Polyhedron Vol. 8, No. 13/14, pp. 1774–1777, 1989
Printed in Great Britain

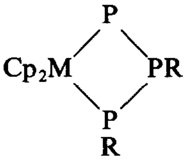
0277–5387/89 \$3.00+.00

TRIPHOSPHANATO ($R_3P_3^{2-}$), PRIMARY PHOSPHIDO (RPH^-) AND DIPHOSPHANATO (DIPHOSPHENE) ($R_2P_2^{2-}$) COMPLEXES OF ZIRCONIUM AND HAFNIUM METALLOCENES

BRIAN L. BENAC and RICHARD A. JONES†

Department of Chemistry, The University of Texas at Austin, Austin,
TX 78712-1167, U.S.A.

Abstract—A variety of triphosphanato ($R_3P_3^{2-}$), primary phosphido (RPH^-) and diphosphanato (diphosphene) ($R_2P_2^{2-}$) derivatives of zirconium and hafnium (I–IV) have been prepared via reactions of primary phosphides LiPH(R) (R = Ph, *t*-Bu) with Cp_2MCl_2 (Cp = η^5-C_5H_5, C_5Me_5, $C_5H_3(SiMe_3)_2$). The products depend on the steric bulk of the P—R group and the Cp (or substituted Cp) group. When Cp = C_5H_5 or C_5Me_5 and R = Ph, triphosphanato complexes of type I are produced (E. Hey, S. G. Bott and J. L. Atwood, *Chem. Ber.* 1988, **121**, 561). When R = *t*-Bu, types II and III are also formed. For Cp = $C_5H_3(SiMe_3)_2$ diphosphanato complexes IV and the diphosphides III are formed.



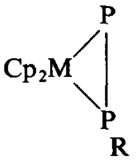
I

$\{Cp_2M(\mu_2\text{-}PHR)\}_2$

II

$Cp_2M(t\text{-}BuPH)_2$

III



IV

There are several classes of diorganophosphide (R_2P^-) and related complexes of the group 4 metals. Homoleptic complexes such as [Li(DME)][Hf$(PCy_2)_5$] (Cy = *c*-C_6H_{11}) were reported by Baker *et al.*[1] In addition, Bercaw and co-workers have described complexes of mono-pentamethylcyclopentadienyl (Cp*) hafnium such as Cp*HfCl{P$(CMe_3)_2\}_2$.[2] The largest class of group 4 metal phosphides is comprised of dicyclopentadienyl derivatives of the type $Cp_2M(PRR')_2$ (Cp = C_5H_5; M = Zr, Hf; R, R′ = alkyl, aryl, $SiMe_3$).[3]

The $Cp_2M(PR_2)_2$ compounds have been used primarily as diphosphine ligands in heterobimetallic complexes such as $Cp_2Hf(\mu\text{-}PEt_2)_2Ni(CO)_2$,[4] $Cp_2Zr(\mu\text{-}PEt_2)_2Rh(\eta\text{-indenyl})$[5] and $Cp_2Zr(\mu\text{-}P(C_6H_5)_2)_2Pt\{P(C_6H_5)_3\}$.[6] The heterobimetallics, $Cp_2M(\mu\text{-}PR_2)_2Mo(CO)_4$ (M = Ti, Zr), had been previously prepared by Johannsen and Stelzer[7] and were studied further by others.[8] The only reported primary phosphides of the group 4 metals are the heterobimetallics, $Cp_2M\{\mu\text{-}PH(C_6H_5)\}_2Mo(CO)_4$, made by Johannsen and Stelzer by treating Cp_2MCl_2 (M = Ti, Zr) with *cis*-$Mo(CO)_4(PhPHLi)_2$.[7] We chose to investigate the chemistry of primary phosphido (RPH^-) ligands, since these should possess an additional site of reactivity in the P—H bond which could lead to unusual new phosphinidene (RP^{2-}) complexes.

