In memory of S. M. Nelson

Subvalent Group 14 Metal Compounds.* Part 10.[1] Syntheses and Structures of Some Bis(metallo)plumbylenes $[Pb\{Mo(R)(CO)_3\}_2(OC_4H_8)]$ [R = η-C_5H_5, η-$C_5H_3(SiMe_3)_2$-1,3, or η-C_5Me_5]; *X*-Ray Crystal Structures of $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2(OC_4H_8)]$ and $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ †‡

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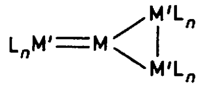
Treatment of $Pb[N(SiMe_3)_2]_2$ with $[Mo(R)(CO)_3H]$ in tetrahydrofuran (thf) affords the green complexes $[Pb\{Mo(R)(CO)_3\}_2(thf)]$ [R = η-C_5Me_5 (**1a**), η-$C_5H_3(SiMe_3)_2$-1,3 (**1b**), or η-C_5H_5 (**1c**)]. The brown thf-free analogues $[Pb\{Mo(R)(CO)_3\}_2]$ (**2**) are obtained from (**1**) at 25 °C and 10^{-2} Torr for R = η-$C_5H_3(SiMe_3)_2$ (**2b**) or η-C_5H_5 (**2c**), but slightly more forcing conditions (40 °C, 10^{-2} Torr) are required to convert complex (**1a**) to $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2]$ (**2a**). The dimeric green bis(isocarbonyl)-bridged complex $\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ (**3**), containing a pair of MoCO–Pb linkages, was obtained from $Pb[N(SiMe_3)_2]_2$ and $[Mo(\eta\text{-}C_5Me_5)(CO)_3H]$ in a hydrocarbon solvent. The brown toluene solution of complex (**3**) shows i.r. characteristics similar to those of complexes (**2b**) or (**2c**), and is thus believed to contain an isoleptic complex of structure (**2a**). Addition of triethylphosphine to the brown (**2b**) yields a green transient believed to be $[Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_3\}_2(PEt_3)]$, which is rapidly converted to the brown $[Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_2(PEt_3)\}_2]$. The complexes (**2**) are thermally labile, decomposing to Pb + $[\{Mo(R)(CO)_3\}_2]$, with decreasing facility in the sequence R = η-C_5H_5 > η-C_5Me_5 > η-$C_5H_3(SiMe_3)_2$, which is attributed to steric considerations. Complex (**3**) has three co-ordinate Pb^{II}, whereas complexes (**1**) and (**2**) are assigned as monomers having three- or two-co-ordinate Pb^{II} environments, respectively; all are diamagnetic, whence it is inferred that complexes (**2**) are V-shaped, having ground-state singlet structures. These structural conclusions are supported by the i.r. and n.m.r. spectra, and by single-crystal *X*-ray data on the pentamethylcyclopentadienyl complexes (**1a**) and (**3**). Complexes (**1a**) and (**3**) crystallise in space groups $P2_1/c$ and $P\bar{1}$, respectively. Both show a pyramidal three-co-ordinate Pb^{II} environment, with Mo–Pb 2.989(2) and 3.019(2) Å [(**1a**)] [or for (**3**): 2.935(1) and 2.989(1) Å] and Pb–O 2.75([illegible]) Å [(**1a**)] [2.918(8) Å in (**3**)], and Mo–Pb–Mo 118.33(5)° [(**1a**)] [120.71(2)° in (**3**)].

The synthesis and characterisation of stable Group 14 (Ölander numbering) analogues of carbenes has for some time been a subject of considerable interest.[2] Many examples of C-, N-, O-, or S-centred bivalent compounds MX_2 (M = Ge, Sn, or Pb; X^- = a monodentate ligand) are known (see, for example, ref. 3). However, few examples exist where the main-group metal is bound to two transition metal (M′)-centred moieties, *i.e.* of formula $[M(M'L_n)_2]$.[4]

Carbenes $\ddot{C}X_2$ have triplet (linear) or singlet (bent) electronic ground-state configurations, depending on the nature of X. The same alternatives are, in principle, available to their heavy Group 14 metal congeners $\ddot{M}X_2$. In practice, all such compounds have proved to be diamagnetic and, with the exception of $Sn(\eta\text{-}C_5Ph_5)_2$ (which in any event, having pentahapto ligands X^-, is not within our present scope),[5] are V-shaped molecules.

$$L_nM'{=}M{=}M'L_n$$

(I)



(II)

Of the complexes $[M(M'L_n)_2]$, only the linear, diamagnetic $[Ge\{Mn(\eta\text{-}C_5H_4Me)(CO)_2\}_2]$,[6] $[Ge\{Mn(\eta\text{-}C_5Me_5)(CO)_2\}_2]$,[7] and $[Pb\{Mn(\eta\text{-}C_5H_5)(CO)_2\}_2]$[8] have been *X*-ray authenticated, and are best considered as being derived from Ge^{IV} or Pb^{IV} and the 18-electron ligands $[Mn(R)(CO)_2]^{2-}$, thus having M=Mn double bonds (**I**). Other compounds postulated as having double bonds between Ge or Sn and a transition metal have the formula $[M(M'L_n)_3]$ [$M'L_n$ = $Mn(R)(CO)_2$

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* Previous parts in this series had the general title 'Subvalent Group 4B Metal Alkyls and Amides.'

† (Tetrahydrofuran)bis[tricarbonyl(η-pentamethylcyclopentadienyl)-molybdenio]lead(II) and 2,3;1,4-di-μ-[carbonyl-*C*(Mo)*O*(Pb)]-2,2,4,4-tetracarbonyl-2,4-bis(η-pentamethylcyclopentadienyl)-1,3-bis-[tricarbonyl(η-pentamethylcyclopentadienyl)molybdenio]di-lead(II)dimolybdenum(0).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

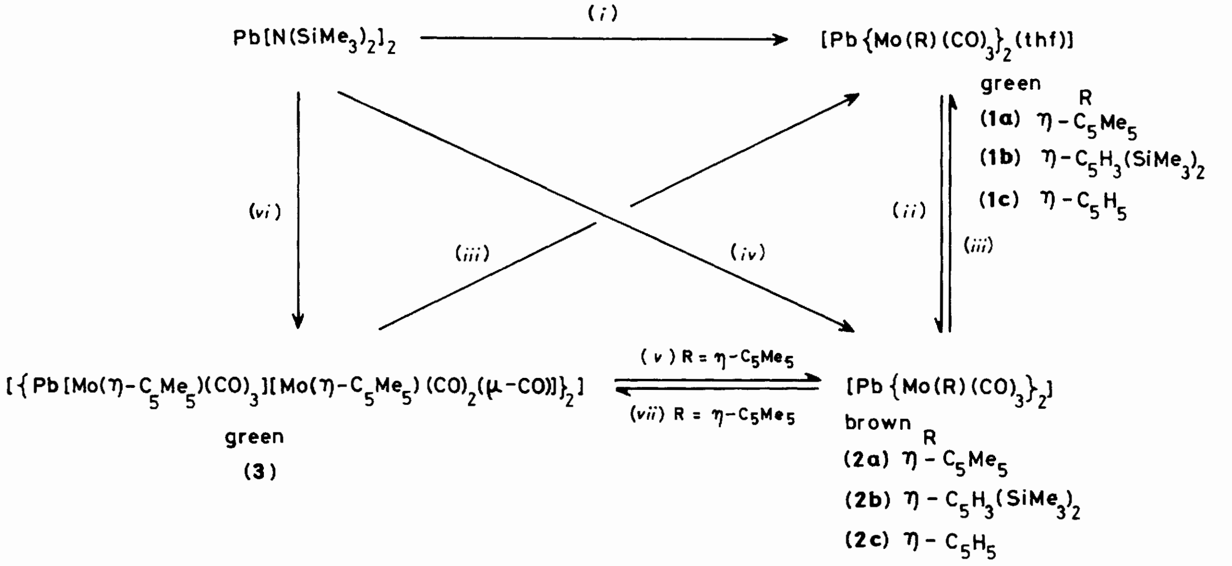
Non-S.I. unit employed: Torr = (101 325)/760 Pa.

‡ No reprints available.

