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SYNTHESES AND MOLECULAR STRUCTURES OF MOLYBDENUM COMPLEXES WITH PHOSPHIDO, DIPHOSPHANYL AND DIPHOSPHENE LIGANDS

EVAMARIE HEY-HAWKINS*

Institut für Anorganische Chemie der Universität, Talstr. 35, D-04103 Leipzig,
Germany

and

KATHARINA FROMM

Institut für Anorganische Chemie der Universität, Engesserstr. 7, D-76131 Karlsruhe,
Germany

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Abstract—The reaction of $\mathrm{Cp^\circ MoCl_2(PMe_3)_2}$ ($\mathrm{Cp^\circ = C_5EtMe_4}$) with $\mathrm{LiPH(2,4,6\text{-}Bu^t{}_3C_6H_2)}$ (1 : 2) yielded the terminal molybdenum(II) phosphido complex $\mathrm{Cp^\circ Mo\{PH(2,4,6\text{-}Bu^t{}_3C_6H_2)\}(PMe_3)_2}$ (**1**). Complex **1** crystallized with one molecule of $\mathrm{Li(2,4,6\text{-}Bu^t{}_3C_6H_2)}$ (**2**), in which there is a rare example of a one-coordinate Li, in the asymmetric unit. In contrast, the reaction of $\mathrm{Cp^\circ MoCl_2(PMe_3)_2}$ with $\mathrm{LiPH(2,4,6\text{-}Me_3C_6H_2)}$ (1 : 2) gave the diphosphanyl complex $\mathrm{Cp^\circ Mo\{P(2,4,6\text{-}Me_3C_6H_2)PH(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**3**). When $\mathrm{Cp'MoCl_2(PMe_3)_2}$ (**4**) ($\mathrm{Cp' = C_5H_4Me}$) was reacted with $\mathrm{LiPH(2,4,6\text{-}Me_3C_6H_2)}$ (1 : 1) the diphosphene complex $\mathrm{Cp'\overline{Mo\{P(2,4,6\text{-}Me_3C_6H_2)P}(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**5**) was obtained. Crystal structure determinations were carried out on **1**–**3** and **5**. The Mo—P(aryl) distances are 2.250 (3) (**1**), 2.253(2) (**3**), and 2.512(2) and 2.624(2) Å (**5**).

The reaction of zirconocene dichlorides $\mathrm{Cp^R{}_2ZrCl_2}$ with PH-functionalized lithium phosphides yields a wide variety of products, whose formation depends on the nature of the organic substituents R′ of LiPHR′ and R of $\mathrm{Cp^R}$.[1] Thus, the following are obtained: complexes with a terminal Zr—PHR′ group,[2] metallacyclic systems with a $\overline{\mathrm{Zr—P—P—P}}$ (triphosphane-1,3-diyl complexes)[2d,3] or $\overline{\mathrm{Zr—P—P}}$ (diphosphene complexes)[2d,4] arrangement, and dimeric phosphido-bridged $\mathrm{Zr^{III}}$ complexes.[5]

We now report our attempts to extend our work on zirconocene chemistry to cyclopentadienyl molybdenum complexes, and the results obtained indicate that the diverse chemistry of zirconocene complexes and PH-functionalized phosphido ligands is paralleled in the reactions of differently substituted cyclopentadienyl molybdenum complexes $\mathrm{Cp^RMoCl_2(PMe_3)_2}$ ($\mathrm{Cp^R = Cp^\circ, Cp'}$) with PH-functionalized phosphido ligands, yielding a terminal phosphido complex as well as a diphosphanyl and a diphosphene complex.

RESULTS AND DISCUSSION

Synthesis and properties of $\mathrm{Cp^\circ Mo\{PH(2,4,6\text{-}Bu^t{}_3C_6H_2)\}(PMe_3)_2}$ (1) · $\mathrm{Li(2,4,6\text{-}Bu^t{}_3C_6H_2)}$ (2)

The reaction of $\mathrm{Cp^\circ MoCl_2(PMe_3)_2}$[6] with $\mathrm{LiPH(2,4,6\text{-}Bu^t{}_3C_6H_2)}$ (1 : 2) gave a small yield of the terminal molybdenum(II) phosphido complex $\mathrm{Cp^\circ Mo\{PH(2,4,6\text{-}Bu^t{}_3C_6H_2)\}(PMe_3)_2}$ (**1**) which crystallized with one equivalent of $\mathrm{Li(2,4,6\text{-}Bu^t{}_3C_6H_2)}$ (**2**); the deep green crystals were highly soluble in all common organic solvents. The pres-

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*Author to whom correspondence should be addressed.

ence of $Li(2,4,6\text{-}Bu^t_3C_6H_2)$ (**2**) can be explained by the fact that this lithium aryl is also formed in the synthesis of $LiPH(2,4,6\text{-}Bu^t_3C_6H_2)$, and we were earlier able to isolate and structurally characterize the adduct $[LiPH(2,4,6\text{-}Bu^t_3C_6H_2)\cdot Li(2,4,6\text{-}Bu^t_3C_6H_2)]_2$.[7] Apparently, the lithium aryl is needed for crystallization, as we were unable to obtain pure **1** in crystalline form.

Molecular structure of $Cp^{\circ}Mo\{PH(2,4,6\text{-}Bu^t_3C_6H_2)\}(PMe_3)_2$ (**1**)·$Li(2,4,6\text{-}Bu^t_3C_6H_2)$ (**2**)

A crystal structure determination was carried out on green rhombic single crystals of **1**·**2**. The product crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. There are two molecules present in the asymmetric unit: one molecule of $Cp^{\circ}Mo\{PH(2,4,6\text{-}Bu^t_3C_6H_2)\}(PMe_3)_2$ (**1**) (Fig. 1) and one of $Li(2,4,6\text{-}Bu^t_3C_6H_2)$ (**2**) (Fig. 2 and Table 1). There are no bonding interactions between the two.

In **1**, the coordination of the molybdenum atom can be regarded as a three-legged piano stool, the "seat" being the cyclopentadienyl ring (Cp°), and the P atom of the phosphido ligand and two P atoms of the PMe_3 ligands as "legs". The Mo(1)—C(Cp°) distances are between 2.292(8) and 2.406(8) Å. The alkyl substituents of the Cp° ligand are displaced out of the plane of the cyclopentadienyl C atoms by 0.2 to 0.3 Å.

