Synthesis and Reactivity of Mononuclear Molybdenum Phosphido Complexes, $[\text{Mo(CO)}_2\{\text{P(Cl)R}\}(\eta\text{-C}_5\text{H}_5)]$ [R = $\text{CH(SiMe}_3)_2$ or $\overline{\text{NCMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CMe}_2}$]. *X*-Ray Crystal Structures of $[\text{Mo(CO)}_2\{\text{P(X)}(\overline{\text{NCMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CMe}_2})\}(\eta\text{-C}_5\text{H}_5)]$ (X = Cl or NMe_2) and $[\text{Mo}_2(\text{CO})_4\{\mu\text{-P}_2[\text{CH(SiMe}_3)_2]_2\}(\eta\text{-C}_5\text{H}_5)_2]$†

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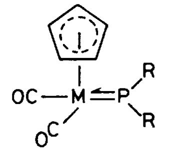
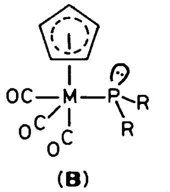
Reaction of $\text{K[Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]$ with PCl_2R affords the mono-chlorophosphido species, $[\text{Mo(CO)}_2\{\text{P(Cl)R}\}(\eta\text{-C}_5\text{H}_5)]$ [R = 2,2,6,6-tetramethyl-1-piperidyl (tmp), (**1**), or $\text{CH(SiMe}_3)_2$, (**3**)]. Both (**1**) and (**3**) contain a three-electron donor phosphido ligand featuring Mo–P multiple bonding and a trigonal-planar configuration at phosphorus. Compound (**1**) has been characterised by *X*-ray diffraction. The reaction of (**1**) with $\text{Li[NMe}_2]$ affords $[\text{Mo(CO)}_2\{\text{P(NMe}_2)(\text{tmp})\}(\eta\text{-C}_5\text{H}_5)]$ (**7**), which has also been characterised by *X*-ray crystallography. The synthesis of (**7**) demonstrates the reactivity of the P–Cl functionality but (**7**) may also be prepared by direct reaction between $\text{K[Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]$ and $\text{PCl(NMe}_2)(\text{tmp})$. Reduction of (**3**) with sodium dihydronaphthylide leads to a coupling reaction *via* P–P bond formation resulting in the *cis*-diphosphene complex $[\text{Mo}_2(\text{CO})_4\{\mu\text{-P}_2[\text{CH(SiMe}_3)_2]_2\}(\eta\text{-C}_5\text{H}_5)_2]$ (**8**), which was characterised by *X*-ray diffraction. Spectroscopic evidence is also presented for a dimolybdenum diphosphinidene complex, isomeric with (**8**).

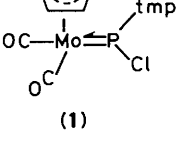
Mononuclear transition metal complexes containing the phosphido ligand (PR_2) are now increasingly common (see ref. 1 for a recent review). Of particular interest to the present work are those involving the organometallic fragments $\text{M(CO)}_n(\eta\text{-C}_5\text{H}_5)$ (n = 2 or 3) where M = Mo or W. In the case where the metal fragment contains only two carbonyls, the phosphido ligand formally donates three electrons to the metal centre and the phosphorus adopts a trigonal-planar geometry, type (**A**). The alternative form, type (**B**), contains three carbonyls and a formal one-electron donor phosphido group with a trigonal-pyramidal phosphorus. Examples of type (**A**) have been extensively studied by Paine and co-workers[2] and more recently by Malisch[3] and Cowley[4] and co-workers while compounds of type (**B**) have been investigated primarily by Malisch *et al.*[5] Reactivity studies have been confined mostly to compounds of type (**B**) and centre around the phosphorus lone pair,[6] such chemistry being similar to that observed for the related iron compounds, $[\text{Fe(CO)}_2(\text{PR}_2)(\eta\text{-C}_5\text{H}_5)]$.[7] The chemistry of the corresponding type (**A**) complexes has been explored to a much lesser degree[2f,3,8] and is associated more with the metal–phosphorus multiple bond functionality. Herein we report additional modes of reactivity for type (**A**) complexes containing a reactive chlorine group, $[\text{Mo(CO)}_2\{\text{P(Cl)R}\}(\eta\text{-C}_5\text{H}_5)]$.


(**A**)

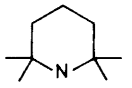

(**B**)

Results and Discussion

Treatment of a tetrahydrofuran (thf) solution of $\text{PCl}_2(\text{tmp})$ (tmp = 2,2,6,6-tetramethyl-1-piperidyl) with one equivalent of $\text{K[Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]$ leads to a clean reaction which affords, after work-up, purple crystals of (**1**). Spectroscopic data (Tables 1 and 2) were consistent with the proposed structure and this was confirmed by a single-crystal *X*-ray diffraction study, the results of which are shown in Figure 1. Selected bond distances and angles are given in Table 3 and atomic co-ordinates are presented in Table 4. The molecule consists of a single molybdenum atom bonded to a cyclopentadienyl group, two terminal carbonyls and a terminal phosphido ligand, P(Cl)(tmp). The molybdenum–phosphorus bond length [Mo(1)–P(1) 2.214(2) Å] is short and indicative of substantial multiple-bond character. It is almost identical to that found in the related compound $[\text{Mo(CO)}_2(\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}})(\eta\text{-C}_5\text{H}_5)]$ (**2**) [Mo–P 2.213(1) Å][2c] and is considerably


(**1**)

tmp =



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† [Chloro- and dimethylamino-(2,2,6,6-tetramethyl-1-piperidyl)-phosphido]dicarbonyl(η-cyclopentadienyl)molybdenum(II) and μ-{1,2-bis[bis(trimethylsilyl)methyl]diphosphenediyl-$P^1(\text{Mo}^{1,2})P^2(\text{Mo}^{1,2})$}-bis[dicarbonyl(η-cyclopentadienyl)molybdenum(II)] respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 Pa.