Table 1. Comparison of some *X*-ray structural parameters for two- or three-co-ordinate lead(II) complexes of formula $PbX_2[\{Pb(\mu\text{-}X)Y\}_2]$ [or Li(thf) adduct], PbX_2L, or $[\{Pb(SR')_2\}_3]$ (X^-, Y^-, L, or L^- are monodentate ligands)

Compound	Bonds to Pb/Å	Angles at Pb/°	Sum of angles at Pb, Σ/°	Ref.
$Pb[N(SiMe_3)_2]_2$	2.24(2)	103.6(7)	103.6(7)	17
$Pb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$	2.13(1), 2.15(1)	86.2(4)	86.2(4)	18
$[AsPh_4][Pb(SPh)_3]$	2.619(1), 2.647(1), 2.623(1)	90.32(4), 91.08(5), 96.14(5)	277.5	19
$[AsPh_4][Pb(SePh)_3]$	2.727(1), 2.762(1), 2.733(1)	88.82(4), 90.11(4), 96.57(4)	275.5	19
$[Pb(PBu^t_2)(\mu\text{-}PBu^t_2)_2Li(thf)]$	2.814(6), 2.766(7), 2.758(9)	82.2(3), 118.4(2), 103.7(3)	304.3	20
$[\{Pb[\mu\text{-}SC(SiMe_3)_3][N(SiMe_3)_2]\}_2]$	2.88(2), 2.74(2), 2.07(5) or 2.35(5)	108(1), 113(1), 76.3(4) or 81.2(4)	297.3, 302.2	21
$[\{Pb[\mu\text{-}SSi(OBu^t)_3][SSi(OBu^t)_3]\}_2]$	2.581(10), 2.786(6), 2.811(6)	89.3(2), 92.5(3), 78.7(2)	260.5	22
$[Pb\{CH(PPh_2)_2\}\{(PPh_2)_2CH\}]$	2.371(12), 2.782(4), 2.758(4)	61.5(1), 96.6(3), 88.7(3)	246.8	23
$[Pb(SR')(\mu\text{-}SR')_2Pb(\mu\text{-}SR')_2Pb(SR')]$ *	2.780(3), 2.673(3), 2.554(4)	73.5(1), 92.8(1), 92.6(1)	258.9	24
(**1a**) $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2(thf)]$	2.989(2), 3.019(2), 2.75(2)	118.33(5), 105.5(3), 98.0(3)	321.8	This work
(**3**) $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$	2.935(1), 2.989(1), 2.918(8)	120.71(2), 100.3(2), 92.9(2)	313.7	This work

* $R' = C_6H_3Pr^i_2\text{-}2,6$; the cited parameters refer to the co-ordination geometry around the terminal three-co-ordinate Pb^{II} atoms.



Scheme. The reaction of $Pb[N(SiMe_3)_2]_2$ with $[Mo(R)(CO)_3H]$. Reagents and conditions: (*i*) $2[Mo(R)(CO)_3H]$, thf, 0 °C; (*ii*) (**1a**): 40 °C, 10^{-2} Torr, but for (**1b**) or (**1c**): 25 °C, 10^{-2} Torr; (*iii*), thf, 25 °C; (*iv*), $2[Mo\{\eta\text{-}C_5H_3(SiMe_3)_2\}(CO)_3H]$, n-$C_5H_{12}$, 25 °C; (*v*), toluene, 25 °C; (*vi*) $2[Mo(\eta\text{-}C_5Me_5)(CO)_3H]$, n-$C_5H_{12}$–n-$C_6H_{14}$, 25 °C; (*vii*), toluene 40 °C, 10^{-2} Torr

($R = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5H_4Me$)[6,9] or $W(CO)_5$[10]] (II), and hence have the Group 14 element in the tetravalent state; they fall outside the scope of this paper.

Compounds formulated as bis(metallo)carbene analogues: (*a*) $[Sn\{(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[11] obtained from $Sn(\eta\text{-}C_5H_4Me)_2$ + $2[W(\eta\text{-}C_5H_5)(CO)_3H]$ and subsequent recrystallisation from CH_2Cl_2; and (*b*) $[Sn\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[4] prepared from $Sn[N(SiMe_3)_2]_2$ and $2[Mo(\eta\text{-}C_5H_5)(CO)_3H]$ and recrystallisation from CH_2Cl_2, have been claimed, but probably erroneously. Thus, reaction of $Sn(\eta\text{-}C_5H_5)_2$ with $2[W(\eta\text{-}C_5H_5)(CO)_3H]$ afforded the Sn^{IV} complex $[SnH\{W(\eta\text{-}C_5H_5)(CO)_3\}_3]$, which with CH_2Cl_2 yielded $[SnCl\{W(\eta\text{-}C_5H_5)(CO)_3\}_3]$.[12]

An objective of the present study was to prepare authentic bis(metallo)carbene analogues $[M(M'L_n)_2]$. As Pb^{II} is less prone to undergo oxidative addition than Sn^{II}, this paper is concerned with lead chemistry. A feature of interest was anticipated to be the possibility of realising a triplet plumbylene $[Pb(M'L_n)_2]$, as a consequence of the considerable steric requirements of the octahedrally ligated transition-metal centres M′; a further prospect was a two-electron oxidation to $[Pb^{IV}{=}(M'L'_m)_2]$, *e.g.*, by a 2NO/2CO exchange reaction (L = CO, L′ = NO). These aspects will be developed in a later paper. In due course, we shall also describe experiments devoted to tin systems, which *inter alia* will show that $[Sn(M'L_n)_2]$ complexes can be obtained, but that the complex in (*b*) above should be reformulated as $[SnCl\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_3]$.

We exclude from our present discussion Pb^{II} complexes which involve polyhapto ligands, including various cyclopentadienyls such as $Pb[\eta\text{-}C_5H_4(CH_2Ph)]_2$[13] or $[Pb(AlCl_4)_2(\eta\text{-}C_6H_6)]\cdot C_6H_6$.[14] Also omitted are complexes having $PbPh_3^-$ as a ligand, *e.g.* *cis*-$[Pt(PbPh_3)(Ph)(PPh_3)_2]$,[15] or four-co-ordinate Pb^{II} complexes such as $[Pb\{C_6H_4(CH_2NMe_2)\text{-}o\}_2]$.[16]

We now report the synthesis of three new bis(metallo)plumbylenes (plumbanediyls) $[Pb\{Mo(R)(CO)_3\}_2]$ [$R = \eta\text{-}C_5Me_5$, $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$, or $\eta\text{-}C_5H_5$], which were isolated as stable 1:1 adducts with tetrahydrofuran (thf), (**1a**)—(**1c**), or as the free monomers (**2a**)—(**2c**). We also provide *X*-ray data on two $\eta\text{-}C_5Me_5$ complexes: the thf adduct (**1a**) and the remarkable 'isocarbonyl'-bridged dimer $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ (**3**). *X*-Ray authenticated two- or three-co-ordinate Pb^{II} compounds are rare; they have the formula $PbX_2[\{Pb(\mu\text{-}X)Y\}_2]$, PbX_2L, or [{Pb-

$(SR')_2\}_3]$ (X^-, Y^-, L, or L^- represent two-electron donors), and some key parameters are summarised in Table 1 (from refs. 17—24, and the present work). Compounds relevant to this study, but not crystallographically characterised, are $[NEt_4]_2[Pb\{Fe(CO)_4\}_2]$,[25] $[\overline{Sn\{M(\eta\text{-}C_5H_5)(CO)_3\}\{(P}R'_2)_2CX\}]$ (M, X, R' = W, Ph, PPh_2; or Mo, Me, $SiMe_3$),[26] and the transient compounds $[GeX\{Co(CO)_4\}]$ [X = F or $Co(CO)_4$].[27]

Results

Synthetic Chemistry.—The reaction of a Group 14 metal amide with a transition-metal hydride is an easy and straightforward method of making a metal–metal bond-containing substance, with only the volatile amine as the by-product.[28] We have used this route to synthesise compounds (**1**)—(**3**), Scheme. In tetrahydrofuran (thf), the reaction of the lead(II) amide $Pb[N(SiMe_3)_2]_2$[29] and two equivalents of the appropriate molybdenum hydride $[Mo(R)(CO)_3H]$ [R = η-C_5Me_5, η-$C_5H_3(SiMe_3)_2$-1,3, or η-C_5H_5] produced the green, crystalline, three-co-ordinate Pb^{II} complexes $[Pb\{Mo(R)(CO)_3\}_2(thf)]$ (**1a**)—(**1c**) respectively. The thf was found not to be tightly bound to the Pb atom in complexes (**1a**)—(**1c**), and was removed *in vacuo* [10^{-2} Torr; at 25 °C, (**1b**) or (**1c**), or 40 °C, (**1a**)] to yield the appropriate brown monomers $[Pb\{Mo(R)(CO)_3\}_2]$ (**2a**)—(**2c**) respectively. Alternatively, $[Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_3\}_2]$ (**2b**) was obtained from the reaction of $Pb[N(SiMe_3)_2]_2$ and $[Mo\{\eta\text{-}C_5H_3(SiMe_3)_2\}(CO)_3H]$ in n-C_5H_{12}.

