Reactions of Bis(η-cyclopentadienyl)dihydrido-molybdenum and -tungsten with Acetatotrimethyl-lead. *X*-Ray Structure and Reactivity of the Demethylated Lead Product containing Molybdenum–Lead Bonds: μ-Diacetatoplumbio-bis[bis(η-cyclopentadienyl)hydrido-molybdenum](2 *Pb–Mo*) †

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Novel transition metal–lead bonded complexes of the bis(η-cyclopentadienyl) class of organometallic compounds have been formed by the demethylation of acetatotrimethyl-lead in the presence of the molybdenum and tungsten dihydrides. An *X*-ray structure analysis of the molybdenum derivative has established the presence of a Mo–Pb–Mo linkage and a hydride ligand. The complex reacts with cyano-acetylene (HC≡CCN) giving a bis(alkenyl) compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\sigma\text{-}\mathrm{CH{=}CHCN})_2]$.

Treatment of $[\mathrm{MH_2}(\eta\text{-}\mathrm{C_5H_5})_2]$ [M = Mo (1a) or W (1b)] with alkyl derivatives of main group metals has given a number of compounds with M–M′ bonds (M′ = Li,[1] Mg,[2] Al,[3] or Zn [4]) proceeding from alkane elimination reactions. The M–Sn bond was formed by an amine and not an alkane elimination reaction of (1) with $\mathrm{Me_2NSnMe_3}$.[5] No defined product was isolated from the reaction of (1) with $\mathrm{HgMe_2}$ or HgMeX but two M–Hg bonds were formed upon the action of the mercury(II) salts $\mathrm{HgX_2}$ on (1).[6] Here we describe the reactions of (1) with acetatotrimethyl-lead leading to the formation of a novel type of bonding in bis(η-cyclopentadienyl) complexes containing M–M′ bonds.

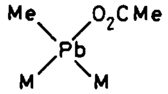
Results and Discussion

The reaction of $[\mathrm{MH_2}(\eta\text{-}\mathrm{C_5H_5})_2]$ (1) in acetone or toluene with acetatotrimethyl-lead $\mathrm{PbMe_3(O_2CMe)}$ gives a violet crystalline compound, $[\{(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{HM}\}_2\mathrm{Pb(O_2CMe)_2}]$ [M = Mo (2a) or W (2b)] in *ca.* 70% yield, together with methane, tetramethyl-lead and other unidentified products: equation (i).

$$[\mathrm{MH_2}(\eta\text{-}\mathrm{C_5H_5})_2] \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{PbMe_3(O_2CMe)}} [\{(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{HM}\}_2\mathrm{Pb(O_2CMe)_2}] + \mathrm{CH_4} + \mathrm{PbMe_4} + \text{other products} \qquad \text{(i)}$$

(1a) M = Mo (2a) M = Mo
(1b) M = W (2b) M = W

The exact stoicheiometry of this reaction cannot be determined because of the formation of insoluble decomposition products. However, it is reasonable to assume that two equivalents of both (1) and $\mathrm{PbMe_3(O_2CMe)}$ are involved. We suppose that the M–Pb bonds are formed by alkane elimination leading to a low-symmetry intermediate with the skeleton shown below. Such an unstable intermediate should readily undergo a symmetrization comprising acetate ligand transfer from the second $\mathrm{PbMe_3(O_2CMe)}$ molecule which in turn accepts the liberated methyl group, giving $\mathrm{PbMe_4}$.



The presence of methane was detected by gas chromatography of a sample from the reaction atmosphere. ^{207}Pb N.m.r. spectroscopy enabled the identification of tetramethyl-lead in the solution after the separation of (2). A spectrum recorded after stirring (1) for 4 h with $\mathrm{PbMe_3(O_2CMe)}$ exhibited a single resonance at δ −272 p.p.m. This resonance is interpreted in terms of exchange between the unreacted $\mathrm{PbMe_3(O_2CMe)}$ (−143 p.p.m.) ‡ and $\mathrm{PbMe_4}$ (−432 p.p.m.).[7] A single resonance at −430 p.p.m. corresponding to $\mathrm{PbMe_4}$ is observed in the spectrum recorded after stirring overnight.