Table 1. Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	ν(CO)/cm^{-1} [b]	Analysis (%) C	Analysis (%) H
(**1**) $[\mathrm{Mo(CO)_2\{P(Cl)(tmp)\}(\eta\text{-}C_5H_5)}]$	Purple	73	1 932s, 1 850m	45.5 (45.1)	5.6 (5.5)[c]
(**3**) $[\mathrm{Mo(CO)_2\{P(Cl)CH(SiMe_3)_2\}(\eta\text{-}C_5H_5)}]$	Red-brown	69	1 979s, 1 895m	37.2 (37.9)	5.5 (5.9)
(**7**) $[\mathrm{Mo(CO)_2\{P(NMe_2)(tmp)\}(\eta\text{-}C_5H_5)}]$	Orange	81	1 906s, 1 825s	50.0 (50.0)	6.8 (6.8)[d]
(**8**) $[\mathrm{Mo_2(CO)_4\{\mu\text{-}P_2[CH(SiMe_3)_2]_2\}(\eta\text{-}C_5H_5)_2}]$	Brown	39	1 938m, 1 934s, 1 837m, 1 826m	40.6 (41.3)	5.9 (5.9)

[a] Calculated values are given in parentheses. [b] Measured as Nujol mulls. [c] Analysis for Cl, 7.9 (8.2%). [d] Analysis for N, 6.3 (6.5%).

Table 2. ^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H} n.m.r. data[a] for the complexes

Compound	$\delta(^1\mathrm{H})$[b]	$\delta(^{13}\mathrm{C})$[b,c]	$\delta(^{31}\mathrm{P})$[b,d]
(**1**)	5.04 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$); 1.59 and 1.43 (s, 6 H, tmp ring *Me*); 1.39 (m, 6 H, tmp ring $\mathrm{C}\mathit{H}_2$)	239.1 (d, *C*O, $^2J_{\mathrm{PC}}$ = 22); 93.5 (s, $\mathit{C}_5\mathrm{H}_5$); 40.2 (d, $\mathit{C}^3\mathrm{H}_2$, $^3J_{\mathrm{PC}}$ = 4.5); 32.9 (d, *Me*, $^3J_{\mathrm{PC}}$ = 4.5); 30.2 (d, *Me*, $^3J_{\mathrm{PC}}$ = 5.9); 17.2 (s, $\mathit{C}^4\mathrm{H}_2$)	218[e]
(**3**)	5.01 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$); 1.71 [d, 1 H, $\mathrm{C}\mathit{H}\mathrm{(SiMe_3)_2}$, $^2J_{\mathrm{PH}}$ = 6.0]; 0.23 [s, 18 H, $\mathrm{CH(Si}\mathit{Me}_3)_2$]	95.2 (s, $\mathit{C}_5\mathrm{H}_5$); 14.1 [d, $\mathit{C}\mathrm{H(SiMe_3)_2}$, $^1J_{\mathrm{PC}}$ = 75]; 1.1 and 1.0 [s, $\mathrm{CH(Si}\mathit{Me}_3)_2$]	293[f]
(**7**)	5.14 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$); 2.74 and 2.71 (s, 3 H, $\mathrm{N}\mathit{Me}_2$); 1.34 and 1.20 (s, 6 H, tmp ring *Me*); 1.09 (m, 6 H, tmp ring $\mathrm{C}\mathit{H}_2$)	90.8 (s, $\mathit{C}_5\mathrm{H}_5$); 55.6 (s, tmp ring $\mathit{C}\mathrm{Me_2}$); 40.7 (s, $\mathrm{N}\mathit{Me}_2$); 39.9 (s, $\mathit{C}^3\mathrm{H}_2$); 32.7 and 27.9 (s, $\mathrm{C}\mathit{Me}_2$); 17.9 ($\mathit{C}^4\mathrm{H}_2$)	290
(**8**)	4.90 (s, 10 H, $\mathrm{C_5}\mathit{H}_5$); 2.05 [m, 2 H, $\mathrm{C}\mathit{H}\mathrm{(SiMe_3)_2}$]; 0.35 [s, 36 H, $\mathrm{CH(Si}\mathit{Me}_3)_2$]	93.5 (s, $\mathit{C}_5\mathrm{H}_5$); 14.3 [m, $\mathit{C}\mathrm{H(SiMe_3)_2}$]; 1.7 [s, $\mathrm{CH(Si}\mathit{Me}_3)_2$]	604[f]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz; measurements at room temperature. [b] Measured in $\mathrm{C_6D_6}$ unless otherwise stated. [c] ^{1}H-Decoupled; chemical shifts are positive to high frequency of $\mathrm{SiMe_4}$. [d] ^{1}H-Decoupled; chemical shifts are positive to high frequency of 85% $\mathrm{H_3PO_4}$ (external). [e] Measured in thf. [f] Measured in hexane.

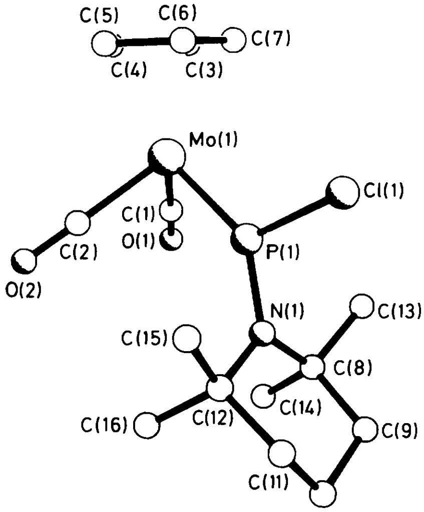


Figure 1. A view of the molecular structure of (**1**) showing the atom-numbering scheme adopted. Hydrogen atoms are omitted for clarity

shorter than typical Mo–P distances (2.40—2.57 Å)[9] normally associated with single bonding. The phosphorus adopts a trigonal-planar geometry [sum of angles 360.1(2)°] being bonded to Mo(1), Cl(1), and the nitrogen atom of the tmp ring, although some, presumably steric, distortion of the angles from idealised values of 120° is evident. The geometry at phosphorus, the shortness of the Mo–P bond, and the possession of only two carbonyls clearly identify (**1**) as a type (**A**) complex as described in the Introduction.