The unsubstituted cyclopentadienyl compounds (**1c**) and (**2c**) were found to be unstable at ambient temperature both in the solid state and in solution, decomposing within 1 d to give lead and $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (**4c**), equation (1). The more

$$(\mathbf{1c})\text{ or }(\mathbf{2a})\text{—}(\mathbf{2c}) \longrightarrow Pb + [\{Mo(R)(CO)_3\}_2] \qquad (1)$$

(**4a**) R = η-C_5Me_5
(**4b**) R = η-$C_5H_3(SiMe_3)_2$
(**4c**) R = η-C_5H_5

sterically hindered pentamethylcyclopentadienyl complex (**1a**) was noticeably more stable, both in solution and in the solid; however, toluene solutions of (**2a**) decomposed slowly (3—4 d) at *ca.* 25 °C in a similar fashion. In contrast, the bis(trimethylsilyl)cyclopentadienyl complexes (**1b**) and (**2b**) were indefinitely stable at 25 °C, and only decomposed in the solid state above 130 °C. Thus, it appears that steric effects fall in the sequence η-$C_5H_3(SiMe_3)_2$ > η-C_5Me_5 > η-C_5H_5, as has previously been shown for the case of $[\{U(R)_2(\mu\text{-}Cl)\}_n]$ [$n = 2$ for R = η-$C_5H_3(SiMe_3)_2$, but $n = 3$ for R = η-C_5Me_5].[30]

The ease of elimination of the lead atom from complexes (**1a**) or (**2a**) is also evident from their electron-impact mass spectra, which showed identical fragmentation patterns to that for $[\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2]$ (**4a**). In contrast, the mass spectrum of (**2b**) showed $[P - 2CO]^+$ (P^+ = parent ion) as the highest *m/e* peak. It had previously been observed that some tetravalent lead complexes $[Pb(M'L_n)Me_3]$ [$M'L_n$ = $Fe(\eta\text{-}C_5H_5)(CO)_2$ or $M''(\eta\text{-}C_5H_5)(CO)_3$ (M'' = Cr, Mo, or W)] decomposed thermally to yield Pb, $PbMe_4$, and $[(M'L_n)_2]$.[31]

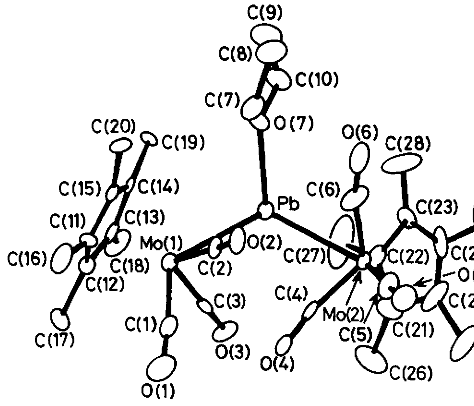


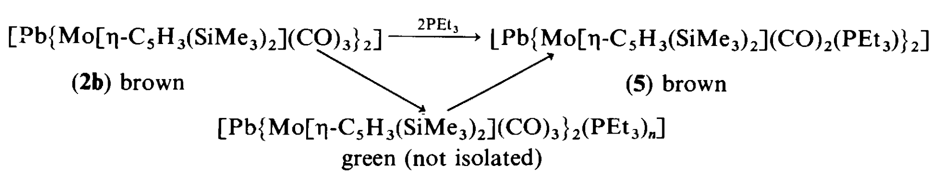
Figure 1. The molecular structure of $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2(thf)]$ (**1a**), showing the atom-numbering scheme

It appears that solvated Pb^{II} complexes $[Pb\{Mo(R)(CO)_3\}_2(L)_n]$ are green, and not only for L_n = thf. Thus, addition of acetone or PEt_3 to the brown solid, or solution, of (**2a**) or (**2b**) produced an instant green colour. In the case of PEt_3 addition to (**2b**), a further rapid (*ca.* 15 s at 25 °C) colour change took place, giving the phosphine-substituted metal complex (**5**), equation (2). The latter was also unstable, and decomposed to give lead and $[\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_2(PEt_3)\}_2]$. Addition of other Lewis bases NEt_2H, OEt_2, or $Me_2N(CH_2)_2NMe_2$ produced only very slight colour changes, and hence it is inferred that weak or no complexation had taken place. This is further demonstrated by the observation that dropwise addition of thf to brown hydrocarbon solutions containing (**2a**) or (**2b**) and $NHEt_2$ or OEt_2 caused immediate formation of the appropriate green thf adduct (**1a**) or (**1b**).

When the reaction of $Pb[N(SiMe_3)_2]_2$ and $[Mo(\eta\text{-}C_5Me_5)(CO)_3H]$ was carried out in a 1:1 mixture of n-C_5H_{12}–n-C_6H_{14}, complex (**2a**) was not obtained, but instead a green precipitate (81%) of the dimeric compound (**3**). The latter showed a different solid-state i.r. spectrum from that of (**2a**); however, in toluene solution the i.r. spectra of (**2b**) and (**3**) were identical. The thf adduct (**1a**) was isolated from a thf solution of compound (**3**). In order to learn more about the structure of these new bivalent lead compounds, single-crystal *X*-ray data were obtained on the green pentamethylcyclopentadienyl complexes (**1a**) and (**3**).

Structural Commentary.—(*a*) $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2(thf)]$ (**1a**). Molecules of (**1a**) crystallised in the space group $P2_1/c$ without molecular symmetry. The molecular structure is illustrated in Figure 1. The lead atom is pyramidal and occupies the centre of a trigonal pyramid, as expected for a compound containing a three-co-ordinate lead(II) atom and a stereochemically active lone pair of electrons. The two independent Mo–Pb distances are 2.989(2) and 3.019(2) Å and the Mo–Pb–Mo angle is 118.33(5)°. The lead–oxygen distance is 2.75(2) Å, and the angle formed by the Pb–O bond and the bisector of the Mo–Pb–Mo angle is 102°. The six independent Mo–CO distances range from 1.86(2) to 1.99(2) Å. The planes of the two pentamethylcyclopentadienyl rings intersect at an angle of 114°. Other bond distances and angles are unexceptional, Table 2.

(*b*) $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ (**3**). This dimeric complex crystallised in the space group $P\bar{1}$, with a centre of symmetry relating the two lead



$$[Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_3\}_2] \xrightarrow{2PEt_3} [Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_2(PEt_3)\}_2] \qquad (2)$$

(**2b**) brown

(**5**) brown

$$[Pb\{Mo[\eta\text{-}C_5H_3(SiMe_3)_2](CO)_3\}_2(PEt_3)_n]$$

green (not isolated)

Table 2. Intramolecular distances (Å) and angles (°) for $[Pb\{Mo(\eta\text{-}C_5Me_5)(CO)_3\}_2(thf)]$ (**1a**), with estimated standard deviations in parentheses [Cp(1) and Cp(2) are the centroids of the pentamethylcyclopentadienyl rings C(11)—C(15) and C(21)—C(25), respectively]

Pb–Mo(1)	2.989(2)	Pb–Mo(2)	3.019(2)	C(11)–C(12)	1.47(3)	C(11)–C(15)	1.36(3)
Pb–O(7)	2.75(2)	Mo(1)–C(1)	1.86(2)	C(11)–C(16)	1.55(3)	C(12)–C(13)	1.38(3)
Mo(1)–C(2)	1.95(2)	Mo(1)–C(3)	1.96(2)	C(12)–C(17)	1.56(3)	C(13)–C(14)	1.47(3)
Mo(1)–Cp(1)	2.02	Mo(2)–C(4)	1.99(2)	C(13)–C(18)	1.54(3)	C(14)–C(15)	1.46(3)
Mo(2)–C(5)	1.97(2)	Mo(2)–C(6)	1.92(2)	C(14)–C(19)	1.49(3)	C(15)–C(20)	1.61(3)
Mo(2)–Cp(2)	2.02	O(1)–C(1)	1.22(3)	C(21)–C(22)	1.45(4)	C(21)–C(25)	1.49(4)
O(2)–C(2)	1.15(2)	O(3)–C(3)	1.13(2)	C(21)–C(26)	1.51(4)	C(22)–C(23)	1.40(3)
O(4)–C(4)	1.14(3)	O(5)–C(5)	1.10(3)	C(22)–C(27)	1.53(3)	C(23)–C(24)	1.36(3)
O(6)–C(6)	1.22(3)	O(7)–C(7)	1.50(3)	C(23)–C(28)	1.47(4)	C(24)–C(25)	1.35(3)
O(7)–C(10)	1.42(3)	C(7)–C(8)	1.50(4)	C(24)–C(29)	1.50(4)	C(25)–C(30)	1.60(4)
C(8)–C(9)	1.43(4)	C(9)–C(10)	1.49(4)				