The i.r. spectrum of (2) gave no evidence for the presence of hydride ligands. However their existence was suggested by the ^{1}H n.m.r. spectrum of (2a) recorded in $\mathrm{D_2O}$ [complexes (2) are sparingly soluble in common organic solvents] but the integration does not show the expected amounts. Three singlets are observed at δ 5.03, 1.87, and −12.3 p.p.m. with relative intensities 10 ($\mathrm{C_5H_5}$), 3 ($\mathrm{CH_3}$), and 0.6 ($\mathrm{H^-}$) respectively. Thus we decided to determine the structure of (2) by *X*-ray diffraction.

The structure of the molybdenum derivative (2a) consists of discrete trimetallic molecules with a lead atom bridging two $\mathrm{MoH}(\eta\text{-}\mathrm{C_5H_5})_2$ moieties (Figure 1) and located on the two-fold axis. The molybdenum–lead bond lengths [2.808(1) Å, Table 1] are shorter than the Mo–Pb bond (2.90 Å) found in $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{MoPbPh_3}]$.[8] This shortening is consistent with the difference of the atomic radii of $\mathrm{Mo^{IV}}$ in the bis(cyclopentadienyl) complexes (close to 1.44 Å)[9] and of $\mathrm{Mo^{II}}$ in the monocyclopentadienyls {equal to at least 1.51 Å, as derived from the Mo–Cl distance in $[\mathrm{MoCl(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$ [10]}.

The molybdenum–hydride distance of 1.7 Å is of the same order as that found in $[\mathrm{H}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Mo}(\mu\text{-}\sigma:\eta\text{-}\mathrm{C_5H_4})\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})]$.[11] The angle Pb–Mo(1)–H(Mo) of 76.3° is smaller than the Cl–Mo–Cl angle in $[\mathrm{MoCl_2}(\eta\text{-}\mathrm{C_5H_5})_2]$ (82.0°) [12] but similar to the H–Mo–H angle in $[\mathrm{MoH_2}(\eta^5\text{-}\mathrm{C_5H_5})_2]$ (75.5°) [13] and

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† *Supplementary data available* (No. SUP 23987, 10 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ The ^{207}Pb resonance was recorded with a saturated solution of $\mathrm{PbMe_3(O_2CMe)}$ in acetone with an internal lock of $\mathrm{C_6D_6}$.

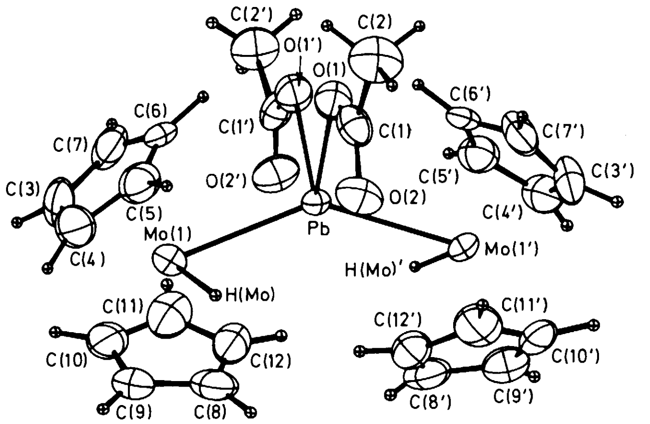


Figure 1. ORTEP drawing of $[\{(\eta\text{-}C_5H_5)_2HMo\}_2Pb(O_2CMe)_2]$ showing the atom labelling scheme. Symmetry code for primed atoms: $\frac{1}{2} - x, y, \frac{1}{2} - z$

