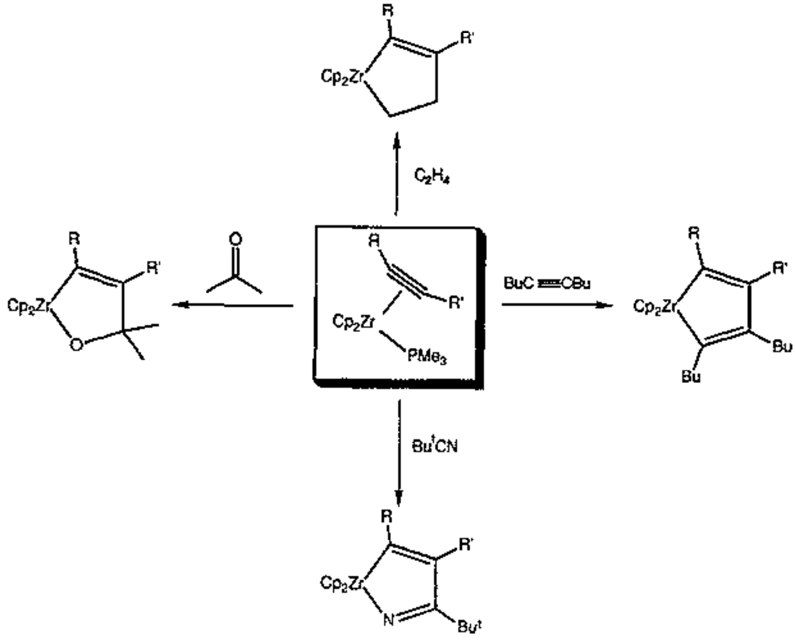


(42)

The lower solubility of the *trans* isomer facilitated separation from the *cis* isomer.

These zirconocene alkyne complexes have a rich reaction chemistry. Because this area has been just recently reviewed [157], only some of the more important reactions are summarized in Scheme 4. Reactions with unsaturated substrates such as alkenes, alkynes, ketones and nitriles lead to insertion of the unsaturated linkage into a Zr–C bond of the metallocyclopropene ring. In the case of ketones and nitriles, the heteroatom always bonds to the electropositive zirconium atom in the product. In all these reactions, the phosphine serves to stabilize the reactive starting material but is ultimately lost.

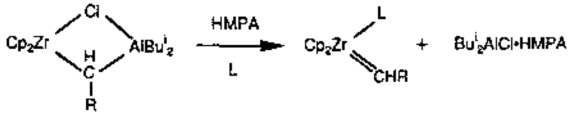
Olefins react with $Cp_2Zr(PMe_3)_2$ to give the complexes $Cp_2Zr(RHC{=}CHR)(PMe_3)$ (R = H [151], Ph [158]) which can be formally considered as π,η^2-alkene derivatives. However, $^{13}C\{^1H\}$ NMR spectra of these derivatives are more consistent with a metallocyclopropane structure having sp^3-hybridized carbon atoms. The X-ray crystal structure of the ethylene complex $Cp_2Zr(H_2C{=}CH_2)(PMe_3)$ [151] reveals a C–C bond length of 1.486(8)



Scheme 4.

Å which is considerably longer than a typical coordinated carbon–carbon double bond (1.36 Å [159]) and further supports this proposal. A simple procedure for the preparation of the 1-butene complex $Cp_2Zr(H_2C{=}CH\text{-}CH_2CH_3)(PMe_3)$ involves reaction of two equivalents of BuLi and Cp_2ZrCl_2 in the presence of PMe_3 [152]. The reaction chemistry of these π,η^2-alkene or metallocyclopropene derivatives has not yet been explored in detail; however, some preliminary reactions indicate that insertion into one of the Zr–C bonds occurs, as is observed for the metallocyclopropene complexes [151,158].

A number of zirconium carbene complexes stabilized by phosphine ligands have been reported. The methylidene complex $Cp_2Zr{=}CH_2(PMePh_2)$ [160] was generated in situ from $Cp_2Zr(PMePh_2)_2$ and a large excess of $Ph_3P{=}CH_2$ with mild heating (42° C). Although the dark solution containing this methylidene complex decomposed over a period of 1 h at room temperature, the formation of the methylidene was clearly evident by the observation of characteristic resonances attributable to the $Zr{=}CH_2$ unit ($C\underline{H}_2$: 11.0 ppm; $\underline{C}H_2$: 248.6 ppm). More stable alkylidene complexes [161] were obtained by cleaving alkylidene-bridged Zr–Al complexes with HMPA in the presence of added phosphine as shown in eqn. (43):

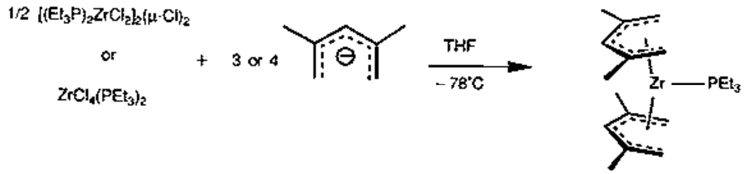


(43)

Although these bulkier alkylidene complexes $Cp_2Zr{=}CHR(L)$ were thermally more stable than the parent methylidene discussed above, none of these complexes were isolated as crystalline solids, precluding any crystallographic studies. Nevertheless, $Cp_2Zr{=}CHCH_2Bu^t(PPh_3)$ was obtained as a pure yellow–orange oil with appropriate spectroscopic parameters for an alkylidene complex. These alkylidene complexes of zirconium are useful "Wittig-like" reagent for the stoichiometric preparation of olefins from aldehydes and aldimines [162].

Addition of PF_3 to the dinitrogen dimer $[Cp_2^*ZrN_2]_2(\mu\text{-}N_2)$ results in the formation of $[Cp_2^*Zr(PF_3)]_2(\mu\text{-}N_2)$ [163] which is stable only at low temperature. Other phosphines such as PMe_3 and $P(OMe)_3$ are reported not to form detectable adducts.

The bis(pentadienyl) complex, $Zr(\eta^5\text{-}2,4\text{-}C_5H_5Me_2)_2PEt_3$, has been prepared from zirconium(III) or zirconium(IV) precursors [164] (eqn. (44)):

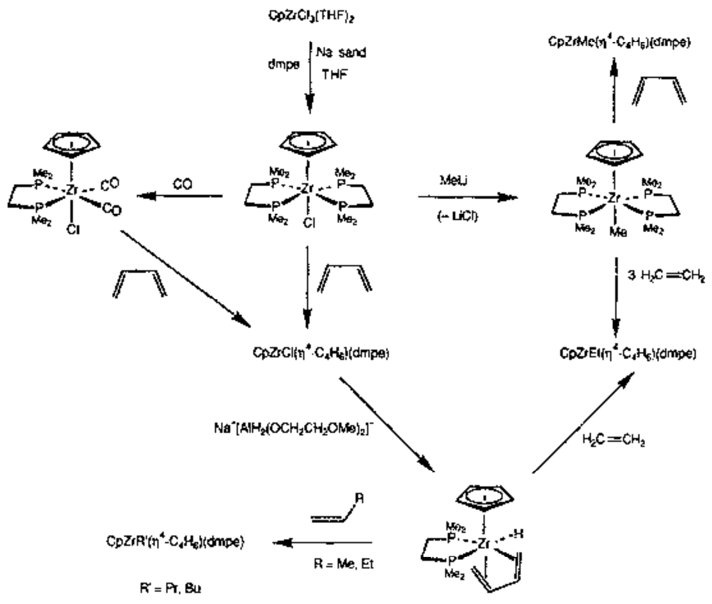


(44)

The X-ray crystal structure of this complex shows an eclipsed geometry for the pentadienyl ligands.

Mono(cyclopentadienyl) zirconium(II) phosphine complexes have been recently reported. Reduction of $CpZrCl_3$ with sodium sand in the presence of dmpe affords $CpZrCl(dmpe)_2$ [121,165] in high yield (Scheme 5). The X-ray crystal structure of this complex reveals a distorted octahedral geometry with equatorial dmpe ligands. Metathesis with MeLi gives $CpZrMe(dmpe)_2$ [166] which has also been structurally characterized; the Zr–C bond length of 2.47(2) Å for the methyl ligand is longer than that found in Cp_2ZrMe_2 ($Zr\text{–}CH_3$, 2.273(5) Å), and this has been attributed to the greater steric crowding in $CpZrMe(dmpe)_2$. Indeed, it is observed that the dmpe ligands in both the chloride and methyl complexes are quite labile. For example, 1,3-butadiene displaces one dmpe to give $CpZrX(\eta^4\text{-}C_4H_6)(dmpe)$ ($X = Cl, CH_3$) [166]. Similarly, CO reacts with $CpZrCl(dmpe)_2$ to give $CpZrCl(CO)_2(dmpe)$. The latter complex has been structurally characterized and again shows a distorted octahedral environment with equatorial dmpe and CO ligands [121].

The pentamethylcyclopentadienyl complex $Cp^*ZrCl(CO)_2(dmpe)$ [99] has also been prepared by reduction of Cp^*ZrCl_3 with sodium naphthalenide in



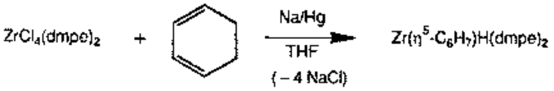
Scheme 5.

the presence of dmpe and CO. The hafnium analogue has been structurally characterized in the solid state and it shows that one arm of the dmpe chelate is axial, presumably due to the greater steric crowding of the Cp* ligand compared with the Cp derivative.

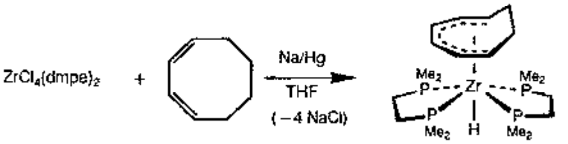
The carbonyl ligands of $CpZrCl(CO)_2(dmpe)$ are also labile as evidenced by the facile exchange with free ^{13}CO and the relatively easy substitution with 1,3-butadiene. In addition, the reaction of $CpZrCl(dmpe)_2$ with $CpZrCl(CO)_2(dmpe)$ leads to an insoluble binuclear product with the formula $[CpZrCl(CO)(dmpe)]_2(\mu\text{-dmpe})$. This same product is also obtained if the carbonylation of $CpZrCl(dmpe)_2$ is carried out on saturated solutions [121].

The related hydride complex $CpZrH(\eta^4\text{-}C_4H_6)(dmpe)$ [167], prepared by metathesis of the chloride with $Na^+[AlH_2(OCH_2CH_2OMe)_2]^-$ (Red-Al), undergoes smooth insertion reactions with small alkenes to generate the corresponding alkyl complexes $CpZrR(\eta^4\text{-}C_4H_6)(dmpe)$ (R = Et, Pr, Bu) (Scheme 5). The ethyl derivative is also formed via reaction of $CpZrMe(dmpe)_2$ with three equivalents of ethylene [166]; this interesting reaction involves coupling of ethylene and loss of methane. Presumably the hydride $CpZrH(\eta^4\text{-}C_4H_6)(dmpe)$ is an intermediate in this transformation and it further reacts with ethylene to give the observed product. The ethyl complex is also a catalyst for the dimerization of ethylene to 1-butene, albeit a rather slow one (ca. 3 turnovers per day) [166].

Wreford's group has reported some closely related zirconium(II) phosphine complexes containing dienyl ligands. The reduction of $ZrCl_4(dmpe)_2$ in the presence of cyclohexadiene or cyclooctadiene produces zirconium(II) dienyl-hydrides stabilized with dmpe [108,168] (eqns. (45) and (46)):



(45)



(46)

In the cyclohexadiene reaction (eqn. (45)), the zirconium(II) dichloride–diene complex $[ZrCl_2(\eta^4\text{-}C_6H_8)dmpe]_2$ [168] was isolated in low yield as an intermediate which upon further reduction generates the observed cyclohexadienyl hydride complex, $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. Reduction to a zirconium(0) cyclohexadiene complex followed by oxidative addition of an allylic C–H bond is a reasonable proposal for the formation of these derivatives. Both dienyl hydrides give molecular ions in the gas phase and the cyclooctadienyl complex has been crystallographically characterized. The cyclohexadienyl complex catalyzes the disproportionation of cyclohexadiene to cyclohexane and benzene. In addition, this complex is a catalyst for the low pressure hydrogenation of 1-octene and the isomerization of 1-pentene [108].

(viii) Zirconium(0)

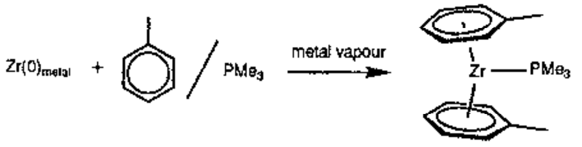
Very few zerovalent zirconium phosphine complexes have been reported. A number of 1,3-butadiene complexes have been prepared (eqn. (47)) and the phosphine ligand of choice is dmpe [108,109]. Reduction of $ZrCl_4(dmpe)_2$ with sodium amalgam in the presence of excess 1,3-butadiene generates $[Zr(\eta^4\text{-}C_4H_6)_2dmpe]_2(\mu\text{-dmpe})$. The bridging dmpe can be removed by addition of CO at low temperature to generate $Zr(\eta^4\text{-}C_4H_6)_2dmpe(CO)$, which decomposes violently at room temperature. Instead, slow warming of the CO adduct at −22 °C under vacuum produces the 16-electron complex $Zr(\eta^4\text{-}C_4H_6)_2dmpe$:

$$ZrCl_4(dmpe)_2 \xrightarrow[\text{THF}\atop \text{1,3-butadiene}]{\text{Na/Hg}} \left[Zr(\eta^4\text{-}C_4H_6)_2dmpe\right]_2(\mu\text{-dmpe}) \xrightarrow[-45\,°\text{C}]{\text{CO}}$$

$$Zr(\eta^4\text{-}C_4H_6)_2dmpe(CO) \xrightarrow[(-\text{CO})]{-22\,°\text{C}} Zr(\eta^4\text{-}C_4H_6)_2dmpe \quad (47)$$

This complex is stable at ambient temperatures and gives a molecular ion in the mass spectrum. Phosphine adducts $Zr(\eta^4\text{-}C_4H_6)_2dmpe(PR_3)$ can be precipitated at −78°C, but again these adducts are unstable at room temperature.

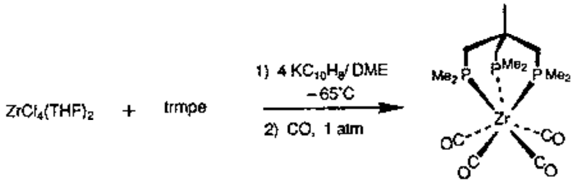
The bis(toluene) zirconium(0) complex, $Zr(\eta^6\text{-}C_7H_8)_2PMe_3$, can be prepared by co-condensation of zirconium metal with toluene and PMe_3 [169,170] (eqn. (48)):



(48)

The proton NMR spectrum indicates that the PMe_3 does not dissociate in solution although it is readily lost in the mass spectrum.

The tetracarbonyl complex $Zr(CO)_4$trmpe [105] was prepared by reduction of $ZrCl_4(THF)_2$ with potassium naphthalenide as shown in eqn. (49):



(49)

The X-ray crystal structure shows that the structure is the expected four-legged piano stool.

(ix) Hafnium(IV)

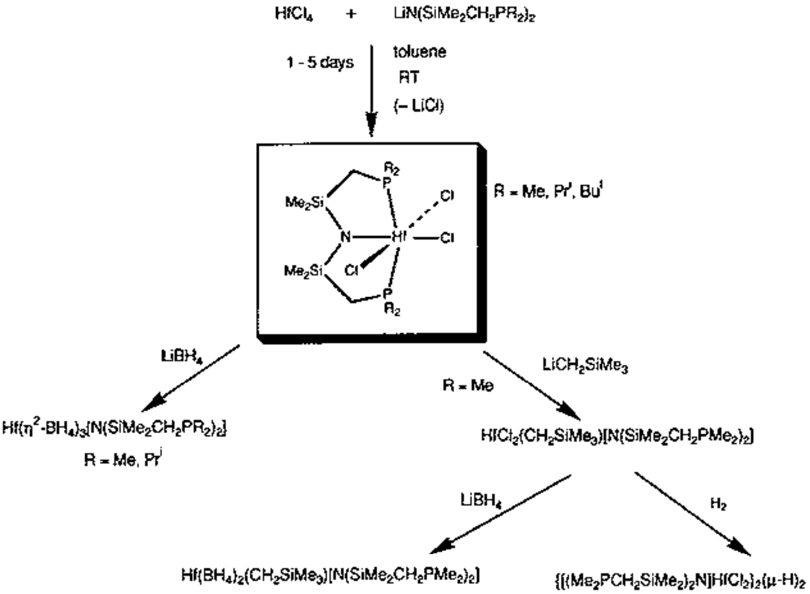
The number of hafnium phosphine complexes characterized is far fewer than for either titanium or zirconium. In the tetravalent state, phosphine adducts of $HfCl_4$ have been prepared. The bis(chelating ligand) adduct $HfCl_4(dmpe)_2$ [171] is formed with dmpe while the more sterically demanding dppe ligand only affords a mono adduct $HfCl_4(dppe)$ [110]. Treating $HfCl_4(dmpe)_2$ with methyllithium produces $HfMe_4(dmpe)_2$ [113] which, on the basis of spectroscopic data, appears to be isostructural with $ZrMe_4(dmpe)_2$ discussed earlier [113]. There is NMR evidence to suggest that $HfBz_4$ forms a mono PMe_3 adduct in solution but no complex has been isolated [115].

In sharp contrast with titanium and zirconium, no hafnium(IV) phosphine complexes containing cyclopentadienyl ligands are known. Only the mono(pentamethylcyclopentadienyl) derivative, $Cp^*HfCl_2Et(PMe_3)$, has been reported. It was prepared by hydrogenation of a hafnium phosphide in the presence of ethylene and PMe_3 [172] (eqn. (50)):

$$Cp^*HfCl_2(PBu^t_2) + H_2C{=}CH_2 + PMe_3 \underset{(-HPBu^t_2)}{\xrightarrow[\text{toluene}]{H_2}} Cp^*HfCl_2Et(PMe_3) \tag{50}$$

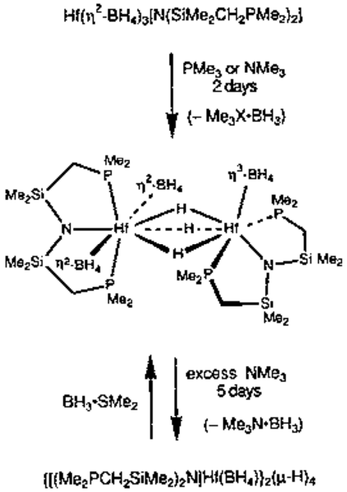
A number of hafnium(IV) phosphine complexes containing hybrid amido-phosphine ligands have been prepared [131,132,173,174]. The bis(ligand) complexes $HfCl_2[N(SiMe_2CH_2PR_2)_2]_2$ (R = Me, Ph) have been isolated from the reaction of the corresponding lithium ligand salt with $HfCl_4$ in diethyl ether [132]. The hafnium complex appears to have the same structure as the crystallographically characterized zirconium analogue (R = Me) on the basis of NMR spectroscopy. As discussed previously, the bis(ligand) complexes do not undergo metathetical reactions with Grignard or alkyl lithium reagents, lithium borohydride or Me_3SiCN, again presumably for steric reasons.