Mo(1)–Pb–Mo(2)	118.33(5)	Mo(1)–Pb–O(7)	98.0(3)	C(8)–C(9)–C(10)	111(3)	O(7)–C(10)–C(9)	97(2)
Mo(2)–Pb–O(7)	105.5(3)	Pb–Mo(1)–C(1)	121.9(7)	C(12)–C(11)–C(15)	108(2)	C(12)–C(11)–C(16)	129(2)
Pb–Mo(1)–C(2)	67.3(6)	Pb–Mo(1)–C(3)	69.2(5)	C(15)–C(11)–C(16)	123(2)	C(11)–C(12)–C(13)	107(2)
Pb–Mo(1)–Cp(1)	117.0	C(1)–Mo(1)–C(2)	80.3(9)	C(11)–C(12)–C(17)	121(2)	C(13)–C(12)–C(17)	131(2)
C(1)–Mo(1)–C(3)	77.2(9)	C(1)–Mo(1)–Cp(1)	121.0	C(12)–C(13)–C(14)	110(2)	C(12)–C(13)–C(18)	124(2)
C(2)–Mo(1)–C(3)	107.5(8)	C(2)–Mo(1)–Cp(1)	127.5	C(14)–C(13)–C(18)	125(2)	C(13)–C(14)–C(15)	103(2)
C(3)–Mo(1)–Cp(1)	123.2	Pb–Mo(2)–C(4)	73.9(5)	C(13)–C(14)–C(19)	123(2)	C(15)–C(14)–C(19)	132(2)
Pb–Mo(2)–C(5)	132.3(7)	Pb–Mo(2)–C(6)	71.7(7)	C(11)–C(15)–C(14)	111(2)	C(11)–C(15)–C(20)	131(2)
Pb–Mo(2)–Cp(2)	108.7	C(4)–Mo(2)–C(5)	79.0(8)	C(14)–C(15)–C(20)	118(2)	C(22)–C(21)–C(25)	103(2)
C(4)–Mo(2)–C(6)	108(1)	C(4)–Mo(2)–Cp(2)	127.8	C(22)–C(21)–C(26)	124(3)	C(25)–C(21)–C(26)	131(3)
C(5)–Mo(2)–C(6)	81(1)	C(5)–Mo(2)–Cp(2)	118.9	C(21)–C(22)–C(23)	108(2)	C(21)–C(22)–C(27)	130(2)
C(6)–Mo(2)–Cp(2)	122.3	Pb–O(7)–C(7)	136(1)	C(23)–C(22)–C(27)	121(2)	C(22)–C(23)–C(24)	109(2)
Pb–O(7)–C(10)	107(1)	C(7)–O(7)–C(10)	114(2)	C(22)–C(23)–C(28)	122(2)	C(24)–C(23)–C(28)	129(2)
Mo(1)–C(1)–O(1)	172(2)	Mo(1)–C(2)–O(2)	173(2)	C(23)–C(24)–C(25)	111(2)	C(23)–C(24)–C(29)	132(2)
Mo(1)–C(3)–O(3)	179(2)	Mo(2)–C(4)–O(4)	170(2)	C(25)–C(24)–C(29)	117(2)	C(21)–C(25)–C(24)	109(2)
Mo(2)–C(5)–O(5)	176(2)	Mo(2)–C(6)–O(6)	167(2)	C(21)–C(25)–C(30)	119(2)	C(24)–C(25)–C(30)	133(2)
O(7)–C(7)–C(8)	102(2)	C(7)–C(8)–C(9)	103(2)				

Table 3. Intramolecular distances (Å) and angles (°) for $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ (**3**), with estimated standard deviations in parentheses [Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings C(7)—C(11) and C(17)—C(21), respectively]

Pb–Mo(1)	2.935(1)	Pb–Mo(2)	2.989(1)	C(7)–C(8)	1.48(2)	C(7)–C(11)	1.38(2)
Mo(1)–C(1)	1.947(11)	Mo(1)–C(2)	2.000(9)	C(7)–C(12)	1.50(2)	C(8)–C(9)	1.364(13)
Mo(1)–C(3)	1.949(8)	Mo(1)–C(7)	2.289(11)	C(8)–C(13)	1.51(2)	C(9)–C(10)	1.40(2)
Mo(1)–C(8)	2.316(10)	Mo(1)–C(9)	2.351(10)	C(9)–C(14)	1.524(15)	C(10)–C(11)	1.356(13)
Mo(1)–C(10)	2.400(12)	Mo(1)–C(11)	2.368(12)	C(10)–C(15)	1.50(2)	C(11)–C(16)	1.51(2)
Mo(2)–C(4)	1.966(9)	Mo(2)–C(5)	1.937(10)	C(17)–C(18)	1.421(13)	C(17)–C(21)	1.424(12)
Mo(2)–C(6)	1.942(8)	Mo(2)–C(17)	2.367(7)	C(17)–C(22)	1.514(13)	C(18)–C(19)	1.437(14)
Mo(2)–C(18)	2.371(8)	Mo(2)–C(19)	2.333(9)	C(18)–C(23)	1.517(14)	C(19)–C(20)	1.41(2)
Mo(2)–C(20)	2.330(7)	Mo(2)–C(21)	2.354(8)	C(19)–C(24)	1.55(2)	C(20)–C(21)	1.423(14)
O(1)–C(1)	1.142(14)	O(2)–C(2)	1.149(11)	C(20)–C(25)	1.52(2)	C(21)–C(26)	1.49(2)
O(3)–C(3)	1.159(10)	O(4)–C(4)	1.159(11)	C(27)–C(28)	1.28(4)	C(27)–C(29)	1.50(4)
O(5)–C(5)	1.144(12)	O(6)–C(6)	1.158(11)	C(28)–C(29)	1.53(4)	Mo(1)–Cp(1)	2.02
				Mo(2)–Cp(2)	2.01		

Mo(1)–Pb–Mo(2)	120.71(2)	Cp(1)–Mo(1)–Pb	112.9	C(7)–C(8)–C(9)	105(1)	C(7)–C(8)–C(13)	128.6(9)
Cp(1)–Mo(1)–C(1)	120.4	Cp(1)–Mo(1)–C(2)	126.2(3)	C(9)–C(8)–C(13)	126(1)	C(8)–C(9)–C(10)	109.7(8)
Cp(1)–Mo(1)–C(3)	125.9	Pb–Mo(1)–C(1)	126.7(3)	C(8)–C(9)–C(14)	124(1)	C(10)–C(9)–C(14)	126(1)
Pb–Mo(1)–C(2)	70.4(2)	Pb–Mo(1)–C(3)	70.3(3)	C(9)–C(10)–C(11)	108.8(9)	C(9)–C(10)–C(15)	122(1)
C(1)–Mo(1)–C(2)	79.4(4)	C(1)–Mo(1)–C(3)	77.8(4)	C(11)–C(10)–C(15)	129(1)	C(7)–C(11)–C(10)	109(1)
C(2)–Mo(1)–C(3)	106.3(4)	Cp(2)–Mo(2)–Pb	108.4	C(7)–C(11)–C(16)	128(1)	C(10)–C(11)–C(16)	123(1)
Cp(2)–Mo(2)–C(4)	126.7	Cp(2)–Mo(2)–C(5)	117.8	C(18)–C(17)–C(21)	108.9(8)	C(18)–C(17)–C(22)	124.9(8)
Cp(2)–Mo(2)–C(6)	127.8	Pb–Mo(2)–C(4)	74.3(3)	C(21)–C(17)–C(22)	125.9(9)	C(17)–C(18)–C(19)	106.5(8)
Pb–Mo(2)–C(5)	133.9(3)	Pb–Mo(2)–C(6)	70.9(3)	C(17)–C(18)–C(23)	125.4(9)	C(19)–C(18)–C(23)	127(1)
C(4)–Mo(2)–C(5)	78.6(4)	C(4)–Mo(2)–C(6)	103.9(3)	C(18)–C(19)–C(20)	109.1(9)	C(18)–C(19)–C(24)	123(1)
C(5)–Mo(2)–C(6)	80.5(4)	Mo(1)–C(1)–O(1)	180(1)	C(20)–C(19)–C(24)	128.0(9)	C(19)–C(20)–C(21)	107.6(8)
Mo(1)–C(2)–O(2)	172.5(8)	Mo(1)–C(3)–O(3)	171.1(8)	C(19)–C(20)–C(25)	126(1)	C(21)–C(20)–C(25)	126(1)
Mo(2)–C(4)–O(4)	172.2(7)	Mo(2)–C(5)–O(5)	177(1)	C(17)–C(21)–C(20)	107.9(8)	C(17)–C(21)–C(26)	126.2(9)
Mo(2)–C(6)–O(6)	173.2(8)	C(8)–C(7)–C(11)	106.9(8)	C(20)–C(21)–C(26)	125.6(9)		
C(8)–C(7)–C(12)	126(1)	C(11)–C(7)–C(12)	126(1)				

atoms. The molecular structure is shown in Figure 2. The dimer consists of two $Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3]_2$ units joined by two bridging 'isocarbonyl' groups, *i.e.* one CO group from each moiety is joined to the other by an O–Pb linkage. Each lead atom has trigonal pyramidal co-ordination, being attached to two molybdenum atoms and the isocarbonyl oxygen atom; the Pb^{II} lone pair of electrons may again be assumed to be stereochemically active. The two independent Mo–Pb distances are 2.935(1) and 2.989(1) Å and the Mo–Pb–Mo angle is 120.71(2)°. The Pb–μ-OC bond length is 2.918(8) Å. The μ-C–O

