# Transition Metal–Phosphide Chemistry: Synthesis of $[M(\eta\text{-}C_5H_5)_2(PR_2)_2]$ (M = Zr, R = Ph; M = Hf, R = Ph or cyclo-$C_6H_{11}$) and $[\{M(\eta\text{-}C_5H_5)_2(PR_2)\}_2]$ (M = Ti, R = Ph or Me; M = Zr or Hf, R = Me), and their Reactions with Protic and Halogen-containing Species

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Reactions of the metallocene dichlorides $[M(cp)_2Cl_2]$ (M = Ti, Zr, or Hf; cp = $\eta$-$C_5H_5$) with stoicheiometric amounts of $LiPR_2$ (R = Me, Ph, or cyclo-$C_6H_{11}$) yield either the direct exchange products $[M^{IV}(cp)_2(PR_2)_2]$ (M = Zr, R = Ph; M = Hf, R = Ph or $C_6H_{11}$) or the reduced species $[\{M^{III}(cp)_2(PR_2)\}_2]$ (M = Ti, R = Me or Ph; M = Zr or Hf, R = Me). Spectral (i.r. and $^1H$ n.m.r.) characterisation of these compounds is presented and discussed with suggestions of possible structures. Treatment of $[Zr(cp)_2(PPh_2)_2]$ with $PPh_2Cl$ affords the 'mixed' chloro–phosphido-compound $[Zr(cp)_2Cl(PPh_2)]$. Reactions of both the $M^{IV}$ and $M^{III}$ species with halogen-containing and protic reagents have been investigated. Each series reacts with smooth cleavage of the M–P bond(s), but whereas the compounds $[M(cp)_2(PR_2)_2]$ (M = Ti, Zr, or Hf) show simple metathetical exchange, $[\{M(cp)_2(PR_2)\}_2]$ usually (and in the case of M = Zr or Hf exclusively) also incorporate metal oxidation $M^{III} \rightarrow M^{IV}$ into their reactions.

Compounds containing a Group 4A metal–nitrogen bond have been thoroughly investigated, and much of their versatile chemistry has been recently reviewed.[1] In stark contrast, only a few complexes containing a metal–phosphorus bond have been isolated, and little is known of their chemical reactivity. As part of a general investigation into the chemistry of early transition-metal cyclopentadienyl (cp) complexes we have examined the reactions of $[M(cp)_2Cl_2]$ (M = Ti, Zr, or Hf) with a number of lithium dialkyl- and diaryl-phosphides. Subsequent investigations of the chemical reactivity of the $M^{IV}$–P and $M^{III}$–P bonds in the various products isolated are also reported and discussed.

## Results and Discussion

Treatment of the Group 4A metallocene dichlorides $[M(cp)_2Cl_2]$ (M = Ti, Zr, or Hf) with stoicheiometric amounts of lithium dimethyl-, diphenyl-, or dicyclohexyl-phosphides has provided both $M^{IV}$ and $M^{III}$ species [equations (1) and (2)].

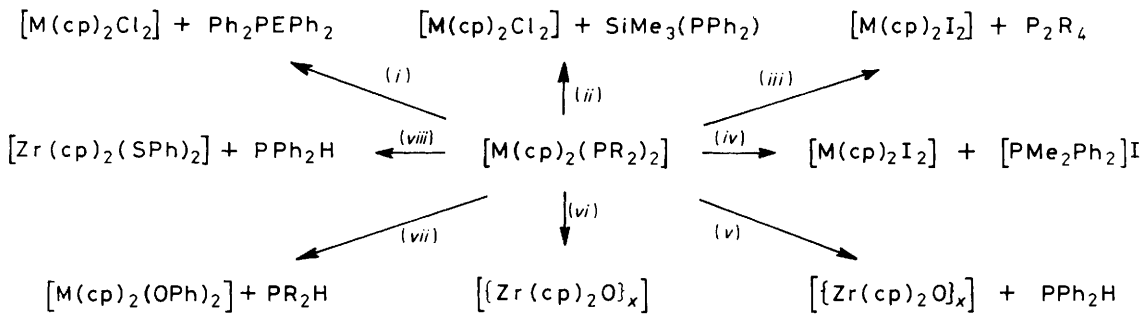
$$[M(cp)_2Cl_2] + 2LiPR_2 \longrightarrow [M(cp)_2(PR_2)_2] + 2LiCl \quad (1)$$
(M = Zr, R = Ph; M = Hf, R = Ph or $C_6H_{11}$)

$$[M(cp)_2Cl_2] + 2LiPR_2 \longrightarrow \tfrac{1}{2}[\{M(cp)_2(PR_2)\}_2] + 2LiCl + \tfrac{1}{2}P_2R_4 \quad (2)$$
(M = Ti, Zr, or Hf, R = Me; M = Ti, R = Ph)