The Mo—PMe_3 bond distances of 2.409(3) and 2.419(3) Å are in the range observed for comparable trimethylphosphine complexes [e.g. **3**, **5**, $CpMoCl_2(PMe_3)_2$ Mo—P 2.459(2) Å[8]]. Compared to the Mo—phosphine bond distances, the Mo(1)—P(1) bond length of 2.250(3) Å is extremely short. For steric reasons, the Mo(1)—P(1)—C(101) bond angle is rather large [133.0(3)°], resulting in small Mo(1)—P(1)—H(999) [128(3)°] and C(101)—P(1)—H(999) [98(3)°] bond angles. The presence of the P—*H* proton of the terminal phosphido group was shown crystallographically. The proton was located by difference Fourier maps and refined isotropically. The P—H bond distance of **1** [1.36(7) Å] is in the range observed for other terminal PH-functionalized phosphido ligands.[2] The geometry of the phosphido group P atom, P(1), is almost trigonal planar, the sum of bond angles being *ca* 360°. Thus, the phosphido ligand can be regarded as a three-electron donor, so that the molybdenum achieves a valence electron number of 18. Comparable structural data have been obtained for related phosphido complexes [e.g. $CpMo(CO)_2PR_2$][9] in which the phosphido ligand acts as a three-electron donor, and the phosphinidene complex $Cp_2Mo\{P(2,4,6\text{-}Bu^t_3C_6H_2)\}$ [Mo—P 2.370(2)

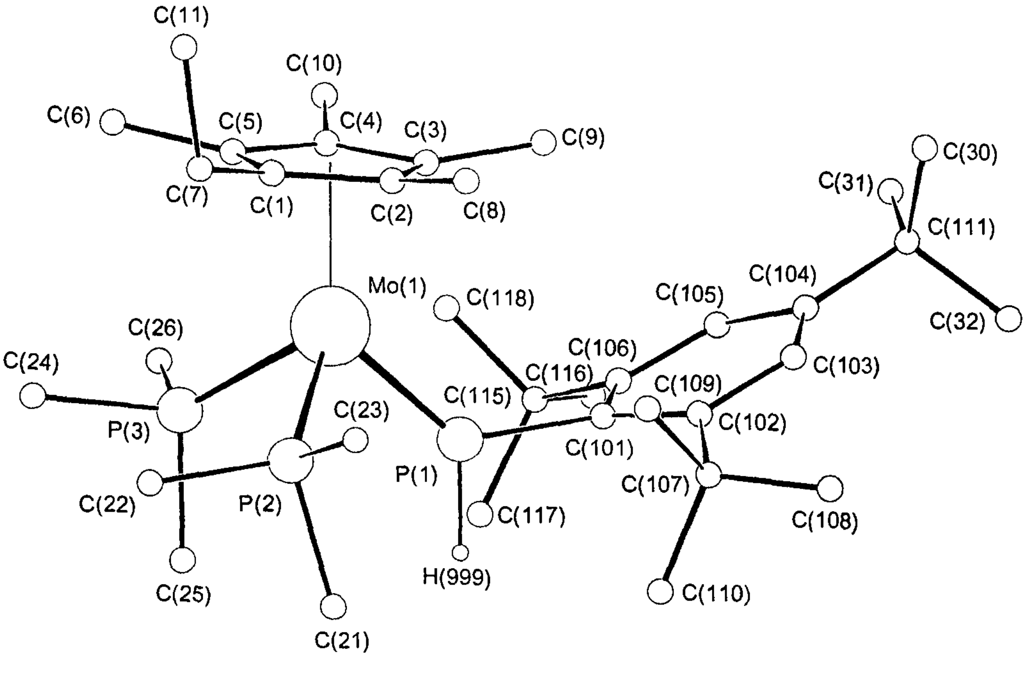


Fig. 1. Molecular structure of $Cp^{\circ}Mo\{PH(2,4,6\text{-}Bu^t_3C_6H_2)\}(PMe_3)_2$ (**1**) (Schakal plot). Hydrogen atoms are omitted (except P—H) for clarity. Only one orientation of the disordered *p*-Bu^t group of the aryl ligand is shown.

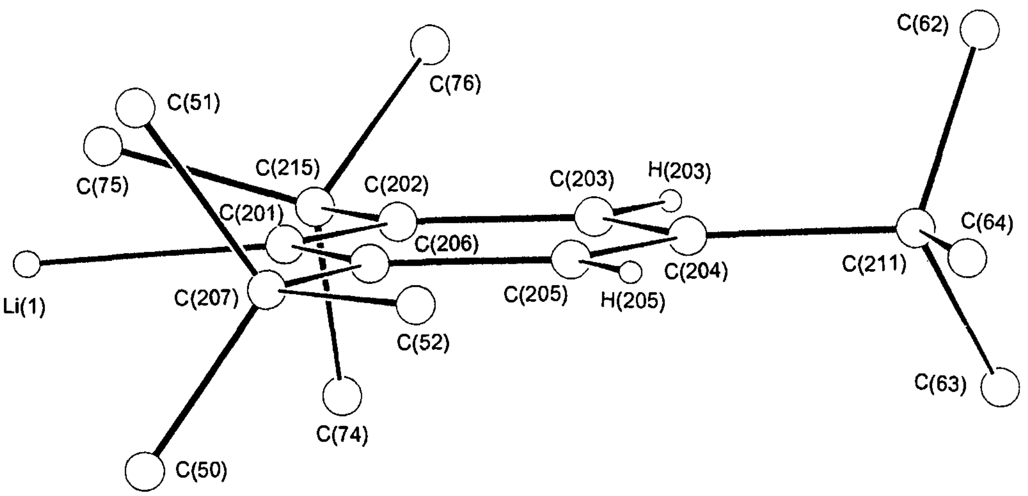


Fig. 2. Molecular structure of Li(2,4,6-Bu$^t_3$C$_6$H$_2$) (**2**) (Schakal plot). Only one orientation of the disordered Bu^t groups of the aryl ligand is shown.

Å, Mo—P—C 115.8(2)°,[10] which contains a Mo—P double bond.

The steric demand of the bulky phosphido ligand PH(2,4,6-Bu$^t_3$C$_6$H$_2$) results in a small P(2)—Mo(1)—P(3) bond angle of 86.42(10)° and large P(1)—Mo(1)—P(phosphine) bond angles [90.95(9) and 92.84(12)°].

The P(1)—C(101) bond length [1.871(9) Å] is in the range expected for phosphorus–aryl carbon bonds. The Bu^t group in the *para* position of the aryl ligand is strongly disordered. Each methyl group can adopt one of four possible orientations (occupational factor 1/4); only one orientation is shown in Fig. 1.