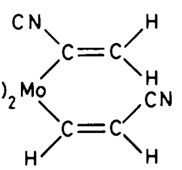
Table 1. Selected interatomic distances (Å) and angles (°)

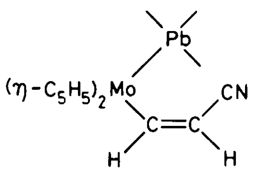
Mo(1)-Pb	2.808(1)	Mo(1)-H(Mo)	1.7 [a]
Mo(1)-C(3)	2.238(12)	Mo(1)-C(8)	2.330(14)
Mo(1)-C(4)	2.240(13)	Mo(1)-C(9)	2.239(14)
Mo(1)-C(5)	2.304(13)	Mo(1)-C(10)	2.235(13)
Mo(1)-C(6)	2.342(11)	Mo(1)-C(11)	2.282(13)
Mo(1)-C(7)	2.295(13)	Mo(1)-C(12)	2.338(14)
Mo(1)-C_5H_5 [b]	1.946	Mo(1)-C_5H_5 [c]	1.946
Pb-O(1)	2.342(8)	Pb-Mo(1)-H(Mo)	76.3
Pb···O(2)	3.041(9)	Mo(1)-Pb-Mo(1')	141.4(1)
C(1)-O(1)	1.281(14)	Mo(1)-Pb-O(1)	102.3(2)
C(1)-O(2)	1.244(14)	Mo(1)-Pb-O(1')	108.0(2)
C(1)-C(2)	1.513(17)	O(1)-Pb-O(1')	75.3(4)

[a] Not refined. [b] Perpendicular distance to C(3)—C(7) ring plane. [c] Perpendicular distance to C(8)—C(12) ring plane.

the Hg-Mo-Hg angles in mercury-containing complexes of the type $[(\eta\text{-}C_5H_5)_2Mo(HgX)_2]$ (*ca.* 73°).[9] The expected value of the angle between the C_5H_5 planes (*ca.* 140°) is observed.

The reactivity of the residual hydride ligand of (2) was checked with some electrophilic reagents like thiols, mercury thiolates, and cyano-activated alkyne. This study was restricted by the low solubility of (2) in the solvents. No reaction, or decomposition, of (2) occurred with all reagents containing SR groups [HSMe, HSEt, HSPh, $Hg(SEt)_2$, and $Hg(SPh)_2$]. However, the reaction of (2a) with HC≡CCN in toluene permitted the isolation after chromatography on a Florisil column of a small amount [<3% yield based on (2a)] of a red compound (3a). Hydrogen-1 and ^{13}C n.m.r. data (Figure 2) of (3a) suggested it to be a bis(alkenyl)bis(cyclopentadienyl)-molybdenum(IV) complex in which both the β-carbon atoms bear one nitrile group. The proposed structure contrasts with that of the known di-insertion product, shown above, in which α- and β-metallated vinylic ligands are present.[14] However, the formation of (3) from (2) seems plausible on the basis of the mechanisms proposed for alkyne insertion reactions into the M-H bonds of the $[MH_2(\eta\text{-}C_5H_5)_2]$ and $[MH(\eta\text{-}C_5H_5)_2(\sigma\text{-}R)]$ complexes (R = vinylic ligand).[14,15] The insertion of HC≡CCN into the Mo-H bond of (2a), analogous to $[MH(\eta\text{-}C_5H_5)_2(\sigma\text{-}R)]$, affords a β-metallated complex (see below) in which the Mo-Pb bond is immediately broken. Once formed, such an intermediate species undergoes attack by a second HC≡CCN molecule on the 'vacant' Mo site giving the second β-metallated σ-vinylic ligand, with the hydrogen atom provided probably by the solvent.