Table 4. Selected i.r. data [ν(CO)/cm^{-1}] for [Pb{Mo(R)(CO)$_3$}$_2$] complexes

Complex	
(**1a**) [Pb{Mo(η-C_5Me_5)(CO)$_3$}$_2$(thf)]	1 969s, 1 935s, 1 877s, 1 875s, 1 862s, 1 846s^{a}
	1 974s, 1 940s, 1 902(sh), 1 898s, 1 860s, 1 845s^{b}
(**1b**) [Pb{Mo[η-$C_5H_3(SiMe_3)_2$](CO)$_3$}$_2$(thf)]	1 972s, 1 945s, 1 890s, 1 878s, 1 860s^{b}
(**1c**) [Pb{Mo(η-C_5H_5)(CO)$_3$}$_2$(thf)]	1 981s, 1 950br, 1 915s, 1 870br^{a}
(**2a**) [Pb{Mo(η-C_5Me_5)(CO)$_3$}$_2$]	1 989s, 1 951s, 1 908s, 1 867br, 1 855(sh)^{c}
	1 974s, 1 940s, 1 898s, 1 860s, 1 846s^{b}
(**2b**) [Pb{Mo[η-$C_5H_3(SiMe_3)_2$](CO)$_3$}$_2$]	1 979s, 1 947s, 1 908br, 1 880s^{b}
	1 989s, 1 950s, 1 901s, 1 865br^{d}
(**3**) [{Pb[Mo(η-C_5Me_5)(CO)$_3$][Mo(η-C_5Me_5)(CO)$_2$(μ-CO)]}$_2$]	1 972s, 1 939s, 1 901s, 1 889s, 1 861s, 1 819s^{b,e}
	1 970s, 1 931s, 1 885s, 1 849s, 1 821s^{b,f}

^{a} In thf solution. ^{b} In Nujol. ^{c} In toluene solution. ^{d} In C_6H_6 solution. ^{e} Powder. ^{f} Crystals.

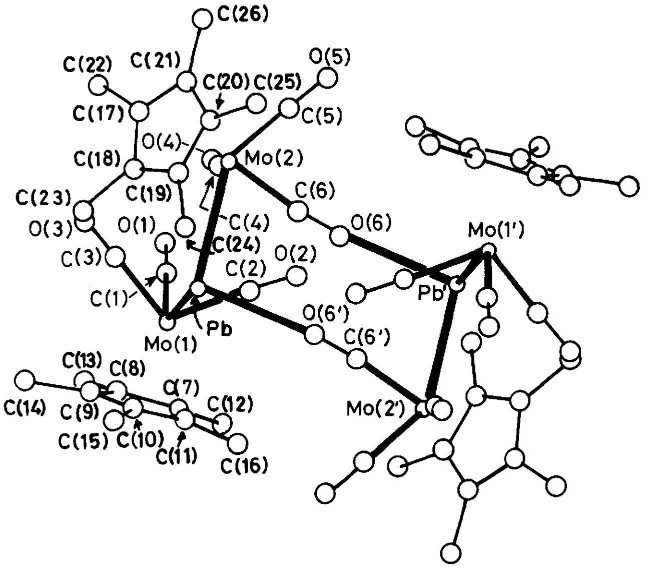


Figure 2. The molecular structure of [{Pb[Mo(η-C_5Me_5)(CO)$_3$][Mo(η-C_5Me_5)(CO)$_2$(μ-CO)]}$_2$] (**3**), showing the atom numbering scheme (primed atoms correspond to $\bar{x}$, $1 - \bar{y}$, $\bar{z}$)

bond at 1.158(11) Å is within the range seen for the five terminal carbonyls, 1.142(14)—1.159(11) Å. The six Mo–CO distances fall between 1.937(10) and 2.000(9) Å. The planes of the two pentamethylcyclopentadienyl rings within each Pb[Mo(η-C_5Me_5)(CO)$_3$]$_2$ unit intersect at an angle of 76°. Bond lengths and angles are shown in Table 3.

Discussion

The molecular structure of [Pb{Mo(η-C_5Me_5)(CO)$_3$}$_2$(thf)] (**1a**) is appropriate for a three-co-ordinate lead(II) complex containing a stereochemically active Pb-centred lone pair of electrons. Other examples of such trigonal-pyramidal co-ordination for Pb^{II} include the anions [Pb(EPh)$_3$]$^-$ (E = S or Se),[19] [Pb(PBu$^t_2$)(μ-PBu$^t_2$)$_2$Li(thf)],[20] [{Pb[μ-SC(SiMe$_3$)$_3$][N(SiMe$_3$)$_2$]}$_2$],[21] [{Pb[μ-SSi(OBu^t)$_3$][SSi(OBu^t)$_3$]}$_2$],[22] [Pb{CH(PPh$_2$)$_2$}{(PPh$_2$)$_2$CH}] (in which one of the formally identical ligands is C- and the other P$_2$-centred; in solution there is fluxionality[32]),[23] and the terminal Pb atoms in [Pb(SR′)(μ-SR′)$_2$Pb(μ-SR′)$_2$Pb(SR′)] (R′ = $C_6H_3Pr^i_2$-2,6);[24] relevant *X*-ray data are in Table 1. The ability of Pb^{II} in compounds (**1**) to co-ordinate a 'hard' donor, *i.e.* the oxygen atom of thf, is surprising. Nevertheless, Lewis-base adducts of Ge^{II} and Sn^{II} are known, *e.g.* GeCl$_2$(diox) (diox = 1,4-dioxane)[3] or the labile Sn[CH(SiMe$_3$)$_2$]$_2$(NC$_5$H$_5$),[33] but, to the best of our knowledge, such adducts of lead(II) compounds have not previously been isolated.

Trigonal-pyramidal geometry around lead is also featured in the structure of [{Pb[Mo(η-C_5Me_5)(CO)$_3$][Mo(η-C_5Me_5)(CO)$_2$(μ-CO)]}$_2$] (**3**). However, there is slight distortion compared with (**1a**), due to the requirements of a bound isocarbonyl group in (**3**) compared with the independent thf ligand in (**1a**). The Pb–O distances in (**3**) [2.918(8) Å] or (**1a**) [2.75(2) Å] are significantly longer than the Pb–O bonds in the two-co-ordinate Pb^{II} complex Pb(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$ [2.13(1), 2.15(1) Å].[18] Thus a weak lead–oxygen bond is implied in both (**1a**) and, especially, (**3**).

The ability of a carbonyl oxygen to function as a Lewis base (*i.e.* to behave as an isocarbonyl, σ-CO bonding)[34] towards a lead(II) acceptor atom is unprecedented. Many structurally authenticated examples of this type of isocarbonyl co-ordination with hard acceptors (M) are, however, known, *e.g.* with Al^{III},[34] La^{III}, Mg^{II}, Mn^{II}, Yb^{III}, or Zr^{IV}.[35] In all of these complexes, the isocarbonyl ν(CO) was at low energy, in the range 1 600—1 700 cm^{-1}. The isocarbonyl C–O bond was usually elongated and the M′–COM bond shortened relative to the corresponding free terminal M′–CO bonds, which may be attributed to the significance of the canonical form $\overset{+}{M'}\text{–C=O–}\overset{-}{M}$. Thus, typical ranges for the former are 1.189—1.25 Å compared with 1.14—1.16 Å for a terminal carbonyl M′C–O. In complex (**3**), however, the isocarbonyl MoC–OPb length of 1.158(11) Å is not significantly longer than the mean of the five terminal C–O distances, 1.142(14)—1.159(11) Å. Likewise, the Mo–COPb bond, 1.942(8) Å, is not unusually short compared with the other Mo–CO bonds, 1.937(10)—2.000(9) Å. This absence of any pronounced distortion of the Mo–C and C–O isocarbonyl, compared with carbonyl, bonds implies that the O–Pb bonding derives primarily from donation from the isocarbonyl lone pair of electrons on oxygen and does not significantly involve the carbonyl π electrons. This view is consistent with the i.r. spectrum of complex (**3**), which shows the isocarbonyl ν(CO) at 1 819 cm^{-1}, Table 4.