Mono(ligand) derivatives, having methyl substituents at phosphorus, were initially accessed by conproportionation of the bis(ligand) complexes and excess $HfCl_4$ to generate materials with the formula $HfCl_3[N(SiMe_2CH_2PMe_2)_2] \cdot HfCl_4$. Nevertheless, treatment of this material with excess $LiBH_4$ allows isolation of $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ from the volatile $Hf(BH_4)_4$ also produced. More recently, mono ligand derivatives free of excess $HfCl_4$ have been prepared by carrying out the stoichiometric reaction of one equivalent of $LiN(SiMe_2CH_2PR_2)_2$ (R = Me, Pr^i, Bu^t) with $HfCl_4$ in toluene [131] (Scheme 6). With R = Me, the reaction is best done under conditions of high dilution. Two crystalline forms (monoclinic and orthorhomic) of $HfCl_3[N(SiMe_2CH_2PMe_2)_2]$ were isolated, both having the *fac* octahedral geometry. In solution, both crystalline forms isomerize to the *mer* geometry on the basis of NMR (^1H, ^{13}C) spectroscopy. Unlike the bis(ligand) derivatives, the mono ligand complexes readily undergo metathesis with $LiCH_2Sie_3$, MeLi and $LiBH_4$ [173] (Scheme 6). Hydrogenolysis of $HfCl_2(CH_2SiMe_3)[N(SiMe_2CH_2PMe_2)_2]$ produces the binuclear dihydride $\{[(Me_2CH_2SiMe_2)_2N]HfCl_2\}_2(\mu\text{-}H)_2$ (Scheme 6). The above-mentioned tris(borohydride) complex $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ is monomeric in benzene (solution molecular weight measurements) while IR and ^{31}P NMR spectroscopy suggest meridional octahedral geometry with bidentate BH_4^- ligands. ^{11}B NMR does, however, show that exchange occurs between the two inequivalent BH_4^- sites at room temperature. Treatment of $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ with excess PMe_3 or NMe_3 cleaves some of the borohydride ligands, producing the binuclear tris(borohydride)–trihydride complex $\{[(Me_2PCH_2SiMe_2)_2N]Hf(BH_4)_2\}(\mu\text{-}H)_3\{Hf(BH_4)[N(SiMe_2CH_2$-



Scheme 6.

$PMe_2)_2]\}$ [173] (Scheme 7). The X-ray structure of this compound reveals three bridging hydrides and monodentate (distorted), bidentate and tridentate BH_4^- ligands in the same molecule. In solution, all three borohydride resonances are equivalent, indicating a fluxional process involving transfer of borohydride ligands between the inequivalent hafnium centers. Upon further reaction with excess NMe_3 over long reaction times, the binuclear



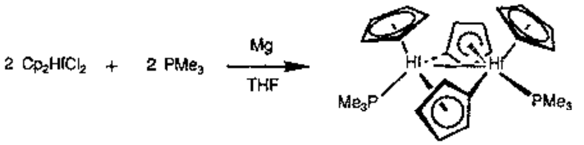
Scheme 7.

tetrahydride $\{[(\mathrm{Me_2CH_2SiMe_2})_2\mathrm{N}]\mathrm{Hf(BH_4)}\}_2(\mu\text{-H})_4$ is obtained. This complex has not been structurally characterized but NMR data suggest a symmetrical structure with rapidly rotating hydride ligands [173].

The only other hafnium(IV) phosphine complexes reported were prepared by phosphine cleavage of binuclear hafnium(IV) species. The metallated silyl amide complex $\mathrm{Hf[CH_2SiMe_2N(SiMe_3)]_2dmpe}$ appears to be isostructural with the structurally characterized zirconium analogue (see eqn. (34)) on the basis of spectroscopy [130]. Reaction of dppe with $\{\mathrm{HfCl_3[C(Cl)}{=}\mathrm{NBu}^t]\}_2$ is reported to generate $\mathrm{HfCl_3[C(Cl)}{=}\mathrm{NBu}^t\mathrm{](dppe)}$, in which the mode of bonding is unknown [30,175].

(x) *Hafnium(III)*

The only known hafnium(III) complex is the $\eta^1:\eta^5\text{-C}_5\mathrm{H}_4$ binuclear species shown in eqn. (51):



(51)

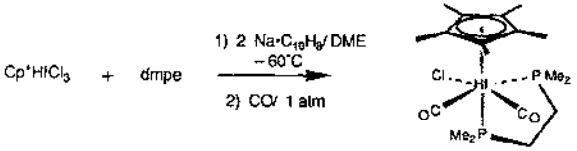
This compound was prepared in excellent yield by the magnesium metal reduction of $\mathrm{Cp_2HfCl_2}$ in the presence of one equivalent of $\mathrm{PMe_3}$ [69]. Like the titanium and zirconium analogues discussed earlier, this complex is diamagnetic, indicating either a metal–metal bond or spin pairing through the bridging ligands. The NMR (^{1}H, ^{13}C) spectra do not indicate any fluxional behaviour in solution.

(xi) *Hafnium(II)*

In contrast with the lighter congeners of group 4, phosphine complexes of hafnium(II) are still quite rare. In most cases, this appears to reflect the inherent difficulty in reducing hafnium rather than a lack of research in this area. A good illustration of this appears to be the formation of $\mathrm{Cp_2Hf(PR_3)_2}$-type derivatives. The titanium and zirconium compounds are very well known and have been utilized as convenient precursors in the preparation of other divalent complexes. However, to date, $\mathrm{Cp_2Hf(PMe_3)_2}$ is the only compound in this class and has been reported to form in trace quantities during the reduction of $\mathrm{Cp_2HfCl_2}$ with magnesium metal [69] (see eqn. (51)). It appears that complexes of this type readily convert to $[\mathrm{CpHf(PMe_3)}]_2(\mu\text{-}\eta^1:\eta^5\text{-C}_5\mathrm{H}_4)_2$ as discussed earlier.

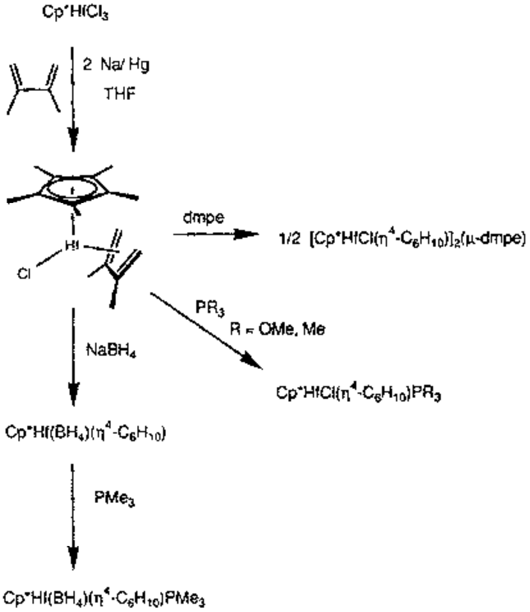
Compounds of the type $\mathrm{Cp_2Hf(L)(CO)}$ (L = $\mathrm{PMe_3}$, $\mathrm{PF_3}$, $\mathrm{PPh_3}$, dppe) have been prepared by thermal [80] and photochemical [119,149,176] phosphine substitution of CO in $Cp_2Hf(CO)_2$. The PPh_3 complex reacts with alkynes to produce a hafnacyclopentadiene complex with loss of PPh_3 [149]. No alkyne or alkene (hafnacyclopropene or hafnacyclopropane respectively) phosphine complexes have been reported as yet.

Some mono(cyclopentadienyl) phosphine hafnium(II) complexes have been reported and are analogous to those already discussed for zirconium(II) in Scheme 5. Reduction of $CpHfCl_3(THF)_2$ in the presence of dmpe produces $CpHfCl(dmpe)_2$ [121]. This complex readily loses one dmpe ligand on exposure to CO to give $CpHfCl(dmpe)(CO)_2$. The structure of this complex is probably similar to the crystallographically characterized zirconium analogue [121]. The Cp* derivative has been prepared directly from Cp^*HfCl_3 as shown in eqn. (52) [99]:



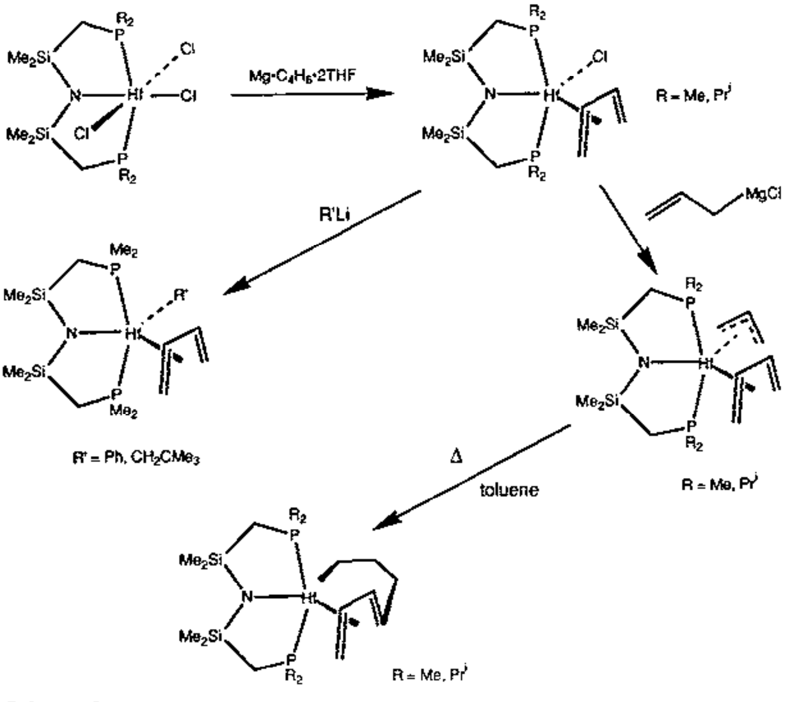
(52)

Unlike $CpMCl(dmpe)(CO)_2$ (M = Zr, Hf), one phosphorus atom of the dmpe ligand occupies an axial site, *trans* to the Cp* ring. This is probably a result of the increased steric bulk of the Cp* relative to Cp. The preparation of phosphine adducts of mono Cp* complexes of formally hafnium(II) incorporating 2,3-dimethylbutadiene has been reported (Scheme 8) [99,177,178]. Attempts to generate a hydride by Lewis base cleavage of a BH_4^- complex failed.



Scheme 8.

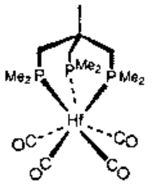
Finally, the preparation of formally hafnium(II) complexes incorporating the amide–phosphine hybrid ligand $^{-}\mathrm{N(SiMe_2CH_2PR_2)_2}$] (R = Me, Pr^i) has been achieved by reduction of $\mathrm{HfCl_3[N(SiMe_2CH_2PR_2)_2]}$ with magnesium butadiene to generate $\mathrm{Hf(\eta^4\text{-}C_4H_6)Cl[N(SiMe_2CH_2PMe_2)_2]}$ [179(a)] (Scheme 9). The phenyl hafnium butadiene complex $\mathrm{Hf(\eta^4\text{-}C_4H_6)Ph[N(SiMe_2CH_2PMe_2)_2]}$ has been structurally characterized and shows that the butadiene is π,η^4 bound to the hafnium center [179(b)]. Although the C–C bond alternation pattern in the butadiene unit does suggest some contribution from the σ^2,π resonance form, this contribution is significantly less than that observed for other early transition metal diene complexes [180]. The diene complexes react with allyl Grignard to produce a mixed allyl–butadiene complex having the formula $\mathrm{Hf(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_3H_5)[N(SiMe_2CH_2PR_2)_2]}$. While the less sterically crowded derivative, with R = Me, has been spectroscopically characterized, for R = Pr^i, rapid coupling of the allyl and butadiene ligands occurs to give an $\eta^1:\eta^5\text{-}C_7H_{11}$ fragment. The structure of the latter complex has been confirmed by X-ray crystallography [179(a)]. The R = Me complex converts in solution to the analogous compound over a period of several days. The coupling of an allyl and a butadiene ligand is apparently unique and has implications in the polymerization of butadiene by metal allyl complexes [12].

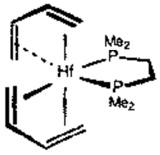


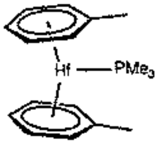
Scheme 9.

(xii) Hafnium(0)

At the time of writing, only three hafnium(0) phosphine complexes have been reported. $Hf(CO)_4(trmpe)$ has been prepared by reductive carbonylation in the presence of the tridentate phosphine trmpe [105]. The butadiene complex, $Hf(\eta^4\text{-}C_4H_6)_2(dmpe)$ has been prepared by two different routes [100,101]. The crystal structure of this complex has been determined. The average Hf–C (terminal) distance is 0.035(6) Å shorter than the Hf–C (internal) distance for the butadiene ligand, reflecting a small contribution from the σ^2,π resonance form. Finally, the bis(arene) complexes $Hf(\eta^6\text{-arene})_2PMe_3$ were prepared by the metal vapour synthesis [169,170]. No structural data have been reported yet, but a bent sandwich structure is assumed:





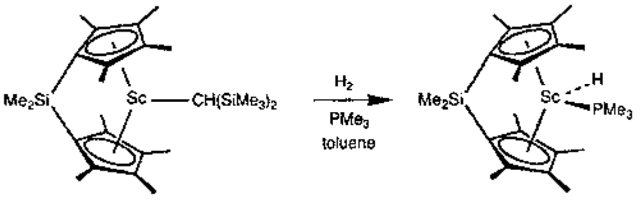


E. GROUP 3: SCANDIUM, YTTRIUM, LANTHANUM AND ACTINIUM

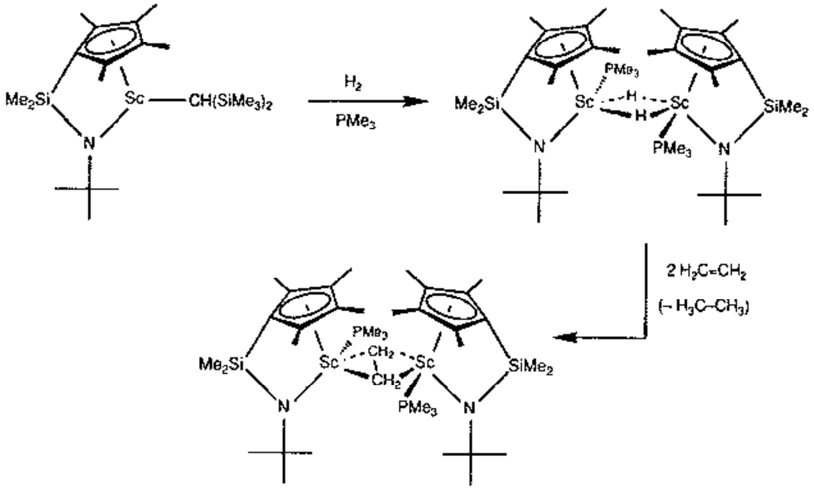
(i) Scandium

The first reports of phosphine complexes of a group 3 element are from 1969 [181]. White powders with the empirical formulae $ScCl_3(dppe)$ and $ScBr_3(dppe)_{1.5}$ were isolated from the reaction of the anhydrous scandium halides with excess dppe. Although the structures are unconfirmed and the analytical data rather poor, oligomeric electrolytes were proposed on the basis of solution molecular weight and conductivity studies in nitromethane.

Very recently, three authentic phosphine complexes of scandium were synthesized and crystallographically characterized [182,183]. Hydrogenation of the alkyl complex, shown in eqn. (53), in the presence of PMe_3 (1 equivalent) produced a monomeric scandium hydride of the formula $\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}ScH(PMe_3)$ [182]:



(53)

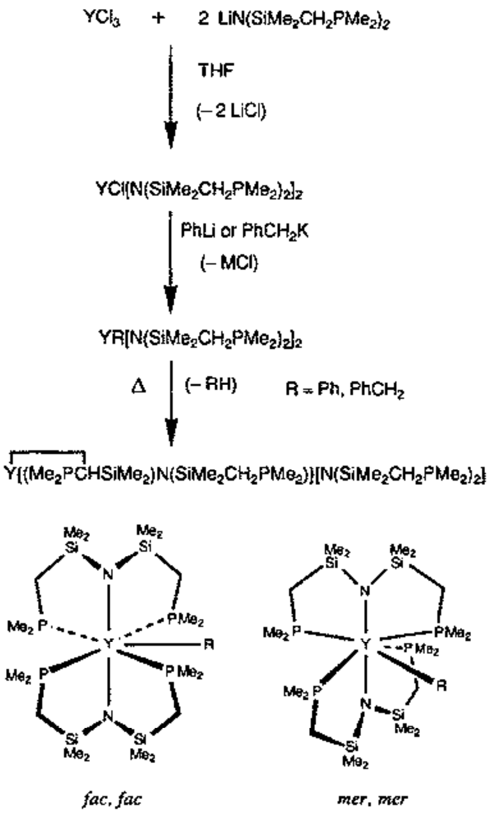


Scheme 10.

The PMe_3 ligand apparently stabilizes the complex by preventing oligomerization and decomposition reactions. This is the first structurally characterized phosphine or hydride complex of scandium. The Sc–P distance of 2.752(1) Å is 0.21 Å larger than the sum of the covalent radii, indicating a weak Sc–P bond. A related scandium alkyl stabilized by the $Bu^tN(SiMe_2)C_5Me_4$ ligand shown in Scheme 10 also undergoes hydrogenation in the presence of PMe_3, but this less bulky Cp*SiNR ligand results in the formation of a binuclear hydride [183]. The X-ray structure of this complex shows a very long Sc–P distance of 2.996(1) Å which probably reflects increased steric crowding in the binuclear framework. This compound reacts with ethylene to give an ethylene sandwich complex (Scheme 10). The ethylene unit is nearly perpendicular to the Sc–Sc vector, similar to the geometry found in $[ZrX_3(PEt_3)_2]_2[\mu\text{-}C_2H_4]$ (X = Cl, Br). The ethylene C–C distance of 1.433(12) Å is intermediate between a single and a double bond distance and is considerably shorter than that found in zirconium compounds [136] (1.69(3)Å, X = Cl; 1.56(4) Å, X = Br).

(ii) Yttrium

The first yttrium phosphine complexes were reported in 1988. The bis(amido diphosphine) hybrid ligand complex $YCl[N(SiMe_2CH_2PMe_2)_2]_2$ was prepared as shown in Scheme 11 [184(a)]. Low temperature (−85 °C) ^{31}P NMR data suggest a structure based on a pentagonal bipyramid; two possible isomeric stereochemistries are illustrated in Scheme 11. At higher temperatures, the complex is fluxional, probably due to phosphine dissocia-

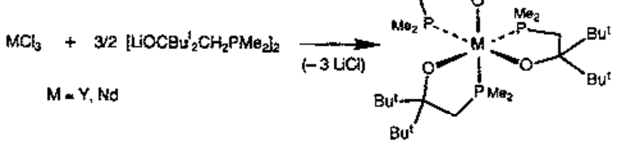


fac, fac *mer, mer*

Scheme 11.

tion processes. The ^{89}Y NMR spectrum, showing the expected binomial quintet ($^1J_{Y-P} = 52$ Hz), was obtained. Metathesis with phenyllithium and benzylpotassium produces the corresponding hydrocarbyl complexes which upon thermolysis eliminate RH to give the metallated species $\overline{\text{Y(Me}_2\text{PC}}\text{HSi-Me}_2\text{)N(SiMe}_2\text{CH}_2\text{PMe}_2\text{)[N(SiMe}_2\text{CH}_2\text{PMe}_2\text{)}_2\text{]}$. That the metallation occurred at the methylene carbon of the backbone and not at one of the phosphorus methyls was shown by ^{13}C{^{1}H} NMR spectroscopy and confirmed by an X-ray crystal structure [184(b)].

