Synthetic Pathways in Binuclear Molybdenum Chemistry: μ-Acetato-, Chloro-, and Tertiary Phosphine Derivatives; *X*-Ray Structure Determination of *trans*-$[\{MoCl(PBu^n_3)(\mu-O_2CMe)\}_2]$†

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The reaction between $[\{Mo(\mu-OCOMe)_2\}_2]$ and $SiMe_3Cl$ in the presence of a variety of donor ligands L [tetrahydrofuran (thf), Me_2S, Et_2S, PEt_3, PPh_3, PBu^n_3, or $Ph_2P(CH_2)_nPPh_2$, where n = 1 or 2] yields binuclear compounds such as $[\{MoLCl(\mu-OCOMe)\}_2]$ or $[(MoL_2Cl_2)_2]$. The products may vary according to the stoicheiometry of the reaction. The new compounds described are $[\{MoCl(\mu-OCOMe)(thf)\}_2]$, $[\{MoCl(PPh_3)(\mu-OCOMe)\}_2]$, isomers of $[\{MoCl(PEt_3)(\mu-OCOMe)\}_2]$, *trans*-$[\{MoCl(PBu^n_3)(\mu-OCOMe)\}_2]$, and $[Mo_2Cl_2(OCOMe)_2(dppm)]$. Interconversion of some of these compounds by ligand-replacement reactions is also demonstrated. The crystal structure of *trans*-$[\{MoCl(PBu^n_3)(\mu-OCOMe)\}_2]$ is described; the crystals are monoclinic, space group $P2_1/n$, with a = 14.969(2), b = 15.146(2), c = 8.920(2) Å, β = 105.14(1)°, and Z = 2. Refinement converged with R = 0.048, R' = 0.063, for 1 762 observed reflections [$I > 3\sigma(I)$]. The Mo–Mo separation is 2.099(1) Å. The presence of isomers of the various compounds is demonstrated from the hydrogen-1 n.m.r. spectra.

The dimer $[\{Mo(\mu-OCOMe)_2\}_2]$ (1) has been shown to act as a precursor for the formation of molybdenocene dimers *via* reaction with sodium cyclopentadienide.[1] During a study of this reaction we added triphenylphosphine to a mixture of (1) and $Na(C_5H_5)$ to try to trap out intermediates in the reaction. This work led to the isolation of a new black molybdenocene dimer.[2] In order further to understand the role of the PPh_3 in the formation of this dimer we wished to synthesise the compounds $[\{MoCl(PPh_3)(\mu-OCOMe)\}_2]$ and $[\{MoCl_2(PPh_3)_2\}_2]$. We noticed a report by McCarley *et al.*[3] of the synthesis of $[Mo_4Cl_8(PEt_3)_4]$ from the reaction between $[\{Mo(\mu-OCOMe)_2\}_2]$ and chlorotrimethylsilane in the presence of triethylphosphine. This led us to investigate the synthesis of related binuclear compounds using the same general principles.

We have found that $SiMe_3Cl$ can act as a mild and selective reagent for the replacement of the acetato-groups in (1) by chlorine and thereby can provide a simple and very convenient route to the synthesis of a variety of new and known dimolybdenum compounds, as described below.

Results

First the synthetic routes will be described and the products will be indicated by their molecular formulae. Then the structures of the new compounds will be discussed in the light of the spectroscopic data. Most of the reactions described proceed in excellent yields under mild conditions.

Treatment of $[\{Mo(\mu-OCOMe)_2\}_2]$ (1) in tetrahydrofuran (thf) with $SiMe_3Cl$ deposits slightly air-sensitive orange microcrystals of stoicheiometry corresponding to $[\{MoCl(\mu-OCOMe)(thf)\}_2]$ (2). The thf ligands of (2) readily undergo exchange with tertiary phosphines and treatment of (2) with PR_3, where $R_3 = Ph_3$ or Et_3, gives pink-red crystals of $[\{MoCl(PPh_3)(\mu-OCOMe)\}_2]$ (3) or air-sensitive red crystals, designated the α isomer, of $[\{MoCl(PEt_3)(\mu-OCOMe)\}_2]$ (4) respectively. The reaction between (2) and $Ph_2PCH_2PPh_2$ is more complex, see below. Direct reaction between (1) and $SiMe_3Cl$ in thf in the presence of PPh_3 rapidly forms (3) in >98% yield. The compound (3) is only slightly soluble in common solvents, being most soluble in dichloromethane.

When (1) is treated with 1 equivalent of $SiMe_3Cl$ in the presence of PBu^n_3 then *trans*-$[\{MoCl(PBu^n_3)(\mu-OCOMe)\}_2]$ (5) is formed in excellent yield. Similarly, when (1) and PEt_3 in thf are treated with 2 mole equivalents of $SiMe_3Cl$ then the orange compound β-$[\{MoCl(PEt_3)(\mu-OCOMe)\}_2]$ (6) is formed which is an isomer of α-$[\{MoCl(PEt_3)(\mu-OCOMe)\}_2]$(4).

The triphenylphosphine ligands of $[\{MoCl(PPh_3)(\mu-OCOMe)\}_2]$ (3) are labile and can be replaced readily by tri-n-butylphosphine or triethylphosphine giving red-orange crystals of (5) (>90% yield) or (6) respectively. The compounds (5) and (6) are air sensitive and soluble in dichloromethane, acetone, acetonitrile, and tetrahydrofuran.