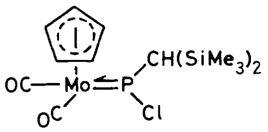
A final point of interest concerns the relative conformation within (**1**). This is such that the plane defined by Mo(1), P(1), Cl(1), and N(1) coincides with the symmetry plane of the $\mathrm{Mo(CO)_2(\eta\text{-}C_5H_5)}$ fragment (1.0°) and is very similar to the arrangement found in (**2**). The $\mathrm{Mo(CO)_2(\eta\text{-}C_5H_5)}$ fragment is isolobal with CH and contains two orthogonal metal-based orbitals of π symmetry. Unlike CH, however, they are not degenerate and differ, albeit slightly, in energy leading to a slight orientational preference in $\mathrm{ML_2(ligand)(C_5H_5)}$ complexes.[10] It might be assumed that the orientation found in (**1**) and (**2**), rather than an alternative conformation at 90°, is the result of electronic effects which maximise the π interaction between molybdenum and phosphorus. The steric bulk of the groups attached to phosphorus, however, is not insignificant and steric factors may, and probably do, play a major role in determining the lowest energy conformation. A full molecular orbital treatment of (**2**) has been provided by Paine and co-workers,[2c] although no specific mention is made of conformational preferences. We note finally that the nitrogen atom in the tmp ligand, N(1), also adopts a trigonal-planar configuration. Any conjugation with the Mo–P π system is, however, precluded by the relative orientation of the planes at N(1) and P(1), 89.1°.

Table 3. Selected bond distances (Å) and angles (°) for $[\mathrm{Mo(CO)_2\{P(Cl)(tmp)\}(\eta\text{-}C_5H_5)}]$ (**1**)*

Mo(1)–C(1)	1.952(6)	P(1)–Cl(1)	2.122(2)
Mo(1)–C(2)	1.964(7)	P(1)–N(1)	1.647(6)
Mo(1)–P(1)	2.214(2)		
C(1)–Mo(1)–C(2)	81.1(3)	N(1)–P(1)–Cl(1)	103.1(2)
C(1)–Mo(1)–P(1)	92.1(2)	P(1)–N(1)–C(8)	121.1(4)
C(2)–Mo(1)–P(1)	92.2(2)	P(1)–N(1)–C(12)	119.0(4)
Mo(1)–P(1)–N(1)	140.0(2)	C(8)–N(1)–C(12)	119.8(5)
Mo(1)–P(1)–Cl(1)	116.97(9)		

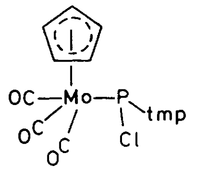
* Values in parentheses are estimated standard deviations in the least significant digit in this and all subsequent Tables.

A similar reaction between $\mathrm{K[Mo(CO)_3(\eta\text{-}C_5H_5)]}$ and $\mathrm{(Me_3Si)_2CHPCl_2}$ proceeds in an analogous manner and results in the formation of (**3**), isolated as red crystals. The supposition that (**3**) adopts a type (**A**) structure analogous to (**1**) is consistent with the spectroscopic data obtained (Tables 1 and 2), most notably the deshielded ^{31}P n.m.r. chemical shift which is characteristic of type (**A**) compounds.



(3)

The two reactions described above both afford type (**A**) complexes, *i.e.* (**1**) and (**3**), which contain two carbonyl ligands attached to the molybdenum. However, both reactions presumably proceed *via* the type (**B**), tricarbonyl species, (**4**) and (**5**), as intermediates which then readily lose CO to afford the observed products, although we have not been able to detect (**4**) and (**5**) spectroscopically.



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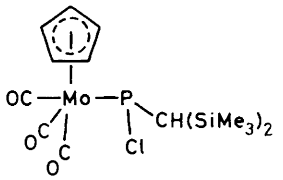
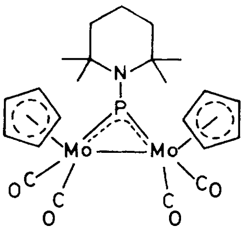


(5)

We note also that (**1**) itself can be viewed as an intermediate since the reaction of PCl_2(tmp) with *two* equivalents of K[Mo(CO)$_3$(η-C$_5$H$_5$)] affords the dimolybdenum phosphinidene complex, (**6**).[11] Analogous behaviour is not observed however, in the corresponding reaction with (Me$_3$Si)$_2$CHPCl$_2$, details of which are discussed later.



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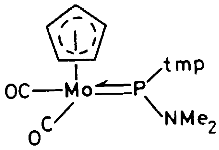


(7)

The availability of (**1**) and (**3**) containing a potentially reactive chloro group attached to phosphorus prompted a study of their reactivity. Previous examples of mononuclear phosphido complexes containing chloro groups are scarce. Malisch *et al.* have reported the complexes [Mo(CO)$_3$(PCl$_2$)(η-C$_5$Me$_5$)][5c] and [Fe(CO)$_2${P(Cl)Bu^t}(η-C$_5$Me$_5$)][7] together with studies on their reactivity, although in both cases it is primarily the phosphorus lone pair rather than the P–Cl bond which is the reactive site.

Nevertheless, the expected reactivity of the P–Cl functionality is demonstrated in the reaction of (**1**) with Li[NMe$_2$] which cleanly affords the simple substitution product, (**7**). The nature of (**7**) was evident from spectroscopic data (Tables 1 and 2) and was confirmed by *X*-ray diffraction (Figure 2). Selected bond distances and angles are given in Table 5 and atomic co-ordinates are presented in Table 6. The structure of (**7**) does not differ from that of (**1**) in any fundamental way. In addition to the cyclopentadienyl and two carbonyl ligands, the molybdenum atom is also bonded to the phosphido moiety, P(NMe$_2$)(tmp). The angle between the plane defined by Mo(1),P(1),N(1),N(2) and the symmetry plane of the Mo(CO)$_2$(η-C$_5$H$_5$) fragment is 12.2°. Thus the conformation of the phosphido fragment is similar to that found in (**1**). However in (**1**) the tmp group adopts a transoid orientation, with respect to the cyclopentadienyl ligand, whereas in (**7**) a cisoid geometry is observed. The phosphorus and both nitrogen atoms adopt trigonal-planar geometries [sum of angles for P(1), 359.7(3); N(1), 357.6(6); N(2), 359.9(7)°]. As found with (**1**), the tmp nitrogen plane is almost orthogonal to the plane at phosphorus (91.6°) but the plane of the NMe$_2$ group is much more nearly coplanar (4.4°). While this might suggest some degree of conjugation between N(2) and the Mo–P π system, any effect is not reflected in the P–N bond lengths which are not different within experimental error [P(1)–N(1) 1.685(6), P(1)–N(2) 1.678(7) Å]. Moreover, the overall molecular geometry is strongly suggestive of one which minimises intramolecular steric interactions, particularly between the various methyl groups. Finally, the Mo–P bond length [Mo(1)–P(1) 2.243(2) Å] is substantially longer than that found in (**1**), but is nevertheless still short and consistent with a modicum of Mo–P multiple bonding.