Lappert's group recently reported an yttrium complex containing hybrid phosphine–alkoxy ligands as shown in eqn. (54) [185]:



(54)

This derivative has been structurally characterized; the Y–P bond distance is 3.045(2) Å. A ^{31}P–^{89}Y coupling constant of 59 Hz was obtained from the ^{31}P NMR spectrum, in good agreement with our result.

(iii) Lanthanum and actinium

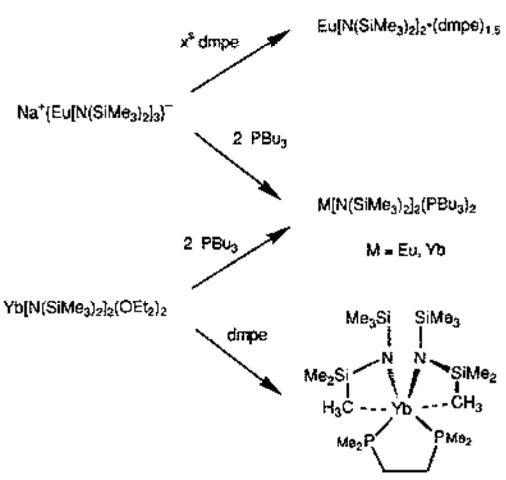
There have been no phosphine complexes of lanthanum or actinium reported to date.

F. LANTHANIDES

The first evidence for phosphine adduct formation with a lanthanide element was reported in 1965 [186]. The adduct $Cp_3Yb(PPh_3)$ was claimed on the basis of changes in the UVVIS spectrum upon addition of PPh_3 to Cp_3Yb [186]. This adduct was subsequently isolated and characterized by elemental analysis [187]. More than a decade later, Bielang and Fischer reported the formation of several other phosphine adducts ($L = PCy_3$, $PHCy_2$, PH_2Cy, PMe_2Ph, PH_2Ph, $PHPh_2$) of Cp_3Yb in solution by UVVIS spectroscopy [188]. These workers were able to isolate only the cyclohexylphosphine adduct, and the elemental analysis on this compound was quite poor. Attempts to isolate adducts of other simple phosphines led to complex mixtures, apparently containing ytterbium(III) phosphides. In fact, with dicyclohexylphosphine, the corresponding phosphide $Cp_2Yb(PCy_2)$ was isolated in analytically pure form.

The first fully characterized lanthanide phosphine complexes were prepared in 1982 [189]. Dmpe and PBu_3 displace diethyl ether in $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ to give isolable phosphine complexes (Scheme 12). The dmpe complex has been characterized by NMR spectroscopy and X-ray crystallography, and shows that agostic interactions between one methyl group of each silyl amide and the ytterbium(II) center increase the formal coordination number to six. Similar complexes were also prepared for europium(II) as shown in Scheme 12. The larger size of the europium atom, compared with the ytterbium atom, allows coordination of 1.5 dmpe ligands per metal atom. The structure of this complex is not known but its high pentane solubility precludes a polymeric formulation. The NMR spectra of the paramagnetic ($\mu = 7.4$ BM) europium(II) complexes were not observable.

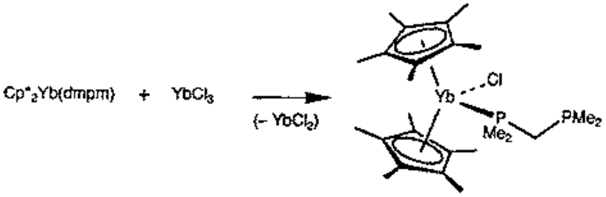
Diethyl ether is also readily displaced from $Cp^*_2M(OEt_2)$ ($M = Eu$, Yb) by chelating phosphines such as dmpe and dmpm [190]. The dmpe complexes are highly insoluble, suggesting a polymeric structure with bridging dmpe units, ie. $[Cp^*_2M(\mu\text{-dmpe})]_x$. Dmpm forms soluble 1 : 1 complexes of the formula $Cp^*_2M(dmpm)$. Presumably, the one carbon backbone of dmpm



Scheme 12.

prevents bridging due to unfavorable steric interactions between the Cp* rings on adjacent metal centers (M = Eu, Yb). In addition, the smaller bite angle of dmpm results in a less-crowded coordination environment. Nevertheless, dmpm is still rather weakly bound since addition of excess diethyl ether completely displaces the phosphine. No complexes were observed with dppe or the monodentate phosphines, PMe_3 and PBu_3. Cyclohexylphosphine forms a soluble lime-green adduct with base-free Cp_2^*Yb, but the phosphine is readily displaced either by diethyl ether or by warming the solid adduct under vacuum, regenerating Cp_2^*Yb [191].

$Cp_2^*Yb(dmpm)$ undergoes a ligand-exchange redox reaction with $YbCl_3$ to generate an ytterbium(III) phosphine complex as shown in eqn. (55) [190]:



(55)

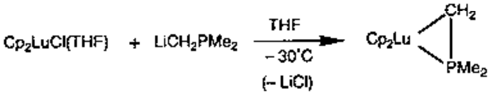
The crystal structure of this complex reveals that only one phosphorus atom of the dmpm ligand is coordinated to the ytterbium center. No ^{31}P NMR resonances were observable.

More recently, the phosphine and phosphite derivatives of cerium(III), $Cp'_3Ce(PR_3)$ ($Cp' = C_5H_4Me$; $PR_3 = PMe_3$ [192]; $PR_3 = P(OCH_2)_3CCH_2CH_3$ [194]) have been prepared by the displacement of THF from $Cp'_3Ce(THF)$. Both complexes have been structurally characterized and the

Ce–P distances of 3.072(4) Å and 3.086(3) Å (L = PMe_3, $P(OCH_2)_3CEt$ respectively) are nearly identical. It is noteworthy that these phosphorus donors will displace a hard (class a) ligand such as THF. Equilibrium studies suggest that PEt_3 is approximately as good a ligand as pyrrolidine and a better ligand than THF towards Cp_3Yb [194]. These findings parallel the gas phase basicities of the ligands and strongly imply that phosphines and phosphites are not inherently poor donors towards lanthanide elements.

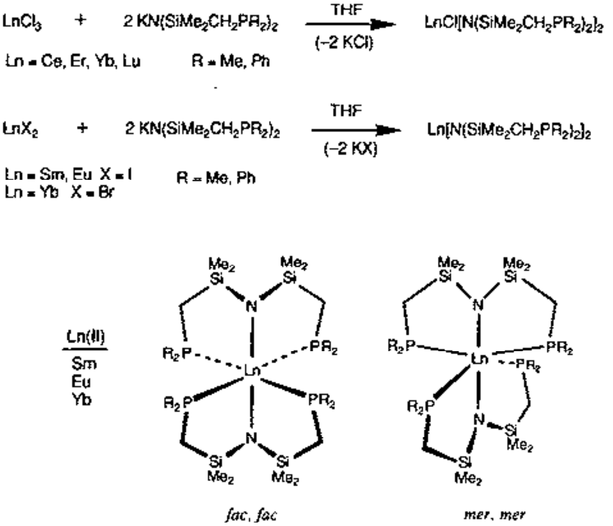
The tris(methylborohydride) complexes of holmium and ytterbium containing dmpe as a stabilizing ligand, $M(BH_3Me)_3(dmpe)_{1.5}$, have been prepared, although no structural data have been obtained for these compounds as yet [195].

Ligands that contain both phosphine and alkyl, oxo or amido functionalities have also been synthesized. A dimethylphosphinomethyl complex of lutetium has been prepared by metathesis of Cp_2LuCl by $LiCH_2PMe_2$ [196] (eqn. (56)):



(56)

^{31}P NMR spectroscopy clearly indicates coordination by the PMe_2 moiety to the lutetium(III) center. As already mentioned, mixed alkoxy–phosphine ligands allow isolation of the neodymium derivative $Nd(OCBu^t_2CH_2PMe_2)_3$ [185]. The X-ray structure of this complex has been determined, and it shows that the Nd–P bond length of 3.154(2) Å is considerably longer than expected for neodymium(III) in six coordination (ca. 3.09 Å).



Scheme 13.

The now familiar strategy of combining amide and phosphine donors into a chelating array allows the preparation of a wide variety of lanthanide phosphine complexes [197] (Scheme 13). It has proven possible to observe the paramagnetic $^{31}P\{^1H\}$ NMR spectra of $MCl[N(SiMe_2CH_2PMe_2)_2]_2$ (M = Ce, Yb).

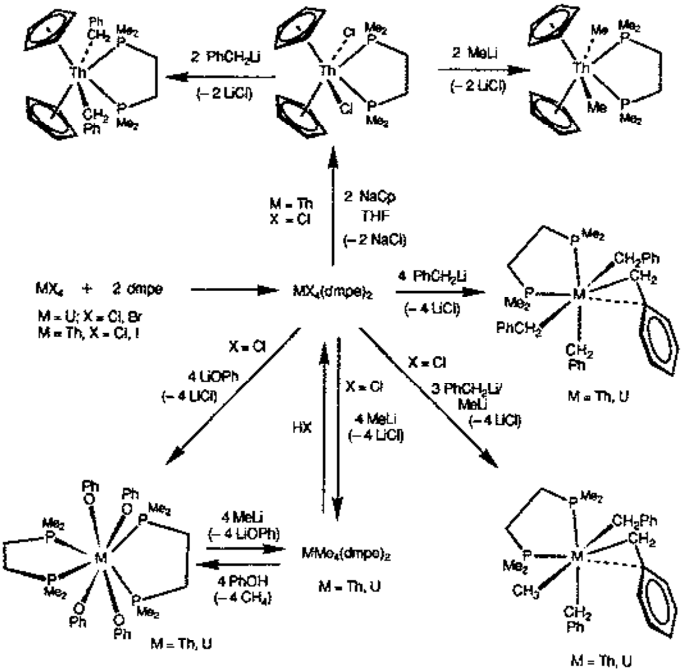
The bis(ligand) complexes of europium(II), samarium(II) and ytterbium(II), $M[N(SiMe_2CH_2PR_2)_2]_2$, have also been synthesized (Scheme 13). The paramagnetic samarium complexes give observable ^1H NMR spectra but no ^{31}P NMR spectral resonances could be located. No NMR (^1H, ^{31}P) signals were observed for the divalent europium complexes. The ^{31}P NMR spectra of the divalent ytterbium(II) complexes show coupling to ^{171}Yb ($I = 1/2$, 14.3% natural abundance); for R = Me, $^1J_{Yb-P} = 665$ Hz and for R = Ph, $^1J_{Yb-P} = 522$ Hz. This is the first ^{31}P–^{171}Yb coupling to be observed [198]. Work is continuing in our laboratories to prepare mono(ligand) derivatives and to explore the chemistry of the bis(ligand) derivatives prepared thus far.

G. ACTINIDES

Several phosphine complexes of UCl_4 were reported in the 1960s [199–201], but most of these were later shown to contain phosphonium salts or phosphine oxides [202–206]. Selbin and Ortego [207] described the preparation of a material with the molecular formula $[UCl_4]_2$(dppe) in 1967 and this appears to be the first reported actinide phosphine complex. These same authors also claim to have prepared PPh_3 and dppe adducts of UCl_5 [208]. However, the rather poor analytical data obtained and the high magnetic moment of the dppe adduct ($\mu = 2.76$ BM) cast considerable doubt on this formulation. There is also a brief mention of a PBu_3 adduct of $U[OC(Ph)CHC(CF_3)O]_4$ [209]. Addition of PMe_3 to the trimer $[Cp^*_2U]_3(\mu\text{-}Cl)_3$ results in the formation of $Cp^*_2UCl(PMe_3)_x$, but no data could be obtained to clarify its formulation because of the ease of loss of PMe_3 [210,211].

The first well-characterized actinide phosphine complexes were reported 1981. The isolation of dmpe adducts of uranium(IV) and thorium(IV) halides [212] (Scheme 14) allowed access to a whole series of intriguing complexes. The halide derivatives $MX_4(dmpe)_2$ were prepared in CH_2Cl_2 or in neat dmpe at elevated temperatures and are hydrocarbon soluble. The uranium complexes sublime under high vacuum, supporting a monomeric eight-coordinate structure. The tris(trimethylphosphine) adduct of UCl_4, $UCl_4(PMe_3)_2$, was also isolated and crystallized from neat trimethylphosphine [212].

The $MX_4(dmpe)_2$ complexes have been used as convenient precursors in

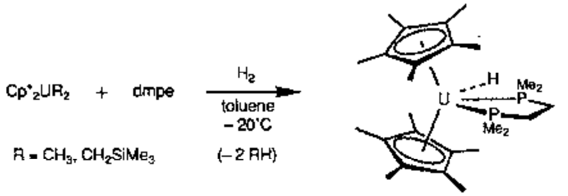


Scheme 14.

the preparation of other actinide phosphines (Scheme 14). Metathesis with lithium reagents yields cyclopentadienyl [214,215], alkyl [213] and alkoxy [212] complexes. The structure of $U(OPh)_4(dmpe)_2$ [212] may be viewed as consisting of an equatorial plane containing the four phenoxide ligands with axially disposed dmpe ligands twisted 90° with respect to each other. The tetrabenzyl and tribenzylmethyl complexes contain only one dmpe ligand owing to the larger size of the benzyl group. Even so, the remaining dmpe ligand in the thorium complex is labile at room temperature as shown by ^{31}P NMR spectroscopy. The crystal structure of $Th(CH_2Ph)_4(dmpe)$ reveals a formally six-coordinate structure with one distorted benzyl group [213]. The Th–C–C angle for the distorted benzyl is ca. 90° vs. 110–114° for the "normal" benzyl groups. The X-ray structure of $U(CH_2Ph)_3Me(dmpe)$ similarly shows one distorted benzyl ligand [213]. This unusual bonding pattern has been explained electrostatically since Hückel theory suggests that the charge on the benzyl ligand is mainly on the α-carbon and also on the *ortho* carbon atoms as well. Thus close approach of the *ortho* carbon atoms, bearing a partial negative charge, satisfies the coordinative unsaturation at the metal center. No distortion was observed in $U(OPh)_4(dmpe)_2$ [212] or $Cp_2Th(CH_2Ph)_4(dmpe)$ [215] because the metal centers in these complexes are coordinatively saturated.

A number of actinide borohydride phosphines have been reported. The preparations of $U(BH_4)_3(dmpe)_2$ [216] and $U(BH_4)_3(o\text{-dppy})_2$ [217] from $U(BH_4)_3(THF)_x$ have been reported. The structures of both complexes are quite similar except that the bonding mode of the unique BH_4^- unit is bidentate in the dmpe complex and tridentate in the *o*-dppy derivative. The remaining borohydride ligands are tridentate in both structures. The addition of dmpe to $U(BH_3Me)_4$ generates the adduct $U(BH_3Me)_4(dmpe)$ [218]. All the borohydride units are tridentate on the basis of the observed U–B bond distances and IR data. The thermal decomposition of this complex in the presence of excess dmpe affords $U(BH_3Me)_3(dmpe)_2$ in low yield. As expected, the structure of this complex is quite similar to that of $U(BH_4)_3(dmpe)_2$ except that in this case all the BH_3Me^- ligands are tridentate. It is apparent from these results that very subtle changes in the steric or electronic environment are sufficient to alter the bonding mode of the borohydride ligands. The NMR behavior of $U(BH_3Me)_4(dmpe)$ and $U(BH_3Me)_3(dmpe)_2$ deserves some comment. The former, a pseudo-six-coordinate species, is fluxional at room temperature but the *cis*- and *trans*-BH_3Me^- ligands can be frozen out at low temperature. The latter complex, a pseudo-seven-coordinate species, is fluxional even at −95 °C. These results are therefore in keeping with the behavior of transition metal complexes where six-coordinate molecules are generally regarded as rigid while seven-coordinate species are usually fluxional on the NMR time scale.

Very few actinide cyclopentadienyl complexes containing phosphines are known. Besides the $Cp_2ThX_2(dmpe)$ (X = Cl, Me, Bz) series mentioned above, dmpe has been utilized to stabilize the novel, monomeric uranium(III) hydride complex shown in eqn. (57) [219]:



(57)

The structure of this complex was determined but the terminal hydride could not be located. A band at 1219 cm^{-1} in the IR was assigned to the U–H stretching frequency which shifted to 870 cm^{-1} upon deuterium substitution. This complex is fluxional in solution and the authors have suggested a mechanism involving spinning or dissociation of one arm of the dmpe ligand to account for this observation. The previously mentioned unstable complex $Cp_2^*UCl(PMe_3)_x$ [210,211] may be structurally similar to $Cp_2^*UH(dmpe)$ but the lability of the PMe_3 ligands has prevented full characterization of this complex.

Finally, Cp'_3U ($Cp' = \eta^5\text{-}C_5H_4Me$) forms adducts with PMe_3 [220] and $P(OCH_2)_3CEt$ [193] while Cp_3U forms the binuclear dmpe-bridged structure $[Cp_3U]_2(\mu\text{-dmpe})$ [221]. These complexes have been structurally characterized and show U–P distances of 2.972(6) Å (L = PMe_3), 2.988(6) Å (L = $P(OCH_2)_3CEt$), and 3.022(2) Å (L = dmpe). It has been noted that the corresponding distance in $Cp'_3Ce[P(OCH_2)_3CEt]$ is 3.086(3) Å [193], nearly 0.1 Å longer than the corresponding uranium derivative, despite the fact that the ionic radii of cerium(II) and uranium(III) in ten-coordination are listed as 1.07 Å and 1.09 Å respectively, a difference of only 0.02 Å. It has been suggested that this discrepancy reflects some U(5*f*) to P(3*d*) π-backbonding which is not possible for the 4*f* orbitals of cerium(III) owing to their limited radial extension. Further evidence for this proposal is found in the structure of the analogous quinuclidine complexes. In this case, where the ligand cannot engage in π-backbonding, the U–N and Ce–N distances of 2.789(3) Å and 2.764(4) Å respectively differ only by 0.025 Å [193]. Regardless of the identity of the empty orbital on phosphorus, this topic is sure to receive considerable attention as more structural comparisons become available.

H. CONCLUSIONS

The ability of a neutral phosphorus donor to bind to the metals of groups 3 and 4, the lanthanides and the actinides is now well established. While there are still no examples of lanthanum or actinium phosphine complexes, such derivatives should be accessible at least for lanthanum. Similarly, there are gaps in the lanthanide series since no phosphine complexes of praseodymium, gadolinium, terbium, dysprosium, holmium and thulium have yet been reported. However, there is no obvious chemical reason to suggest that such derivatives cannot be generated given strategies that have worked for other members of the lanthanide series. It is clear that more work in this area is required.

Not surprisingly, the phosphine ligands that appear to generate the most stable phosphine–metal interaction are chelating phosphines such as dmpe, trmpe and trimpsi. In addition, the use of the chelate effect in conjunction with a hard ligand such as the amide in $^-N(SiMe_2CH_2PMe_2)_2$, or an alkoxide as found in $^-OC(Bu^t)_2CH_2PMe_2$, also appears to be effective in anchoring the phosphine donor to the metal.

It is remarkable that the majority of low oxidation state derivatives of the group 4 elements are stabilized by phosphine donors. This is in contrast with other parts of the transition series where one finds that classic π-acceptor-type ligands such as CO or RNC are utilized. In fact, the binary carbonyl complexes $M(CO)_7$ of the group 4 elements are unknown, and only combinations of phosphines with CO, 1,3-butadiene or naphthalene can apparently generate the formal oxidation states of M(0) for these elements.