Previous examples of direct Cl/$PR_2$ exchange [equation (1)] include the simple phosphides $[Ti(PR^1_2)(NR^2_2)_3]$ ($R^1$ = Et or $SiMe_3$; $R^2$ = Me or Et),[2,3] $[M\{P(C_6H_{11})_2\}_3]$ (M = V or Cr),[4] the chelate compounds $[M(cp)_2(\eta^2\text{-}P_3Ph_3)]$ (M = Ti or Zr),[5] and the spiro compound $[Zr(cp)_2\{(PhPCH_2)_2C(CH_2PPh)_2\}\text{-}Zr(cp)_2]$.[6] Reactions involving reduction [as in equation (2)] have led to $[Ti\{P(C_6H_{11})_2\}_2]$[4] and the $M^{III}$ species $[\{M(cp)_2(PR_2)\}_2]$ (M = Ti or Zr).[7] The observed lack of reduction of $Zr^{IV}$ and $Hf^{IV}$ by $LiPR_2$ (R = Ph or $C_6H_{11}$) [equation (1)] was surprising since earlier work had suggested that, firstly, reduction of $Zr^{IV}$ to $Zr^{II}$ was probable,[7] and secondly, in the presence of an excess of the diphenylphosphide, solutions of $[M(cp)_2Cl_2]$ (M = Ti or Zr) have been reported to give rise to strong e.s.r. signals signifying $M^{III}$ species, postulated [8,9] as $[M(cp)_2(PPh_2)_2]^-$. It should be pointed out that all of our experiments have been carried out at room temperature. The effects of higher temperatures on the reaction solutions have not been investigated but we did note that $[Zr(cp)_2(PPh_2)_2]$ does not appear to change on attempted sublimation up to 140 °C. In contrast to the reactions involving zirconium and hafnium no $Ti^{IV}$ species were isolated in any of the reactions. The reduction potentials of $[M(cp)_2Cl_2]$ (M = Ti or Zr) have recently been measured in tetrahydrofuran (thf) solution by cyclic voltammetry; the value obtained for M = Zr (−1.70 V) was found to be almost 1.0 V higher than that for the corresponding Ti complex under similar conditions.[10] Evidently in reactions of the $PR_2$ anion featuring R = Me and R = Ph or $C_6H_{11}$ groups there must be a subtle balance of electronic and steric factors for the former to espouse formation of the $M^{III}$ dimer [equation (2)]. Such a dimer, $[\{Zr(cp)_2(PPh_2)\}_2]$, has been suggested by Schwartz and co-workers [11] to result from the oxidative addition of $PPh_2H$ to $[\{Zr(cp)(\mu\text{-}\sigma\text{:}\eta^5\text{-}C_5H_4)(PMePh_2)\}_2]$.

*Properties and Reactions of* $[M(cp)_2(PR_2)_2]$.—The complexes $[M(cp)_2(PPh_2)_2]$ (M = Zr or Hf) were prepared by addition of benzene solutions of $[M(cp)_2Cl_2]$ to $LiPPh_2$ in either hexane or thf; $LiPPh_2$ can be conveniently prepared either by the action of LiBu on $PPh_2H$ in hexane solution, or by the treatment of $PPh_3$ with two mol equiv. of lithium metal in thf (the accompanying LiPh formed can be removed by treatment with t-butyl chloride: LiPh + $Bu^tCl \longrightarrow C_6H_6 + Me_2C{=}CH_2$ + LiCl).[12] The corresponding cyclohexyl derivatives proved more difficult to isolate. Reaction of $P(C_6H_{11})_2H$ with LiBu in hexane gave pale yellow solutions of $LiP(C_6H_{11})_2$ which on treatment with $[M(cp)_2Cl_2]$ (M = Zr or Hf) gave bright red solutions. Work up of these reaction mixtures, however, generally resulted in deep red oils; only in the case of M = Hf was a solid product obtained but then only in low yield (*ca.* 6%).

All the $M^{IV}$ derivatives are oxygen- and moisture-sensitive, especially in solution. They dissolve in hydrocarbons such as $C_6H_6$ and toluene and in ethers (thf and $Et_2O$) to give intensely coloured solutions {*e.g.* purple $[Zr(cp)_2(PPh_2)_2]$, deep red $[Hf(cp)_2(PR_2)_2]$ (R = Ph or $C_6H_{11}$)}, but decompose rapidly in halogenated solvents. Molecular weight measurements determined cryoscopically in $C_6H_6$ confirm a monomeric formulation (see Experimental section).




**Scheme 1.** Reactions of $[M(cp)_2(PR_2)_2]$ (M = Zr, R = Ph; M = Hf, R = Ph or $C_6H_{11}$): (*i*) 2 mol equiv. of $EPh_2Cl$ (M = Zr or Hf, R = Ph; M = Hf, R = $C_6H_{11}$; E = Ph or As); (*ii*) equimolar amount of $SiMe_3Cl$ (M = Zr or Hf, R = Ph); (*iii*) equimolar amount of $I_2$ (M = Zr or Hf, R = Ph; M = Hf, R = $C_6H_{11}$); (*iv*) 4 mol equiv. of MeI (M = Zr or Hf, R = Ph); (*v*) equimolar amount of $H_2O$ (M = Zr, R = Ph); (*vi*) excess dry $O_2$ (M = Zr, R = Ph); (*vii*) 2 mol equiv. of PhOH (M = Zr or Hf, R = Ph; M = Hf, R = $C_6H_{11}$); (*viii*) 2 mol equiv. of PhSH (M = Zr, R = Ph)