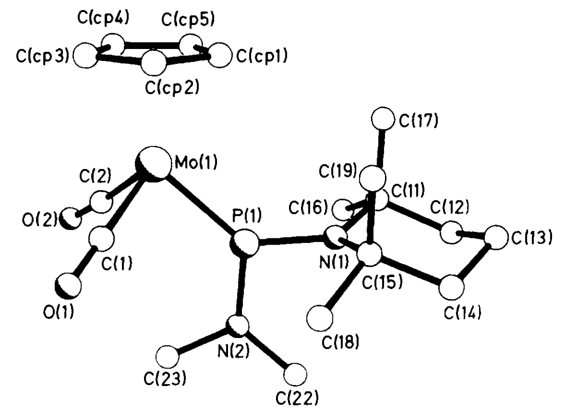
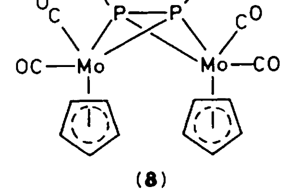


Figure 2. A view of the molecular structure of (**7**) showing the atom-numbering scheme adopted. Hydrogen atoms are omitted for clarity

We note also that (**7**) is readily synthesised by an alternative route involving the reaction of K[Mo(CO)$_3$(η-C$_5$H$_5$)] with PCl(NMe$_2$)(tmp) and is quite similar to a known, although not structurally characterised complex, [Mo(CO)$_2${P(NMe$_2$)$_2$}(η-C$_5$H$_5$)].[3]

Compound (**1**) is also reactive towards a number of metal carbonylate anions, resulting in hetero-binuclear complexes with a bridging phosphido ligand. Details of these compounds will be reported in a future publication.

It was also of interest to study the reactivity of (**1**) and (**3**) with a view to potential coupling reactions. Accordingly, the reaction of (**3**) with one equivalent of sodium dihydronaphthylide was investigated. This proceeds cleanly and affords, after work-up, brown crystalline (**8**). Although it was apparent from



(8)

Table 4. Fractional atomic co-ordinates for $[Mo(CO)_2\{P(Cl)(tmp)\}(\eta\text{-}C_5H_5)]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	0.024 72(6)	0.123 20(3)	0.176 86(4)	C(6)	−0.037 7(9)	0.166 1(6)	0.005 4(5)
Cl(1)	−0.390 7(2)	0.172 5(1)	0.088 5(1)	C(7)	−0.010(1)	0.243 3(5)	0.064 5(5)
P(1)	−0.203 6(2)	0.109 8(1)	0.197 2(1)	C(8)	−0.298 5(8)	0.110 5(4)	0.366 1(4)
O(1)	0.187 2(7)	0.149 2(4)	0.408 0(4)	C(9)	−0.454 8(8)	0.094 4(5)	0.377 3(5)
O(2)	0.111 5(6)	−0.070 4(3)	0.239 5(4)	C(10)	−0.500 5(9)	−0.002 9(5)	0.371 8(5)
N(1)	−0.284 8(6)	0.062 9(3)	0.273 8(3)	C(11)	−0.499 7(8)	−0.038 2(5)	0.268 5(5)
C(1)	0.125 1(8)	0.140 6(5)	0.322 0(5)	C(12)	−0.342 9(8)	−0.031 5(4)	0.252 6(4)
C(2)	0.078 0(8)	0.000 9(5)	0.216 5(5)	C(13)	−0.280(1)	0.210 5(4)	0.353 3(6)
C(3)	0.145 9(9)	0.241 6(5)	0.127 2(5)	C(14)	−0.167 8(9)	0.081 8(5)	0.463 1(5)
C(4)	0.213 8(9)	0.163 2(5)	0.105 5(5)	C(15)	−0.361(1)	−0.056 7(5)	0.142 0(5)
C(5)	0.098(1)	0.116 5(5)	0.029 6(5)	C(16)	−0.224 0(9)	−0.095 3(4)	0.323 0(6)

Table 5. Selected bond distances (Å) and angles (°) for $[Mo(CO)_2\{P(NMe_2)(tmp)\}(\eta\text{-}C_5H_5)]$ (7)

Mo(1)-C(1)	1.929(9)	P(1)-N(1)	1.685(6)
Mo(1)-C(2)	1.940(9)	P(1)-N(2)	1.678(7)
Mo(1)-P(1)	2.243(2)		
C(1)-Mo(1)-C(2)	86.6(4)	P(1)-N(1)-C(11)	119.7(5)
C(1)-Mo(1)-P(1)	87.9(3)	P(1)-N(1)-C(15)	117.6(5)
C(2)-Mo(1)-P(1)	93.3(3)	C(11)-N(1)-C(15)	120.3(6)
Mo(1)-P(1)-N(1)	130.0(2)	P(1)-N(2)-C(22)	126.8(6)
Mo(1)-P(1)-N(2)	127.9(2)	P(1)-N(2)-C(23)	120.6(6)
N(1)-P(1)-N(2)	101.8(3)	C(22)-N(2)-C(23)	112.5(7)

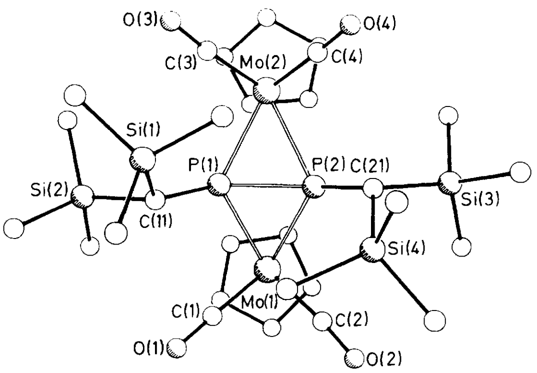


Figure 3. A view of the molecular structure of (**8**) showing the atom-numbering scheme adopted. Hydrogen atoms are omitted for clarity