It has been known for some time that the reaction of Cp_2MCl_2 (Cp = C_5H_5; M = Zr, Hf) with LiPH(Ph) gives the triphosphanato metallocycles $Cp_2M[P(Ph)]_3$ (**Ia**: M = Zr; **Ib**: M = Hf).[9] Even treatment of $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(CH_3)Cl$ with $PhPH_2$ gives only $Cp_2Zr[P(Ph)]_3$ (**Ia**) and no primary phosphido zirconium complexes.[9] These types of compounds I were previously made by the reaction of Cp_2MCl_2 with $K_2(PR)_n$ (M = Ti, Zr, Hf).[10]

In our hands, the reaction of Cp_2MCl_2 with $LiPH(C_6H_5)$ also gives the triphosphanato complexes, **Ia** (Cp = C_5H_5; M = Zr; R = C_6H_5) and **Ib** (Cp = C_5H_5; M = Hf; R = C_6H_5). However,

---

† Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR data for new compounds[a]

Compound	Colour	Signal	^{1}H (δ)	J_{PH} (Hz)
{$Cp_2Zr(\mu_2$-*t*-BuPH)}$_2$ (**II**)	Red	$C_5\mathit{H}_5$	4.99 s	—
		t-BuP*H*	3.00 d	259.22
		*t-Bu*PH	1.45 d	11.71
Cp_2Hf(*t*-BuPH)$_2$ (**IIIa**)	Red	$C_5\mathit{H}_5$	5.60 t	1.71
		t-BuP*H*	4.10 d	242.28
		*t-Bu*PH	1.43 d	11.76
$Cp^*_2Zr[P(C_6H_5)]_3$ (**Ie**)	Red	$(C_6\mathit{H}_5)P$	6.8–8.25 m	—
		$C_5(C\mathit{H}_3)_5$	1.83 s	—
		$C_5(C\mathit{H}_3)_5$	1.49 s	—
$Cp^*_2Hf[P(C_6H_5)]_3$ (**If**)	Red	$(C_6\mathit{H}_5)P$	6.8–8.25 m	—
		$C_5(C\mathit{H}_3)_5$	1.94 s	—
		$C_5(C\mathit{H}_3)_5$	1.60 s	—
Cp^*_2Zr(*t*-BuPH)$_2$ (**IIIb**)	Purple	*t*-BuP*H*	3.83 d	239.61
		$C_5(C\mathit{H}_3)_5$	1.95 s	—
		*t-Bu*PH	1.53 d	11.20
Cp^*_2Hf(*t*-BuPH)$_2$ (**IIIc**)	Red	*t*-BuP*H*	3.63 d	245.91
		$C_5(C\mathit{H}_3)_5$	2.02 s	—
		*t-Bu*PH	1.56 d	11.10
$Cp''_2Zr[P(Ph)]_2$ (**IVa**)	Orange	$C_5\mathit{H}_3(SiMe_3)_2$	6.2–6.7 br	—
		$C_6\mathit{H}_5$	6.9–7.5 br	—
		$C_5H_3(Si\mathit{Me}_3)_2$	0.1–0.3 br	—
$Cp''_2Hf[P(Ph)]_2$ (**IVb**)	Green	$C_5\mathit{H}_3(SiMe_3)_2$	6.2–6.7 br	—
		$C_6\mathit{H}_5$	6.9–7.5 br	—
		$C_5H_3(Si\mathit{Me}_3)_2$	0.1–0.3 br	—
Cp''_2Zr[P(*t*-Bu)]$_2$ (**IVc**)	Red–orange	$C_5\mathit{H}_3(SiMe_3)_2$	6.2–6.7	—
		*t-Bu*P	1.62 t	5.5
		$C_5H_3(Si\mathit{Me}_3)_2$	0.1–0.3	—
Cp''_2Zr(*t*-BuPH)$_2$ (**IIId**)	Red	$C_5\mathit{H}_3(SiMe_3)_2$	6.70 br s	—
		$C_5\mathit{H}_3(SiMe_3)_2$	6.26 br s	—
		t-BuP*H*	4.38 d	239.90
		*t-Bu*PH	1.51 d	11.46
		$C_5H_3(Si\mathit{Me}_3)_2$	0.38 s	—
Cp''_2Hf(*t*-BuPH)$_2$ (**IIIe**)	Red	$C_5\mathit{H}_3(SiMe_3)_2$	6.68 br s	—
		$C_5\mathit{H}_3(SiMe_3)_2$	6.23 br s	—
		t-BuP*H*	4.33 d	247.63
		*t-Bu*PH	1.53 d	11.29
		$C_5H_3(Si\mathit{Me}_3)_2$	0.39 s	—

[a] C_6D_6, 25°C, 300.15 MHz.