The i.r. spectra of $[M(cp)_2(PPh_2)_2]$ (M = Zr or Hf) in the range 4 000—400 $cm^{-1}$ are similar (most bands differing by $<5$ $cm^{-1}$), and show characteristic absorptions of the M–cp and phenyl groups as expected. Single weak bands at the lower frequencies of 356 (M = Zr) and 305 $cm^{-1}$ (M = Hf) are tentatively assigned as ν(M–P) stretching vibrations. $[Hf(cp)_2\{P(C_6H_{11})_2\}_2]$ shows weak bands at 299 and 270 $cm^{-1}$ which possibly arise from ν(Hf–P) stretching modes. The $^1H$ n.m.r. spectra (thf) of $[M(cp)_2(PPh_2)_2]$ show single resonances at δ 5.80 (M = Zr) and 5.78 (M = Hf) corresponding to the equivalent protons of the cyclopentadienyl ring, and a complex multiplet at δ 7.03—7.47 (M = Zr) and 7.05—7.51 (M = Hf) from the phenyl protons. In aromatic media interactions between the cp and phenyl groups and solvent molecules cause an upfield shift in the cp resonance, and split the broad phenyl multiplet into three distinct sets. $[Hf(cp)_2\{P(C_6H_{11})_2\}_2]$ shows a single resonance at δ 5.88 from the cp protons with the cyclohexyl protons being obscured by the solvent absorptions.

The complexes $[M(cp)_2(PR_2)_2]$ (M = Zr or Hf, R = Ph; M = Hf, R = $C_6H_{11}$) react with a variety of protic and halogen-containing species with cleavage of the metal–phosphorus bond in each case. These reactions are summarised in Scheme 1. The reactions were monitored by their $^1H$ n.m.r. spectra, and were found to be both quantitative and relatively slow compared with those of their nitrogen analogues; [1] most take about 1 min to go to completion. $[M(cp)_2(PPh_2)_2]$ (M = Zr or Hf) gave smooth metathetical reactions with (*i*) $EPh_2Cl$ (E = P or As) and (*ii*) $SiMe_3Cl$, with formation of $[M(cp)_2Cl_2]$ as the common product. The side products $Ph_2PPPh_2$, $Ph_2AsPPh_2$, and $SiMe_3(PPh_2)$, respectively, were identified by their characteristic $^1H$ n.m.r. spectra. It is noteworthy that reactions with one mol equiv. of $SiMe_2Cl_2$ produced an equilibrium mixture: equation (3). This is directly comparable

$$2[Zr(cp)_2(PPh_2)_2] + 2SiMe_2Cl_2 \rightleftharpoons [Zr(cp)_2Cl(PPh_2)] + [Zr(cp)_2Cl_2] + SiMe_2Cl(PPh_2) + SiMe_2(PPh_2)_2 \quad (3)$$

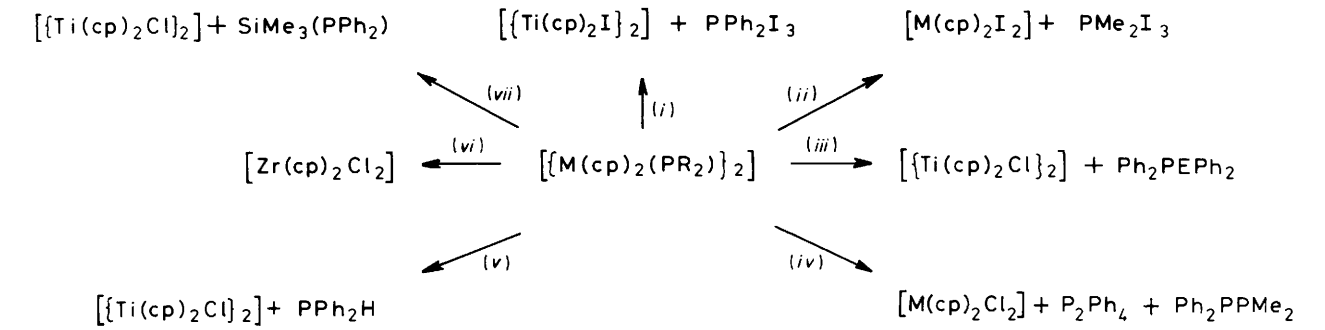
to the partial Cl/$NMe_2$ exchange situation which is a feature of the $SiMe_2(NMe_2)_2/TiCl_4$ system.[13] Reaction of $[M(cp)_2(PR_2)_2]$ with $I_2$ as in (*iii*) proceeds through a mauve intermediate to give yellow $[M(cp)_2I_2]$, and the appropriate diphosphine $P_2R_4$. Addition of a further 3 mol equiv. of iodine breaks the diphosphine P–P bond *via* the oxidation $P^{III} \rightarrow P^V$, and eventually gives the pale yellow solids $PR_2I_3$ (R = Ph or $C_6H_{11}$). Reaction with MeI in (*iv*) leads directly to the phosphonium salt $[PMe_2Ph_2]I$. Rapid decolourisation of the purple thf solution of $[Zr(cp)_2(PPh_2)_2]$ occurs on addition of $H_2O$ (*v*), and dry $O_2$ (*vi*), and is followed by precipitation of a white solid which was insoluble in all common solvents. The i.r. spectrum showed characteristic cp ring absorptions, and a strong band at 725 $cm^{-1}$ (assigned to a Zr–O–Zr stretch [14]) suggesting a polymeric formulation $[\{Zr(cp)_2O\}_x]$. Reactions of $[M(cp)_2(PR_2)_2]$ with a two-fold excess of phenol (*vii*), and thiophenol (*viii*), gave $[M(cp)_2(OPh)_2]$ [15] and $[M(cp)_2(SPh)_2]$ [16] respectively in high yield, which could be conveniently recrystallised from n-hexane. The free phosphine $PR_2H$ was isolated from the mother-liquor, and characterised by its i.r. spectrum. Aliphatic alcohols (MeOH, EtOH, and Bu$^t$OH) and secondary amines ($NEt_2H$) displace the $PPh_2$ groups from $[Zr(cp)_2(PPh_2)_2]$ as $PPh_2H$, but in each case the Zr product was poorly defined.