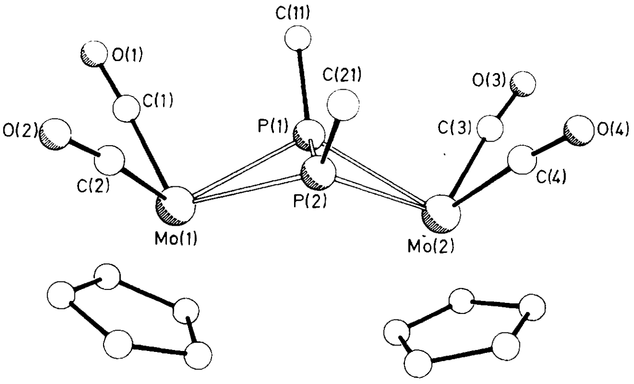
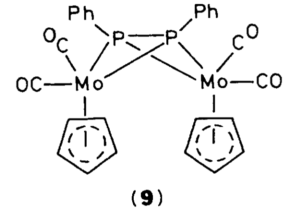


Figure 4. An alternative view of (**8**) with hydrogen atoms and $SiMe_3$ groups omitted

spectroscopic evidence (Tables 1 and 2) that the desired coupling had occurred, the precise structure of (**8**) was not obvious and so a single-crystal *X*-ray diffraction study was undertaken, the results of which are shown in Figures 3 and 4. Selected bond distances and angles are given in Table 7 and atomic co-ordinates are presented in Table 8.

The molecule comprises a *cis*-diphosphene unit, $(Me_3Si)_2HCP{=}PCH(SiMe_3)_2$ bonded to two $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments in such a way that the central Mo_2P_2 core adopts a 'butterfly' arrangement with the 'hinge' defined by the P(1)–P(2) vector and molybdenum atoms as 'wing-tips'. The P–P bond length [P(1)–P(2) 2.123(4) Å] is short and lies mid-way between values typical for an unsupported double bond (2.0 Å), as found in diphosphenes, and a single bond (2.2 Å).[12] A residual degree of multiple bonding is thus implied. The molybdenum–phosphorus bond lengths are all similar [average Mo–P 2.538(3) Å] and fairly long in comparison with standard Mo–P single bonds (2.40—2.57 Å).[9] The molybdenum–molybdenum separation [Mo(1)–Mo(2) 4.203(2) Å] is a full 1 Å longer than typical values for Mo–Mo single bonds, *e.g.* 3.235 Å in $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$,[13] and is thus clearly non-bonding. The angle between the planes defined by Mo(1)P(1),P(2) and Mo(2),P(1),P(2) is 131.4°. The overall molecular geometry is such that (**8**) possesses an approximate (non-crystallographic) two-fold axis passing through the mid-points of the P–P and Mo–Mo vectors. Figure 3 provides a view of (**8**) in which this symmetry is clearly revealed. In addition, the orientation of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments is such that the cyclopentadienyl groups adopt a *syn* orientation with respect to the Mo–Mo vector (Figure 4). While this may be electronic in origin, such an orientation also minimises any intramolecular steric interaction between the C_5H_5 and $CH(SiMe_3)_2$ groups.

As mentioned above, (**8**) contains a ligated diphosphene in a *cis* configuration. All known unco-ordinated diphosphenes adopt *trans* geometries[12] but a few examples exist in which diphosphenes functioning as ligands to transition metal centres adopt *cis* configurations. Of particular interest is (**9**) reported by Fenske and Merzweiler[14] which is very similar in structure to (**8**), differing only in the substituents attached to phosphorus, *viz.* $CH(SiMe_3)_2$ in (**8**) and Ph in (**9**). All aspects of the molecular geometry of (**9**) are similar to those found in (**8**)



(**9**)

Table 6. Fractional atomic co-ordinates for [Mo(CO)$_2${P(NMe$_2$)(tmp)}(η-C$_5$H$_5$)] (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	0.971 72(9)	0.271 47(5)	0.084 75(4)	C(cp5)	0.901(1)	0.391 2(6)	0.167 8(5)
P(1)	1.148 1(3)	0.169 3(1)	0.140 6(1)	C(11)	1.230(1)	0.177 6(5)	0.292 0(4)
O(1)	0.870(1)	0.127 4(6)	−0.032 9(4)	C(12)	1.298(1)	0.109 4(6)	0.351 8(4)
O(2)	1.254 1(9)	0.339 1(6)	−0.024 1(4)	C(13)	1.154(1)	0.043 7(6)	0.375 6(5)
N(1)	1.144 3(8)	0.126 9(4)	0.228 3(3)	C(14)	1.089(1)	−0.008 3(6)	0.305 5(5)
N(2)	1.305 9(9)	0.107 0(5)	0.101 4(4)	C(15)	1.012(1)	0.053 8(5)	0.243 7(4)
C(1)	0.912(1)	0.181 8(7)	0.010 3(5)	C(16)	1.393(1)	0.228 4(6)	0.263 7(5)
C(2)	1.153(1)	0.310 8(7)	0.016 9(5)	C(17)	1.106(1)	0.248 3(5)	0.328 1(5)
C(cp1)	0.789(1)	0.316 3(6)	0.185 5(4)	C(18)	0.980(1)	−0.004 8(6)	0.172 5(5)
C(cp2)	0.676(1)	0.296 9(6)	0.121 1(5)	C(19)	0.829(1)	0.092 0(6)	0.266 1(5)
C(cp3)	0.717(1)	0.361 5(7)	0.064 2(5)	C(22)	1.416(1)	0.038 1(6)	0.139 0(5)
C(cp4)	0.854(1)	0.418 5(6)	0.093 3(6)	C(23)	1.340(1)	0.113 9(8)	0.019 6(5)

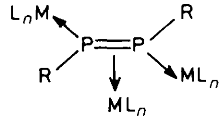
Table 7. Selected bond distances (Å) and angles (°)* for [Mo$_2$(CO)$_4${μ-P$_2$[CH(SiMe$_3$)$_2$]$_2$}(η-C$_5$H$_5$)$_2$] (**8**)

Mo(1)–P(1)	2.549(3)	Mo(2)–P(1)	2.512(3)
Mo(1)–P(2)	2.528(3)	Mo(2)–P(2)	2.563(3)
P(1)–P(2)	2.123(4)	P(1)–C(11)	1.86(1)
P(2)–C(21)	1.87(1)		
Mo(1)–P(1)–Mo(2)	112.3(1)	Mo(1)–P(2)–Mo(2)	111.3(1)
Mo(1)–P(1)–P(2)	64.8(1)	Mo(1)–P(2)–P(1)	65.8(1)
Mo(1)–P(1)–C(11)	118.5(3)	Mo(1)–P(2)–C(21)	128.6(4)
Mo(2)–P(1)–P(2)	66.5(1)	Mo(2)–P(2)–P(1)	64.0(1)
Mo(2)–P(1)–C(11)	128.9(3)	Mo(2)–P(2)–C(21)	119.7(4)
P(2)–P(1)–C(11)	132.8(3)	P(1)–P(2)–C(21)	132.4(4)

* Torsion angle C(11)–P(1)–P(2)–C(21) −14.5(4)°.