The second molecule in the asymmetric unit is Li(2,4,6-Bu$^t_3$C$_6$H$_2$) (**2**) (Fig. 2). In **2**, the lithium atom Li(1) shows the unusual coordination number of 1[11] and exhibits a short Li(1)—C(201) bond [1.80(2) Å] {*cf.* 2.09(1) Å in the adduct [LiPH(2,4,6-Bu$^t_3$C$_6$H$_2$) · Li(2,4,6-Bu$^t_3$C$_6$H$_2$)]$_2$[7]}. All Bu^t groups of the aryl ligand are disordered and could be refined in four different orientations (occupational factor 1/4). Only one arrangement of the Bu^t groups is shown in Fig. 2.

Synthesis and properties of Cp$^\circ$Mo{P(2,4,6-Me$_3$C$_6$H$_2$)PH(2,4,6-Me$_3$C$_6$H$_2$)}(PMe$_3$)$_2$ (**3**)

The reaction of Cp$^\circ$MoCl$_2$(PMe$_3$)$_2$[6] with LiPH(2,4,6-Me$_3$C$_6$H$_2$) (1 : 2) at room temperature in pentane gave the diphosphanyl complex Cp$^\circ$Mo{P(2,4,6-Me$_3$C$_6$H$_2$)PH(2,4,6-Me$_3$C$_6$H$_2$)}(PMe$_3$)$_2$ (**3**) as green, rhombic crystals in low yield, as well as brown twinned crystals, which could not be characterized. Complex **3** is highly soluble in common organic solvents.

Molecular structure of Cp$^\circ$Mo{P(2,4,6-Me$_3$C$_6$H$_2$)PH(2,4,6-Me$_3$C$_6$H$_2$)}(PMe$_3$)$_2$ (**3**)

Single crystals of **3** were obtained from pentane solution at −25°C. The complex crystallizes triclinic in the space group $P\bar{1}$. The overall structure of **3** is comparable to that of the Cp$^\circ$Mo(PMe$_3$)$_2$P fragment of **1**, showing the piano stool arrangement with the Cp$^\circ$ ligand forming the "seat", and the three P atoms the "legs" (Fig. 3, Table 2). The Mo—C(Cp$^\circ$) distances range from 2.328(3) to 2.390(3) Å. The Mo—P bond distances in **3** are similar to those observed in **1** [Mo—PMe$_3$ 2.4079(14), 2.418(2); Mo—P(3) 2.253(2) Å]. As in **1**, the steric demand of the diphosphanyl ligand results in large P(3)—Mo—P(phosphine) angles [93.22(5) and 95.45(5)°] and a small P(1)—Mo—P(2) angle of 87.98(5)°. The geometry of the diphosphanyl P atom P(3) is trigonal planar, the sum of the bond angles being *ca* 360° [Mo(1)—P(3)—C(101) 126.09(8)°, Mo(1)—P(3)—P(4) 136.53(5)°, P(4)—P(3)—C(101) 95.84(9)°]. Thus, the diphosphanyl ligand can be regarded as a three-electron donor, giving a total of 18 valence electrons for the molybdenum atom.

A view along the Mo—C$_5$ centre axis (C$_5$ centre = centre of the cyclopentadienyl ring; Fig. 4) shows that the diphosphanyl ligand is located in such a way that the Mo—P(3) bond intersects the C(3)—C(4) bond of the Cp$^\circ$ ring, thus minimizing steric interaction between the diphosphanyl ligand and the Cp$^\circ$ ring. However, due to interaction of one aryl ring [C(101)—C(106)] of the diphosphanyl ligand with the alkyl groups C(8) and C(9) of the Cp$^\circ$ ring the methyl groups are displaced from the mean plane of the cyclopentadienyl carbon atoms by *ca* 0.2 Å.

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**·**2**

	1		**2**
Mo(1)—P(1)	2.250(3)	Li(1)—C(201)	1.80(2)
Mo(1)—P(2)	2.409(3)	C(201)—C(202)	1.398(14)
Mo(1)—P(3)	2.419(3)	C(202)—C(203)	1.371(13)
P(1)—C(101)	1.871(9)	C(203)—C(204)	1.381(13)
P(1)—H(999)	1.36(7)	C(204)—C(205)	1.400(14)
P(2)—C(21)	1.847(10)	C(205)—C(206)	1.400(14)
P(2)—C(22)	1.806(10)	C(206)—C(201)	1.404(13)
P(2)—C(23)	1.829(10)	C(202)—C(215)	1.574(12)
P(3)—C(24)	1.844(10)	C(204)—C(211)	1.585(12)
P(3)—C(25)	1.839(10)	C(206)—C(207)	1.565(11)
P(3)—C(26)	1.846(10)		
C(1)—C(7)	1.507(12)	Li(1)—C(201)—C(202)	119.8(9)
C(7)—C(11)	1.537(13)	Li(1)—C(201)—C(206)	118.9(9)
C(102)—C(107)	1.544(12)	C(202)—C(201)—C(206)	121.2(9)
C(104)—C(111)	1.534(10)	C(203)—C(202)—C(201)	118.1(9)
C(106)—C(115)	1.533(12)	C(202)—C(203)—C(204)	123.7(9)
Mo(1)—C(Cp°)	2.292(8)-2.406(8)	C(203)—C(204)—C(205)	117.3(9)
C(Cp°)—C(Cp°)	1.404(12)-1.452(12)	C(204)—C(205)—C(206)	121.7(9)
C(Cp°)—C(Me, Cp°)	1.494(11)-1.518(12)	C(205)—C(206)—C(201)	118.1(9)
C(aryl)—C(aryl)	1.378(12)-1.441(11)	C(203)—C(202)—C(215)	117.4(9)
C(Bu^t)—C(Bu^t)	1.524(13)-1.547(13)	C(201)—C(202)—C(215)	124.5(9)
		C(203)—C(204)—C(211)	121.6(9)
		C(205)—C(204)—C(211)	121.0(9)
		C(205)—C(206)—C(207)	114.0(9)
		C(201)—C(206)—C(207)	127.9(9)
P(1)—Mo(1)—P(2)	90.95(9)		
P(1)—Mo(1)—P(3)	92.84(12)		
P(2)—Mo(1)—P(3)	86.42(10)		
C(101)—P(1)—Mo(1)	133.0(3)		
C(101)—P(1)—H(999)	98(3)		
Mo(1)—P(1)—H(999)	128(3)		
C(21)—P(2)—Mo(1)	120.4(3)		
C(22)—P(2)—Mo(1)	121.6(4)		
C(23)—P(2)—Mo(1)	117.3(3)		
C(22)—P(2)—C(23)	97.0(6)		
C(22)—P(2)—C(21)	98.5(6)		
C(21)—P(2)—C(23)	96.8(5)		
C(24)—P(3)—Mo(1)	120.5(4)		
C(25)—P(3)—Mo(1)	119.8(4)		
C(26)—P(3)—Mo(1)	116.7(4)		
C(25)—P(3)—C(24)	99.5(6)		
C(25)—P(3)—C(26)	98.5(5)		
C(24)—P(3)—C(26)	97.1(6)		
C(106)—C(101)—P(1)	120.8(6)		
C(102)—C(101)—P(1)	121.1(6)		
C(5)—C(1)—C(7)	124.6(8)		
C(2)—C(1)—C(7)	126.6(8)		
C(1)—C(7)—C(11)	111.3(8)		
C(101)—C(102)—C(107)	124.9(8)		
C(103)—C(102)—C(107)	117.0(8)		
C(103)—C(104)—C(111)	123.6(8)		
C(105)—C(104)—C(111)	120.8(8)		
C(105)—C(106)—C(115)	116.5(7)		
C(101)—C(106)—C(115)	124.9(7)		
C(Cp°)—C(Cp°)—C(Cp°)	107.1(7)-108.7(7)		
C(Cp°)—C(Cp°)—C(Me)	123.8(7)-126.7(8)		
C(aryl)—C(aryl)—C(aryl)	115.6(8)-125.3(8)		
C(Bu^t)—C(Bu^t)—C(Bu^t)	106.4(8)-112.5(8)		