— Signifies no coupling observed.

the reaction of Cp_2ZrCl_2 with 2 equivalents of the bulkier primary phosphide, LiPH(*t*-Bu), in toluene–ether (70 : 30) at −78°C, results in formation not only of the previously characterized[10b] triphosphanato complex **Ic** (Cp = C_5H_5; M = Zr; R = *t*-Bu) in 15% yield, but also the reduced complex **II** (Cp = C_5H_5; M = Zr; R = *t*-Bu). Compound **II** may be isolated as red crystals in 50% yield after recrystallization from hexane and is very air-sensitive† in the solid-state and in solution. Compound **II** is diamagnetic like other Zr^{III} complexes[12] and NMR data are obtainable. (^{1}H and ^{31}P NMR data for **II** and all other new compounds reported are given in Tables 1 and 2 respectively.) The corresponding reaction of Cp_2HfCl_2[12] with 2

---

† Since most of all the new complexes were very air-sensitive, all manipulations were performed using either standard Schlenk line or dry-box techniques.

Table 2. ^{31}P{^{1}H} data for new compounds[a]

Compound	^{31}P{^{1}H} δ
{Cp$_2$Zr(μ_2-*t*-BuPH)}$_2$ (**II**)	121.85
Cp$_2$Hf(*t*-BuPH)$_2$ (**IIIa**)	101.97
Cp$^*_2$Zr(*t*-BuPH)$_2$ (**IIIb**)	126.41
Cp$^*_2$Hf(*t*-BuPH)$_2$ (**IIIc**)	101.58
Cp$''_2$Zr[P(Ph)]$_2$ (**IVa**)	228.91
Cp$''_2$Hf[P(Ph)]$_2$ (**IVb**)	193.22
Cp$''_2$Zr[P(*t*-Bu)]$_2$ (**IVc**)	270.56
Cp$''_2$Zr(*t*-BuPH)$_2$ (**IIId**)	130.65
Cp$''_2$Hf(*t*-BuPH)$_2$ (**IIIe**)	109.06

[a] C_6D_6 solutions, 30°C, 121.51 MHz. Referenced to external 85% H_3PO_4 ($\delta = 0.0$) with high field increasingly negative.

equivalents of LiPH(*t*-Bu) in toluene–THF (60 : 40) also yields the previously characterized[10b] triphosphanato complex **Id** (Cp = C_5H_5; M = Hf; R = *t*-Bu) in 15% yield and the new diphosphido complex **IIIa** (Cp = C_5H_5; M = Hf). Complex **IIIa** can be isolated in 60% yield as red, hexane-soluble, air-sensitive crystals from toluene at −30°C.

Utilizing the bis-pentamethylcyclopentadienyl metal dichlorides, Cp$^*_2$ZrCl$_2$[13] and Cp$^*_2$HfCl$_2$,[14] it was hoped that the steric effect of the pentamethylcyclopentadienyl groups would help to stabilize other primary phosphido compounds of zirconium and hafnium. However, reaction of the Cp$^*_2$ZrCl$_2$ with LiPH(Ph) in toluene–THF (60 : 40) at −78°C, yields upon crystallization from toluene at −30°C, the triphosphanato complex Cp$^*_2$Zr{P(C_6H_5)}$_3$ (**Ie**) in 27% yield. Similarly, for the reaction of Cp$^*_2$HfCl$_2$ with LiPH(Ph) in THF at room temperature, Cp$^*_2$Hf{P(C_6H_5)}$_3$ (**If**) is isolated in 19% yield from the reaction mixture after recrystallization from toluene at −30°C.

Both compounds **Ie** and **If** are red in solution and the ^{1}H NMR spectra for both complexes exhibit two distinctly different Cp* resonances. This is due to the orientation of the triphosphanato unit with respect to the Cp* groups. This type of inequivalence of the Cp groups has been extensively studied by Köpf and Voigtländer for the analogous Cp (Cp = C_5H_5) compound.[10b] Table 3 compares the ^{31}P data for the compounds **Ia**, **Ie**, **Ib** and **If**. The ^{31}P resonances for the phosphorus nuclei directly attached to the metal (P_A) for compounds **Ie** and **If** are at higher field than in the normal cyclopentadienyl analogues, compounds **Ia** and **Ib**. This shift to higher field is indicative of less phosphorus lone pair donation to the empty $1a_1$ orbital[15] at the metal centres. Also noticeable is that the resonances for the apical phosphorus nuclei (P_B) shift downfield by ~55 ppm. The other interesting fact from Table 3 is the reduced coupling constant between the phosphorus nuclei (P_A and P_B) in compounds **Ie** and **If** when compared to compounds **Ia** and **Ib**. Nonetheless, despite the steric effect of the pentamethylcyclopentadienyl groups, the driving force of the reaction is the formation of the triphosphanato metallocycle.†