Reactions (*i*)—(*iv*) were observed to proceed *via* intensely coloured intermediates on the addition of 0.5 mol ($I_2$ or $SiMe_2Cl_2$), 1 mol ($SiMe_3Cl$, $PPh_2Cl$, or $AsPh_2Cl$), or 2 mol (MeI) of reagent. In the case of the zirconium compound, the original purple colour intensified to a red-purple shade, while for the hafnium analogue the deep red colouration intensified to give a slightly darker solution. These intermediate solutions, which could equally be obtained either from the reaction of $[M(cp)_2Cl_2]$ (M = Zr or Hf) with one mol equiv. of $LiPPh_2$ or by straightforward mixing of equimolar amounts of $[M(cp)_2(PR_2)_2]$ and $[M(cp)_2X_2]$ (X = Cl or I), are best thought of in terms of a labile equilibrium: equation (4). Hydrogen-1 n.m.r.

$$[M(cp)_2(PR_2)_2] + [M(cp)_2X_2] \rightleftharpoons 2[M(cp)_2X(PR_2)] \quad (4)$$

studies reveal cp resonances corresponding to $[M(cp)_2(PR_2)_2]$, $[M(cp)_2X_2]$, and one of intermediate chemical shift assigned to the mixed species $[M(cp)_2X(PR_2)]$ (see Experimental section). The equilibrium evidently favours the $[M(cp)_2X(PR_2)]$ derivative more for the Zr than for the Hf species since the mixed $PR_2/X$ hafnium species never accounted for more than 10% of the total cp intensity. Attempts to isolate any of the mixed $PR_2/X$ species were largely unsuccessful, the majority giving intractable tarry solids. On leaving the purple solution formed from $[Zr(cp)_2(PPh_2)_2]$ and $PPh_2Cl$ at 0 °C for several days, however, purple crystals of $[Zr(cp)_2Cl(PPh_2)]$ were obtained in low yield (5%). The i.r. spectrum is very similar to that of the parent $[Zr(cp)_2(PPh_2)_2]$, but shows an additional intense ν(Zr–Cl) stretching band at 330 $cm^{-1}$. The $[M(cp)_2X_2]$–$[M(cp)_2(PR_2)_2]$ equilibria solutions were particularly susceptible to oxidation/hydrolysis, since the purple colour rapidly disappeared in the presence of both dry $O_2$ and water; work up of these solutions gave $[\{Zr(cp)_2Cl\}_2O]$ as a colourless crystalline solid (60%).

*Properties and Reactions of* $[\{M(cp)_2(PR_2)\}_2]$.—$[Ti(cp)_2Cl_2]$




**Scheme 2.** Reactions of $[\{M(cp)_2(PR_2)\}_2]$ (M = Ti, Zr, or Hf, R = Me; M = Ti, R = Ph): (*i*) 2 mol equiv. of $I_2$ (M = Ti, R = Ph); (*ii*) 2.5 mol equiv. of $I_2$ (M = Zr or Hf, R = Me); (*iii*) 2 mol equiv. of $EPh_2Cl$ (M = Ti, R = Ph; E = P or As); (*iv*) 4 mol equiv. of $PPh_2Cl$; (M = Zr or Hf, R = Me); (*v*) 2 mol equiv. of HCl (M = Ti, R = Ph); (*vi*) equimolar amount of $BCl_3$ (M = Zr, R = Me); (*vii*) equimolar amount of $SiMe_3Cl$ (M = Ti, R = Ph)