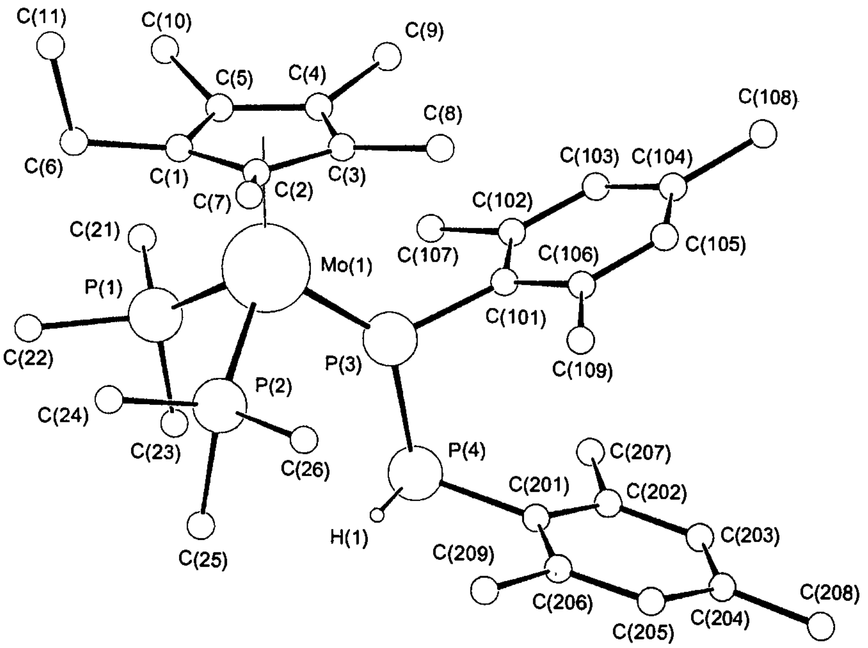


Fig. 3. Molecular structure of $Cp^{\circ}Mo\{P(2,4,6\text{-}Me_3C_6H_2)PH(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (**3**) (Schakal plot). Hydrogen atoms (except P—H) are omitted for clarity.

The P(3)—P(4) bond [2.2646(14) Å] of the diphosphanyl ligand is elongated compared with known distances for P—P single bonds (*ca* 2.21 Å)[12] due to the fact that the two bulky $2,4,6\text{-}Me_3C_6H_2$ ligands are arranged so as to minimize their steric interaction [Fig. 4, torsion angle C(101)—P(3)—P(4)—C(201) 46.3(1)°]. The angle of the mean planes of the two aryl ligands is 33.2°. The proton H(1), coordinated to the P atom P(4), was located crystallographically by difference Fourier maps and refined isotropically [P(4)—H(1) 1.08(3) Å]. While the geometry of P(3) is almost planar, P(4) has a pyramidal environment, the sum of bond angles being *ca* 295° [P(3)—P(4)—C(201) 107.17(10)°, P(3)—P(4)—H(1) 91.1(14)°, H(1)—P(4)—C(201) 97.2(14)°].

A diphosphanyl complex of zirconium, $Cp^*_2Zr(H)(PPhPHPh)$ ($Cp^* = C_5Me_5$) was assumed to be the intermediate in the formation of the diphosphene complex $Cp^*_2Zr(PPhPPh)$ from Cp^*_2ZrPPh and PH_2Ph.[2d]

Synthesis and properties of $Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (5)

When $Cp'MoCl_2(PMe_3)_2$ (**4**) was reacted with $LiPH(2,4,6\text{-}Me_3C_6H_2)$ (1 : 1) the diphosphene complex $Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (**5**) was obtained as orange needles. In the mass spectrum the molecular ion peak and fragments due to loss of PMe_3 were observed.

Molecular structure of $Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (5)

An X-ray structure determination was carried out on orange single crystals of **5**, obtained from a toluene solution layered with *n*-heptane. The observed extinctions suggested the orthorhombic space groups *Pbcm* (No. 57) or $Pca2_1$ (No. 29). The structure was solved and refined in the acentric space group $Pca2_1$.