Reaction of CP$^*_2$ZrCl$_2$ with 2 equivalents of LiPH(*t*-Bu) in toluene–ether (70 : 30) at room temperature for 4 h, affords purple Cp$^*_2$Zr(*t*-BuPH)$_2$ (**IIIb**). Complex **IIIb** can be isolated in 71% yield as purple blocks by crystallization from hexane at −30°C. Similarly, reaction of Cp$^*_2$HfCl$_2$ with 2 equivalents of LiPH(*t*-Bu) in THF for 2 days affords, after the appropriate work-up, red, crystalline Cp$^*_2$Hf(*t*-BuPH)$_2$ (**IIIc**) in 63% yield. Both compounds **IIIb** and **IIIc** are highly air-sensitive in solution and the solid state. In addition, both of these compounds reductively eliminate the diphosphine, (*t*-Bu)PHPH(*t*-Bu), when treated with CO (3 atm) at room temperature in toluene solution, to form the dicarbonyls, Cp$^*_2$M(CO)$_2$.[17] This reaction demonstrates the weakness of the metal–phosphorus bonds in these complexes and the ease with which the metal centres are reduced.

The reaction of Cp$''_2$MCl$_2$[18] (Cp$''$ = $C_5H_3(SiMe_3)_2$) with 2 equivalents of LiPH(Ph) in toluene–THF (60 : 40) for 2 h, produces the orange crystalline Cp$''_2$Zr[P(Ph)]$_2$ (**IVa**) and green crystalline Cp$''_2$Hf[P(Ph)]$_2$ (**IVb**) diphosphanato (diphosphene) complexes in good yield (60–70%), after recrystallization from toluene at −30°C. The ^{1}H NMR signals at 25°C for **IVa** and **IVb** are very broad and make the assignment and integration of the resonances difficult. The ^{31}P{^{1}H} NMR signals for **IVa** and **IVb** are also very broad (**IVa**, $\Delta w_{1/2} = 37$ Hz; **IVb**, $\Delta w_{1/2} = 40$ Hz) at 25°C and indicate that there is some fluctionality of the diphosphanato metallocycle. In contrast to the triphosphanato metallocycles (**I**), complexes **IVa** and **IVb** are easily hydrolysed to Cp$''_2$M(OH)$_2$ and the *meso* and D,L isomers of diphenyldiphosphine.[19]

Reaction of Cp$''_2$ZrCl$_2$ with 2 equivalents of LiPH(*t*-Bu) in toluene at room temperature for 2 days yields, after work-up and crystallization from hexane at −30°C, the red microcrystalline diphos-

---

† The mechanisms for the formation of the triphosphanato metallacycle are not clear. Professor G. L. Hillhouse and co-workers have synthesized Cp$^*_2$HfH(PHPh) from the reaction of Cp$^*_2$HfH$_2$ with PhPH$_2$ and Cp$^*_2$Hf(I)(PHPh) from the reaction of Cp$^*_2$HfI$_2$ with LiPH(Ph).[16]

Table 3. ^{31}P data for $(C_5R_5)_2M[P(C_6H_5)]_3$ complexes[a]

Complex	R	M	P_A	P_B	J_{AB} (Hz)
Ia	H	Zr	92.94	−189.78	349.45[b]
Ie	CH_3	Zr	60.87	−134.89	244.95[c]
Ib	H	Hf	67.32	−193.92	330.45[b]
If	CH_3	Hf	36.37	−128.75	215.80[c]

[a] All complexes display an A_2X pattern.
[b] Data from ref. 10b.
[c] Data from this work.

phido compound $Cp_2''Zr(t\text{-}BuPH)_2$ (**IIId**) in 11% yield and the red–orange diphosphanato complex $Cp_2''Zr[P(t\text{-}Bu)]_2$ (**IVc**) in 48% yield. The $^{31}P\{^1H\}$ NMR resonance for **IVc** at δ 270.56 is much sharper ($\Delta w_{1/2} = 3$ Hz) than in the phenyl analogue **IVa**. The ^{1}H NMR for **IVc** is also sharper than for **IVa** and **IVb**, and hydrolysis of complex **IVc** yields mainly the D,L isomer of the diphosphine, (t-Bu)PHPH(tBu), in addition to $Cp_2''Zr(OH)_2$. In contrast, reaction of $Cp_2''HfCl_2$ with 2 equivalents of LiPH(t-Bu) does not give a diphosphanato complex, but instead only the red diphosphido complex, $Cp_2''Hf(t\text{-}BuPH)_2$ (**IIIe**), which is isolated in 55% yield after crystallization from hexane.