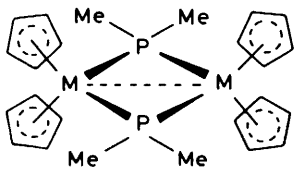
reacts with 1 mol equiv. of $LiPR_2$ (R = Me or Ph) to give initially $[\{Ti(cp)_2Cl\}_2]$. This then reacts with a further mol of $LiPR_2$ to give deep green $[\{Ti(cp)_2(PPh_2)\}_2]$ or pale mauve $[\{Ti(cp)_2(PMe_2)\}_2]$ [equation (5)]. In practice, the separation of

$$[Ti(cp)_2Cl_2] \xrightarrow{LiPR_2} \tfrac{1}{2}[\{Ti(cp)_2Cl\}_2] + LiCl + \tfrac{1}{2}P_2R_4$$
$$\downarrow LiPR_2$$
$$\tfrac{1}{2}[\{Ti(cp)_2(PR_2)\}_2] + LiCl \qquad (5)$$

$[\{Ti(cp)_2(PR_2)\}_2]$ from $P_2Ph_4$ proved to be difficult, and analytically pure samples were best prepared from $[\{Ti(cp)_2Cl\}_2]$ and $LiPPh_2$ in $C_6H_6$ solution. By way of contrast, treatment of $[M(cp)_2Cl_2]$ (M = Zr or Hf) with 1 mol equiv. of $LiPMe_2$ gave a mixture of $[M(cp)_2Cl_2]$ and $[\{M(cp)_2(PMe_2)\}_2]$ rather than the reduced $[\{M(cp)_2Cl\}_2]$ species. However, addition of 2 mol equiv. of $LiPMe_2$ readily gave $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) as red-brown microcrystalline solids [equation (2)]. Isslieb and Häckert [7] have reported similar ethyl and butyl species. The $P_2Me_4$ side product was isolated as $PMe_2I_3$ by reaction with excess iodine.

The $[\{M(cp)_2(PMe_2)\}_2]$ (M = Ti, Zr, or Hf) series of complexes inflame immediately on contact with air, presumably as a result of oxidation/hydrolysis to give M–O–M bonds with consequent release of highly flammable $PMe_2H$ and $P_2Me_4$. They are soluble in thf, slightly soluble in $C_6H_6$, toluene and $Et_2O$, and insoluble in hexane; they react violently on contact with chlorocarbons. The phenyl derivative $[\{Ti(cp)_2(PPh_2)\}_2]$ was sufficiently soluble in $C_6H_6$ to allow a molecular weight determination (cryoscopic), which indicated dimer formation.

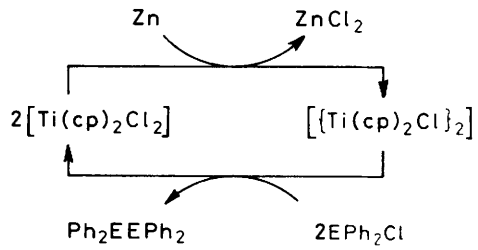
The $^1H$ n.m.r. spectra of the titanium species $[\{Ti(cp)_2(PR_2)\}_2]$ (R = Ph or Me) show only very broad resonances as expected for paramagnetic $Ti^{III}$ compounds. A sharpening of resonances following oxidation with dry $O_2$ is commensurate with $Ti^{III} \longrightarrow Ti^{IV}$ oxidation. Interestingly, in contrast the compounds $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) are diamagnetic in solution; each $^1H$ n.m.r. spectrum shows a sharp singlet (equivalent cp groups), and a triplet due to virtual coupling of $PMe_2$ groups to two P nuclei, consistent with the existence of a dimeric structure, as shown below. The higher alkyl derivatives $[\{Zr(cp)_2(PR_2)\}_2]$ (R = Et or Bu) have also




been confirmed as dimers.[7] Schrock and co-workers [17] have recently determined the crystal structure of the diamagnetic $Zr^{III}$ dimer $[\{ZrCl_3(PBu_3)_2\}_2]$ which has a significant Zr ··· Zr interaction. The diamagnetic behaviour of $[\{M(cp)_2(PMe_2)\}_2]$ can be explained in similar fashion. By comparison, monomeric $Zr^{III}$ species [8,10,17,18] are paramagnetic and give e.s.r. signals characteristic of a $d^1$ metal centre.

Reactions of $[\{M(cp)_2(PR_2)\}_2]$ (M = Ti, Zr, or Hf, R = Me; M = Ti, R = Ph) with a number of halogen sources show a general feature of $M^{III} \longrightarrow M^{IV}$ oxidation in addition to the facile metal–phosphorus bond cleavage. This is especially so for the zirconium and hafnium species. Indeed, refusal of $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) to give the parent $[\{M(cp)_2Cl\}_2]$ on treatment with a halogen source is a common trait (see Scheme 2).