In **5**, the Mo atom is coordinated in a distorted square-pyramidal fashion, with the Cp′ ligand occupying the apical position and the four P atoms of the two PMe_3 ligands and the diphosphene ligand occupying the basal positions (Fig. 5, Table 3). The Mo—PMe_3 bond distances [2.425(2), 2.456(3) Å] are in the same range as those observed for **1**, **3** and related complexes.[8]

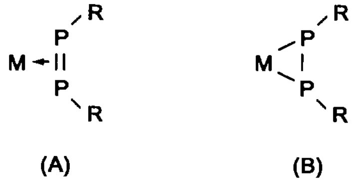
The free ligand $(2,4,6\text{-}Me_3C_6H_2)P{=}P(2,4,6\text{-}Me_3C_6H_2)$ is unstable. As in the comparable complexes $Cp^R_2Zr\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}$ ($Cp^R = Cp^{\circ}$, Cp^*)[2d,4] and $Cp_2Mo(PHPH)$,[13] the diphosphene ligand is kinetically stabilized by interaction of the π electrons with a transition metal centre.[14] The coordinated diphosphene shows the *trans* orientation of the two aryl ligands. Similarly,

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**

Mo(1)—P(1)	2.418(2)
Mo(1)—P(2)	2.4079(14)
Mo(1)—P(3)	2.253(2)
Mo(1)—C(Cp°)	2.328(3)–2.390(3)
P(1)—C(21)	1.848(4)
P(1)—C(22)	1.825(4)
P(1)—C(23)	1.820(3)
P(2)—C(24)	1.847(3)
P(2)—C(25)	1.844(3)
P(2)—C(26)	1.846(3)
P(3)—C(101)	1.851(3)
P(3)—P(4)	2.2646(14)
P(4)—C(201)	1.851(3)
P(4)—H(1)	1.08(3)
C(1)—C(6)	1.514(4)
C(6)—C(11)	1.528(4)
C(102)—C(107)	1.508(4)
C(104)—C(108)	1.519(4)
C(106)—C(109)	1.514(4)
C(202)—C(207)	1.515(4)
C(204)—C(208)	1.525(5)
C(206)—C(209)	1.512(4)
C(Cp°)—C(Cp°)	1.414(4)–1.439(4)
C(Cp°)—C(Me, Cp°)	1.505(4)–1.510(4)
C(aryl)—C(aryl)	1.380(5)–1.412(4)
P(1)—Mo(1)—P(2)	87.98(5)
P(1)—Mo(1)—P(3)	93.22(5)
P(2)—Mo(1)—P(3)	95.45(5)
C(21)—P(1)—Mo(1)	117.86(13)
C(22)—P(1)—Mo(1)	119.57(13)
C(23)—P(1)—Mo(1)	121.41(12)
C(23)—P(1)—C(22)	99.8(2)
C(23)—P(1)—C(21)	94.5(2)
C(22)—P(1)—C(21)	98.5(2)
C(24)—P(2)—Mo(1)	118.71(12)
C(25)—P(2)—Mo(1)	125.29(11)
C(26)—P(2)—Mo(1)	113.60(11)
C(24)—P(2)—C(25)	97.1(2)
C(24)—P(2)—C(26)	99.4(2)
C(25)—P(2)—C(26)	97.9(2)
C(101)—P(3)—Mo(1)	126.09(8)
C(101)—P(3)—P(4)	95.84(9)
Mo(1)—P(3)—P(4)	136.53(5)
C(201)—P(4)—P(3)	107.17(10)
C(201)—P(4)—H(1)	97.2(14)
P(3)—P(4)—H(1)	91.1(14)
C(106)—C(101)—P(3)	120.7(2)
C(102)—C(101)—P(3)	119.9(2)
C(206)—C(201)—P(4)	123.8(2)
C(202)—C(201)—P(4)	117.2(2)
C(5)—C(1)—C(6)	125.4(3)
C(2)—C(1)—C(6)	125.5(3)
C(1)—C(6)—C(11)	111.8(2)
C(Cp°)—C(Cp°)—C(Cp°)	107.2(2)–108.5(2)
C(Cp°)—C(Cp°)—C(Me)	124.2(3)–126.0(3)
C(aryl)—C(aryl)—C(aryl)	117.6(3)–122.7(3)
C(aryl)—C(aryl)—C(Me)	118.1(3)–122.7(3)

the *trans*-configuration is observed for most stable diphosphenes in the solid state.[15]

According to the isolobal concept, the diphosphene ligand and its coordination to a metal atom is comparable to alkenes and alkene complexes.[16] As for the organic ligand, two structures can be discussed for diphosphene complexes: (**A**) diphosphene ligand as σ donor, and (**B**) diphosphene ligand as σ donor and π acceptor ligand:[17]



(A) **(B)**

The M—P and P—P bond lengths as well as the P—P—R bond angles in diphosphene complexes should allow a differentiation between structure (**A**) and (**B**), as the synergistic effect of the donor–acceptor bond in (**B**) should result in a longer P—P bond. According to this formulation, the P_2R_2 ligand in **5** can be regarded as (i) a neutral ligand coordinated to a Mo^{I} centre or (ii) a $P_2R_2^{2-}$ ligand, coordinated to a Mo^{III} centre.

As the Mo—P bond lengths of the MoP_2 metallacycle are longer [2.512(2) and 2.624(2) Å] than the P—P bond length [2.158(3) Å], the corresponding P(1)—Mo—P(2) bond angle [49.63(6)°] is small, while the P—P—Mo bond angles [67.87(7) and 62.49(8)°] are much larger. Comparable structural parameters are observed for $Cp_2Mo(PHPH)$ [Mo—P 2.536(5), 2.550(4), P—P 2.146(3) Å, P—Mo—P 49.91(7), Mo—P—P 64.7(2), 65.4(2)°].[13]

The P—P bond length of 2.158(3) Å is closer to the values observed for P—P single bonds [e.g. 2.217(6) Å in $(PPh)_5$],[12] while P=P double bonds [2.00–2.03 Å][15a] are much shorter. Thus, structure (**B**) seems to be more appropriate for describing the coordination of the diphosphene ligand to the Mo centre.

CONCLUSION

The reaction of substituted cyclopentadienyl molybdenum complexes $Cp^RMoCl_2(PMe_3)_2$ (Cp^R = Cp°, Cp′) with PH-functionalized lithium phosphides LiPHR′ (R′ = 2,4,6-$Bu^t_3C_6H_2$ or 2,4,6-$Me_3C_6H_2$) yields a terminal phosphido complex, a diphosphanyl complex and a diphosphene complex. Apparently, as with zirconocene complexes, the product of these reactions depends on the bulk and electronic properties of the ligands Cp^R on molybdenum and R′ of the lithium phosphide. We are