The major reactivity of a metal-to-phosphine linkage, as defined in this review, is dissociation. Although a number of cases were singled out where dissociation was not observed, generally speaking the phosphine ligand is labile for these elements. In many cases this is useful, since reactive fragments such as η^2-alkynes, carbenes and benzynes can be stabilized by the presence of the phosphine ligand. However, these complexes can react further, generally with phosphine dissociation as the first step. The reactivity of the phosphine complexes themselves is still an area open to investigation. Unlike the later transition elements where one finds that catalysis by phosphine-containing complexes is common, with the elements discussed here, catalysis has only been seen in relatively few cases thus far.

TABLE 1

Crystal structure data for phosphine complexes of the early metals

Complex	M–P distance (Å)	Ref.
$TiMeCl_3(dmpe)$	2.582(2) 2.585(1)	36, 40
$TiMeCl_3(dmpe)$ (NEUT)	2.589(2) 2.591(2)	40
$TiEtCl_3(dmpe)$	2.570(3) 2.560(3)	35, 40
$CpTiCl_3(dmpe)$	2.609(11) 2.602(12) 2.636(9) 2.624(12)	43
$Cp_2Ti(\eta^2\text{-}OC{=}C(Ph)C(SiMe_3){=}CH_2)(PMe_3)$	2.592	45
$Ti(BH_4)_3(PMe_3)_2$	2.571(3) 2.539(3)	55, 56
$CpTiCl_2(PMe_3)_2$	2.599(2)	65
$Cp_2TiCl(PMe_2SiMe_3)$	2.639(1)	63
$Cp_2TiCl(PMe_3)$	2.599(1)	62
$[CpTi(PMe_3)(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)]_2$	2.589(1) 2.565(1)	69
$[Cp_2TiCl]_2(\mu\text{-}Ph_2P(CH_2)_2AsPh_2)$ (disorder in P and As)	2.677(3)	60
$TiCl_2(dmpe)_2$	2.586(5)	72
$Ti(Me)_{1.3}(Cl)_{0.7}(dmpe)_2$ (disorder in Me and Cl)	2.520(1) 2.529(1)	72
$TiMe_2(dmpe)_2$	2.510(1) 2.518(1)	73
$TiMe_2(dmpe)_2$ (NEUT)	2.529(4) 2.517(5)	73
$Ti(BH_4)_2(dmpe)_2$	2.625(1) 2.627(1)	73
$Cp_2Ti(PMe_3)_2$	2.527(3) 2.524(4) 2.527(2)	81
$Cp_2Ti(PF_3)_2$	2.340(6) 2.349(6)	76, 78
$Cp_2TiCO(PMe_3)$	2.544(1)	62
$Cp_2TiCO(PEt_3)$	2.585(1)	76
$Cp_2Ti(\eta^1\text{-}N_2CPh_2)(PMe_3)$	2.534(3)	89
$Cp'_2Ti(dmpe)$	2.527(4) 2.540(4)	75
$[Cp_2Ti(PMe_3)]_2[\mu\text{-}N_2]$	2.538(2) 2.525(2)	88
$CpTi(CO)_2H(dmpe)$	2.505(2) 2.520(2)	98

TABLE 1 (continued)

Complex		M–P distance (Å)	Ref.
$CpTi[\eta^5\text{-}2,4\text{-}Me_2(pd)](PMe_3)$		Not reported	95
$Ti(CO)_2(PF_3)(dmpe)_2$	dmpe (1)	2.621(2) 2.636(2)	102
	dmpe (2)	2.509(2) 2.671(2)	
	PF_3	N.R.	
$Ti(CO)_3(dmpe)_2$	dmpe (1)	2.567(1) 2.637(1)	104
	dmpe (2)	2.523(1) 2.630(1)	
$Ti(CO)_4(trimpsi)$		2.632(5) 2.612(3)	52(a)
$Ti(\eta^6\text{-}C_{10}H_8)(trimpsi)$		2.523(2) 2.532(2) 2.552(2)	52(b)
$(CHT)TiEt(dmpe)$		2.673(1) 2.636(1)	106, 107
$ZrBz_4(dmpe)$		2.862(4) 2.885(4)	113
$Zr(CH_2SiMe_3)_4(dmpe)$		2.876(2) 2.972(2)	114
$ZrMe_4(dmpe)_2$		2.812(6) 2.815(5)	113
$Cp_2Zr[\eta^2\text{-}SC(Me)(H)](PMe_3)$		2.731(3)	223
$[Cp_2ZrH(PMe_3)_2]^+[BPh_4]^-$		2.676(3) 2.684(3)	122
$[Cp_2ZrCl]_2[\mu\text{-}\eta^2:\eta^2\text{-}OCCH(PMe)_2]$		2.724(5)	126
$[Cp_2ZrCl]_2[\mu\text{-}\eta^2:\eta^2\text{-}OCCH(PPh)_2]$		2.752(3)	127
$[Cp_2ZrCl]_2[\mu\text{-}\eta^2:\eta^2\text{-}OCCH(PPh)_2]$		2.761(2)	128
$[Cp^*_2ZrI][\mu\text{-}\eta^1:\eta^1\text{-}OCH][Cp_2Zr(PMe_3)]$		2.693(2)	129
$Zr[CH_2SiMe_2N(SiMe_3)]_2(dmpe)$		2.848(1) 2.855(1)	130
$ZrCl_2[N(SiMe_2CH_2PMe_2)_2]_2$		2.794(1) 2.803(1)	131
$ZrCl_3[N(SiMe_2CH_2PPr^i_2)_2]$		2.765(1) 2.783(1)	132
$[ZrCl_3(PEt_3)_2]_2$		2.806(2) 2.820(2)	134
$[ZrCl_3(PMe_2Ph)_2]_2$		2.760(3) 2.770(3)	134
$[ZrCl_3(PBu_3)_2]_2$		2.830(2) 2.839(2)	116
$[ZrCl_3(dppe)]_2$	dppe (1)	2.771(3) 2.785(3)	134
	dppe (2)	2.808(3) 2.762(3)	
$[ZrCl_3(PEt_3)_2]_2[\mu\text{-}CH_2CH_2]$		2.780(5) 2.793(6)	136
$[ZrBr_3(PEt_3)_2]_2[\mu\text{-}CH_2CH_2]$		2.798(6) 2.785(6)	136
$Zr_6Cl_{12}(PMe_2Ph)_6$		Not reported	135
$Zr(\eta^5\text{-}C_8H_{11})H(dmpe)_2$	dmpe (1)	2.730(4) 2.805(4)	168
	dmpe (2)	2.787(4) 2.758(4)	
$CpZrCl(dmpe)_2$	dmpe (1)	2.728(3) 2.692(3)	165
	dmpe (2)	2.701(3) 2.710(3)	
$CpZrMe(dmpe)_2$	dmpe (1)	2.676(7) 2.687(7)	166
	dmpe (2)	2.679(7) 2.714(7)	
$CpZr(\eta^4\text{-}C_4H_6)H(dmpe)$		2.725(1) 2.704(1)	167
$CpZr(CO)_2Cl(dmpe)$		2.742(3) 2.750(3)	121
$Cp_2Zr(PMe_3)_2$		2.650(0) 2.638(2)	70
$Cp_2Zr(CO)[P(OMe)_3]$		2.619(1) 2.630(1)	150
$Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$		2.687(3)	154
$Cp_2Zr(\eta^2\text{-}C_6H_8)(PMe_3)$		2.689(3)	153
$Cp_2Zr(\eta^2\text{-}C_2H_4)(PMe_3)$		2.693(2)	158
$Cp_2Zr(\eta^2\text{-}CHCBu)(PMe_3)$		2.658(1)	152
$Cp_2Zr[\eta^2\text{-}CPHCPh](PMe_3)$		2.70(1)	151
$[Cp_2Zr(PMe_3)]_2[\mu\text{-}\eta^2:\eta^2\text{-}C_6(OMe)_2]$		2.667(2)	156
$Zr[\eta^5\text{-}(2,4\text{-}dimethyl(pd)]_2(PEt_3)$		2.721(2)	164
$Zr(\eta^4\text{-}C_4H_6)Ph[N(SiMe_2CH_2PMe_2)_2]$		2.730(2) 2.752(2)	179(b)

TABLE 1 (continued)

Complex	M–P distance (Å)	Ref.
$Zr(CO)_4(trmpe)$	2.755(3) 2.760(3) 2.762(3)	105
$HfCl_3[N(SiMe_2CH_2PMe_2)_2]$ Monoclinic	2.712(1) 2.725(2)	132
Orthorhombic	2.736(2) 2.706(2)	
$HfMe_3[N(SiMe_2CH_2PMe_2)_2]$	2.761(2) 2.806(2)	133
$Hf_2(\mu\text{-}H)_3(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]_2$	2.732(2) 2.786(2) 2.712(2) 2.717(2)	173
$Cp^*Hf(CO)_2Cl(dmpe)$	2.775(1) 2.764(1)	99
$Hf(\eta^4\text{-}C_4H_6)Ph[N(SiMe_2CH_2PMe_2)_2]$	2.707(2) 2.720(2)	179(b)
$Hf(\eta^1:\eta^4\text{-}C_7H_{11})[N(SiMe_2CH_2PPr^i_2)_2]$	2.767(6) 2.812(6)	179(a)
$Hf(C_4H_6)_2(dmpe)$	2.685(1) 2.698(1) 2.692(1) 2.675(1)	101
$[Me_2Si(C_5Me_4)_2]Sc(H)(PMe_3)$	2.752(1)	182
$\{[(C_5Me_4)SiMe_2NBu^t]Sc(\mu\text{-}H)(PMe_3)\}_2$	2.996(1)	183
$\{[(C_5Me_4)SiMe_2NBu^t]Sc(PMe_3)\}_2(\mu\text{-}C_2H_2)$	2.825(3)	183
$\{Y(\mu\text{-}Cl)(allyl)[N(SiMe_2CH_2PMe_2)_2]\}_2$	2.892(1) 2.931(1)	184(b)
$Y[N(SiMe_2CH_2PMe_2)(SiMe_2CHPMe_2)][N(SiMe_2CH_2PMe_2)_2]$	2.817(3) 2.896(3) 2.903(3) 3.005(3)	184(b)
$Y(OCBu^t_2CH_2PMe_2)_3$	3.045(2)	185
$Cp'_3Ce(PMe_3)$	3.072(4)	192
$Cp'_3Ce[P(OCH_2)_3CEt]$	3.086(3)	193
$Nd(OCBu^t_2CH_2PMe_2)_3$	3.154(2)	185
$Cp^*_2YbCl(dmpm)$	2.941(3)	190
$Yb[N(SiMe_3)_2]_2(dmpe)$	3.012(4)	189
$ThBz_4(dmpe)$	3.16(1) 3.15(1) 3.21(1) 3.15(1)	213
$Cp_2ThCl_2(dmpe)$	3.122(2) 3.121(2)	214
$Cp_2ThMe_2(dmpe)$	3.146(2) 3.147(2)	214
$Cp_2ThBz_2(dmpe)$	3.142(2) 3.237(2)	215
$U(BH_4)_3(dmpe)_2$	3.139(9) 3.051(9)	216
$U(BH_3Me)_3(dmpe)_2$	3.174(3) 3.085(3)	218
$U(BH_4)_3[o\text{-}PPh_2(C_6H_4N)]_2$	3.162(1)	217
$Cp^*_2UH(dmpe)$	3.211(8) 3.092(8)	219
$Cp'_3U(PMe_3)$	2.972(6)	220
$Cp'_3U[P(OCH_2)_3CEt]$	2.988(6)	193
$[Cp_3U]_2[\mu\text{-}dmpe]$	3.020(6) 3.024(6)	221
$UBz_3Me(dmpe)$	3.020(2) 3.010(2)	213
$U(BH_3Me)_4(dmpe)$	3.029(2) 3.017(2)	218
$U(OPh)_4(dmpe)_2$	3.104(6) (average)	212

I. TABULATED DATA FOR PHOSPHINE COMPLEXES OF THE EARLY METALS

The data are tabulated in Table 2.

TABLE 2

Phosphine complexes of the early metals

Complex	Characterization	Synthesis	Ref.
Titanium(IV)			
$TiCl_4L$		$TiCl_4 + L$	
$L = PH_3$, PH_2Me, $PHMe_2$, PMe_3	IR, MW		20
$L = PMe_3$, PMe_2Ph, PPh_3, PCy_3	IR, MW, NMR(H,P)		26
$L = PPh_3$	IR		25
$L = P(OBu)_3$			28
$TiCl_4L_2$		$TiCl_4 + 2L$	
$L = PMe_3$, PMe_2Ph, PPh_3, PCy_3	IR, NMR(H:VT)		21
$L = PMe_3$, PMe_2Ph, PEt_3, $PEtPh_2$, PCy_3, PPh_3	IR, NMR(H,P)		26
$L = PPh_3$, PEt_3; L_2 = dmpe, depe, depbz			22
$L = PPh_3$; L_2 = dppe	IR		23
$L = PPh_3$; L_2 = dppe	IR		24
$L = PPh_3$	IR		25
$L = PBu_3$; L_2 = dbpe	NMR(P)		27
$L = P(OBu)_3$			28
L_2 = dppm	IR, NMR(H)		31
L_2 = dppe		$\{TiCl_3[C(Cl)NBu^t](CNBu^t)\}_2 + 2$dppe	30
$TiCl_4(dmpbz)_2$	IR, POWDIFF	$TiCl_4 + 2$dmpbz	29
$(TiCl_4)_x(dppe)_y$, $y/x = 2/3, 1/2, 3/1$	IR	$TiCl_4 + y/x$ dppe	25
$(TiCl_4)_2(PR_3)$: R = Et, Bu	NMR(P)	Solution equilibrium NMR study of $TiCl_4 + PR_3$	27
$(TiCl_4)_5[Pt(PPh_3)_3]$	IR	$TiCl_4 + Pt(PPh_3)_3$	224
$CpTiCl_3(dmpe)$	XRAY, NMR(H,C,P)	$CpTiCl_3 +$ dmpe	43
$TiMeCl_3(PH_3)$		A model for ab initio MO calculations	37
$TiEt(H)Cl_2(PH_3)$		A model for ab initio MO calculations	38
$Ti(R)X_3L_n$		$Ti(R)X_3 + nL$	
R = Me; X = Cl; $L = PPh_3$, dppe; $n = 1$	IR, UVVIS, NMR(H)		33
R = Me; X = Cl, Br; $L = PPh_3$, dppe, dppm; $n = 1$	IR, NMR(H), MW		34
R = Ph, p = tol; X = Br; $L = PPh_3$; $n = 1$	IR, NMR(H), MW		34
R = Ph, p-tol; X = Br; L = dppe; $n = 1/2$	IR, NMR(H), MW		34
R = Me; X = Cl; L = dmpe; $n = 1$	XRAY		36

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$R = Me, Et; X = Cl; L = dmpe; n = 1$	XRAY, NEUT, NMR(H:VT,C,P)		40
$R = Me; X = Cl; L = dppe; n = 1$	IR		32
$R = Et; X = Cl; L = dmpe; n = 1$	XRAY, NMR(H)		35
$R =$ trimethylphenoxy; $X = Cl; L = dppe; n = 1$	IR		41
$R = Cp, OPr; X = Cl; L = PMe_2Ph; n = 1, 2$	NMR(H)		42
$R = Me; X = Cl; L = PMe_2Ph; n = 1$	NMR(H)		42
$TiR_2Cl_2L_2$			
$R = SBu^t; L_2 = dmpe, dppe$	IR, NMR(H,P)	$TiCl_4 + L_2 + 2LiSBu^t$	39
$R = OPh; L_2 = 2PMe_3, 2PPh_3, dmpe, dppe$	IR, NMR(P)	$Ti(OPh)_2Cl_2 + nL$	27
$[R_2TiMe(L)]^+[BPh_4]^-$		$R_2TiMeCl + L + NaBH_4$	
$R = Cp; L = PMe_3, PMe_2Ph, PMePh_2, PBu_3$	IR, NMR(H,C)		47
$R = Ind; L = PMe_3, PMe_2Ph$	IR, NMR(H,C)		47
$[Cp_2TiCl(PMe_2Ph)]^+$	CV	Electrochemical oxidation of $Cp_2TiCl(PMe_2Ph)$	48
$[Cp_2Ti(\eta^2\text{-}OCCH_3)(PMe_2Ph)]^+[BPh_4]^-$	IR, NMR(H,C)	$[Cp_2Ti(\eta^2\text{-}OCCH_3)CH_3CN]^+[BPh_4]^- + PMe_2Ph$	47
$Cp_2Ti(\eta^2\text{-}OCCH_2)(PMe_2Ph)$	NMR(H)	$[Cp_2Ti(\eta^2\text{-}OCCH_2)]_n + PMe_2Ph$	44
$Cp_2Ti(\eta^2\text{-}OCO)(PMe_3)$	IR, NMR(H,C,P) MS	$Cp_2Ti(PMe_3)_2 + CO_2$	46
$Cp_2Ti(\eta^2\text{-}SCS)(PMe_3)$	IR, NMR(H,C,P) MS	$Cp_2Ti(PMe_3)_2 + CS_2$	46
$Cp_2Ti(\eta^2\text{-}OC{=}CRCR'{=}CH_2)(PMe_3)$	XRAY, IR, NMR (H,C,P)	$Cp_2Ti(\eta^1{:}\eta^1\text{-}CH_2CR'{=}CR) + CO + PMe_3$	45
$R = R' = Me, Et, Ph$			
$R = Ph; R' = Me, SiMe_3$			
Titanium(III)			
$TiCl_3L_n$		$TiCl_3 + nL$	
$L = depe; n = 1$			22
$L = PMe_3, PEt_3, PH_2Me, PHMe_2; n = 2$	IR, UVVIS, MW, ESR		49
$L = trimpsi; n = 1$			52
$L = PCy_3, PPr^i_3, PBu_3; n = 2, 3$	NMR(H), ESR, UVVIS		50
$TiCl_3(PEt_3)_2(CO)$	IR	$TiCl_3(PEt_3)_2 +$ 800 psi CO	51
$[\eta^2\text{-}OC(Bu^t)CHC(Bu^t)O]TiCl_2(PMe_3)_2$	ESR, EVANS, UVVIS	$[\eta^2\text{-}OC(Bu^t)CHC(Bu^t)O]TiCl_2(THF)_2 + 2PMe_3$	54
$[\eta^2\text{-}OC(Bu^t)CHC(Bu^t)O]TiMe_2(PMe_3)_2$		$[\eta^2\text{-}OC(Bu^t)CHC(Bu^t)O]TiCl_2(PMe_3)_2 + 2MeLi$	54
$RTiCl_2(PPh_3)_2$		$RTiCl_2(THF)_2 + 2PPh_3$	53
$R =$ acac, benzoylacetone, dipivolylmethane			