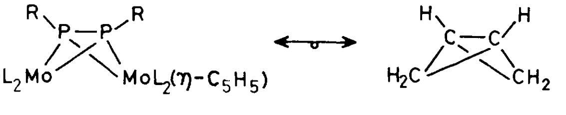
including the P–P bond length (2.136 Å).[14] Compound (**9**) is, however, synthesised by an entirely different route to (**8**) involving diphosphene transfer from a nickel complex to [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$]. Other examples of co-ordinated *cis*-diphosphene complexes are [Fe$_2$(CO)$_6$(μ-P$_2$Ph$_2$)],[15] [Ni$_5$(CO)$_6$Cl{μ-P$_2$[CH(SiMe$_3$)$_2$]$_2$}$_2$],[16] [Cr$_3$(CO)$_{10}$(μ-PBu^t)(μ-P$_2$Bu$^t_2$)],[17] [{Mo(CO)$_5$}$_2${P$_2$(C$_6$H$_2$Me$_3$-2,4,6)$_2$}],[18] and [{Cr(CO)$_5$}(2,4,6-Bu$^t_3$C$_6$H$_2$P=PC$_6$H$_2$Me$_3$-2,4,6)].[19]

In (**8**) and (**9**) formal electron-counting procedures indicate that the diphosphene behaves as a six-electron donor (three to each molybdenum). Six-electron donation is not uncommon for diphosphene ligands and occurs, for example, in [Fe$_2$(CO)$_6$(μ-P$_2$Ph$_2$)] (see above). However it is more usually found in complexes with the structural form (**C**).[12]

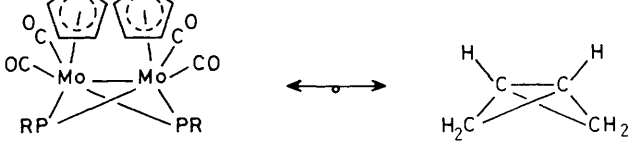


(**C**)

The bonding in (**8**) is interesting and may be understood in simple terms by reference to the isolobal analogy.[20] If the molecule is considered to be made up of the fragments [Mo(CO)$_2$(η-C$_5$H$_5$)]$^-$ and [PCH(SiMe$_3$)$_2$]$^+$, these are isolobal with CH$_2$ and CH respectively. Combination of these fragments gives C$_4$H$_6$, for which the organic analogue is bicyclobutane. This analogy has also been made by Fenske and Merzweiler[14] with regard to (**9**), see below. An alternative isolobal mapping is Mo(CO)$_2$(η-C$_5$H$_5$) with CH and CHP(SiMe$_3$)$_2$ with CH$_2$. The former is well documented[10,20] and the ability of the phosphinidene fragment to behave either as CH$^-$ or CH$_2$ has been discussed previously.[21] This so called 'ambilobal' behaviour depends on whether the phosphorus lone pairs are both involved in bonding (*i.e.* analogous to CH$^-$) or whether one is non-bonding (*i.e.* it behaves in a manner analogous to CH$_2$). Combination of the molybdenum and phosphorus fragments in which this alternative isolobal mapping is adopted also leads to an analogy with bicyclobutane but one in which the molybdenum and phosphorus positions are reversed, *i.e.* (**10**) [R = CH(SiMe$_3$)$_2$]. The structure of (**10**) is isomeric with (**8**) and may be regarded as a diphosphinidene complex.



(**8**) L = CO, R = CH(SiMe$_3$)$_2$
(**9**) L = CO, R = Ph

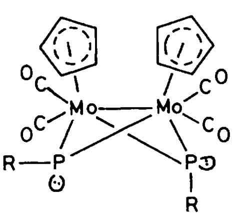


(**10**)

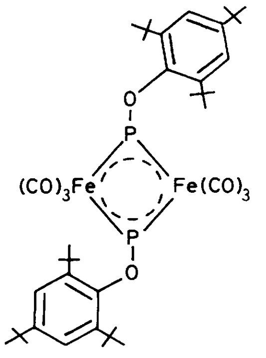
Evidence that this isomer may exist was obtained from a reaction between (Me$_3$Si)$_2$CHPCl$_2$ and two equivalents of K[Mo(CO)$_3$(η-C$_5$H$_5$)]. Reaction at room temperature, followed by column chromatography (Florisil/Et$_2$O) of the crude product afforded, after crystallisation, an orange solid but this proved difficult to purify and satisfactory analytical data were not obtained. However ^{31}P n.m.r. data indicated the predominance of a single phosphorus-containing product. The ^{1}H-decoupled ^{31}P n.m.r. spectrum revealed an AX system with δ(P$_A$) +330.7, δ(P$_B$) +321.1, and J_{PP} = 17 Hz. The corresponding ^{1}H-coupled ^{31}P spectrum indicated no hydrogens directly bound to phosphorus. However the resonance at 330.7 p.p.m. appeared as a triplet due to a J_{PH} coupling of *ca.* 17 Hz (accidentally similar to the P–P coupling) while the resonance at 321.1 p.p.m. remained unchanged. The ^{1}H n.m.r. revealed a single cyclopentadienyl resonance (5.50 p.p.m.) and signals corresponding to two chemically inequivalent CH(SiMe$_3$)$_2$ groups (0.35 and 0.33 p.p.m.). Moreover, the signals for the two C*H*(SiMe$_3$)$_2$ protons (1.88 and 2.28 p.p.m.) showed that only the latter was coupled to phosphorus ($^2J_{PH}$ ~ 17 Hz) in agreement with the ^{1}H-coupled ^{31}P spectrum. The overall integration indicated a ratio of two cyclopentadienyl ligands (equivalent) to two CH(SiMe$_3$)$_2$ groups (inequivalent). Collectively, the foregoing data are consistent with a dimolybdenum diphosphinidene complex such as (**10**). Specifically, a structure as shown in (**10a**) [R = CH(SiMe$_3$)$_2$] would be required to account for the chemically-equivalent cyclopentadienyl ligands and inequivalent CH(SiMe$_3$)$_2$ groups and phosphorus resonances. The proposed geometry is