The brown solution of complex (**3**) in toluene or benzene showed no i.r. isocarbonyl ν(CO) absorbance at 1 819 cm^{-1}. We believe that in such a solution, (**3**) exists primarily as the monomer [Pb{Mo(η-C_5Me_5)(CO)$_3$}$_2$] (**2a**). Although solution molecular weight determination of (**2a**) in benzene met with failure due to its instability [see equation (1)], the ^{13}C-{^{1}H} n.m.r. spectrum at 38 °C showed the presence of one signal for each of the two types of cyclopentadienyl carbons and only one carbonyl resonance, at 221.9 p.p.m. When the temperature was lowered to -60 °C, the latter signal split into two peaks, at 222.1 and 227.8 p.p.m., in the ratio of 2:1 (Figure 3). We attribute this to a frozen, static conformation about the molybdenum in which one CO is *trans* and two are *cis* to Pb. There was no evidence for any noticeable equilibrium

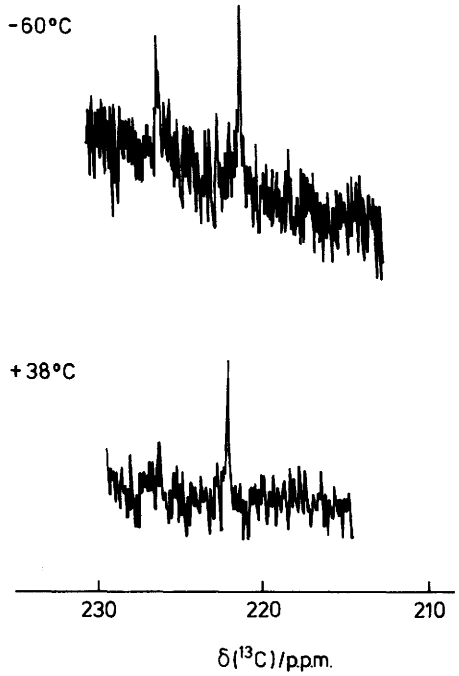


Figure 3. Variable-temperature ^{13}C n.m.r. spectrum of [{Pb[Mo(η-C_5Me_5)$(CO)_3$][Mo(η-C_5Me_5)$(CO)_2$(μ-CO)]}$_2$] (3) in $C_6D_5CD_3$, showing the carbonyl region

concentration of (3) in the solution of (**2a**), although its presence is inferred because (3) was obtained by recrystallisation of solutions of (**2a**). We have no explanation to offer for the existence of (3) in the solid state but of (**2a**) in solution in an inert solvent. However, we do not consider that the formation of the green complex (3) is due to any inherent instability of the brown complex (**2a**) in the solid state, since the brown powder obtained by removal of thf (*in vacuo*) from the green [Pb{Mo(η-C_5Me_5)$(CO)_3$}$_2$(thf)] (**1a**) is believed to be (**2a**), and showed no sign of decomposition to lead and [{Mo(η-C_5Me_5)$(CO)_3$}$_2$] at ambient temperature.

The more sterically hindered [Pb{Mo[η-$C_5H_3(SiMe_3)_2$]-$(CO)_3$}$_2$] (**2b**) was not only stable at 25 °C but also showed no evidence of isocarbonyl bridging, either in solution or in the solid state. Solution molecular weight determination (30 °C, C_6H_6; Signer method) indicated that (**2b**) is probably monomeric in benzene solution. The lack of any bridged dimer for the η-$C_5H_3(SiMe_3)_2$ complex may be related to the observation that thf is more tightly bound in the η-C_5Me_5 complex (**1a**) than in the η-$C_5H_3(SiMe_3)_2$ analogue (**1b**); both results may be related to the greater steric bulk of η-$C_5H_3(SiMe_3)_2$ than η-C_5Me_5.

It is useful to compare the *X*-ray structures of the $PbMo_2$ complexes (**1a**) and (3) with the known [Pb{Mn(η-C_5H_5)-$(CO)_2$}$_2$] [(**I**); M = Pb, $M'L_n$ = Mn(η-C_5H_5)$(CO)_2$].[8] In the latter, the manganese atoms are disposed about the lead in a linear fashion, Mn-Pb-Mn 177.2(1)°, and there was evidence for double- and possibly even triple-bonding between the Mn and Pb. For each of (**1a**) and (3), the Mo-Pb-Mo angles are near 120° and there is no need to invoke multiple bonding between Mo and Pb, since the molybdenum atoms achieve an 18-electron count on the basis of forming single bonds to lead. For a two-co-ordinate $Pb^{II}(Mo^0)_2$ complex, we calculate a Pb^{II}–Mo^0 single bond length of 3.09 Å, using known Pb^{IV}–O,[36] Pb^{II}–O,[18] and Pb^{IV}–Mo^0[37] distances. This is slightly higher than the value of the Pb^{II}–Mo^0 lengths (2.98 ± 0.05) in the three-co-ordinate $Pb^{II}(Mo^0)_2L$ complexes (**1a**) or (3).

Experimental

All the manipulative operations were carried out as described in previous Parts.[3] Proton n.m.r. spectra were recorded on a Bruker WP-FT80 spectrometer and carbon-13 spectra using a Bruker WM-360 FT instrument, both at *ca.* 305 K unless otherwise stated. Analyses were carried out by Miss K. Plowman (University of Sussex) or by Elemental Microanalysis Ltd., Beaworthy, Devon.

The lead amide $Pb[N(SiMe_3)_2]_2$ was synthesised as previously reported.[29] The molybdenum hydrides [Mo{η-$C_5H_3(SiMe_3)_2$}$(CO)_3$H] and [Mo(η-C_5Me_5)$(CO)_3$H] were prepared using the procedure described for [Mo(η-C_5H_5)$(CO)_3$H],[38] but replacing Na(η-C_5H_5) by Li[η-$C_5H_3(SiMe_3)_2$](OEt_2) or Li(η-C_5Me_5); an alternative preparation for [Mo(η-C_5Me_5)$(CO)_3$H] is also available.[39]

Preparation of [Pb{Mo(η-C_5Me_5)$(CO)_3$}$_2$(thf)] (**1a**).—Tricarbonylhydrido(η-pentamethylcyclopentadienyl)molybdenum (1.31 g, 4.12 mmol) was dissolved in thf (7 cm^3) and added to a cooled (0 °C) thf solution (18 cm^3) of $Pb[N(SiMe_3)_2]_2$ (1.09 g, 2.06 mmol). Formation of an immediate green colour was observed. The resulting dark green mixture was stirred for 1 h at 0 °C and slowly warmed to 25 °C during 1 h. The volatiles were removed *in vacuo*, leaving a green-brown solid which became brown when warmed to 40 °C under vacuum. The green colour was regenerated by the addition of fresh thf–n-C_5H_{12} (10:3) to the solid. Cooling this solution to −30 °C afforded the dark green, air-sensitive *compound* (**1a**) (0.92 g, 53%) (Found: C, 39.4; H, 4.45. $C_{30}H_{38}Mo_2O_7Pb$ requires C, 39.6; H, 4.20%), m.p. *ca.* 300 °C (decomp.); ^1H n.m.r. (C_4D_8O): δ 2.04.

Preparation of [{Pb[Mo(η-C_5Me_5)$(CO)_3$][Mo(η-C_5Me_5)-$(CO)_2$(μ-CO)]}$_2$] (3) *and* [Pb{Mo(η-C_5Me_5)$(CO)_3$}$_2$] (**2a**).—A solution of tricarbonylhydrido(η-pentamethylcyclopentadienyl)molybdenum (0.74 g, 2.34 mmol) in n-C_6H_{12}–n-C_6H_{14} (1:1, 10 cm^3) was added to a cooled (0 °C) solution of $Pb[N(SiMe_3)_2]_2$ (0.60 g, 1.14 mmol) in n-C_5H_{12}–n-C_6H_{14} (12 cm^3). A green precipitate formed during the addition. The reaction mixture was warmed to 25 °C over a period of 2.5 h, and filtered. The isolated green solid was washed twice with small (5 cm^3) portions of n-C_5H_{12} and dried *in vacuo* to give the air-sensitive, green powder of *complex* (3) (0.77 g, 81%) (Found: C, 36.9; H, 3.85. $C_{26}H_{30}Mo_2O_6Pb$ requires C, 37.3; H, 3.60%), m.p. *ca.* 137 °C (decomp.).

The monomer (**2a**) was obtained by dissolving complex (3) in either toluene or benzene. However, solutions of (**2a**) [n.m.r.: ^1H (C_6D_6), δ 1.79; ^{13}C-{^1H} ($C_6D_5CD_3$), δ 10.01 (Me), 105.07 (C_5Me_5), 221.85 (CO)] readily decomposed to lead and [{Mo(η-C_5Me_5)$(CO)_3$}$_2$] (**4a**) (Found: C, 49.0; H, 5.00. $C_{26}H_{30}Mo_2O_6$ requires C, 49.5; H, 4.80%); ν(CO) (C_6D_6) at 1 941s and 1 909s cm^{-1}; ^1H n.m.r. (C_6D_6): δ 1.77.

Preparation of [Pb{Mo[η-$C_5H_3(SiMe_3)_2$]$(CO)_3$}$_2$(thf)] (**1b**) *and* [Pb{Mo[η-$C_5H_3(SiMe_3)_2$]$(CO)_3$}$_2$] (**2b**).—The molybdenum hydride [Mo{η-$C_5H_3(SiMe_3)_2$}$(CO)_3$H] (1.65 g, 4.23 mmol) was dissolved in thf (11 cm^3) and slowly added to a cooled (0 °C) solution of $Pb[N(SiMe_3)_2]_2$ (1.10 g, 2.08 mmol) in thf (8 cm^3). An immediate green colour was produced. The reaction was stirred for 1 h and the volatiles removed *in vacuo*, leaving a brown solid. Addition of fresh thf regenerated the green colour. Cooling to −30 °C gave moist, air-sensitive, brown needles of *complex* (**1b**) (0.7 g, 34%); ^1H n.m.r. (C_4D_8O): δ 0.15 (s, 18 H, $SiMe_3$), 5.05 [d, 2 H, $^4J(^1H^1H)$ 1.6 Hz], 5.73 [t, 1 H, $^4J(^1H^1H)$ 1.6 Hz].