Titanium(III)			
(TPP)TiF(PBu$_3^n$)	ESR	(TPP)TiF$_2$ + PBu$_3^n$ + Zn/Hg	225
Ti(BH$_4$)$_3$L$_2$		Ti(BH$_4$)$_3$(Et$_2$O) + 2L	
L = PMe$_3$, PEt$_3$	XRAY, IR, ESR, SUSC		55
L = PMe$_3$, PEt$_3$, PMe$_2$Ph, P(OMe)$_3$	XRAY, IR, ESR, NMR(H)		56
L$_2$ = dmpe	IR		56
CpTiCl$_2$L$_2$			
L = PMe$_2$Ph, PMePh$_2$; L$_2$ = dmpe, dppe	IR	[CpTiCl$_2$]$_n$ + 2L	64
L = PPh$_3$, PPr$_3^i$	ESR	Cp$_2$TiCl$_2$ + PR$_3$ + $h\nu$	66
L = PMe$_3$	XRAY, IR, ESR	CpTiCl$_3$ + Mg + excess PMe$_3$	65
CpTi(CH$_2$PPh$_2$)$_2$	ESR	Electrochemical reduction of Cp$_2$Ti(CH$_2$PPh$_2$)$_2$	68
Cp$_2$TiX(L)			
X = H; L = PPh$_3$	ESR	[Cp$_2$TiH]$_2$ + 2PPh$_3$	57
X = H; L = PPh$_3$	ESR		58
X = Cl; L = PMe$_2$Ph	ESR	Cp$_2$TiCl$_2$ + L + e$^-$	61
X = Cl; L = PMe$_2$Ph, PMePh$_2$	MW, ESR	[Cp$_2$TiCl]$_2$ + 2L	59
X = Cl; L = PMe$_3$	XRAY, MS	Cp$_2$TiCl$_2$ + PMe$_3$ + Mg + HgCl$_2$ or [Cp$_2$TiCl]$_2$ + PMe$_3$	62 62
X = Cl; L = PMe$_2$(SiMe$_3$)	XRAY, IR, ESR	Cp$_2$TiCl$_2$ + 2PMe$_2$(SiMe$_3$)	63
X = H; L = PBu$_3$	ESR	Cp$_2$TiCl$_2$ + 2BuLi + H$_2$ + PBu$_3$	226
[Cp$_2$TiCl]$_2$[μ-L$_2$]			
L$_2$ = dppe	ESR	Cp$_2$TiCl$_2$ + dppe	59
L$_2$ = Ph$_2$P(CH$_2$)$_2$AsPh$_2$	XRAY	[Cp$_2$TiCl]$_2$ + L + Mn + KOBu^t + diglyme	60
[CpTi(PMe$_3$)(μ-η^5:η^1-C$_5$H$_4$)]$_2$	XRAY, MS, NMR(H,C,P)	Cp$_2$TiCl$_2$ + PMe$_3$ + Mg	69, 70
Cp(η^5:η^1 – C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)TiCl	ESR	Cp(C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)TiCl$_2$ + Al powder	71
(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$TiCl	ESR	(C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$TiCl$_2$ + Al powder	71
[Cp$_2$TiCl$_2$(PMe$_2$Ph)]$^-$	ESR	Electrochemical reduction of Cp$_2$TiCl$_2$(PMe$_2$Ph)	67
[Cp$_2$Ti(PMe$_2$Ph)$_2$]$^+$	ESR	Electrochemical oxidation of Cp$_2$TiCl(PMe$_2$Ph)	
Titanium(II)			
TiCl$_2$(dmpe)$_2$	XRAY, IR, NMR(H), SUSC	TiCl$_4$ + Mg + dmpe	72

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$Ti(Me)_{1.3}(Cl)_{0.7}(dmpe)_2$	XRAY, IR	$TiCl_2(dmpe) + MeLi$ or Me_2Mg	72
$Ti(BH_4)_2(dmpe)_2$	XRAY, IR, NMR(H)	$TiCl_2(dmpe) + 2LiBH_4$	73
$TiMe_2(dmpe)_2$	XRAY, NEUT, CMAS, NMR(H,C,P)	$TiCl_2(dmpe) + 2MeLi$	73
Cp_2TiL_2			
$L = PF_3$	XRAY, IR, NMR(H), MS	$Cp_2Ti(CO)_2 + 2PF_3 + h\nu$	76, 78
$L = PMe_3$	XRAY, NMR(H,C,P), MS	$Cp_2TiCl_2 + Mg + 2PMe_3$	81, 227
$L = PMe_3$	NMR(H,C,P)	$Cp_2TiCl_2 + Mg + 2PMe_3$	62
$L = PMe_3$	NMR(H,C,P), MS	$Cp_2TiCl_2 + Mg + 2PMe_3$	70
$L = P(OMe)_3$	NMR(H)	$Cp_2TiCl_2 + 2Na(g) +$ excess $P(OME)_3$ at −100 °C	74
$Cp'_2Ti(dmpe)$: Cp′ = Cp or MeCp	XRAY, NMR(H,P)	$TiCl_4 + Mg + dmpe + NaCp'$	75
$[Cp_2Ti(PPh_3)]_2$		$[Cp_2TiH]_2 + 2PPh_3$ or $[Cp_2Ti]_2 + 2PPh_3$ or $Cp_2TiMe_2 + H_2 + 2PPh_3$	77
$[Cp_2Ti(PMe_3)]_2[\mu\text{-}N_2]$	XRAY, NMR(H,P)	$Cp_2Ti(PMe_3)_2 + N_2$	88
$Cp_2Ti(PR_3)L$			
R = Ph; L = THF		$[Cp_2Ti(PPh_3)]_2 + THF$	77
R = Me; L = CO	IR	$Cp_2Ti(CO)_2 +$ excess $PMe_3 + \Delta$	79
R = Me; L = PhCCPh	IR, NMR(H)	$Cp_2Ti(CO)_2 + PhC{\equiv}CPH + PMe_3$	84
R = Et, Ph; L = CO	IR, NMR(H)	$Cp_2Ti(CO)_2 + PR_3 + \Delta$	78
R = F; L = CO	IR, NMR(H), MS	$Cp_2Ti(CO)(L') + PF_3$; $L' = PEt_3$ or PPh_3	78
R = F; L = CO	IR, NMR(H),	$Cp_2Ti(CO)(PEt_3) + PF_3$	76
R = Ph, Et; L = CO	XRAY, IR, NMR(H)	$Cp_2Ti(CO)_2 + PR_3 + \Delta$	76
R = Me; L = CO, PhCCPh, HCCH, H_2CCH_2		$Cp_2Ti(PMe_3)_2 + L$	81
R = Me; L = PhCCPh, HCCH	IR, NMR(H,P)	$Cp_2Ti(PMe_3)_2 + L$	82, 83
R = Me; L = CO	XRAY, IR, NMR(H,C,P), MS	$Cp_2Ti(CO)_2 + PMe_3 + h\nu$	62

R = Me; L = N_2CPh_2	XRAY, NMR(H,C)	$Cp_2Ti(PMe_3)_2 + L$	89
$R_3 = Me_3, Ph_3, Me_2Ph, MePh_2, Bu_3$;			
L = CO	IR	$Cp_2Ti(CO)_2 + PR_3$	80
R = Me; L = MeCN, Bu^tCN	IR, NMR(H), MS	$Cp_2Ti(PMe_3)_2 + RCN$	70
Titanium(II)			
$CpCp^*Ti(PMe_3)(PhCCPh)$		$CpCp^*Ti(CO)_2 + PME_3 + PhC{\equiv}CPh$	85
$Cp'_2Ti(PMe_3)(PhCCPh)$;	NMR(H,P)	$Cp'_2Ti(CO)_2 + PhC{\equiv}CPh + PMe_3$	86
$Cp'_2 = Cp_2, Cp^*Cp, MeCp_2$			
$[Cp_2TiX(PPhMe_2)]^-$	CV	Electrochemical reduction of $[Cp_2TiX_2(PPhMe_2)]$	57
$(Ind)_2Ti(CO)(PMe_3)$	IR, NMR(H,C,P), MS	$(Ind)_2TiCl_2 + Mg + CO$, then $PMe_3 + h\nu$	62
$(\eta^5\text{-}R)_2Ti(L)$		$(\eta^5\text{-}R)_2Ti + L$ or $TiCl_4 + Mg + L + K(R)$	96
R = 2,4-Me_2(pd); L = PMe_3, PEt_3, PMe_2Ph	IR, NMR(H,C,P), MS		
R = Pd, 3-Me(pd); L = PEt_3	NMR(P)		
$CpTi(\eta^5\text{-}R)L$		$CpTiCl_2 + L + KR$	95
R = 2,4-Me_2(pd); L = PMe_3, PEt_3	XRAY, IR,		
R = pd; L = PEt_3	NMR(H,C,P)		
$(dmCh)_2TiL$: L = $PMe_3, PF_3, P(OMe_3)$	NMR(H)	$(\eta^5\text{-}C_8H_{11})_2Ti = L$ at − 80 °C	97
$Cp^*Ti(CO)_2X(dmpe)$: X = Cl, I			228
$Cp^*Ti(CO)_2Cl(dmpe)$	IR, NMR(C,P)	$Cp^*TiCl_3 + dmpe + 2NaC_{10}H_8 + CO$	99
$CpTi(CO)_2H(dmpe)$	XRAY, IR, NMR(H,C)	$[K(2\cdot2\cdot2)]^+ [CpTi(CO)_2(dmpe)] + CH_3COOH$	98
$Cp_2Ti{=}CHCMe_2CH{=}CH_2(L)$	IR, NMR(H,C,P)	$Cp_2Ti(\eta^1{:}\eta^1\text{-}CH_2CHCMe_2CH) + L$	93
L = $PMe_3, PMe_2Ph, PMePh_2$			94
$Cp_2Ti{=}CH_2(L)$: L = PMe_3, PMe_2Ph		$Cp_2Ti(\eta^1{:}\eta^1\text{-}CH_2CR_2CH_2) + L$	91
$Cp_2Ti{=}CH_2(PMe_3)$	NMR(H,C,P)	$[Cp_2Ti(\mu\text{-}CH_2)]_2 + 2PMe_3$	92
Titanium(0)			
$Ti(CO)_2(PF_3)(dmpe)_2$	XRAY	$Ti(CO)_3(dmpe)_2 + PF_3 + dmpe$	102
$Ti(CO)_3L_2$			
L = dmpe, depe	IR	$Ti(C_4H_6)_2L + CO$ for 12 h at 0 °C	102
L = dmpe	XRAY, NMR(C,P)	$Ti(C_4H_6)_2L + CO$ for 12 h at 0 °C	104
L = dmpe	IR, NMR(H,C,P)	$TiCl_4(dmpe) + NaC_{10}H_8$ at − 70 °C then 1 atm CO at 0 °C followed by Ar purge	103
$Ti(\eta^6\text{-}C_{10}H_8)(trimpsi)$	XRAY	$TiCl_3(trimpsi)(THF) + 3NaC_{10}H_8$	52(b)
$Ti(CO)_4(trimpsi)$	XRAY, IR, NMR(H,C,P)	$TiCl_3(trimpsi)(THF) + 3NaC_{10}H_8 + 4CO$	52(a)

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$Ti(CO)_4(trmpe)$	IR, NMR(H,C,P), MS	$TiCl_4(THF)_2 + trmpe + 4NaC_{10}H_8 + 4CO$	103, 105
$Ti(CO)_5(dmpe)$	IR, NMR(H,C,P)	$Ti(CO)_3(dmpe)_2 + 2CO + 2BH_3(THF)$	103
$[Ph_4AsCl]^+[Ti(Ph_3E)(CO)_4(dmpe)]^-$:			
E = Sn, Ge	IR, NMR(H,P)	$Ti(CO)_5(dmpe) + AsPh_4Cl + NaEPh_3$	103
$[K(2\cdot2\cdot2)]^+[CpTi(CO)_2(dmpe)]^-$	IR, NMR(H,P)	$Cp_2Ti(CO)_2 + dmpe + KC_{10}H_8 + (2\cdot2\cdot2)$	98
$Ti(C_4H_6)_2L$			
L = dmpe	NMR(H,C,P), MS	$TiCl_4(dmpe) + C_4H_6 + Na/Hg$	171
L = dmpe		$TiCl_4 + 4LiCH{=}CH_2 + dmpe$	100
L = depe, dppe, dmope	NMR(H,P)	$TiCl_4(THF)_2 + L + 2Mg(C_4H_6)(THF)_2$	101
$(CHT)TiXL_2$			
X = Cl; L_2 = dmpe	NMR(H)	$[(CHT)TiCl(THF)]_2 + 2dmpe$	107
X = Me, Et; L_2 = dmpe	XRAY, NMR(H)	$(CHT)TiCl(dmpe) + XMgCl$	107
X = Cl; L = PMe_3	NMR(H)	$[(CHT)TiCl(THF)]_2 + 4PMe_3$	107
X = Cl; L_2 = dmpe, dppe, dippe, dmpcp, $2PMe_3$	NMR(H)	$[(CHT)TiCl(THF)]_2 + L_2$	106
X = Me, Et; L_2 = dmpe	XRAY, NMR(H,C)	$(CHT)TiCl(dmpe) + XMgBr$	106
X = Me; L_2 = dmpcp	NMR(H,C)	$(CHT)TiClL_2 + MeMgBr$	106
X = BH_4; L_2 = dmpcp	IR, NMR(H)	$(CHT)TiClL_2 + NaBH_4$	106
$[(CHT)TiCl]_2[PMe_3]$	NMR(H)	$(CHT)Ti(PMe_3)_2Cl$ + toluene + vacuum	106
Zirconium (IV)			
$ZrX_4(dppe)$: X = Cl, Br	IR	$ZrX_4 + dppe$	110
$ZrCl_4(dmpe)_2$	NMR(P), MS	$ZrCl_4 + 2dmpe$	108, 109
$ZrCl_4(PR_3)_2$: R = Et, Bu^n	IR, NMR(P)	$ZrCl_4 + 2PR_3$	27
$ZrCl_4(dbpe)$	IR, NMR(P)	$ZrCl_4 + dbpe$	27
$Zr(Ph)Cl_3(PPh_3)(THF)$	IR, NMR(H)	$Zr(Ph)Cl_3(THF)_3 + PPh_3$	111
$Zr(Ph)Cl_3(dppe)$	IR, NMR(H)	$Zr(Ph)Cl_3(CH_3CN)_2 + dppe$	111
$ZrCl_3$(*O*-trimethylphenoxy)(dppe)	IR	$ZrCl_3\{O[C_6H_3(Me)_3]\} + dppe$	41
$ZrR_2X_2L_2$	NMR(H,C,P)	$ZrR_2X_2(ether)_2 + 2L$	112
R = Bz; X = Cl; L = PMe_3			
R = Np; X = Br; L = PMe_3			
R = Np; X = Cl; L_2 = $2PMe_3$, $2PMe_2Ph$, dmpe			
R = Me; X = Cl; L_2 = dmpe	NMR(H)	$ZrCl_4(dmpe)_2 + Me_2Mg$	113, 114

Zirconium (IV)			
$Zr(\eta^3:\eta^3\text{-}C_8H_{12})(PEt_3)$	IR, NMR(C,P)	$[ZrCl_3(PEt_3)]_2$ + excess C_4H_6	116
$ZrNp_3Cl(PMe_3)$	NMR(H)	$ZrNp_3Cl + PMe_3$	112
$ZrBz_4(PMe_3)$	NMR(H)	Not isolated	115
$ZrBz_4(dmpe)$	XRAY, IR, NMR(H)	$ZrBz_4$ + dmpe	113, 114
$Zr(CH_2SiMe_3)_4(dmpe)$	XRAY, IR, NMR(H)	$ZrCl_4(dmpe)_2$ + excess $LiCH_2SiMe_3$	113, 114
$ZrMe_4(dmpe)_2$	XRAY, IR, NMR(H,C,P)	$ZrCl_4(dmpe)_2$ + 4MeLi	113, 114
$CpZrCl_3(PEt_3)_2$	NMR(H)	$CpZrCl_3 + 2PEt_3$ or $[ZrCl_3(PEt_3)]_2$ + TlCp	116
$CpZrCl(\eta^2$-cyclopentanone)(dmpe)$_{1/2}$	NMR(H)	$CpZr(CO)_2Cl(dmpe) + 2H_2C{=}CH_2$	121
$Cp^*ZrNpCl_2(PMe_3)$	NMR(H,C,P)	$Cp^*ZrNpCl_2 + PMe_3$	112
$Cp^*ZrMe_3(PMe_3)_2$	NMR(H)	$Cp^*ZrMe_3 + 2PMe_3$(in situ)	117
$Cp^*ZrMe_3(dmpe)$	NMR(H)	Cp^*ZrMe_3 + dmpe	117
$\{[Cp_2ZrCl]_2[\mu\text{-dppe}]\}\{ClO_4\}_2$	NMR(H), COND	$[Cp_2ZrCl]_2(ClO_4)_2$ + dppe	229
$Cp^*_2ZrH_2(PF_3)$	NMR(H)	$Cp^*_2ZrH_2 + PF_3$ at −80 °C (in situ)	118, 119
$Cp_2Zr[\eta^2\text{-}SC(R)(H)](PMe_3)$: R = Me, Ph	XRAY, IR, NMR(H,C,P)	$Cp_2ZrMe_2 + RCH_2SH + PMe_3 + \Delta$	223
$Cp_2Zr[\eta^2\text{-}SC(R)(H)](PMe_3)$: R = Me, R′Ph R′ = H, CF_3, NH_2, Cl, OMe	IR, NMR(H,C,P,F), MS	$Cp_2ZrMe(SCH_2R) + PMe_3$	120
$[Cp_2ZrMe(PMe_3)_2]^+[BPh_4]^-$	NMR(H,C,P)	$[Cp_2ZrMe(THF)]^+[BPh_4]^- + 2PMe_3$	122
$[Cp_2ZrH(PMe_3)_2]^+[BPh_4]^-$	XRAY, IR, NMR(H,C)	$[Cp_2ZrMe(PMe_3)_2]^+[BPh_4]^- + H_2$	122
$[Cp_2ZrMe(THF)(PMe_2Ph)]^+[BPh_4]^-$	NMR(H,P)	$[Cp_2ZrMe(THF)]^+[BPh_4]^- + PMe_2Ph$	122
$[Cp_2ZrH(PMe_2Ph)_2]^+[BPh_4]^-$	NMR(H,P)	$[Cp_2ZrMe(THF)PMe_2Ph]^+[BPh_4]^-$ $+ H_2 + PMe_2Ph$	122
$[Cp_2ZrH(PMePh_2)_2]^+[BPh_4]^-$	NMR(H,P)	$[Cp_2ZrMe(THF)]^+[BPh_4]^- + H_2 + 2PMePh_2$	122
$[Cp_2ZrMe(dmpe)]^+[BPh_4]^-$	NMR(H,C,P)	$[Cp_2ZrMe(THF)]^+[BPh_4]^-$ + dmpe	122
$[Cp_2Zr(MeCN)_{3-n}(PMe_3)_n]^{2+}$: $n = 0, 1, 2$	NMR(H,P)	$[Cp_2Zr(MeCN)_3]^{2+}[BPh_4)_2^- + 2PMe_3$	124
$[Cp_2ZrCl]_2[\mu\text{-}\eta^2:\eta^2\text{-}OCCH(PMe_2)]$	XRAY, IR	$2Cp_2Zr(CH_2PMe_2)Cl + CO(-PMe_3)$	126
$[Cp_2ZrCl]_2[\mu\text{-}\eta^2:\eta^2\text{-}OCCH(PPh_2)]$	XRAY, NMR(H,P)	$2Cp_2Zr(CH_2PPh_2)Cl + CO(-PMePh_2)$	127, 128
$[Cp^*_2ZrI][\mu\text{-}\eta^1:\eta^1-OCH][Cp_2Zr(PMe_3)]$	XRAY, IR, NMR(H,C)	$[Cp^*_2ZrH][\mu\text{-}\eta^1:\eta^1-OCH][Cp_2Zr(PMe_3)]$ $+ CH_3I$	129
$[Cp^*_2ZrH][\mu\text{-}\eta^1:\eta^1\text{-}OCH][Cp_2Zr(PMe_3)]$	IR, NMR(H,C)	$Cp_2Zr(CO)(PMe_3) + Cp^*_2ZrH_2$	129