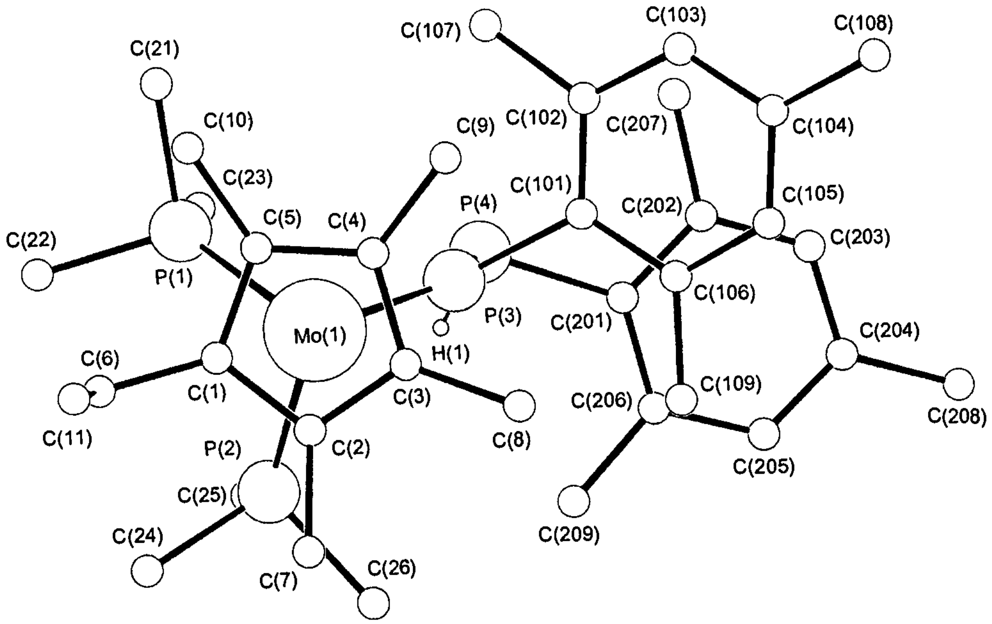


Fig. 4. View along the Mo—C_5 centre axis (C_5 centre = centre of the cyclopentadienyl ring) of $Cp^{\circ}Mo\{P(2,4,6\text{-}Me_3C_6H_2)PH(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (**3**) (Schakal plot). Hydrogen atoms (except P—H) are omitted for clarity.

presently attempting to extend our investigations to other ligands R′ and Cp^R.

EXPERIMENTAL

All manipulations were carried out under purified and dried nitrogen. All solvents were rigorously purified and distilled under nitrogen prior to use. The IR spectra were recorded with CsI windows in the range 200–4000 cm^{-1}. MS: Varian MAT 711 (EI, 70eV, 180°C). The melting points were determined on samples sealed in capillaries under nitrogen and are uncorrected. $Cp^{\circ}MoCl_2(PMe_3)_2$,[6] $LiPH(2,4,6\text{-}Bu^t_3C_6H_2)$,[7] and $LiPH(2,4,6\text{-}Me_3C_6H_2)$[18] were prepared according to literature procedures.

Synthesis of $Cp^{\circ}Mo\{PH(2,4,6\text{-}Bu^t_3C_6H_2)\}(PMe_3)_2$ (**1**) · $Li(2,4,6\text{-}Bu^t_3C_6H_2)$ (**2**)

Pentane (15 cm^3) was added to a mixture of 0.58 g $Cp^{\circ}MoCl_2(PMe_3)_2$ (1.24 mmol) and 0.70 g $LiPH(2,4,6\text{-}Bu^t_3C_6H_2)$ (2.47 mmol) at −30°C and the resulting solution stirred at this temperature for 6 h, then at room temperature for 12 h. A green solution and a green solid were obtained. The solvent was then removed and 15 cm^3 *n*-heptane added to the residue followed by filtration. On concentrating the filtrate slowly, a few green crystals of **1**·**2** were obtained, which were characterized by X-ray crystallography. The product is highly soluble in polar and non-polar organic solvents.

Synthesis of $Cp^{\circ}Mo\{P(2,4,6\text{-}Me_3C_6H_2)PH(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2$ (**3**)

Pentane (35 cm^3) was added to a mixture of 1.74 g $Cp^{\circ}MoCl_2(PMe_3)_2$ (3.72 mmol) and 1.18 g $LiPH(2,4,6\text{-}Me_3C_6H_2)$ (7.44 mmol) at room temperature and the resulting solution stirred for 12 h. Then, the green–brown solution was filtered, followed by concentration and cooling the solution to −25°C which yielded small crystals (yield: 0.25 g). Under the microscope, two types of crystals can be seen: twinned brown crystals (*ca* 95%) and green rhombic crystals (*ca* 5%). The latter were shown to be complex **3** by X-ray crystallography.

Synthesis of $Cp'MoCl_2(PMe_3)_2$ (**4**)

In a 100 cm^3 flask 3.82 g of $[Cp'Mo(\mu\text{-}Cl)_2]_2$[19] (7.76 mmol) was dissolved in 20 cm^3 THF and 2.36 g PMe_3 (31.06 mmol) added with stirring. After several hours a deep red solution was obtained. Concentrating yielded red crystals of **4**. Yield: 4.18 g (75%). M. p. 173°C; IR (CsI, cm^{-1}) 3095w, 2983m, 2911m, 1755vw, 1739vw, 1728vw, 1712vw, 1699vw, 1630m, 1492vw, 1420s, 1295s, 1261m, 1121s, 1020m, 950vs, 862m, 820sh, 726m, 671m, 610w, 470vw, 423m, 403w, 358m. Mass spectrum