Table 8. Fractional atomic co-ordinates for $[Mo_2(CO)_4\{\mu\text{-}P_2[CH(SiMe_3)_2]_2\}(\eta\text{-}C_5H_5)_2]$ (**8**)

Atom	*x*	*y*	*z*
Mo(1)	0.789 51(8)	0.334 31(5)	0.377 09(5)
Mo(2)	0.995 89(8)	0.175 47(5)	0.265 10(5)
P(1)	0.848 7(2)	0.190 9(2)	0.361 3(1)
P(2)	0.815 3(2)	0.252 3(2)	0.261 1(2)
Si(1)	0.722 5(2)	0.015 1(2)	0.372 1(2)
Si(2)	0.851 2(3)	0.097 3(2)	0.504 5(2)
Si(3)	0.746 4(3)	0.312 6(2)	0.110 7(2)
Si(4)	0.562 5(3)	0.214 8(2)	0.200 3(2)
O(1)	0.623 6(7)	0.262 7(5)	0.487 4(5)
O(2)	0.571 4(8)	0.395 1(6)	0.312 0(6)
O(3)	0.493 6(9)	0.502 8(5)	0.699 4(5)
O(4)	0.581 7(8)	−0.101 3(5)	0.617 9(5)
C(1)	0.686 8(9)	0.288 0(6)	0.444 2(6)
C(cp1)	0.955(1)	0.414 5(7)	0.367 4(8)
C(2)	0.653(1)	0.368 3(7)	0.332 3(7)
C(cp2)	0.956(1)	0.375 8(8)	0.439 1(8)
C(3)	0.990(1)	0.064 6(7)	0.289 3(6)
C(cp3)	0.862(1)	0.401 5(9)	0.480 5(8)
C(cp4)	0.801(1)	0.456 2(7)	0.436 3(8)
C(4)	0.941 7(9)	0.128 1(7)	0.173 5(7)
C(cp5)	0.858(1)	0.462 4(7)	0.368 3(9)
C(cp6)	1.106(1)	0.293 3(8)	0.250 2(8)
C(cp7)	1.138(1)	0.235 2(8)	0.198 9(8)
C(cp8)	1.180 2(9)	0.168 0(9)	0.237 9(9)
C(cp9)	1.171(1)	0.186 2(9)	0.316 4(8)
C(cp10)	1.126(1)	0.261 0(8)	0.322 2(8)
C(11)	0.773 3(8)	0.113 0(5)	0.413 2(5)
C(12)	0.720(1)	0.013 6(8)	0.266 5(6)
C(13)	0.577(1)	0.004 8(8)	0.411 3(8)
C(14)	0.801(1)	−0.076 1(6)	0.399 8(7)
C(15)	0.992(1)	0.052 1(8)	0.490 2(7)
C(16)	0.870(1)	0.193 0(7)	0.556 3(6)
C(17)	0.765(1)	0.037 0(8)	0.567 2(7)
C(21)	0.716(1)	0.233 9(6)	0.184 1(6)
C(22)	0.665(1)	0.290(1)	0.024 2(8)
C(23)	0.721(1)	0.415 0(8)	0.143 8(8)
C(24)	0.897(1)	0.308(1)	0.082 7(8)
C(25)	0.465(1)	0.300 3(8)	0.177 7(9)
C(26)	0.529(1)	0.182 1(9)	0.299 4(6)
C(27)	0.524(1)	0.130 5(8)	0.136 7(8)



(**10a**)



(**11**)

consistent with the presence of phosphorus lone pairs and the phosphorus chemical shifts and coupling constants are also appropriate for this structure. A mass spectrum of (**10**) did not show a molecular ion but peaks were observed for the fragment $Mo_2(CO)_4\{PCH(SiMe_3)_2\}(C_5H_5)_2$ and those corresponding to loss of the four carbonyl ligands. Further studies are in progress with other R groups on phosphorus to establish whether other analogues of (**8**), and particularly (**10**), can be synthesised and whether interconversion of the two forms is possible. Further examples of dinuclear complexes containing two bridging phosphinidene ligands would also be of interest since such species are rare, the only previous example being a di-iron complex, (**11**), reported by Power and co-workers[22]

Experimental

All experiments were performed using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. spectra were recorded on a General Electric QE300 instrument operating at 300, 75.48, and 121.5 MHz respectively. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer and mass spectra on Du Pont–Consolidated 21-491 and 21-100 spectrometers (the latter for high-resolution mass spectra, h.r.m.s.).

The salt $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ was prepared by NaK reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$. $PCl_2(tmp)$[23] and $(Me_3Si)_2CHPCl_2$[24] were prepared by literature methods.

Preparation of $[Mo(CO)_2\{P(Cl)(tmp)\}(\eta\text{-}C_5H_5)]$ (**1**).—A solution of $PCl_2(tmp)$ (2.43 g, 10.0 mmol) in methylcyclohexane (50 cm^3) was added to a slurry of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ (2.83 g, 10.0 mmol) in a mixture of toluene (10 cm^3) and methylcyclohexane (50 cm^3) which had been cooled to −78 °C. The resulting pale orange slurry was allowed to warm to room temperature and stirred for 24 h, during which time it assumed a purple-brown colour. Filtration to remove KCl, followed by washing of the filter with methylcyclohexane afforded a purple filtrate (250 cm^3). Reduction of the solvent volume to *ca.* 150 cm^3 and cooling to −20 °C for 12 h gave $[Mo_2(CO)_4\{\mu\text{-}P(tmp)\}(\eta\text{-}C_5H_5)_2]$ (**6**) (0.65 g).[11] Further concentration to 50 cm^3, and cooling to −20 °C for 48 h, gave purple crystals of (**1**) (3.11 g, 73% yield). A low-resolution electron impact mass spectrum showed a molecular ion, M^+, 426, plus additional fragments of (M^+ − Cl) 390, (M^+ − 2CO) 370, and (M^+ − Cl + CO) 363. Full spectroscopic data for this and all other compounds are given in Tables 1 and 2.