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$[CpZr(CH_2PPh_2)][\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)]\text{-}$ $[\mu\text{-}CH_2PPh_2][Cp_2ZrH]$	NMR(H,P)	$Cp_2Zr(CH_2PPh_2)Cl + Na/Hg$ (minor product)	125
$Zr[CH_2SiMe_2N(SiMe_3)]_2(dmpe)$	XRAY, NMR(H,C,P)	$\{Zr[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2[N(SiMe_3)_2]$ + dmpe	130
$Zr[OC(CH_2)SiMe_2N(SiMe_3)]_2(dmpe)$	IR, NMR(H,C,P)	$Zr[CH_2SiMe_2N(SiMe_3)]_2(dmpe)$ + CO (20 atm)	130
$ZrCl_2[N(SiMe_2CH_2PR_2)_2]_2$: R = Me, Ph	XRAY, NMR(H,P)	$ZrCl_4 + 2Li[N(SiMe_2CH_2PR_2)_2]$	131
$ZrCl_3[N(SiMe_2CH_2PR_2)_2]$: R = Me, Pr^i, Bu^t	XRAY, IR, NMR(H,C,P)	$ZrCl_4 + Li[N(SiMe_2CH_2PR_2)_2]$	132
Zirconium(III)			
$[ZrCl_3L_2]_2$			
L = PMe_3	NMR(H)	$ZrNp_2Cl_2(PMe_3)_2 + h\nu$ (10 h)	112
L = PMe_3, PEt_3, PPr_3, PBu_3	XRAY, NMR(P), ESR	$ZrCl_4 + 2L + Na/Hg$	116
$L_2 = 2PMe_2Ph$, $2PEt_3$, dppe	XRAY	$ZrCl_4 + L_2 + Na/Hg$	134
$[ZrCl_3(PBu_3)_2]_2[\mu\text{-}CH_2CH_2]$	NMR(P)	$[ZrCl_3(PBu_3)_2]_2 + H_2C{=}CH_2$	116
$[ZrX_3(PEt_3)_2]_2[\mu\text{-}CH_2CH_2]$: X = Cl, Br	XRAY	$Zr_2X_6(PEt_3)_4 + H_2C{=}CH_2$ or XCH_2CH_2X	136
$[ZrCl_3(PEt_3)_2]_2[\mu\text{-}CH_2CH(Me)]$	NMR(C,P)	$[ZrCl_3(PEt_3)_2]_2 + H_2C{=}CH(Me)$	116
$CpZrPh_2(PEt_3)$	ESR	$Cp_2ZrPh_2 + PEt_3 + h\nu$ at −64°C (minor product)	140
$CpZr(\eta^2\text{-}CH_2PPh_2)_2$	ESR	$Cp_2Zr(\eta^2\text{-}CH_2PPh_2)_2 + e^-$ (in situ)	68
$CpZr(\eta^2\text{-}O_2CCH_2PPh_2)_2$	ESR	$Cp_2Zr(\eta^2 - O_2CCH_2PPh_2)_2 + e^-$ (in situ)	68
$[CpZr(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(L)]_2$	IR, NMR(H,C,P)	$Cp_2ZrL_2 + \Delta$ or $Cp_2ZrCl_2 + Na/Hg + 2L$	137, 138
L = $PMePh_2$, PMe_2Ph	MW, Evans		
$[CpZr(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(PMe_3)]_2$	NMR(H,C,P), MS	$Cp_2Zr(PMe_3)_2 + \Delta$ or $Cp_2ZrCl_2 + 2Mg + 2PMe_3$	69
$Cp_2ZrX(PMePh_2)$: X = Cl, Br	ESR	$Cp_2Zr(PMePh_2)_2 + RX$	139
$Cp_2ZrX(PMe_3)$: X = Cl, Br	ESR	$Cp_2ZrX_2 + PMe_3 + e^-$	143
$Cp_2ZrR(L)$	ESR	$Cp_2ZrR_2 + h\nu + L$ at −64°C	140
R = Ph; L = PEt_3, PPh_3			
R = Bz; L = PPh_3			
R = CH_2SiMe_3; L = PEt_3			
R = Me; L = PPh_3		$Cp_2ZrR_2 + h\nu + L$ at −44°C (in situ)	142
R = H; L = PMe_3, PPh_3, dmpm		$Cp_2ZrH(CH_2PPh_2) + L$ at 60°C	146

Zirconium(III)			
$Cp'_2ZrH(PPh_3)$	ESR	$Cp'_2ZrH_2 + h\nu + PPh_3$ (in situ)	141
$Cp_2Zr(\eta^2\text{-}CH_2PMe_2)$	ESR	$Cp_2Zr(CH_2PMe_2)Cl + Na/Hg$	144
$Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$	ESR	$Cp_2Zr(CH_2PPh_2)Cl + Na/Hg$	145
$Cp_2Zr(\eta^2\text{-}C_6H_4PPh_2)$	ESR	Slow decomposition of $Cp_2ZrH(PPh_3)$	146
$Cp_2Zr[\eta^2\text{-}o\text{-}CH(SiMe_3)(C_6H_4PPh_2)]$		$Cp_2Zr[CH(SiMe_3)(C_6H_4PPh_2)]Cl + Na/Hg$	230
$Cp_2Zr[CH(SiMe_3)(\text{anthraceneyl})](PMe_3)$		$Cp_2Zr[CH(SiMe_3)(\text{anthraceneyl})]Cl$ $+ Na/Hg + PMe_3$	230
$Cp_2Zr[CH(SiMe_3)(C_6H_4PPh_2)](PMe_3)$		$Cp_2Zr[CH(SiMe_3)(C_6H_4PPh_2)]Cl$ $+ Na/Hg + PMe_3$	230
$[Cp_2Zr(CH_2PPh_2)(Cl)]^-$	ESR	$Cp_2Zr(CH_2PPh_2)Cl + Na/Hg$	145
Zirconium(II)			
$Zr_6Cl_{12}(PMe_2Ph)_6$	XRAY	$Zr_2Cl_6(PMe_2Ph)_4 + \Delta$	135
$Zr(\eta^5\text{-}C_6H_7)H(dmpe)_2$	NMR(H,P), MS	$ZrCl_4(dmpe)_2$ + 1,3-cyclohexadiene + Na/Hg	108
$Zr(\eta^5\text{-}C_8H_{11})H(dmpe)_2$	XRAY, IR, NMR(H,P), MS	$ZrCl_4(dmpe)_2$ + 1,3-cyclooctadiene + Na/Hg	168
$[Zr(\eta^4\text{-}C_6H_8)Cl_2(dmpe)]_2$	NMR(P)	$ZrCl_4(dmpe)_2 + C_6H_8 + Na/Hg$ isolable intermediate	168
$[CpZr(CO)Cl(dmpe)]_2(dmpe)$	IR	$CpZrCl(dmpe)_2 + CpZr(CO)_2Cl(dmpe)$	121
$Cp^*Zr(C_6H_{10})Cl(PR_3)$: R = Me, OMe	IR, NMR(H,C)	$Cp^*Zr(C_6H_{10})Cl + PR_3$	177, 178
$Cp^*Zr(CO)_2Cl(dmpe)$	IR, NMR(C,P)	$Cp^*ZrCl_3 + dmpe + 2NaC_{10}H_8 + CO$ (in situ)	99
$CpZrCl(dmpe)_2$	XRAY, IR, NMR(H)	$CpZrCl_3 + 2dmpe + 2NaC_{10}H_8$	165
$CpZrCl(dmpe)_2$	NMR(H,C), CV	$CpZrCl_3(THF)_2 + 2Na + 2dmpe$	121
$CpZrMe(dmpe)_2$	XRAY, NMR(H,C)	$CpZrCl(dmpe)_2 + MeLi$	166
$CpZr(CO)_2Cl(dmpe)$	XRAY, IR, NMR(H,C)	$CpZrCl(dmpe)_2 + 2CO$	121
$CpZr(C_4H_6)Cl(dmpe)$	IR, NMR(H,C)	$CpZrCl(dmpe)_2 + C_4H_6$	121, 166
$CpZr(C_4H_6)H(dmpe)$	XRAY, NMR(H), IR	$CpZr(C_4H_6)Cl(dmpe)$ $+ NaH_2Al(OCH_2CH_2OCH_3)_2$	167
$CpZr(C_4H_6)Me(dmpe)$	IR, NMR(H,C,P)	$CpZrMe(dmpe)_2 + C_4H_6$	166
$CpZr(C_4H_6)Et(dmpe)$	IR, NMR(H,C,P)	$CpZrMe(dmpe)_2 + 3H_2C{=}CH_2$	166

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
Cp_2ZrL_2			
$L_2 = 2PMePh_2, 2PMe_2Ph$, dmpe, dppe	IR, NMR(H,C,P), MS	$Cp_2Zr(CH_2Cy)H + 3L$ or Cp_2ZrCl_2 + dmpe + Na/Hg	137, 147
$L = PMe_3$	XRAY, NMR(H,C,P), MS	$Cp_2ZrCl_2 + Mg +$ excess PMe_3	70
$L = P(OMe)_3$	NMR(H), MS	$Cp_2ZrCl_2 + 2Na(g) +$ excess $P(OMe)_3$	74
$Cp_2Zr(CO)L$:			
$L = PMe_3$	IR, MS	$Cp_2Zr(CO)_2 + PMe_3 + \Delta$	62, 148
$L = PPh_3$	IR, NMR(H)	$Cp_2Zr(CO)_2 + PPh_3 + h\nu$	149
$L = PMePh_2$		$Cp_2Zr(PMePh_2)_2 + CO$	137, 138
$L = PMe_3, PMe_2Ph, PMePh_2, PBu_3, PPh_3$	IR	$Cp_2Zr(CO)_2 + L + \Delta$	80
$L = P(OMe)_3$	XRAY, IR, NMR(H,C)	$Cp_2Zr(CO)_2 + P(OMe)_3$ at 50 °C	150
$Cp''_2Zr(CO)(PMe_3)$: $Cp'' = C_5H_3(SiMe_3)_2$	"Impure"	$Cp''_2Zr(CO)_2 + h\nu + PMe_3$	142
$\{Cp^*_2Zr(PF_3)\}_2[\mu\text{-}N_2]$	IR, NMR(H-VT)	$[Cp^*_2Zr(N_2)]_2[\mu\text{-}N_2] + PF_3$ at −80 °C	163
$Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$	XRAY, NMR(H,C,P)	$Cp_2ZrPh_2 + PMe_3$ at 75 °C	154
$Cp_2Zr(\eta^2\text{-}C_6H_8)(PMe_3)$	XRAY, NMR(H,C,P)	$Cp_2Zr(Me)Cl + LiC_6H_9 + PMe_3$	153
$Cp_2Zr(\eta^2\text{-}C_2H_2)(PMe_3)$	IR, NMR(H,P)	$Cp_2Zr(PMe_3)_2 + HC{\equiv}CH$ (in situ)	83
$Cp_2Zr(\eta^2\text{-}C_2H_4)(PMe_3)$	XRAY, NMR(H,C,P)	$Cp_2Zr(PMe_3)_2 + H_2C{=}CH_2$	158
$Cp_2Zr(\eta^2\text{-}CHCBu)(PMe_3)$	XRAY	$Cp_2Zr(H)Cl +$ hexyne $+ MeLi + PMe_3$	152
$Cp_2Zr[\eta^2\text{-}CH_2CH(Et)](PMe_3)$		$Cp_2ZrCl_2 + 2BuLi + PMe_3$	152
$Cp_2Zr[\eta^2\text{-}CH(Ph)CH(Ph)](PMe_3)$	IR, NMR(H,C)	$Cp_2Zr(PMe_3)_2 + Ph(H)C{=}CPh(H)$	151
$Cp_2Zr[\eta^2\text{-}CPhCPh](PMe_3)$	XRAY, IR, NMR(H,C)	$Cp_2ZrCl_2 + 2BuLi + PMe_3 + PhC{\equiv}CPh$	151
$[Cp_2Zr(PMe_3)]_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}\{C_6(OMe)_2\}\}$	XRAY, NMR(H)	$[Cp_2ZrMe]_2\{\mu\text{-}C_6H_2(OMe)_2\} + PMe_3 + \Delta$	156
$Cp_2Zr\{\eta^2\text{-}CHC(CH{=}CHOMe)\}(PMe_3)$	NMR(H,P)	$Cp_2ZrCH{=}CHCH{=}CHOMe(Cl) + MeLi$ + excess PMe_3	155
$Cp_2Zr[\eta^2\text{-}CHC(C_6H_9)](PMe_3)$	NMR(H,P), MS	$Cp_2ZrCH{=}CHC_6H_9(Cl) + MeLi$ + excess PMe_3	155
$Cp_2Zr{=}CH_2(PMePh_2)$	NMR(H,C,P)	$Cp_2Zr(PMePh_2)_2 +$ excess Ph_3PCH_2 at 42 °C	160
$Cp_2Zr{=}C(H)R(L)$	NMR(H,C,P)	$[Cp_2Zr][\mu\text{-}Cl{:}\ \mu\text{-}CHCH_2R][AlBu^i_2] + L$	161
$L = PPh_3, PMe_2Ph$; $R = Bu^n, Bu^s, Bu^t$, Cy			
$Cp_2Zr{=}C(H)CH_2R(L)$			162
$R = Bu^t, L = PPh_3$; $R = Bu^n, L = PMe_2Ph$			
$Zr[\eta^5\text{-}2,4\text{-dimethyl(pd)}]_2(PEt_3)$	XRAY, NMR(H,C)	$[ZrCl_3(PEt_3)_2]_2 + 6pd$ or $ZrCl_4(PEt_3)_2 + 4pd$	164

Zirconium(0)			
$Zr(\eta^6\text{-}C_6H_5CH_3)_2(PMe_3)$	NMR(H), MS	$Zr(g) + 2C_6H_5R + PMe_3$ (metal vapor synthesis)	169, 170
$Zr(CO)_4(trmpe)$	XRAY, IR, NMR(C,P)	$ZrCl_4(THF)_2 + trmpe + 4KC_{10}H_8 + 4CO$ at −60° C	105
$[Zr(C_4H_6)_2(dmpe)]_2(dmpe)$	NMR(H,P), MS	$ZrCl_4(dmpe)_2$ + excess $C_4H_6 + Na/Hg$	108, 109
$Zr(C_4H_6)_2(dmpe)(CO)$	NMR(C,P)	$[Zr(C_4H_6)_2(dmpe)]_2(dmpe) + 2CO$ @ 45° C	108, 109
$Zr(C_4H_6)_2(dmpe)(L)$ $L = PMe_3, PMe_2Ph, POMe_3$	NMR(P)	$Zr(C_4H_6)_2(dmpe)(CO) + L$ at −78° C	108, 109
$Zr(C_4H_6)_2(dmpe)$	NMR(H), MS	$Zr(C_4H_6)_2(dmpe)(CO)$ at −22° C + vacuum	108, 109
$[Zr(C_8H_8)_2\}_2(dmpe)$		$2Zr(C_8H_8)_2$ + dmpe or $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ + COT	168
Hafnium (IV):			
$HfCl_4(dppe)$	IR	$HfCl_4$ + dppe	110
$HfCl_4(dmpe)_2$	NMR(P)	$HfCl_4$ + 2dmpe	171
$HfMe_4(dmpe)_2$	IR, NMR(H,C,P)	$HfCl_4(dmpe)_2 + 4MeLi$	113
$HfBz_4(PMe_3)$	NMR(H)	$HfBz_4 + PMe_3$ (in situ)	115
$HfCl_3[C(Cl){=}NBu^t](dppe)$	IR	$\{HfCl_3[C(Cl){=}NBu^t](CNBu^t)\}_2$ + 2dppe	30, 175
$Hf[CH_2SiMe_2N(SiMe_3)]_2(dmpe)$	NMR(H,C,P)	$\{Hf[\mu\text{-}CHSiMe_2N(SiMe_3)][N(SiMe_3)_2]_2$ + dmpe	130
$Cp^*HfCl_2(Et)(PMe_3)$	IR, NMR(H)	$Cp^*HfCl_2(PBu^t_2) + H_2C{=}CH_2 + PMe_3 + H_2$	172
$HfCl_2[N(SiMe_2CH_2PR_2)_2]_2$: R = Me, Ph	NMR(H,P)	$HfCl_4 + 2LiN(SiMe_2CH_2PR_2)_2$	131
$HfCl_3[N(SiMe_2CH_2PMe_2)_2]\cdot HfCl_4$	NMR(H,P)	$HfCl_2[N(SiMe_2CH_2PMe_2)_2]_2$ + excess $HfCl_4$	173, 174
$HfCl_3[N(SiMe_2CH_2PR_2)_2\}$: R = Me, Pr^i, Bu^t	XRAY, IR, NMR(H,P)	$HfCl_4 + LiN(SiMe_2CH_2PR_2)_2$	132
$Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$	IR, NMR(H,P,B), MW	$HfCl_3[N(SiMe_2CH_2PMe_2)_2\cdot HfCl_4$ + excess $LiBH_4$	173, 174
$Hf(BH_4)_3[N(SiMe_2CH_2PPr^i_2)_2]$	IR, NMR(H,P)	$HfCl_3[N(SiMe_2CH_2PPr^i_2)_2]$ + $3LiBH_4$	173
$Hf_2(\mu\text{-}H)_3(BH_4)_3$-$[N(SiMe_2CH_2PMe_2)_2]_2$	XRAY, IR, NMR(H,P,B)	$Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ + excess PMe_3	173, 174

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$Hf_2(\mu\text{-}H)_4(BH_4)_2$- $[N(SiMe_2CH_2PMe_2)_2]_2$	IR, NMR(H,P)	$Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ + excess PMe_3, 5 days	173
$Hf(BH_4)_2(CH_2SiMe_3)$- $[N(SiMe_2CH_2PMe_2)_2]$	NMR(H,P)	$HfCl_2(CH_2SiMe_3)[N(SiMe_2CH_2PMe_2)_2]$ $+ 2LiBH_4$	173
$HfCl_2(CH_2SiMe_3)$- $[N(SiMe_2CH_2PMe_2)_2]$	NMR(H,P)	$HfCl_3[N(SiMe_2CH_2PMe_2)_2] + LiCH_2SiMe_3$	173
$\{HfCl_2[N(SiMe_2CH_2PMe_2)_2]\}_2$- $\{\mu\text{-}H\}_2$	IR, NMR(H,P)	$HfCl_2(CH_2SiMe_3)[N(SiMe_2CH_2PMe_2)_2] + H_2$	173
Hafnium(III)			
$[CpHf(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(PMe_3)]_2$	MS, NMR(H,C,P)	$2Cp_2HfCl_2 + 2Mg + 2PMe_3$	69
Hafnium(II)			
$Cp^*Hf(CO)_2X(dmpe)$: $X = Cl, I$	XRAY, IR, NMR(H,C,P)	$Cp^*HfCl_3 + dmpe + 2NaC_{10}H_8/DME + CO$	99, 228
$CpHf(CO)_2Cl(dmpe)$	IR, NMR(H,C)	$CpHfCl(dmpe)_2 + CO$	121
$CpHfCl(dmpe)_2$	CV, NMR(H,C)	$CpHfCl_3(THF)_2 + 2Na + 2dmpe$	121
$CpHf(\eta^4\text{-}C_4H_6)H(dmpe)$	IR, NMR(H)	$CpHf(C_4H_6)Cl(dmpe)$ $+ NaH_2Al(OCH_2CH_2OCH_3)_2$	167
$[Cp^*Hf(C_6H_{10})Cl]_2(dmpe)$	NMR(H)	$Cp^*Hf(C_6H_{10})Cl + dmpe$	177, 178
$Cp^*Hf(C_6H_{10})Cl(PR_3)$: $R = Me, OMe$	IR, NMR(H,C)	$Cp^*Hf(C_6H_{10})Cl + PR_3$	177, 178
$Cp^*Hf(C_6H_{10})(BH_4)(PMe_3)$	IR	$Cp^*Hf(C_6H_{10})(BH_4) + PMe_3$	177, 178
$Cp_2Hf(CO)(PMe_2Ph)$	IR	$Cp_2Hf(CO)_2 + PMe_2Ph + \Delta$ in decalin	80
$Cp_2Hf(CO)L$ $L = PPh_3, PMe_3, PF_3$, dppe	IR, NMR(H), MS	$Cp_2Hf(CO)_2 + L + h\nu$ at 0 °C for 4 h	62, 149, 176
$Hf(C_4H_6)Cl[N(SiMe_2CH_2PR_2)_2]$: $R = Me, Pr^i$	XRAY, NMR(H,C,P)	$HfCl_3[N(SiMe_2CH_2PR_2)_2] + Mg(C_4H_6)(THF)_2$	179(b)
$Hf(C_4H_6)R[N(SiMe_2CH_2PMe_2)_2]$: $R = Np, Rh$		$Hf(C_4H_6)Cl[N(SiMe_2CH_2PMe_2)_2] + RLi$	179(b)
$Hf(C_4H_6)(allyl)[N(SiMe_2CH_2PMe_2)_2]$	XRAY, NMR(H,C,P)	$Hf(C_4H_6)Cl[N(SiMe_2CH_2PMe_2)_2] + ClMgC_3H_5$	179(a)
$Hf(\eta^1:\eta^4\text{-}C_7H_{11})[N(SiMe_2CH_2PR_2)_2]$: $R = Me, Pr^i$		$Hf(C_4H_6)(allyl)[N(SiMe_2CH_2PR_2)_2] + \Delta$	179(a)