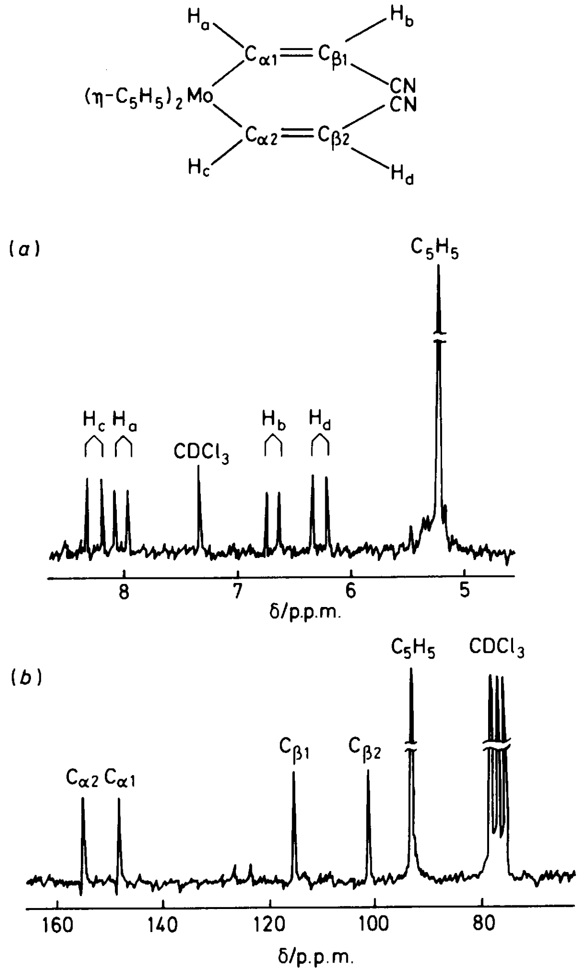


Figure 2. N.m.r. spectra of $[Mo(\eta\text{-}C_5H_5)_2(\sigma\text{-}CH{=}CHCN)_2]$. (*a*) $\delta(^1H)$: H_a 8.01, H_b 6.52, H_c 8.21, H_d 6.25 p.p.m.; $^3J(H_aH_b)$ = 12, $^3J(H_cH_d)$ = 13 Hz. (*b*) $\delta(^{13}C)$: $C_{\alpha1}$ 148.1, $C_{\alpha2}$ 154.6, $C_{\beta1}$ 115.1, $C_{\beta2}$ 101.1 p.p.m.

Experimental

The complexes $[MH_2(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) reacted under nitrogen in acetone or toluene with an equimolar quantity of $PbMe_3(O_2CMe)$, diffused through a glass frit. A

Table 2. Final atomic co-ordinates with estimated standard deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb(1)	0.250 0(0)	0.137 25(8)	0.250 0(0)	C(5)	0.395 9(11)	0.214(2)	0.515 8(10)
Mo(1)	0.257 76(9)	0.018 3(1)	0.455 28(8)	C(6)	0.303 6(12)	0.310(1)	0.470 4(10)
O(1)	0.371 5(6)	0.375(1)	0.249 1(6)	C(7)	0.209 9(11)	0.276(2)	0.524 7(9)
O(2)	0.506 7(7)	0.175(1)	0.247 0(7)	C(8)	0.252 9(13)	−0.266(2)	0.398 5(12)
C(1)	0.474 8(9)	0.328(2)	0.243 5(9)	C(9)	0.252 2(15)	−0.253(2)	0.510 7(12)
C(2)	0.559 8(11)	0.471(2)	0.233 5(13)	C(10)	0.151 3(13)	−0.174(2)	0.529 2(11)
C(3)	0.245 3(11)	0.160(2)	0.603 9(9)	C(11)	0.090 8(12)	−0.132(2)	0.430 8(12)
C(4)	0.360 1(12)	0.118(2)	0.598 5(10)	C(12)	0.157 0(12)	−0.193(2)	0.355 1(11)

progressive colour change of the solution from yellow to red occurred, followed after 1 h by the formation of violet crystals of $[\{(\eta\text{-}C_5H_5)_2HM\}_2Pb(O_2CMe)_2]$ [Found, (2a; M = Mo): C, 36.9; H, 3.5; Mo, 24.7; Pb, 26.5. $C_{24}H_{28}Mo_2O_4Pb$ requires C, 37.0; H, 3.6; Mo, 24.6; Pb, 26.6%. Found, (2b; M = W): C, 30.5; H, 2.8; Pb, 22.5; W, 36.2. $C_{24}H_{28}O_4PbW_2$ requires C, 30.25; H, 2.75; Pb, 21.75; W, 38.55%).