Recrystallisation from toluene–n-C_5H_{12} afforded brown needles of the *complex* (**2b**) (0.28 g, 14%) (Found: C, 34.0; H, 4.40. $C_{28}H_{42}Mo_2O_4PbSi_2$ requires C, 34.1; H, 4.30%); ^1H n.m.r.

Table 5. Fractional atomic co-ordinates (× 10^4 for Pb, Mo; × 10^3 for C, O) for the non-hydrogen atoms of [Pb{Mo(η-C_5Me_5)$(CO)_3$}$_2$(thf)] (**1a**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pb	1 656.4(7)	2 843.3(5)	8 671.1(4)
Mo(1)	−759.5(14)	3 395.1(11)	8 648.2(9)
Mo(2)	2 748.8(15)	1 983.8(11)	10 046.9(9)
O(1)	−232(2)	298(1)	986(1)
O(2)	64(1)	420(1)	1 000(1)
O(3)	−57(1)	137(1)	868(1)
O(4)	21(1)	204(1)	1 034(1)
O(5)	290(2)	249(1)	1 168(1)
O(6)	392(1)	381(1)	1 001(1)
O(7)	261(1)	449(1)	863(1)
C(1)	−165(2)	309(1)	939(1)
C(2)	17(2)	386(1)	950(1)
C(3)	−63(1)	211(1)	868(1)
C(4)	112(2)	207(1)	1 019(1)
C(5)	281(2)	231(2)	1 110(1)
C(6)	335(3)	315(1)	999(1)
C(7)	262(2)	530(1)	911(1)
C(8)	365(3)	577(2)	890(2)
C(9)	383(3)	538(2)	821(2)
C(10)	354(2)	443(2)	820(1)
C(11)	−199(1)	447(1)	815(1)
C(12)	−228(2)	364(1)	776(1)
C(13)	−138(2)	341(1)	738(1)
C(14)	−48(2)	408(1)	749(1)
C(15)	−95(2)	472(1)	797(1)
C(16)	−273(2)	504(2)	862(1)
C(17)	−344(2)	318(2)	783(2)
C(18)	−135(2)	261(1)	688(1)
C(19)	50(2)	411(2)	704(1)
C(20)	−25(2)	561(1)	815(1)
C(21)	271(2)	49(1)	979(2)
C(22)	313(2)	90(1)	915(1)
C(23)	414(2)	134(1)	937(1)
C(24)	441(2)	119(1)	1 010(1)
C(25)	364(2)	66(1)	1 037(1)
C(26)	172(3)	−13(2)	976(3)
C(27)	274(3)	79(2)	833(2)
C(28)	478(3)	181(2)	884(2)
C(29)	544(2)	142(2)	1 060(2)
C(30)	355(3)	23(2)	1 117(2)

Table 6. Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms of [{Pb[Mo(η-C_5Me_5)$(CO)_3$][Mo(η-C_5Me_5)$(CO)_2$(μ-CO)]}$_2$] (**3**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pb	2 549.8(3)	4 547.1(2)	1 483.2(2)
Mo(1)	2 658.0(7)	2 280.2(5)	1 415.7(5)
Mo(2)	666.4(7)	5 778.5(5)	2 716.4(5)
O(1)	869(9)	883(6)	2 457(6)
O(2)	−661(7)	2 553(6)	513(6)
O(3)	3 466(9)	3 405(5)	3 666(5)
O(4)	−97(7)	3 470(5)	2 954(5)
O(5)	−2 714(8)	5 671(8)	2 662(8)
O(6)	−599(10)	5 841(6)	502(5)
C(1)	1 529(11)	1 399(7)	2 072(8)
C(2)	572(10)	2 529(7)	862(7)
C(3)	3 151(10)	3 065(6)	2 807(6)
C(4)	226(9)	4 298(7)	2 806(6)
C(5)	−1 458(10)	5 685(8)	2 693(7)
C(6)	−76(10)	5 768(7)	1 309(6)
C(7)	3 099(11)	1 034(9)	121(9)
C(8)	4 119(11)	936(7)	1 051(9)
C(9)	5 080(10)	1 849(8)	1 337(7)
C(10)	4 753(11)	2 486(7)	635(9)
C(11)	3 566(12)	1 989(10)	−91(8)
C(12)	1 961(16)	181(13)	−565(13)
C(13)	4 210(17)	1(10)	1 543(13)
C(14)	6 415(13)	2 061(16)	2 217(11)
C(15)	5 765(14)	3 462(10)	668(13)
C(16)	2 988(18)	2 416(15)	−1 009(10)
C(17)	2 112(9)	6 375(6)	4 365(6)
C(18)	3 088(9)	6 438(7)	3 691(6)
C(19)	2 564(12)	7 190(7)	3 113(7)
C(20)	1 294(11)	7 577(6)	3 430(7)
C(21)	1 013(10)	7 076(6)	4 212(7)
C(22)	2 321(12)	5 752(7)	5 185(7)
C(23)	4 565(11)	5 980(9)	3 742(9)
C(24)	3 426(14)	7 573(10)	2 367(9)
C(25)	503(17)	8 474(8)	3 089(9)
C(26)	−133(13)	7 324(10)	4 824(9)
C(27)	6 325(32)	125(21)	4 618(16)
C(28)	5 366(29)	788(15)	4 699(14)
C(29)	3 846(31)	865(18)	4 990(16)

(C_6D_6): δ 0.161 (s, 18 H, $SiMe_3$)], 4.90 [br, 2 H, $C_5\mathit{H}_3(SiMe_3)_2$]; 5.59 [br, 1 H, $C_5\mathit{H}_3(SiMe_3)_2$]; ^{13}C-{^1H} (C_6D_6–C_6H_6): δ 0.155 ($SiMe_3$), 103.44 [$\mathit{C}_5H_3(SiMe_3)_2$], 104.81 [$\mathit{C}_5H_3(SiMe_3)_2$], 220.89 (CO); mass spectrum: *m/e* 930 (P − 2CO)$^+$, 850, 595 [P − Mo{η-$C_5H_3(SiMe_3)_2$}$(CO)_3H_2$]$^+$.

Attempted Preparation of [Pb{Mo(η-C_5H_5)$(CO)_3$}$_2$] (**2c**).—A solution of [Mo(η-C_5H_5)$(CO)_3$H] (0.71 g, 2.89 mmol), dissolved in thf (9 cm^3), was added to a cooled (0 °C) solution of Pb$[N(SiMe_3)_2]_2$ (0.77 g, 1.46 mmol) in thf (5 cm^3). The experimental details were similar to those described for (**2b**). The brown-black involatile material was recrystallised from thf–n-C_5H_{12} (2:1) at −30 °C, yielding dark green crystals (*ca.* 0.3 g), which decomposed completely to lead and [{Mo(η-C_5H_5)$(CO)_3$}$_2$] after *ca.* 1 d at 25 °C; the latter was identified by comparison with an authentic sample.[38]

Reaction of Complex (**2b**) *with* PEt_3.—Triethylphosphine (0.13 cm^3, 0.88 mmol) was added dropwise with stirring at 25 °C to a solution of complex (**2b**) (0.40 g, 0.41 mmol) in benzene (5 cm^3). An immediate green colour was produced, which changed to brown after *ca.* 15 s. The reaction mixture was stirred for 14 h, whereafter the volatiles were removed *in vacuo*. A mixture of toluene–n-C_5H_{12} (2:3) was added, and the resulting brown solution was cooled to −30 °C. After two months at −30 °C, red crystals had formed as well as a grey powder. The crystals were separated and identified as [{Mo[η-$C_5H_3(SiMe_3)_2$]$(CO)_2(PEt_3)$}$_2$] (**4d**) (for similar complexes, see ref. 40), the decomposition product of the presumed intermediate [Pb{Mo[η-$C_5H_3(SiMe_3)_2$]$(CO)_2(PEt_3)$}$_2$] (**5**). For (**4d**): ^1H n.m.r. (C_6D_6): δ 0.326 (s, 18 H, $SiMe_3$), 0.97—1.05 (m, 9 H, Me), 1.65—1.74 (m, 6 H, CH_2P), 4.12 [t, 1 H, $C_5\mathit{H}_3(SiMe_3)_2$], 4.90 [dd, 2 H, $C_5\mathit{H}_3(SiMe_3)_2$, $J(^{31}P^1H)$ 3.5 Hz]; ^{31}P n.m.r. (C_6D_6): δ −112.46; ν(CO) (Nujol) at 1 888s, 1 845(sh), 1 830br, 1 795s cm^{-1}.