Hafnium(0)			
$\mathrm{Hf(\eta^6\text{-}C_6H_5R)_2(PMe_3)}$: R = H, $\mathrm{CH_3}$	NMR(H), MS	$\mathrm{Hf(g) + 2C_6H_5R + PMe_3}$ (metal vapor synthesis)	169, 170
$\mathrm{Hf(CO)_4(trmpe)}$	IR, NMR(C,P)	$\mathrm{HfCl_4 \cdot 2THF + trmpe + 4KC_{10}H_8 + 4CO}$	105
$\mathrm{Hf(C_4H_6)_2(dmpe)}$	NMR(C)	$\mathrm{HfCl_4 + 4LiCH{=}CH_2 + dmpe}$	100
$\mathrm{Hf(C_4H_6)_2(dmpe)}$	XRAY, MS, NMR(H,P)	$\mathrm{HfCl_4 + dmpe + 2Mg(C_4H_6)(THF)_2}$	101
Group 3			
$\mathrm{[ScCl_3(dppe)]_x}$	IR, COND, MW	$\mathrm{ScCl_3 + dppe}$	181
$\mathrm{[ScBr_3(dppe)_{1.5}]_x}$	IR, COND, MW	$\mathrm{ScBr_3 + dppe}$	181
$\mathrm{[Me_2Si(C_5Me_4)_2]ScH(PMe_3)}$	XRAY	$\mathrm{[Me_2Si(C_5Me_4)_2]ScR + PMe_3 + H_2}$	182
$\mathrm{\{[(C_5Me_4)SiMe_2NBu^t]Sc(\mu\text{-}H)(PMe_3)\}_2}$	XRAY	$\mathrm{[(C_5Me_4)SiMe_2NBu^t]ScR + PMe_3 + H_2}$	183
$\mathrm{\{[(C_5Me_4)SiMe_2NBu^t]Sc(PMe_3)\}_2(\mu\text{-}C_2H_2)}$	XRAY	$\mathrm{\{[(C_5Me_4)SiMe_2NBu^t]Sc(\mu\text{-}H)(PMe_3)\}_2 + HC{\equiv}CH}$	183
$\mathrm{Y(R)[N(SiMe_2CH_2PMe_2)_2]_2}$	NMR(H,C,P,Y)	$\mathrm{YCl_3 + 2Li[N(SiMe_2CH_2PMe_2)_2]}$	184
R = Cl, Ph, $\mathrm{CH_2Ph}$		$\mathrm{YCl[N(SiMe_2CH_2PMe_2)_2]_2 + RLi}$	
$\mathrm{Y(OCBu^t_2CH_2PMe_2)_3}$	XRAY, NMR(H,P)	$\mathrm{YCl_3 + 3/2(LiOCBu^t_2CH_2PMe_2)_2}$	185
Lanthanides			
$\mathrm{Cp'_3Ce(PMe_3)}$	XRAY	$\mathrm{Cp'_3Ce(THF)}$ + excess $\mathrm{PMe_3}$	192
$\mathrm{Cp'_3Ce[P(OCH_2)_3CEt]}$	XRAY, IR, NMR(H)	$\mathrm{Cp'_3Ce(THF) + P(OCH_2)_3CEt}$	193
$\mathrm{Nd(OCBu^t_2CH_2PMe_2)_3}$	XRAY, NMR(H)	$\mathrm{NdCl_3 + 3/2(LiOCBu^t_2CH_2PMe_2)_2}$	185
$\mathrm{Cp^*_2M(L)}$			
M = Eu, Yb; L = dmpe, dmpm	IR, NMR(H,C,P)	$\mathrm{Cp^*_2M(OEt_2) + L}$	190
$\mathrm{Eu[N(SiMe_3)_2]_2L_n}$	EVANS	$\mathrm{NaEu[N(SiMe_3)_2]_3} + n\mathrm{L}$	189
L = dmpe, $n = 1.5$; L = $\mathrm{PBu_3}$, $n = 2$			
$\mathrm{Yb[N(SiMe_3)_2]_2L_2}$	XRAY, NMR(H,C,P)	$\mathrm{Yb[N(SiMe_3)_2]_2(OEt_2) + L_2}$	189
$\mathrm{L_2}$ = dmpe, $\mathrm{2PBu_3}$			
$\mathrm{M(BH_3Me)_3(dmpe)_{1.5}}$: M = Ho, Yb		$\mathrm{MCl_3 + 3LiBH_3Me + dmpe}$	195
$\mathrm{Cp^*_2YbCl(dmpm)}$	XRAY, IR, EVANS	$\mathrm{Cp^*_2Yb(dmpm) + YbCl_3}$	190
$\mathrm{Cp_3Yb(L)}$			
L = $\mathrm{PPh_3}$	UVVIS	$\mathrm{Cp_3Yb + PPh_3}$	186, 187
L = $\mathrm{PPh_3}$, $\mathrm{PHPh_2}$, $\mathrm{PH_2Ph}$, $\mathrm{PCy_3}$, $\mathrm{PHCy_2}$, $\mathrm{PH_2Cy}$ and $\mathrm{PMe_2Ph}$	UVVIS	$\mathrm{Cp_3Yb + L}$ (in situ except $\mathrm{PH_2Cy}$)	188
L = $\mathrm{PEt_3}$	UVVIS	$\mathrm{Cp_3Yb + PEt_3}$	194

TABLE 2 (continued)

Complex	Characterization	Synthesis	Ref.
$Cp_2Lu(CH_2PMe_2)$	NMR(H,C,P)	$Cp_2LuCl + LiCH_2PMe_2$	196
$M[N(SiMe_2CH_2PMe_2)_2]_2Cl$: M = Ce, Er, Yb, Lu	NMR(H,P)	$MCl_3 + 2KN(SiMe_2CH_2PMe_2)_2$	197
$M[N(SiMe_2CH_2PPh_2)_2]_2Cl$: M = Er, Yb	NMR(H,P)	$MCl_3 + 2KN(SiMe_2CH_2PPh_2)_2$	198
$Yb[N(SiMe_2CH_2PMe_2)_2]_2$	NMR(H,P)	$MI_2 + 2KN(SiMe_2CH_2PMe_2)_2$	198
$M[N(SiMe_2CH_2PPh_2)_2]_2$: M = Sm, Eu, Yb	NMR(H,P)	$MI_2 + 2KN(SiMe_2CH_2PPh_2)_2$	198
$M[N(SiMe_2CH_2PMe_2)_2]Cl_2$: M = Yb, Lu	NMR(H,P)	$MCl_3 + KN(SiMe_2CH_2PMe_2)_2$	197
Actinides			
$ThI_4(dmpe)_2$	NMR(H,P)	$MX_4 + 2dmpe$	212
$Cp_2ThCl_2(dmpe)$	XRAY	$ThCl_4(dmpe)_2 + 2NaCp$	214
$Cp_2ThR_2(dmpe)$: R = Me, Bz	XRAY	$Cp_2ThCl_2 + 2RLi$	214, 215
$ThR_4(dmpe)_n$ and $UR_4(dmpe)_n$			
R = OPh, $n = 2$	XRAY, NMR(H,C,P)	$MX_4(dmpe)_2 + 4LiOPh$ or $MMe_4(dmpe)_2 + 4PhOH$	212
R = Me, $n = 2$	NMR(H,C,P)	$MX_4(dmpe)_2 + 4MeLi$ or $MOPh_4(dmpe)_2 + 4MeLi$	212
R = Bz, $n = 1$	XRAY, IR, NMR(H,P)	$MCl_4(dmpe)_2 + 4BzLi$	213
$R_4 = Bz_3Me$, $n = 1$	XRAY, IR, NMR(H)	$MCl_4(dmpe)_2 + 3BzLi + MeLi$	213
UCl_5L: L = PPh_3, dppe	IR, SUSC, ESR	$UCl_5 + L$	208, 231
$[UCl_4]_2[dppe]$	IR, SUSC	$2UCl_4 + dppe$	207
$UCl_4(PMe_3)_3$		UCl_4 + excess PMe_3	212
$UX_4(dmpe)_2$: X = Cl, Br	NMR(H,P)	$MX_4 + 2dmpe$	212
$UR_n(dmpe)_m$			
R = BH_3Me, $n = 4$, $m = 1$	XRAY, IR, NMR(H:VT)	$U(BH_3Me)_4 + dmpe$	218
R = BH_3Me, $n = 3$, $m = 2$	XRAY, IR, NMR(H:VT)	$U(BH_3Me)_4(dmpe) + dmpe$ at 80 °C	218
R = BH_4, $n = 3$, $m = 2$	XRAY, IR	$U(BH_4)_3(THF)_x + 2dmpe$	216

$U(BH_4)_3[o\text{-}PPh_2(C_6H_4N)]_2$	XRAY, IR	$U(BH_4)_3(THF)_x + 2\,o\text{-}PPh_2(C_6H_4N)$	217
$Cp^*_2UCl(PMe_3)_x$		$[Cp^*_2UCl]_3$ + excess PMe_3	210, 211
$Cp^*_2UH(dmpe)$	XRAY, NMR(H), IR, EVANS	$Cp^*_2UR_2 + 3/2H_2$ + dmpe at −20 °C	219
$[Cp_3U]_2[\mu\text{-}dmpe]$	XRAY	$2Cp_3U(THF)$ + dmpe	221
$Cp'_3U(PMe_3)$	XRAY	$Cp'_3U(THF)$ + excess PMe_3	220
$Cp'_3U[P(OCH_2)_3CEt]$	XRAY, IR, NMR(H)	$Cp'_3U(THF) + P(OCH_2)_3CEt$	193
$CpUCl_3[o\text{-}PPh_2(C_6H_4N)]$	IR, NMR(H)	$CpUCl_3(THF)_x + o\text{-}PPh_2(C_6H_4N)$	217
$U[\eta^2\text{-}OC(CF_3)CHC(Ph)O]_4(PBu)_3$		$U[\eta^2\text{-}OC(CF_3)CHC(Ph)O]_4 + PBu_3$ (in situ)	209
$[UF(PF_3)_2]_2[\mu\text{-}PF_2]_3$	IR, ESCA, MS	$U(g) + PF_3$ at 77 K (metal vapor synthesis)	232
$U(PF_3)_6$	MS	$U(g) + PF_3$ at 77 K (metal vapor synthesis)	233

ACKNOWLEDGEMENTS

We thank the National Science and Engineering Research Council of Canada for financial support (operating grants to M.D.F. and a postdoctoral fellowship to D.J.B.) and the Izaak Walton Killam Foundation for an honorary postdoctoral fellowship to D.J.B. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

REFERENCES

1 C.A. McAuliffe, *in* G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Pergamon, London, 1987, Vol. 2, Chapter 14, p. 989.
2 L.H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum, New York, 1983.
3 P.S. Pregosin and R.W. Kunz, NMR Basic Principles and Progress, Springer-Verlag, Heidelberg, 1979, Vol. 16, p. 55.
4 O. Stelzer, Top. Phosphorus Chem., 9 (1977) 1.
5 C.A. McAuliffe and W.S. Levason, Phosphine, Arsine and Stibine Complexes of the Transition Elements, Elsevier, Amsterdam, 1979, p. 72.
6 G. Wilkinson, R.D. Gillard and J.A. McCleverty (Ed.), Comprehensive Coordination Chemistry, Pergamon, London, 1987, Vol. 3, Chapters 31, 32, 39 and 40.
7 P.J. Fagan, J.M. Manriquez, E.A. Maata, A.M. Seyam and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 6650, and references cited therein.
8 T. Moeller, Chem. Rev., 65 (1965) 1.
9 R.G. Pearson, J. Chem. Educ., 45 (1969) 581, 643.
10 J.E. Huheey, Inorganic Chemistry, (3rd edn.), Harper and Row, New York, 1983, p. 312.
11 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987, Chapter 2, p. 24.
12 H. Yasuda and A. Nakamura, Angew. Chem., Int. Ed. Engl., 29 (1987) 723.
13 C.M. Lukehart, Fundamental Transition Metal Chemistry, Brooks/Cole, Monterey, 1985, p. 156.
14 F.A. Cotton and G. Wilkinson, Comprehensive Inorganic Chemistry, (5th edn.), Wiley, New York, 1988, p. 778.
15 Ref. 1, p. 1030.
16 Ref. 1, p. 1033.
17 S. Xiao, W.C. Trogler, D.E. Ellis and Z. Berkovitch-Yellin, J. Am. Chem. Soc., 105 (1983) 7033.
18 D.S. Marynick, J. Am. Chem. Soc., 106 (1984) 4064.
19 N.M. Golovin, M.M. Rahman, J.E. Belmonte and W.P. Giering, Organometallics, 4 (1985) 1981.
20 I.R. Beattie and R. Collis, J. Chem. Soc. A, (1969) 2960.
21 F. Calderazzo, S. Losi and P.B. Susz, Inorg. Chim. Acta, 3 (1969) 329.
22 J. Chatt and R.G. Hayter, J. Chem. Soc., (1963) 1343.
23 I.R. Beattie and M. Webster, J. Chem. Soc., (1964) 3507.
24 G.W.A. Fowles and R.A. Walton, J. Chem. Soc., (1964) 4330.

25 A.D. Westland and L. Westland, Can. J. Chem., 43 (1965) 426.

26 F. Calderazzo, S.A. Losi and B.P. Susz, Helv. Chim. Acta, 54 (1971) 1156.

27 D. Gordon and M.G.H. Wallbridge, Inorg. Chim. Acta, 111 (1986) 77.

28 A.G. Akhmadullina, E.G. Yarkova, N.A. Mukmeneva, P.A. Kirpichnikov, A.A. Muratova and A.N. Pudovik, Zh. Prikl. Khim., 46 (1973) 1291; Chem. Abstr., 79 (1973) 601085j.

29 R.J.H. Clark, R.H.U. Negrotti and R.S. Nyholm, J. Chem. Soc., Chem. Commun., (1966) 486.

30 B. Crociani, M. Nicolini and R.L. Richards, J. Organomet. Chem., 101 (1975) C1.

31 S.R. Wade and G.R. Willey, J. Chem. Soc., Dalton Trans., (1981) 1264.

32 R.J.H. Clark and A.J. McAlees, J. Chem. Soc. A, (1970) 2026.

33 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc. A, (1971) 1920.

34 G.W.A. Fowles, D.A. Rice and T.G. Sheehan, J. Organomet. Chem., 135 (1977) 321.

35 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1982) 802.

36 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1982) 1410.

37 S. Obara, N. Koga and K. Morokuma, J. Organomet. Chem., 270 (1984) C33.

38 N. Koga, S. Obara and K. Morokuma, J. Am. Chem. Soc., 106 (1984) 4625.

39 R.A. Jones, S.T. Schwab and B.R. Whittlesey, Polyhedron, 3 (1984) 505.

40 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa, K. Prout, A.J. Schultz, J.M. Williams and T.F. Koetzle, J. Chem. Soc., Dalton Trans., (1986) 1629.

41 A. Shah, A. Singh and R.C. Mehrotra, Polyhedron, 5 (1986) 1285.

42 J.L. Pellegatta, M. Basso-Bert and D. Gervais, J. Chim. Phys. Phys.-Chim. Biol., 74 (1977) 311; Chem. Abstr., 87 (1977) 12339b.

43 D.L. Hughes, G.J. Leigh and D.G. Walker, J. Organomet. Chem., 355 (1988) 113.

44 D.A. Straus and R.H. Grubbs, J. Am. Chem. Soc., 104 (1982) 5499.

45 J.D. Meinhart, B.D. Santarsiero and R.H. Grubbs, J. Am. Chem. Soc., 108 (1986) 3318.

46 H.G. Alt, K.-H. Schwind and M.D. Rausch, J. Organomet. Chem., 321 (1987) C9.

47 M. Bochmann, L.M. Wilson, M.B. Hursthouse and R.L. Short, Organometallics, 6 (1987) 2556.

48 Y. Mugnier, C. Moise and E. Laviron, J. Organomet. Chem., 210 (1981) 69.

49 C.D. Schmulbach, C.H. Kolich and C.C. Hinckley, Inorg. Chem., 11 (1972) 2841.

50 N. Koide and K. Iimura, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 20 (1979) 558; Chem. Abstr., 94 (1981) 122023w.

51 T.A. Ballintine and C.D. Schmulbach, J. Organomet. Chem., 164 (1979) 381.

52 (a) T.G. Gardner and G.S. Girolami, Organometallics, 6 (1987) 2251.
(b) T.G. Gardner and G.S. Girolami, Angew. Chem., Int. Ed. Engl., 27 (1988) 1693.

53 A. Dormond and T. Kolavudh, Rev. Chim. Miner., 17 (1980) 131; Chem. Abstr., 93 (1980) 196819m.

54 L.E. Manzer, Inorg. Chem., 17 (1978) 1552.

55 J.A. Jensen and G.S. Girolami, J. Chem. Soc., Chem. Commun., (1986) 1160.

56 J.A. Jensen, S.R. Wilson and G.S. Girolami, J. Am. Chem. Soc., 110 (1988) 4977.

57 J.E. Bercaw and H.H. Brintzinger, J. Am. Chem. Soc., 91 (1969) 7301.

58 J.G. Kenworthy, J. Myatt and M.C.R. Symons, J. Chem. Soc. A, (1971) 3428.

59 M.L.H. Green and C.R. Lucas, J. Chem. Soc., Dalton Trans., (1972) 1000.

60 L.P. Battaglia, A.B. Corradi and M. Nardelli, Inorg. Acta, 50 (1981) 125.

61 Y. Mugnier, C. Moise and E. Laviron, J. Organomet. Chem., 204 (1981) 61.

62 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Wolf and U. Thewalt, J. Organomet. Chem., 297 (1985) 159.

63 R. Payne, J. Hachgenei, G. Fritz and D. Fenske, Z. Naturforsch., Teil B, 41 (1986) 1535.

64 M.L.H. Green and C.R. Lucas, J. Organomet. Chem., 73 (1974) 259.

65 A. Razavi, D.T. Mallin, R.O. Day, M.D. Rausch and H.G. Alt, J. Organomet. Chem., 333 (1987) C48.

66 P.B. Brindley, A.G. Davies and J.A.-A. Hawari, J. Organomet. Chem., 250 (1983) 247.

67 N.E. Murr, A. Chaloyard and J. Tirouflet, J. Chem. Soc., Chem. Commun., (1980) 446.

68 M. Etienne, R. Choukroun and D. Gervais, J. Chem. Soc., Dalton Trans., (1984) 915.

69 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Honold, J. Organomet. Chem., 310 (1986) 27.