Preparation of $[Mo(CO)_2\{P(Cl)CH(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (**3**).—A solution of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ (5.68 g, 20.0 mmol) in thf (250 cm^3) was added dropwise to a solution of $(Me_3Si)_2CHPCl_2$ (5.23 g, 20.0 mmol) in thf (100 cm^3) maintained at −78 °C. After complete addition the reaction mixture was kept at −78 °C for 1 h and then allowed to warm to room temperature. The thf was removed *in vacuo* after which a brown oily residue remained. Extraction with hexane (100 cm^3), followed by filtration (Celite) afforded an orange-red solution. Reduction of the solvent volume to *ca.* 10 cm^3 and cooling for 12 h at −10 °C gave red-brown crystals of (**3**) (5.75 g, 69% yield).

Preparation of $[Mo(CO)_2\{P(NMe_2)(tmp)\}(\eta\text{-}C_5H_5)]$ (**7**).—A solution of $Li[NMe_2]$ in thf (2.0 cm^3 of a 0.5 mol dm^{-3} solution) was added dropwise to a solution of (**1**) (0.426 g, 1.0 mmol) in thf (60 cm^3) which had been cooled to −78 °C. An immediate colour change from purple to orange was observed. The resulting solution was allowed to warm to room temperature and was then filtered (Celite). Reduction of the filtrate volume to *ca.* 10 cm^3 and cooling to −20 °C for 12 h afforded crystals of (7) (0.362 g, 81% yield). H.r.m.s.: *m/e* 434.10296 (calc. for $C_{18}H_{29}MoN_2O_2P$, 434.10207).

Compound (7) may also be prepared by direct reaction of $K[Mo(CO)_3(\eta-C_5H_5)]$ and $PCl(NMe_2)(tmp)$ in a manner identical to that described for the synthesis of (3).

Preparation of $[Mo_2(CO)_4\{\mu-P_2[CH(SiMe_3)_2]_2\}(\eta-C_5H_5)_2]$ **(8)**.—A solution of sodium dihydronaphthylide in thf (25 cm^3 of a 0.8 mol dm^{-3} solution, 20.0 mmol) was added dropwise to a solution of (3) (8.86 g, 20.0 mmol) in thf (50 cm^3) which had been cooled to −78 °C. The resulting solution was stirred for 1 h and then all thf was removed *in vacuo*. Further pumping at 10^{-5} Torr for 12 h at 40 °C was carried out to remove the naphthalene. The resulting solid was redissolved in hexane and purified by column chromatography (silica gel/hexane). The resulting brown solution was concentrated and cooled to −10 °C which afforded brown crystals of **(8)** (3.16 g, 39% yield), m.p. 171—173 °C.

X-Ray Crystallographic Studies.—Compound **(1)**. Crystals were grown from thf–hexane. Diffracted intensities were collected at 293 K on an Enraf-Nonius CAD4-F diffractometer. Of the 2 898 unique data collected (ω—2θ scans, $3.0 \leqslant 2\theta \leqslant 48.0°$), 2 898 had $I > 3.0\sigma(I)$ and only these were used in structure solution and refinement. Data were corrected for Lorentz, polarisation, crystal decay, and *X*-ray absorption, the latter by an empirical ψ-scan method (transmission factors ranging from 95.16 to 99.95%).

Crystal data. $C_{16}H_{23}ClMoNO_2P$, $M = 423.73$, monoclinic, $a = 9.191(2)$, $b = 15.261(6)$, $c = 13.910(5)$ Å, $\beta = 108.53(2)°$, $U = 1\,850(2)$ Å^3, $Z = 4$, $D_c = 1.579$ g cm^{-3}, $F(000) = 864$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,73$ Å, μ(Mo-K_α) = 9.3 cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. All non-hydrogen atoms were refined using anisotropic thermal parameters. Refinement by full-matrix least-squares methods converged smoothly and led to $R = 0.051$ ($R' = 0.056$). A weighting scheme of the form $w = 4F_o^2/\sigma^2(F_o)^2$ and $\sigma^2(F_o)^2 = \sigma_o^2(F_o)^2 + (PF^2)^2$ was used with $P = 0.08$. The final electron-density difference synthesis showed no chemically significant peaks (maximum value 0.71 e Å^{-3}).

Compound (7). Crystals were grown from thf–hexane. Diffracted intensities were collected at 293 K. Of the 3 517 unique data collected (ω—2θ scans, $3.0 \leqslant 2\theta \leqslant 50.0°$), 2 221 had $I > 3.0\sigma(I)$ and only these were used in structure solution and refinement. Data were corrected for Lorentz, polarisation, and *X*-ray absorption using an empirical ψ-scan method (transmission factors ranging from 90.96 to 99.71%).

Crystal data. $C_{18}H_{29}MoN_2O_2P$, $M = 432.35$, monoclinic, $a = 7.576(3)$, $b = 14.902(3)$, $c = 17.790(4)$ Å, $\beta = 91.29(3)°$, $U = 2\,008(2)$ Å^3, $Z = 4$, $D_c = 1.420$ g cm^{-3}, $F(000) = 896$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,73$ Å, μ(Mo-K_α) = 7.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods as described for (**1**). Refinement converged smoothly and led to $R = 0.046$ ($R' = 0.056$). A weighting scheme of the form given for (**1**) was used with $P = 0.08$. No chemically significant peaks were present in the final electron-density difference synthesis (max. value 0.67 e Å^{-3}).

Compound (**8**). Crystals were grown from thf–hexane. Diffracted intensities were collected at 293 K. Of the 3 695 unique data collected (ω—2θ scans, $3.0 \leqslant 2\theta \leqslant 50.0°$), 2 629 had $I > 3.0\sigma(I)$ and only these were used in structure solution and refinement. Data were corrected for Lorentz and polarisation effects.

Crystal data. $C_{28}H_{48}Mo_2O_4P_2Si_4$, $M = 814.86$, orthorhombic, $a = 12.221(4)$, $b = 16.925(3)$, $c = 18.024(2)$ Å, $U = 3\,728(2)$ Å^3, $Z = 4$, $D_c = 1.452$ g cm^{-3}, $F(000) = 1\,560$, space group $P2_12_12_1$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,73$ Å, μ(Mo-K_α) = 8.9 cm^{-1}.

The structure was solved by conventional heavy-atom methods as for (**1**). Refinement converged smoothly and led to $R = 0.039$ ($R' = 0.046$). A weighting scheme of the form given for (**1**) was used with $P = 0.04$. No chemically significant peaks were present in the final difference map (max. value 2.46 e Å^{-3}).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

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