Crystal Structure Determination of [Pb{Mo(η-C_5Me_5)$(CO)_3$}$_2$(thf)] (**1a**).—Crystals of (**1a**) were grown from thf–n-C_5H_{12} solution. A dark green crystal of approximate dimensions 0.2 × 0.2 × 0.05 mm was sealed in a capillary under argon.

Crystal data. $C_{30}H_{38}Mo_2O_7Pb$, M = 909.7, monoclinic, space group $P2_1/c$, $a = 11.886(4)$, $b = 15.225(4)$, $c = 18.248(8)$ Å, $\beta = 95.14(3)°$, $U = 3\,289.1$ Å^3, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000) = 1\,760$; monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 59.2$ cm^{-1}. A unique data set was obtained using an Enraf-Nonius CAD-4 diffractometer, $\Delta\theta = (1.0 + 0.35 \tan\theta)°$, maximum scan time 1 min, yielding 4 667 reflections measured for $2 < \theta < 22°$, $+h +k \pm l$. A total of 2 477 unique reflections with $|F^2| > \sigma(F^2)$ was used in the refinement, $\sigma(F^2) = [\sigma^2(I) + (0.04\ I)^2]^{\frac{1}{2}}/Lp$. No crystal decay was observed during the data collection. Absorption corrections were performed using the program DIFABS.[41]

The structure was solved by routine heavy-atom methods and non-hydrogen atoms refined anisotropically by full-matrix least squares. The hydrogen atoms could not be located and were omitted. The weighting scheme was $w = 1/\sigma^2(F)$. Final residuals were $R = 0.055$, $R' = 0.060$. A final difference map had peaks of up to 0.6 e Å^{-3} near the Mo atoms but elsewhere was featureless. Programs were from the Enraf-Nonius SDP-Plus package run on a PDP 11/34 computer. Atomic co-ordinates are in Table 5.

Crystal Structure Determination of $[\{Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3][Mo(\eta\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)]\}_2]$ (**3**).—Green crystals of (**3**) were grown from a toluene solution cooled to −30 °C. A crystal of dimensions 0.5 × 0.4 × 0.15 mm was mounted and sealed in a capillary under argon.

Crystal data. $C_{26}H_{30}Mo_2O_6Pb{\cdot}0.5C_7H_8$, $M = 883.7$, triclinic, space group $P\bar{1}$, $a = 9.177(4)$, $b = 12.980(2)$, $c = 13.886(2)$ Å, $\alpha = 101.37(2)$, $\beta = 100.83(2)$, $\gamma = 94.45(2)°$, $U = 1\,581.4$ Å^3, $Z = 2$, $D_c = 1.86$ g cm^{-3}, $F(000) = 850$; monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 61.5$ cm^{-1}. A unique data set was obtained using similar methods to those described for complex (**1a**). The diffractometer was in the conventional θ—2θ mode, $\Delta\theta = (0.8 + 0.35 \tan\theta)°$. A total of 5 811 reflections was measured for $2 < \theta < 25°$, $+h +k \pm l$. Refinement was by routine heavy-atom methods using 4 531 unique reflections with $|F^2| > \sigma(F)^2$; $\sigma(F)^2 = [\sigma(I) + (0.04\ I)^2]^{\frac{1}{2}}/Lp$. No crystal decay was observed during the data collection. Full least-squares refinement was performed with all atoms anisotropic after absorption correction using DIFABS.[40] A molecule of toluene lying on an inversion centre was disordered such that its methyl carbon atom could not be located. Final residuals were $R = 0.040$, $R' = 0.052$. A final difference map had maxima at 1.3 e Å^{-3} near the Pb atom. Atomic co-ordinates are in Table 6.

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References

1 Part 9, D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, T. Fjeldberg, A. Haaland, and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387.

2 *cf.* M. F. Lappert, *Silicon, Germanium, Tin Lead Compounds*, 1986, **9**, 129.

3 Part 8, T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert, and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551 and refs. therein.

4 Part 7, M. F. Lappert and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1985, 51 and refs. therein.

5 M. J. Heeg, C. Janiak, and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1984, **106**, 4259.

6 W. Gäde and E. Weiss, *J. Organomet. Chem.*, 1981, **213**, 451; D. Melzer and E. Weiss, *ibid.*, 1984, **263**, 67.

7 J. D. Korp, I. Bernal, R. Hörlein, R. Serrano, and W. A. Herrmann, *Chem. Ber.*, 1985, **118**, 340.

8 W. A. Herrmann, H-J. Kneuper, and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 1062.

9 W. A. Herrmann, J. Weichmann, U. Küsthardt, A. Schäfer, R. Hörlein, C. Hecht, E. Voss, and R. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 979; W. A. Herrmann, *ibid.*, 1986, **25**, 56; H-J. Kneuper, E. Herdtweck, and W. A. Herrmann, *J. Am. Chem. Soc.*, 1987, **109**, 2508.

10 G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang, and L. Zsolnai, *J. Organomet. Chem.*, 1985, **282**, 331; O. Scheidsteger, G. Huttner, K. Dehnicke, and J. Pebler, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 428.

11 P. G. Harrison and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1973, 940.

12 T. S. Dory, J. J. Zuckerman, C. D. Hoff, and J. W. Connolly, *J. Chem. Soc., Chem. Commun.*, 1981, 521.

13 H. Schumann, C. Janiak, E. Hahn, C. Kolax, J. Loebel, M. D. Rausch, J. J. Zuckerman, and M. J. Heeg, *Chem. Ber.*, 1986, **119**, 2656.

14 A. G. Gash, P. F. Rodesiler, and E. L. Amma, *Inorg. Chem.*, 1974, **13**, 2429.

15 N. G. Furmanova, Yu. T. Struchkov, D. N. Kravtsov, and G. M. Rokhlina, *Zh. Strukt. Khim.*, 1979, **20**, 1047.

16 P. H. de Wit, H. O. van der Kooi, and J. Wolters, *J. Organomet. Chem.*, 1981, **216**, C9.

17 T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639.

18 I. Gümrükçu, M. F. Lappert, A. J. Thorne, J. L. Atwood, R. D. Rogers, and M. J. Zaworotko, unpublished work.

19 P. A. W. Dean, J. J. Vittal, and N. C. Payne, *Inorg. Chem.*, 1984, **23**, 4232.

20 A. M. Arif, A. H. Cowley, R. A. Jones, and J. M. Power, *J. Chem. Soc., Chem. Commun.*, 1986, 1446.

21 P. B. Hitchcock, H. A. Jasim, R. E. Kelly, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1985, 1776.

22 W. Wojnowski, M. Wojnowski, K. Peters, E-M. Peters, and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1986, **535**, 56.

23 A. J. Balch and D. E. Oram, *Organometallics*, 1986, **5**, 2159.

24 P. B. Hitchcock, M. F. Lappert, B. J. Samways, and E. L. Weinberg, *J. Chem. Soc., Chem. Commun.*, 1983, 1492.

25 C. B. Lagrone, K. H. Whitmire, M. R. Churchill, and J. C. Fettinger, *Inorg. Chem.*, 1986, **25**, 2080.

26 H. H. Karsch and A. Appelt, *J. Organomet. Chem.*, 1986, **312**, C6.

27 A. Castel, P. Rivière, J. Satgé, J. J. Moreau, and R. J. P. Corriu, *Organometallics*, 1983, **2**, 1498.

28 *cf.* M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' Ellis Horwood, Chichester, 1980, ch. 12.

29 Part 5, M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.

30 P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood, W. E. Hunter, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1394.

31 K. H. Pannell, *J. Organomet. Chem.*, 1980, **198**, 37; K. H. Pannell and R. N. Kapoor, *ibid.*, 1981, **214**, 47.

32 H. H. Karsch, A. Appelt, and G. Hanika, *J. Organomet. Chem.*, 1986, **312**, C1.

33 Part 2, J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2275.

34 *cf.* C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219.

35 W. J. Sartain and J. P. Selegue, *Organometallics*, 1984, **3**, 1922; B. Longato, B. D. Martin, J. R. Norton, and O. Anderson, *Inorg. Chem.*, 1985, **24**, 1389.

36 P. G. Harrison, T. J. King, J. A. Richards, and R. C. Phillips, *J. Organomet. Chem.*, 1976, **116**, 307.

37 Yu. T. Struchkov, K. N. Anisimov, O. P. Osipova, N. E. Kolobova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1967, **172**, 107.

38 R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 107.

39 P. Leoni, E. Grilli, M. Pasquali, and M. Tomassini, *J. Chem. Soc., Dalton Trans.*, 1986, 1041.

40 K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 1967, **6**, 294; R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 4; R. M. Medina, A. Alvarez-Valdés, and J. R. Masaguer, *J. Organomet. Chem.*, 1985, **294**, 209.

41 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 159.

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