In reaction (*i*) iodine initially displaces the $PPh_2$ groups from $[\{Ti(cp)_2(PPh_2)\}_2]$ to give $[\{Ti(cp)_2I\}_2]$ and $P_2Ph_4$; the latter absorbs a further 3 mol equiv. of $I_2$ to give the phosphonium salt. However, $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) were quantitatively oxidized to the $M^{IV}$ species [reaction (*ii*)] with no observable intermediate. Similarly, addition of $EPh_2Cl$ (E = P or As) to $[\{Ti(cp)_2(PPh_2)\}_2]$ [reaction (*iii*)] gave $[\{Ti(cp)_2Cl\}_2]$, whereas $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) were again oxidised to $[M(cp)_2Cl_2]$. Addition of a further 2 mol equiv. of $EPh_2Cl$ brought about oxidation of green $[\{Ti(cp)_2Cl\}_2]$ to red $[Ti(cp)_2Cl_2]$. This latter reaction provides the basis for the catalytic quantitative conversion of $EPh_2Cl$ to $Ph_2EEPh_2$ (E = P or As) in thf using zinc metal as the reducing agent (see below). As the reaction proceeds, and the concentration of




$ZnCl_2$ increases, the pale green colour of $[\{Ti(cp)_2Cl\}_2]$ darkens as $[\{Ti(cp)_2Cl\}_2ZnCl_2]$ [19] (dark green) becomes the dominant $Ti^{III}$ species in solution. Dark red solutions of $[\{Zr(cp)_2(PMe_2)\}_2]$ in benzene are rapidly decolourised on addition of $BCl_3$ [in (*vi*)] to give $[Zr(cp)_2Cl_2]$ in high yield; the boron containing product was not identified. Addition of $SiMe_3Cl$ [in (*vii*)] gave rapid $Cl/PPh_2$ exchange in the case of $[\{Ti(cp)_2(PPh_2)\}_2]$, whereas $[\{M(cp)_2(PMe_2)\}_2]$ (M = Zr or Hf) did not react at all, even after heating at reflux for several hours. Pre-

liminary results indicate that the corresponding $[\{Ti(cp)_2(PMe_2)\}_2]$ compound also reacts with $SiMe_3Cl$, but the products of this reaction were not fully characterised.

The above reactions demonstrate the effect of both the metal centre and the type of phosphido-group on the pattern of reactivity. There is a clear preference for the zirconium and hafnium compounds to exist in the $M^{IV}$ oxidation state, and it is only with the $PMe_2^-$ anion that $M^{III}$ compounds can be isolated. We are examining further the stability of the M–P bonds under various reaction conditions, especially for compounds containing the metal in a lower oxidation state.

## Experimental

All manipulations of materials were carried out under an atmosphere of purified argon using a Schlenk system. The solvents thf and $C_6H_6$ were dried by distillation from Na–benzophenone and $CaH_2$ respectively, and thoroughly degassed by purging with Ar before use. Samples for i.r. analysis were prepared in a nitrogen flushed dry box, and their spectra recorded on a PE 580B spectrophotometer as Nujol mulls held between CsI plates. Hydrogen-1 n.m.r. spectra were obtained using a PE R34 instrument (220 MHz) from either thf or $C_6D_6$ solutions; shifts are relative to $SiMe_4$ ($\delta = 0$) as standard. Microanalyses were obtained from BMAC Limited, Teddington, and chloride was determined by the Volhard method. For the extremely reactive $PMe_2$-substituted derivatives, although commercially obtained data were often unreliable, the metal content (as obtained by careful ashing and weighing the residue as the dioxide) proved satisfactory. The $PMe_2$ content was calculated by titration against $I_2$ in $C_6H_6$ [Scheme 2, equation (*ii*)].

$[M(cp)_2(PR_2)_2]$ (M = Zr, R = Ph; M = Hf, R = Ph *or* $C_6H_{11}$).—As a typical example $PPh_2H$ (2.95 g, 21.2 mmol) was syringed into a Schlenk tube containing LiBu (13.6 $cm^3$, 1.55 mol $dm^{-3}$) in n-hexane (100 $cm^3$) to give a yellow solution, which after a few minutes gave a pale yellow precipitate of $LiPPh_2$. To this suspension was added $[Zr(cp)_2Cl_2]$ (3.1 g, 10.6 mmol) in $C_6H_6$ (200 $cm^3$), which immediately gave a purple solution. After stirring for 2 h, the solution was left to stand (1 h) when the purple solution was filtered to leave a black solid. The residue was extracted with a further 100 $cm^3$ portion of $C_6H_6$, the filtrates combined and reduced in volume to 30 $cm^3$. Slow addition of n-hexane (150 $cm^3$) caused the product to precipitate from solution as a black microcrystalline solid (5.3 g, 84.1%) [Found: C, 68.8; H, 5.2%; *M* (cryoscopic in $C_6H_6$), 576. $C_{34}H_{30}P_2Zr$ requires C, 69.0; H, 5.1%; *M*, 592]; $^1H$ (thf), δ 5.80 (s, cp), 7.03—7.47 (complex multiplet, Ph); $^1H$ ($C_6D_6$), δ 5.56 (s, cp), 6.92—7.17, 7.32—7.45, 7.61—7.72 (multiplets, Ph).