Table 3. Selected bond lengths (Å) and bond angles ( ) for **5**

Mo(1)—P(1)	2.512(2)
Mo(1)—P(2)	2.624(2)
Mo(1)—P(3)	2.456(3)
Mo(1)—P(4)	2.425(2)
Mo(1)—C(Cp′)	2.289(8)–2.426(8)
P(1)—C(101)	1.867(7)
P(1)—P(2)	2.158(3)
P(2)—C(201)	1.858(9)
P(3)—C(11)	1.840(9)
P(3)—C(12)	1.822(9)
P(3)—C(13)	1.838(9)
P(4)—C(14)	1.867(13)
P(4)—C(15)	1.822(10)
P(4)—C(16)	1.865(12)
C(1)—C(6)	1.477(13)
C(102)—C(107)	1.517(12)
C(104)—C(108)	1.506(13)
C(106)—C(109)	1.537(12)
C(202)—C(207)	1.47(2)
C(204)—C(208)	1.53(2)
C(206)—C(209)	1.495(13)
C(Cp′)—C(Cp′)	1.39(2)–1.42(2)
C(aryl)—C(aryl)	1.355(12)–1.450(12)
P(1)—Mo(1)—P(2)	49.63(6)
P(1)—Mo(1)—P(3)	90.47(8)
P(1)—Mo(1)—P(4)	131.09(8)
P(2)—Mo(1)—P(3)	126.58(8)
P(2)—Mo(1)—P(4)	89.99(7)
P(3)—Mo(1)—P(4)	96.25(9)
C(101)—P(1)—P(2)	113.7(2)
C(101)—P(1)—Mo(1)	120.0(2)
P(2)—P(1)—Mo(1)	67.87(7)
C(201)—P(2)—P(1)	103.2(3)
C(201)—P(2)—Mo(1)	113.2(3)
P(1)—P(2)—Mo(1)	62.49(8)
C(11)—P(3)—Mo(1)	119.7(4)
C(12)—P(3)—Mo(1)	116.6(4)
C(13)—P(3)—Mo(1)	116.1(3)
C(11)—P(3)—C(12)	101.1(6)
C(11)—P(3)—C(13)	100.1(5)
C(12)—P(3)—C(13)	99.9(5)
C(14)—P(4)—Mo(1)	118.6(4)
C(15)—P(4)—Mo(1)	119.9(4)
C(16)—P(4)—Mo(1)	118.0(3)
C(14)—P(4)—C(15)	96.7(6)
C(14)—P(4)—C(16)	99.0(7)
C(15)—P(4)—C(16)	100.3(6)
C(106)—C(101)—P(1)	128.3(5)
C(102)—C(101)—P(1)	115.1(6)
C(202)—C(201)—P(2)	119.8(7)
C(206)—C(201)—P(2)	122.6(6)
C(5)—C(1)—C(6)	125.3(10)
C(2)—C(1)—C(6)	128.2(9)
C(Cp′)—C(Cp′)—C(Cp′)	106.3(8)–110.0(10)
C(aryl)—C(aryl)—C(aryl)	115.8(10)–123.3(13)
C(aryl)—C(aryl)—C(Me)	116.0(7)–124.4(7)

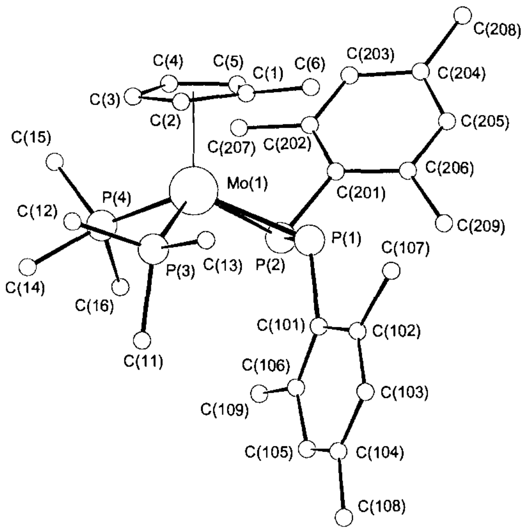


Fig. 5. Molecular structure of $\mathrm{Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**5**) (Schakal plot). Hydrogen atoms are omitted for clarity.

(EI = 70 eV; 140°C, *m*/*z*, Int.) 398 (M^+, 9.8%), 322 (M^+-Cp′, 29.2%), 287 (M^+-Cp′-Cl, 17.8%), 246 (M^+-Cp′-PMe_3, 18.3%), 210 (M^+-Cp′-Cl-PMe_3, 12.8%). The observed isotope pattern of the molecular ion peak at *m*/*z* 398 is in good agreement with the calculated isotope distribution.

Synthesis of $\mathrm{Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**5**)

Toluene (20 cm^3) was added to a mixture of 1.42 g $Cp'MoCl_2(PMe_3)_2$ (**4**) (3.57 mmol) and 0.58 g $LiPH(2,4,6\text{-}Me_3C_6H_2)$ (3.57 mmol) at room temperature. After 10 min a deep brown solution had formed. The solvent was removed until crystallization started, then layered with 10 cm^3 heptane. After 2 days at room temperature **5** crystallized as clusters of orange needles. Yield: 0.8 g (35%). M. p. 82°C (decomp.); IR (KBr, cm^{-1}) 2952m, 2921m, 2851m, 1859w, 1751vw, 1740vw, 1728vw, 1711vw, 1699vw, 1641m, 1603m, 1555w, 1449s, 1372m, 1277m, 1261m, 1151m, 1093m, 1026m, 948vs, 898w, 879vw, 848s, 810m, 771w, 715m, 671m, 626w, 608vw, 572w, 551w, 522w, 484w, 423w, 411w, 358m, 328w, 305w. Mass spectrum (EI = 70 eV; *m*/*z*, Int.) 624 (M^+, 2.1%), 551 (M^+-PMe_3, 0.9%), 475 (M^+-2 PMe_3, 1.3%). The observed isotope pattern of the molecular ion peak at *m*/*z* 624 is in agreement with the calculated isotope distribution.

An additional signal at *m*/*z* 828 (3.5%) is tentatively assigned to the dimeric complex

Table 4. Crystal data and structure refinement for $\mathrm{Cp^{\circ}Mo\{PH(2,4,6\text{-}Bu^t_3C_6H_2)\}(PMe_3)_2 \cdot Li(2,4,6\text{-}Bu^t_3C_6H_2)}$ (**1·2**), $\mathrm{Cp^{\circ}Mo\{P(2,4,6\text{-}Me_3C_6H_2)PH(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**3**) and $\mathrm{Cp'Mo\{P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}(PMe_3)_2}$ (**5**)

	1·2	**3**	**5**
Formula	$C_{53}H_{94}LiMoP_3$	$C_{35}H_{58}MoP_4$	$C_{30}H_{47}MoP_4$
Molecular weight	927.14	698.63	627.50
Temperature (K)	200	200	200
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$Pca2_1$ (no. 29)
Cell constants:			
a (Å)	10.610(8)	10.465(5)	27.706(2)
b (Å)	16.442(11)	13.480(8)	9.142(3)
c (Å)	17.73(3)	13.928(8)	15.749(13)
α (°)	105.34(5)	106.33(4)	90
β (°)	100.75(2)	92.51(4)	90
γ (°)	103.21(4)	91.43(4)	90
V (Å^3)	2802(5)	1882(2)	3989(4)
Z	2	2	4
d_{calc} (g cm^{-3})	1.098	1.233	1.045
Scan technique	ω/Θ-scan	ω/Θ-scan	ω/Θ-scan
2Θ range (°)	3–46	3–52	4–56
h (min., max.)	0/11	−4/12	−1/36
k (min., max.)	−18/17	−16/16	−4/7
l (min., max.)	−19/19	−17/17	−1/20
Total reflections	8251	7963	4229
Independent reflections	7749 [R(int.) 0.0555]	7390 [R(int.) 0.0182]	4014 [R(int.) 0.0225]
F(000)	1004	740	1316
Parameters	459	382	329
Absorption coefficient (μ cm^{-1})	3.50	5.14	4.78
Largest diff. peak/hole (e Å^{-3})	1.2/−0.7	0.4/−0.4	1.3/−0.5
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0663$, $wR2 = 0.1825$	$R1 = 0.0305$, $wR2 = 0.0687$	$R1 = 0.0589$, $wR2 = 0.1725$
R indices (all data)	$R1 = 0.1378$, $wR2 = 0.2217$	$R1 = 0.0520$, $wR2 = 0.0763$	$R1 = 0.0699$, $wR2 = 0.2055$
Goodness-of-fit (F^2)	1.041	1.012	1.072