A suspension of (2a) (0.78 g, (1 mmol) in toluene was frozen in liquid nitrogen, and HC≡CCN [prepared from 0.5 g of HC≡CC(O)NH$_2$ [16]] was trapped on the solidified mixture *via* a vacuum line. The mixture was allowed to warm to room temperature and stirred for 12 h. A red solution was separated from abundant decomposition products by filtration and chromatographed on a Florisil column. The band eluted with dichloromethane–tetrahydrofuran (1 : 1) gave 0.020 g of $[Mo(\eta\text{-}C_5H_5)_2(\sigma\text{-}CH{=}CHCN)_2]$ (3a) (3% yield) identified by its ^1H and ^{13}C n.m.r. spectra and by its high-resolution mass spectrum [parent peak (*m/e*): calc., 332.021 09; found, 332.0209]. Because of the low yield no elemental analysis was performed.

Infrared spectra were recorded on a Pye-Unicam SP2000 spectrophotometer. N.m.r. spectra were recorded on a JEOL JNM-FX 100 spectrometer operating at 99.60 MHz for ^1H, 25.05 MHz for ^{13}C, and 20.80 MHz for ^{207}Pb. Hydrogen-1 chemical shifts of $[\{(\eta\text{-}C_5H_5)_2HM\}_2Pb(O_2CMe)_2]$ were measured relative to residual protons of D_2O and to an external reference of $PbMe_3Cl$ (saturated CH_2Cl_2 solution with an internal lock of C_6D_6) for ^{207}Pb. The mass spectrum was recorded on a Varian Mat 311 spectrometer.

Crystal Structure Determination of (2a).—All calculations were carried out using the Enraf-Nonius SDP program library.[17] Neutral-atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those of Cromer and Waber.[18] Final atomic co-ordinates are given in Table 2.

Crystal data. $C_{24}H_{28}Mo_2O_4Pb$, $M = 799.65$, monoclinic, space group $P2/n$, $a = 11.772(2)$, $b = 7.796(3)$, $c = 12.951(3)$ Å, $\beta = 96.26(3)°$, $U = 1\,181.5$ Å^3, D_m (by flotation) = 2.17(2), $Z = 2$, $D_c = 2.185$ g cm^{-3}, $F(000) = 740$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 82.097$ cm^{-1}.

A violet crystal of dimensions 0.08 × 0.24 × 0.04 mm along [100], [010], and [001], respectively, was mounted on an Enraf-Nonius CAD4 diffractometer. The intensities of 2 604 reflections were measured using an ω—2θ scan ($\theta_{\text{min.}} = 2°$, $\theta_{\text{max.}} = 18°$), from which 1 483 with $F^2 > 3\sigma(F^2)$ were used in the solution and refinement of the structure. The structure was solved by heavy-atom and Fourier methods and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically. Ring and acetate hydrogens were located in difference maps and then placed geometrically [r(C–H) = 1.0 Å, $B_{\text{iso.}} = 5$ Å^2]. The hydride, H(Mo), was located in a difference map and included in the model, but, as with the other hydrogens, its parameters were not refined. The absorption correction applied following a crystal shape did not give any improvement of the results and was not retained in the final refinement. The final R value was 0.039 and R' was 0.047; $w^{-1} = \sigma^2(F) = \frac{1}{4}[\sigma(I)/(I) + (0.06)^2(I)]$.

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