From these studies it is evident that the distribution of products depends upon three factors: (1) the metal used and the reducibility of that metal; (2) the steric and electronic nature of the cyclopentadienyl group utilized in stabilizing the complexes and (3) the bulk of the aryl or alkyl group on the phosphorus. In conclusion, primary phosphido complexes of the group 4 metallocenes can be stabilized given the correct conditions and these new complexes should provide a wealth of new and interesting chemistry. Further studies of these and related compounds are in progress.

Acknowledgements—We thank the Robert A. Welch Foundation and the National Science Foundation for support. R.A.J. also thanks the Alfred P. Sloan Foundation for a fellowship (1985–89). We would also like to thank Professor G. L. Hillhouse for helpful discussions and preprints of related work on primary phosphido complexes of bis(pentamethylcyclopentadienyl)zirconium and hafnium.

REFERENCES

1. R. T. Baker, P. J. Krusic, T. H. Tulip, J. C. Calabrese and S. S. Wreford, *J. Am. Chem. Soc.* 1983, **105**, 6763.
2. D. M. Roddick, B. D. Santarsiero and J. E. Bercaw, *J. Am. Chem. Soc.* 1985, **107**, 4670.
3. (a) J. Ellerman and P. Poersch, *Angew. Chem. Int. Ed. Engl.* 1967, **6**, 355; (b) S. R. Wade, M. G. H. Wallbridge and G. R. Willey, *J. Chem. Soc., Dalton Trans.* 1983, 2555; (c) R. T. Baker, J. F. Whitney and S. S. Wreford, *Organometallics* 1983, **2**, 1049; (d) L. Weber, G. Meine, R. Boese and N. Augart, *Organometallics* 1987, **6**, 2484; (e) H. Köpf and V. Richtering, *J. Organomet. Chem.* 1988, **346**, 355.
4. R. T. Baker, T. H. Tulip and S. S. Wreford, *Inorg. Chem.* 1985, **24**, 1379.
5. R. T. Baker and T. H. Tulip, *Organometallics* 1986, **5**, 839.
6. L. Gelmini and D. W. Stephan, *Inorg. Chim. Acta* 1986, **111**, L17.
7. G. Johannsen and O. Stelzer, *Chem. Ber.* 1977, **110**, 3428.
8. T. S. Targos, R. P. Rosen, R. R. Whittle and G. L. Geoffroy, *Inorg. Chem.* 1985, **24**, 1375.
9. E. Hey, S. G. Bott and J. L. Atwood, *Chem. Ber.* 1988, **121**, 561.
10. (a) K. Issleib, G. Wille and F. Krech, *Angew. Chem.* 1972, **84**, 582; (b) H. Köpf and R. Voigtländer, *Chem. Ber.* 1981, **114**, 2731.
11. For example $\{Cp_2Zr(\mu\text{-}PMe_2)\}_2$ in ref. 3b. For other examples see: (a) J. H. Wengrovius, R. R. Schrock and S. C. Day, *Inorg. Chem.* 1981, **20**, 1844; (b) M. Y. Chiang, S. Gambarotta and F. van Bolhuis, *Organometallics* 1988, **7**, 1864.
12. P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding and R. C. Srivastava, *J. Chem. Soc. A* 1969, 2106.
13. J. M. Manriquez and J. E. Bercaw, *J. Am. Chem. Soc.* 1974, **96**, 6229.
14. D. M. Roddick, M. D. Fryzuk, P. F. Seidler, G. L. Hillhouse and J. E. Bercaw, *Organometallics* 1985, **4**, 1694.
15. J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.* 1976, **98**, 1729.
16. G. L. Hillhouse, personal communication.
17. D. J. Sikora, M. D. Rausch, R. D. Rogers and J. L. Atwood, *J. Am. Chem. Soc.* 1981, **103**, 1265.
18. A. Antiñolo, M. F. Lappert, A. Singh, D. J. W. Winterborn, L. M. Engelhardt, C. L. Raston, A. H. White, A. J. Carty and N. J. Taylor, *J. Chem. Soc., Dalton Trans.* 1987, 1463.
19. M. Baudler, B. Carlsohn, D. Koch and P. K. Medda, *Chem. Ber.* 1978, **111**, 1210.