$Cp'(PMe_3)_2Mo\{\mu\text{-}P(2,4,6\text{-}Me_3C_6H_2)P(2,4,6\text{-}Me_3C_6H_2)\}Mo(PMe_3)_2Cp'$, which is either an impurity or formed under mass spectroscopic conditions.

Data collection and structural refinement

Data (Mo-K_α = 0.71069 Å) were collected with a STOE Stadi IV diffractometer. 25 reflections (2Θ range: 2–25°) were used for determination of the unit cell parameters. Absorption correction: psi-scans. The structure was solved by direct methods (SHELXS-86)[20] and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXL-93).[21] Restrictions for **1**·**2**: Mo, P and C atoms anisotropic. The *para*-Bu^t group of the 2,4,6-$Bu^t_3C_6H_2$ ligand of **1** [C(30), C(31), C(32) with C(111)—C 1.53–1.54 Å, C—C(111)—C 108.9–110.4°] and all Bu^t groups of the 2,4,6-$Bu^t_3C_6H_2$ ligand of **2** [with C(207)—C 1.53–1.59 Å, C—C(207)—C 109.2–111.2°, C(211)—C 1.46–1.58 Å, C—C(211)—C 107.7–114.0°, C(215)—C 1.49–1.58 Å, C—C(215)—C 107.1–112.1°] are disordered and were refined isotropically in four split positions, which were suggested by the program SHELXL-93.[21] H atoms were isotropic in calculated positions, H(999) was located by difference maps and refined isotropically. Restrictions for **3**: Mo, P and C atoms anisotropic, H atoms isotropic in calculated positions, H(1) was located by difference maps and refined isotropically. Restrictions for **5**: Mo, P and C atoms anisotropic, H atoms isotropic in calculated positions. A summary of data collection parameters is given in Table 4. Anisotropic atomic parameters, full lists of bond lengths and angles and lists of F_o/F_c values have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

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REFERENCES

1. E. Hey-Hawkins, *Chem. Rev.* 1994, **94**, 1661.
2. (a) E. Hey and U. Müller, *Z. Naturforsch.* 1989, **44B**, 1538; (b) S. Kurz and E. Hey-Hawkins, *J. Organomet. Chem.* 1994, **479**, 125; (c) S. Kurz, E. Hey-Hawkins and G. Baum, *Z. Naturforsch.* 1995, **50B**, 239; (d) Z. Hou, T. L. Breen and D. W. Stephan, *Organometallics* 1993, **12**, 3158; (e) J. Ho, R. Rousseau and D. W. Stephan, *Organometallics* 1994, **13**, 1918.
3. (a) E. Hey, S. G. Bott and J. L. Atwood, *Chem. Ber.* 1988, **121**, 561; (b) E. Hey, *Z. Naturforsch.* 1988, **43B**, 1271; (c) K. Fromm, G. Baum and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* 1992, **615**, 35; (d) J. Ho, T. L. Breen, A. Ozarowski and D. W. Stephan, *Inorg. Chem.* 1994, **33**, 865.
4. E. Hey-Hawkins and S. Kurz, *J. Organomet. Chem.* 1993, **462**, 203.
5. (a) E. Hey-Hawkins, S. Kurz, J. Sieler and G. Baum, *J. Organomet. Chem.* 1995, **486**, 229; (b) J. Ho, Z. Hou, R. J. Drake and D. W. Stephan, *Organometallics* 1993, **12**, 3145.
6. K. Fromm and E. Hey-Hawkins, *Polyhedron* 1995, **15–16**, 2027.
7. S. Kurz and E. Hey-Hawkins, *Organometallics* 1992, **11**, 2729.
8. S. Krueger, R. Poli, A. Rheingold and D. L. Staley, *Inorg. Chem.* 1989, **28**, 4599.
9. (a) Review: A. H. Cowley and R. A. Kemp, *Chem. Rev.* 1985, **85**, 367 (and literature cited therein); (b) A. H. Cowley, D. M. Giolando, C. M. Nunn, M. Pakulski, D. Westmoreland and N. C. Norman, *J. Chem. Soc., Dalton Trans.* 1988, 2127; (c) A. M. Arif, A. H. Cowley and S. Quashie, *J. Chem. Soc., Chem. Commun.* 1986, 1437; (d) M. Leise, L. Zsolnai and H. Lang, *Polyhedron* 1993, **12**, 1257.
10. P. B. Hitchcock, M. F. Lappert and W. P. Leung, *J. Chem. Soc., Chem. Commun.* 1987, 1282.
11. W. N. Setzer and P. v. Ragué-Schleyer, *Adv. Organomet. Chem.* 1985, **24**, 353 (and literature cited therein).
12. J. J. Daly, *J. Chem. Soc.* 1964, 6147.
13. E. Cannillo, A. Coda, K. Prout and J.-C. Daran, *Acta Cryst.* 1977, **33B**, 2608.
14. Review: L. Weber, *Chem. Rev.* 1992, **92**, 1839.
15. Reviews: (a) A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.* 1986, **34**, 1; (b) A.-M. Caminade, J.-P. Majoral and R. Mathieu, *Chem. Rev.* 1991, **91**, 575 (and literature cited therein).
16. R. Hoffmann, *Angew. Chem.* 1982, **94**, 725.
17. D. M. P. Mingos, in G. Wilkinson, F. G. A. Stone and E. W. Abel (Eds), *Comprehensive Organometallic Chemistry*, Vol. 3, p. 47 ff. Pergamon Press, New York (1982).
18. S. Kurz, Dissertation, Leipzig (1995).
19. K. Fromm and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* 1993, **619**, 261.
20. G. Sheldrick, SHELXS-86, *Program for Crystal Structure Solution.* Göttingen (1986).
21. G. Sheldrick, SHELXL-93, *Program for Crystal Structure Determination.* Göttingen (1993).