$[Hf(cp)_2(PPh_2)_2]$ was obtained similarly as red-brown microcrystals (76.1%) [Found: C, 59.5; H, 4.7%; *M* (cryoscopic in $C_6H_6$), 656. $C_{34}H_{30}HfP_2$ requires C, 60.1; H, 4.5%; *M*, 679.1]; $^1H$ (thf), δ 5.78 (s, cp), 7.05—7.51 (complex multiplet, Ph); $^1H$ ($C_6D_6$), δ 5.61 (s, cp), 6.97—7.17, 7.20—7.40, 7.59—7.69 (multiplets, Ph).

$[Hf(cp)_2\{P(C_6H_{11})_2\}_2]$ was obtained as red crystals (6.3%) (Found: C, 58.2; H, 7.7. $C_{54}H_{54}HfP_2$ requires C, 58.1; H, 7.7%); $^1H$ (thf), δ 5.88 (s, cp).

$[Zr(cp)_2Cl(PPh_2)]$.—The complex $[Zr(cp)_2Cl_2]$ (3.0 g, 10.25 mmol) in $C_6H_6$ (120 $cm^3$) was treated with $LiPPh_2$ (20.5 mmol) in n-hexane (15 $cm^3$) to give a purple-brown solution which was stirred for 30 min. $PPh_2Cl$ (1.84 $cm^3$, 10.25 mmol) was added *via* a syringe to give an intense purple solution. The precipitated lithium chloride was removed by filtration, and the solution concentrated to 20 $cm^3$. Addition of dry n-hexane gave a purple oil, which on trituration at 195 K and warming to room temperature gave a precipitate of $P_2Ph_4$. This was filtered off (3.0 g, 8.1 mmol), and the filtrate refrigerated overnight at 253 K, whereupon purple crystals of $[Zr(cp)_2Cl(PPh_2)]$ deposited (0.23 g, 5%) (Found: C, 59.8; H, 4.9; Cl, 7.8. $C_{24}H_{20}ClPZr$ requires C, 59.8; H, 4.6; Cl, 8.0%); $^1H$ (thf), δ 6.14 (s, cp). $[Zr(cp)_2I(PPh_2)]$: $^1H$ (thf), δ 6.05 (s, cp). $[Hf(cp)_2Cl(PPh_2)]$: $^1H$ (thf), δ 6.04 (s, cp).

$[\{Ti(cp)_2(PPh_2)\}_2]$.—The complex $[\{Ti(cp)_2Cl\}_2]$ (1.9 g, 0.9 mmol) was dissolved in thf (100 $cm^3$), and added dropwise to a suspension of $LiPPh_2$ [prepared from $PPh_2H$ (1.65 g, 0.9 mmol) and LiBu] (5.7 $cm^3$, 1.55 mol $dm^{-3}$) in hexane (50 $cm^3$. An immediate reaction occurred to give a green-brown solution. The solvent was removed, and the tarry solid extracted with $C_6H_6$ (3 × 100 $cm^3$ portions). The resulting green-brown solution was concentrated to 30 $cm^3$, and n-hexane (100 $cm^3$) added to precipitate the product $[\{Ti(cp)_2(PPh_2)\}_2]$ as a black-green powder (2.3 g, 76.4%) [Found: C, 72.0; H, 5.3%; *M* (cryoscopic in $C_6H_6$), 694. $C_{64}H_{60}P_2Ti_2$ requires C, 72.7; H, 5.5%; *M*, 726.5].

$[\{M(cp)_2(PMe_2)\}_2]$ (M = Ti, Zr, *or* Hf).—The compound $P_2Me_4$ was made by the reaction scheme shown below.[20]

$$PSCl_3 + 6MgMeI \xrightarrow{Et_2O} Me_2P(S)-P(S)Me_2 \xrightarrow[Heat]{Fe} P_2Me_4$$

Flattened Li wire (0.13 g, 18.4 mmol) was added to a solution of $P_2Me_4$ (2.26 g, 18.4 mmol) in $Et_2O$ (200 $cm^3$). The mixture was heated to reflux temperature for 6 h, after which time a fine white precipitate of $LiPMe_2$ had formed. To this suspension was added $[Zr(cp)_2Cl_2]$ (2.69 g, 9.2 mmol) in $C_6H_6$ (100 $cm^3$) which immediately reacted to give a red solution. The solution was stirred for 30 min, and the solvent removed *in vacuo* to give a red solid. This was pumped for several hours to remove $P_2Me_4$ which was trapped out as $PMe_2I_3$. The residual solid was extracted with $C_6H_6$ (3 × 100 $cm^3$), and the solution concentrated to 50 $cm^3$. Addition of n-hexane (100 $cm^3$) gave $[\{Zr(cp)_2(PMe_2)\}_2]$ as a brown microcrystalline solid (1.74 g, 66.9%) (Found: Zr, 32.0; $PMe_2$, 20.9. $C_{44}H_{52}P_2Zr_2$ requires Zr, 32.3; $PMe_2$, 21.6%); $^1H$ (thf), δ 5.20 (s, cp), 0.55 [d, *J*(PH) = 7.0 Hz, Me].