70 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Honold and U. Thewalt, J. Organomet. Chem., 320 (1987) 37.

71 J.C. Leblanc, C. Moise, A. Maisonnat and R. Poilblanc, J. Organomet. Chem., 231 (1982) C43.

72 G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 1339.

73 J.A. Jensen, S.R. Wilson, A.J. Schultz and G.S. Girolami, J. Am. Chem. Soc., 109 (1987) 8094.

74 M. Chang, P.L. Timms and R.B. King, J. Organomet. Chem., 199 (1980) C3.

75 G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1984) 2347.

76 B.H. Edwards, R.D. Rogers, D.J. Sikora, J.L. Atwood and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 416.

77 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Am. Chem. Soc., 94 (1972) 1219.

78 D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, J. Am. Chem. Soc., 103 (1981) 982.

79 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 93 (1975) 199.

80 G.T. Palmer, F. Basolo, L.B. Kool and M.D. Rausch, J. Am. Chem. Soc., 108 (1986) 4417.

81 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Wolf, Angew. Chem., Int. Ed. Engl., 24 (1985) 394.

82 H.G. Alf, H.E. Engelhardt, M.D. Rausch and L.B. Kool, J. Am. Chem. Soc., 107 (1985) 3717.

83 H.G. Alt, H.E. Engelhardt, M.D. Rausch and L.B. Kool, J. Organomet. Chem., 329 (1987) 61.

84 B. Demerseman and P.H. Dixneuf, J. Chem. Soc., Chem. Commun., (1981) 665.

85 B. Demerseman, R. Mahe and P.H. Dixneuf, J. Chem. Soc., Chem. Commun., (1984) 1394.

86 B. Demerseman, P. Le Coupanec and P.H. Dixneuf, J. Organomet. Chem., 287 (1985) C35.

87 H.G. Alt, G.S. Herrmann and M.D. Rausch, J. Organomet. Chem., 356 (1988) C50.

88 D.H. Berry, L.J. Procopio and P.J. Carroll, Organometallics, 7 (1988) 570.

89 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, A.F. Hill, U. Thewalt and B. Wolf, J. Chem. Soc., Chem. Commun., (1986) 408.

90 H.G. Alt, G.S. Herrmann, M.D. Rausch and D.T. Mallin, J. Organomet. Chem., 356 (1988) C53.

91 E.V. Anslyn and R.H. Grubbs, J. Am. Chem. Soc., 109 (1987) 4880.

92 B.J.J. Van de Heisteeg, G. Schat, O.S. Akkerman and F. Bickelhaupt, J. Organomet. Chem., 310 (1986) C25.

93 L.R. Gilliom and R.H. Grubbs, Organometallics, 5 (1986) 721.

94 W. Tumas, D.R. Wheeler and R.H. Grubbs, J. Am. Chem. Soc., 109 (1987) 6182.

95 E. Melendez, A.M. Arif, M.L. Ziegler and R.D. Ernst, Angew. Chem., Int. Ed. Engl., 27 (1988) 1099.
96 L. Stahl and R.D. Ernst, J. Am. Chem. Soc., 109 (1987) 5673.
97 P.T. DiMauro and P.T. Wolczanski, Organometallics, 6 (1987) 1947.
98 S.R. Frerichs, B.K. Stein and J.E. Ellis, J. Am. Chem. Soc., 109 (1987) 5558.
99 B.K. Stein, S.R. Frerichs and J.E. Ellis, Organometallics, 6 (1987) 2017.
100 R. Beckhaus and K.-H. Thiele, J. Organomet. Chem., 317 (1986) 23.
101 S.S. Wreford and J.F. Whitney, Inorg. Chem., 20 (1981) 3918.
102 S.S. Wreford, M.B. Fischer, J. Lee, E.J. James and S.C. Nyburg, J. Chem. Soc., Chem. Commun., (1981) 458.
103 K.M. Chi, S.R. Frerichs, B.K. Stein, D.W. Blackburn and J.E. Ellis, J. Am. Chem. Soc., 110 (1988) 163.
104 P.J. Domaille, R.L. Harlow and S.S. Wreford, Organometallics, 1 (1982) 935.
105 D.W. Blackburn, K.M. Chi, S.R. Frerichs, M.L. Tinkham and J.E. Ellis, Angew. Chem., Int. Ed. Engl., 27 (1988) 437.
106 C.E. Davies, I.M. Gardiner, J.C. Green, M.L.H. Green, N.J. Hazel, P.D. Grebenik, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Dalton Trans., (1984) 669.
107 M.L.H. Green, N.J. Hazel, P.D. Grebenik, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1983) 356.
108 S. Datta, S.S. Wreford, R.P. Beatty and T.J. McNeese, J. Am. Chem. Soc., 101 (1979) 1053.
109 R.P. Beatty, S. Datta and S.S. Wreford, Inorg. Chem., 18 (1979) 3139.
110 T.C. Ray and A.D. Westland, Inorg. Chem., 4 (1965) 1501.
111 J.F. Clarke, G.W.A. Fowles and D.A. Rice, J. Organomet. Chem., 76 (1974) 349.
112 J.H. Wengrovius and R.R. Schrock, J. Organomet. Chem., 205 (1981) 319.
113 G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1984) 2789.
114 J.Z. Cayias, E.A. Babaian, D.C. Hrncir, S.G. Bott and J.L. Atwood, J. Chem. Soc., Dalton Trans., (1986) 2743.
115 J.J. Felten and W.P. Anderson, J. Organomet. Chem., 36 (1972) 87.
116 J.H. Wengrovius, R.R. Schrock and C.S. Day, Inorg. Chem., 20 (1981) 1844.
117 P.T. Wolczanski and J.E. Bercaw, Organometallics, 1 (1982) 793.
118 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Am. Chem. Soc., 98 (1976) 6733.
119 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 2716.
120 S.L. Buchwald and R.B. Nielsen, J. Am. Chem. Soc., 110 (1988) 3171.
121 Y. Wielstra, S. Gambarotta, J.B. Roedelof and M.Y. Chiang, Organometallics, 7 (1988) 2177.
122 R.F. Jorden, C.S. Bajgur, W.E. Dasher and A.L. Rheingold, Organometallics, 6 (1987) 1041.
123 K.I. Gell, B. Possin, J. Schwartz and G.M. Williams, J. Am. Chem. Soc., 104 (1982) 1846.
124 R.F. Jordan and S.F. Echols, Inorg. Chem., 26 (1987) 383.
125 C. Blandy, S.A. Locke, S.J. Young and N.E. Schore, J. Am. Chem. Soc., 110 (1988) 7540.
126 L.M. Engelhardt, G.E. Jacobsen, C.L. Raston and A.H. White, J. Chem. Soc., Chem. Commun., (1984) 220.
127 S.J. Young, H. Hope and N.E. Schore, Organometallics, 3 (1984) 1585.
128 R. Choukroun, F. Dahan and D. Gervais, J. Organomet. Chem., 266 (1984) C33.
129 P.T. Barger, B.D. Santarsiero, J. Armantrout and J.E. Bercaw, J. Am. Chem. Soc., 106 (1984) 5178.

130 R.P. Planalp and R.A. Andersen, Organometallics, 2 (1983) 1675.
131 M.D. Fryzuk, H.D. Williams and S.J. Rettig, Inorg. Chem., 22 (1983) 863.
132 M.D. Fryzuk, A. Carter and A. Westerhaus, Inorg. Chem., 24 (1985) 642.
133 A. Carter, M.Sc. Thesis, University of British Columbia, 1985.
134 F.A. Cotton, M.P. Diebold and P.A. Kibala, Inorg. Chem., 27 (1988) 799.
135 F.A. Cotton, P.A. Kibala and W.J. Roth, J. Am. Chem. Soc., 110 (1988) 298.
136 F.A. Cotton and P.A. Kibala, Polyhedron, 6 (1987) 645.
137 K.I. Gell and J. Schwartz, J. Chem. Soc., Chem. Commun., (1979) 244.
138 K.I. Gell, T.V. Harris and J. Schwartz, Inorg. Chem., 20 (1981) 481.
139 G.M. Williams and J. Schwartz, J. Am. Chem. Soc., 104 (1982) 1122.
140 A. Hudson, M.F. Lappert and R. Pichon, J. Chem. Soc., Chem. Commun., (1983) 374.
141 S.B. Jones and J.L. Petterson, J. Am. Chem. Soc., 105 (1983) 5502.
142 J.M. Atkinson, P.B. Brindley, A.G. Davies and J.A.-A. Hawari, J. Organomet. Chem., 264 (1984) 253.
143 E. Samuel, D. Guery, J. Vedel and F. Basile, Organometallics, 4 (1985) 1073.
144 S.J. Young, M.M. Olmstead, M.J. Knudsen and N.E. Schore, Organometallics, 4 (1985) 1432.
145 N.E. Schore and H. Hope, J. Am. Chem. Soc., 102 (1980) 4251.
146 R. Choukroun and D. Gervais, J. Chem. Soc., Chem. Commun., (1985) 224.
147 K.I. Gell and J. Schwartz, J. Am. Chem. Soc., 103 (1981) 2687.
148 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 132 (1977) 223.
149 D.J. Sikora and M.D. Rausch, J. Organomet. Chem., 276 (1984) 21.
150 G. Erker, U. Dorf, C. Kruger and K. Angermund, J. Organomet. Chem., 301 (1986) 299.
151 T. Takahashi, D.R. Swanson and E. Negishi, Chem. Lett., (1987) 623.
152 S.L. Buchwald, B.T. Watson and J.C. Huffman, J. Am. Chem. Soc., 109 (1987) 2544.
153 S.L. Buchwald, R.T. Lum and J.C. Dewan, J. Am. Chem. Soc., 108 (1986) 7441.
154 S.L. Buchwald, B.T. Watson and J.C. Huffman, J. Am. Chem. Soc., 108 (1986) 7411.
155 M.D. Fryzuk, R.A. Alex, R.K. Chadra and C. Stone, Tetrahedron Lett., 29 (1988) 3915.
156 S.L. Buchwald, E.A. Lucas and J.C. Dewan, J. Am. Chem. Soc., 109 (1987) 4396.
157 S.L. Buchwald and R.B. Nielsen, Chem. Rev., 88 (1988) 1047.
158 H.G. Alt, C.E. Denner, U. Thewalt and M.D. Rausch, J. Organomet. Chem., 356 (1988) C83.
159 Ref. 11, p. 150.
160 J. Schwartz and K.I. Gell, J. Organomet. Chem., 184 (1980) C1.
161 F.E. Hartner, Jr., J. Schwartz and S.M. Clift, J. Am. Chem. Soc., 105 (1983) 640.
162 S.M. Clift and J. Schwartz, J. Am. Chem. Soc., 106 (1984) 8300.
163 J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 3078.
164 L. Stahl, J.P. Hutchinson, D.R. Wilson and R.D. Ernst, J. Am. Chem. Soc., 107 (1985) 5016.
165 S. Gambarotta and M.Y. Chiang, J. Chem. Soc., Chem. Commun., (1987) 698.
166 Y. Wielstra, S. Gambarotta and M.Y. Chiang, Organometallics, 7 (1988) 1866.
167 Y. Wielstra, A. Meetsma and S. Gambarotta, Organometallics, 8 (1989) 258.
168 M.B. Fischer, E.J. James, T.J. McNeeze, S.C. Nyburg, B. Posin, W. Wong-Ng and S.S. Wreford, J. Am. Chem. Soc., 102 (1980) 4941.
169 F.G.N. Cloke and M.L.H. Green, J. Chem. Soc., Chem. Commun., (1979) 127.
170 F.G.N. Cloke and M.L.H. Green, J. Chem. Soc., Dalton Trans., (1981) 1938.
171 S. Datta, M.B. Fischer and S.S. Wreford, J. Organomet. Chem., 188 (1980) 353.
172 D.M. Roddick, B.D. Santarsiero and J.E. Bercaw, J. Am. Chem. Soc., 107 (1985) 4670.
173 M.D. Fryzuk, S.J. Rettig, A. Westerhaus and H.D. Williams, Inorg. Chem., 24 (1985) 4316.

174 M.D. Fryzuk and H.D. Williams, Organometallics, 2 (1983) 162.

175 M. Behnam-Dehkordy, B. Crociani, M. Nicolini and R.L. Richards, J. Organomet. Chem., 181 (1979) 69.

176 D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, J. Am. Chem. Soc., 101 (1979) 5079.

177 J. Blenkers, H.J. de Liefde Meijer and J. Teuben, Organometallics, 2 (1983) 1483.

178 J. Blenkers, B. Hassen, F. vanBolhuis, A.J. Wagner and J.H. Teuben, Organometallics, 6 (1987) 459.

179 (a) M.D. Fryzuk, T.S. Haddad and S.J. Rettig, Organometallics, 7 (1988) 1224.
(b) M.D. Fryzuk, T.S. Haddad and S.J. Rettig, Organometallics, 8 (1989) 1723.

180 G. Erker, C. Kruger and G. Muller, Adv. Organomet. Chem., 24 (1985) 1.
(b) H. Yasuda, K. Tatsumi and A. Nakamura, Acc. Chem. Res., 18 (1985) 120.

181 N.N. Greenwood and R.L. Tranter, J. Chem. Soc. A, (1969) 2878.

182 E.E. Bunel, V. Schomaker and J.E. Bercaw, personal communication, 1988.

183 P.J. Shapiro, W.P. Schaefer, and J.E. Bercaw, personal communication, 1988.

184 (a) M.D. Fryzuk and T.S. Haddad, J. Am. Chem. Soc., 110 (1988) 8263.
(b) M.D. Fryzuk, T.S. Haddad and S.J. Rettig, unpublished results, 1988.

185 P.B. Hitchcock, M.F. Lappert and I.A. MacKinnon, J. Chem. Soc., Chem. Commun., (1988) 1557.

186 R.D. Fischer and H. Fischer, J. Organomet. Chem., 4 (1965) 412.

187 E.O. Fischer and H. Fischer, J. Organomet. Chem., 6 (1966) 141.

188 G. Bielang and R.D. Fischer, J. Organomet. Chem., 161 (1978) 335.

189 T.D. Tilley, R.A. Andersen and A. Zalkin, J. Am. Chem. Soc., 104 (1982) 3725.

190 T.D. Tilley, R.A. Andersen and A. Zalkin, Inorg. Chem., 22 (1983) 856.

191 D.J. Berg and R.A. Andersen, unpublished results, 1987.

192 S. Stults and A. Zalkin, Acta Crystallogr., Sect. C, 43 (1987) 430.

193 J.G. Brennan, S.D. Stults, R.A. Andersen and A. Zalkin, Organometallics, 7 (1988) 1329.

194 C.J. Schlesener and A.B. Ellis, Organometallics, 2 (1983) 529.

195 R.S. Shinomoto, Energy. Res. Abstr., 10 (1985) Abstr. No. 10165; Chem. Abstr., 103 (1985) 80844m.

196 H. Schumann, F.-W. Reier, and E. Palamidis, J. Organomet. Chem., 297 (1985) C30.

197 D.J. Berg, T.S. Haddad and M.D. Fryzuk, unpublished results, 1988.

198 D.J. Berg, and M.D. Fryzuk, unpublished results, 1989.

199 A.K. Majumdar, A.K. Mukherjee and R.G. Bhattacharya, J. Inorg. Nucl. Chem., 26 (1964) 386.

200 J.A.C. Allison and F.G. Mann, J. Chem. Soc., (1949) 2915.

201 H.C.E. Mannerskantz, G.W. Parshall and G. Wilkinson, J. Chem. Soc., (1963) 3163.

202 B.W. Fitzsimmons, P. Gans, B. Hayton and B.C. Smith, J. Inorg. Nucl. Chem., 28 (1966) 915.

203 F.A. Hart and J.E. Newberry, J. Inorg. Nucl. Chem., 28 (1966) 1334.

204 A.K. Majumdar and R.G. Bhattacharya, J. Inorg. Nucl. Chem., 29 (1967) 2359.

205 P. Gans and B.C. Smith, J. Chem. Soc., (1964) 4172.

206 J.P. Day and L.M. Venanzi, J. Chem. Soc. A, (1966) 1363.

207 J. Selbin and J.D. Ortego, J. Inorg. Nucl. Chem., 29 (1967) 1449.

208 J. Selbin, N. Ahmad and M.J. Pribble, J. Inorg. Nucl. Chem., 32 (1970) 3249.

209 G. Folcher, J. Paris, P. Plurien, P. Rigny and E. Soulie, J. Chem. Soc., Chem., Commun., (1974) 3.

210 J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day and V.W. Day, J. Am. Chem. Soc., 101 (1979) 5075.

211 P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer and V.W. Day, Organometallics, 1 (1982) 170.

212 P.G. Edwards, R.A. Andersen and A. Zalkin, J. Am. Chem. Soc., 103 (1981) 7792.

213 P.G. Edwards, R.A. Andersen and A. Zalkin, Organometallics, 3 (1984) 293.

214 A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Crystallogr., Sect. C, 43 (1987) 418.

215 A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Crystallogr., Sect. C, 43 (1987) 421.

216 H.J. Wasserman, D.C. Moody and R.R. Ryan, J. Chem. Soc., Chem. Commun., (1984) 532.

217 H.J. Wasserman, D.C. Moody, R.T. Paine, R.R. Ryan and K.V. Salazar, J. Chem. Soc., Chem. Commun., (1984) 533.

218 J. Brennan, R. Shinomoto, A. Zalkin and N. Edelstein, Inorg. Chem., 23 (1984) 4143.

219 M.R. Duttera, P.J. Fagan, T.J. Marks and V.W. Day, J. Am. Chem. Soc., 104 (1982) 865.

220 J.G. Brennan and A. Zalkin, Acta Crystallogr., Sect. C, 41 (1985) 1038.

221 A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Crystallogr., Sect. C, 43 (1987) 1706.

222 R.D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751.

223 S.L. Buchwald, R.B. Nielsen and J.C. Dewan, J. Am. Chem. Soc., 109 (1987) 1590.

224 J.F. Plummer and E.P. Schram, Inorg. Chem., 14 (1975) 1505.

225 J.M. Latour, J.C. Marchon and M. Nakajima, J. Am. Chem. Soc., 101 (1979) 3974.

226 F.A. Shmidt, N.M. Ryntina, V.V. Saraev, V.A. Cruznykh and V.A. Makarov, React. Kinet. Catal. Lett., 5 (1976) 101; Chem. Abstr., 86 (1977) 71377q.

227 A.R. Dias and J.A.M. Simoes, Polyhedron, 6 (1988) 1531.

228 B.A. Kelsey, Ph.D. Thesis, University of Minnesota, 1986; Chem. Abstr., 108 (1988) 6133r.

229 T. Cuenca and P. Royo, J. Organomet. Chem., 293 (1985) 61.

230 S.I. Bailey, D. Colgan, L.M. Engelhardt, W. Leung, R.I. Papasergio, C.L. Raston and A.H. White, J. Chem. Soc., Dalton Trans., (1986) 603.

231 J. Selbin, N. Ahmad and M.J. Pribble, J. Chem. Soc., Chem. Commun., (1969) 759.

232 A.P. Babichev, V.D. Klimov, O.A. Kushlyanskii, V.A. Legasov, A.V. Lebedev, A.I. Nastyukha, S.S. Khoroshev, Dokl. Akad. Nauk SSSR, 259 (1981) 109; Chem. Abstr., 95 (1981) 161183p.

233 V.N. Prusakov, Y.V. Petrov, A.A. Terent'ev and N.F. Simonov, Radiokhimiya, 23 (1981) 319; Chem. Abstr., 95 (1981) 34598c.