$[\{Hf(cp)_2(PMe_2)\}_2]$ was obtained as brown microcrystals (60.2%) (Found: Hf, 47.9; $PMe_2$, 15.9. $C_{44}H_{52}Hf_2P_2$ requires Hf, 48.3; $PMe_2$, 16.5%); $^1H$ (thf), δ 5.18 (s, cp), 0.56 [t, *J*(PH) = 7.0 Hz, Me].

$[\{Ti(cp)_2(PMe_2)\}_2]$ was obtained as a pale violet solid (36.3%) (Found: Ti, 19.7. $C_{44}H_{52}Hf_2P_2$ requires Ti, 20.0%).

*Reactions of* $[M(cp)_2(PR_2)_2]$ *and* $[\{M(cp)_2(PR_2)\}_2]$ *with Protic and Halogenated Species.*—All reactions were carried out on a *ca.* 0.5 g scale and the products investigated by i.r. and $^1H$ n.m.r. spectroscopy. As the work-up procedure was, in general, common to each class of reactions, only a typical example is given in each case.

*Reactions involving* $EPh_2Cl$ (E = Ph *or* As). Typically, $PPh_2Cl$ (0.26 g, 1.18 mmol) was injected through a rubber septum into a solution of $[Hf(cp)_2(PPh_2)_2]$ (0.4 g, 0.59 mmol) in $C_6H_6$ (50 $cm^3$). The solution was stirred for 3 min during which time the deep red colour was discharged. Removal of the solid *in vacuo* gave a white solid, which was extracted with n-hexane (3 × 50 $cm^3$), to leave $[Hf(cp)_2Cl_2]$ (0.21 g, 94.1%). The filtrate was concentrated to *ca.* 5 $cm^3$, when colourless crystals of $P_2Ph_4$ deposited on cooling (identified by its i.r. spectrum by comparison with an authentic sample).

*Reactions involving* $SiMe_3Cl$. The $SiMe_3Cl$ (0.1 $cm^3$, 0.82 mmol) was added *via* a syringe to a solution of $[\{Ti(cp)_2(PPh_2)\}_2]$ (0.3 g, 0.82 mmol) in $C_6H_6$ (5 $cm^3$) giving a green

solution. Removal of the solvent gave an oily green residue which was washed with n-hexane (2 × 50 $cm^3$) to give green [{$Ti(cp)_2Cl$}$_2$] (Found: Cl, 16.4. Calc. for $C_{20}H_{20}Cl_2Ti_2$: Cl, 16.6%). Concentration of the hexane washings gave $SiMe_3(PPh_2)$ which was identified by $^1H$ n.m.r. $SiMe_3(PPh_2)$: $^1H$ (thf), δ 0.15 [d, $J$(PH) = 7.0 Hz, Me]. $SiMe_2(PPh_2)_2$: $^1H$ (thf), δ 0.26 [t, $J$(PH) = 3.0 Hz, Me]. $SiMe_2Cl(PPh_2)$: $^1H$ (thf), δ 0.49 [d, $J$(PH) = 4.5 Hz, Me].

*Reactions involving* $I_2$ *and* MeI. In a typical reaction [$Zr(cp)_2(PPh_2)_2$] (0.33 g, 0.51 mmol) in $C_6H_6$ (50 $cm^3$) in a Schlenk tube was titrated against $I_2$ in $C_6H_6$ (3.15 × $10^{-2}$ mol $dm^{-3}$), the operation being carried out under an atmosphere of Ar. After the addition of 16.2 $cm^3$ (5.1 mmol), the solution turned yellow. Removal of the solvent gave a yellow solid which on washing (3 × 50 $cm^3$) with boiling n-hexane left a residue of [$Zr(cp)_2I_2$] in quantitative yield. The colourless hexane washings were concentrated to *ca.* 5 $cm^3$ whereupon colourless crystals of $P_2Ph_4$ precipitated on cooling.

*Reactions involving* PhOH *and* PhSH. Phenol (0.2 g, 2.1 mmol) in $C_6H_6$ (20 $cm^3$) was added *via* a syringe to a stirred solution of [$Zr(cp)_2(PPh_2)_2$] (0.61 g, 0.13 mmol) also in $C_6H_6$ (20 $cm^3$). After 1 h the solvent was removed, and the resulting white solid redissolved in boiling n-hexane (5 $cm^3$). On cooling colourless crystals of [$Zr(cp)_2(OPh)_2$] were deposited (yield 0.38 g, 90%). The remaining solution was evaporated to give $PPh_2H$, which was identified from its i.r. spectrum (liquid film).

*Reactions involving* $H_2O$ *and* $O_2$. A solution of [$Zr(cp)_2(PPh_2)_2$] (0.3 g, 0.51 mmol) in thf (50 $cm^3$) was treated with $H_2O$ (9.1 mg, 0.51 mmol). Almost immediately, the colour was discharged and a white precipitate of [{$Zr(cp)_2O$}$_x$] (0.11 g) formed. The solution was filtered and evaporated to give $PPh_2H$, identified by i.r. (liquid film).

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