Treatment of (3) with bis(diphenylphosphino)methane (dppm) gives green crystals of the previously described compound $[\{MoCl_2(\mu-dppm)\}_2]$ (7)[4,5] as the tetrahydrofuran solvate. The solvate molecule may be removed by powdering the crystals and drying *in vacuo*. Direct reaction between (1), $SiMe_3Cl$, and dppm in thf gives (7) in 91% yield.

If (1) in the presence of a suitable ligand is treated with more than 4 mole equivalents of $SiMe_3Cl$ then all four acetato-groups can be replaced by chloro-groups. For example, the reaction between (1) and excess of $SiMe_3Cl$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) gives $[\{MoCl_2(\mu-dppe)\}_2]$ (8) which the i.r. spectrum shows to be identical to the previously described β-$[\{MoCl_2(\mu-dppe)\}_2]$.[4] Treatment of solutions of (1) with R_2S (R = Me or Et) in the presence of an excess of $SiMe_3Cl$ forms the previously described compounds $[\{MoCl_2(SMe_2)_2\}_2]$ (9) and $[\{MoCl_2(SEt_2)_2\}_2]$ (10).[6] When an excess of $SiMe_3Cl$ is present then PEt_3 reacts with (1) to give the blue-purple crystalline $[\{MoCl_2(PEt_3)_2\}_2]$ (11),[7] in 79% yield, rather than the compound β-$[\{MoCl(PEt_3)(\mu-OCOMe)\}_2]$ (6).

Finally, treatment of (3) or (5) with sodium cyclopentadienide in thf gave small yields of the compound $[(\eta-C_5H_5)_2HMo(\mu-\sigma:\eta^5-C_5H_4)Mo(\eta-C_5H_5)]$ (12) whose chemistry has been described in detail elsewhere.[2]

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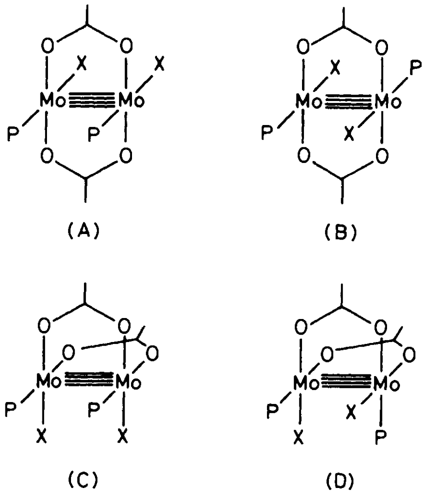
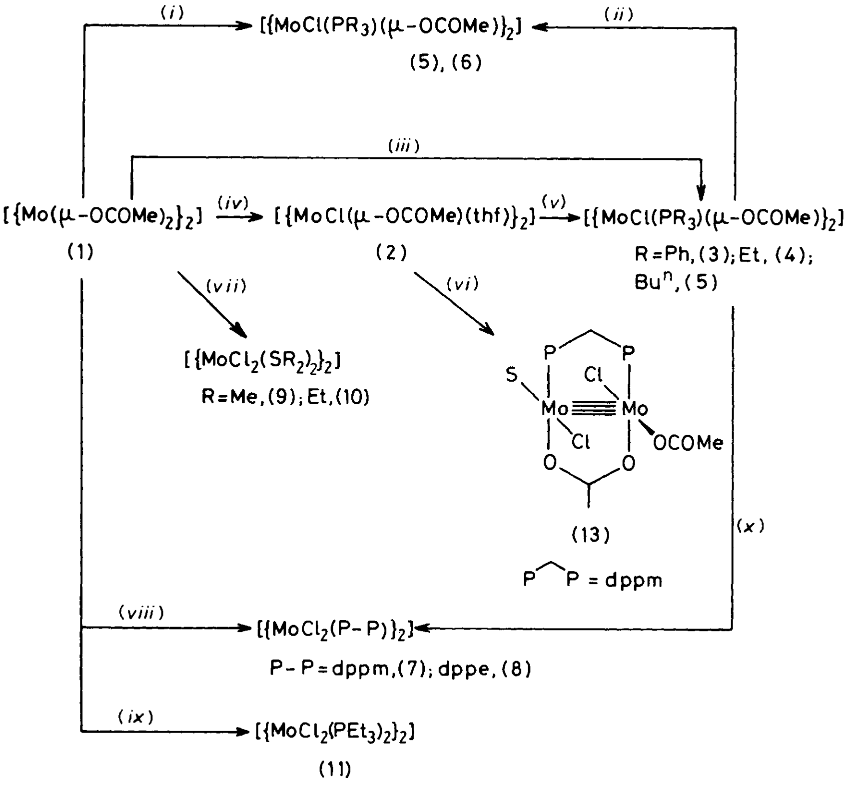
† *trans*-Di-μ-acetato-*OO'*-bis[chloro(tri-n-butylphosphine)-molybdenum(II)](4*Mo–Mo*).

Supplementary data available (No. SUP 23420, 17 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. Possible isomers of [{MoX(PR$_3$)(μ-OCOMe)}$_2$]



Scheme 2. (*i*) For (6) only: PEt$_3$ and SiMe$_3$Cl (2 equivalents) in thf at r.t., yield 92%; (*ii*) for (5) and (6): to (3; R = Ph) add PBu$^n_3$ or PEt$_3$, respectively, in thf at r.t. for 10 min, 94%; (*iii*) R = Ph or Bu^n: SiMe$_3$Cl in thf with PR$_3$, 85—98%; (*iv*) SiMe$_3$Cl in thf at 50 °C for 30 min, 75%; (*v*) for R = Et or Ph: add PR$_3$ in thf at r.t. >85%; (*vi*) dppm in thf at r.t. for 10 min, 60%; (*vii*) SEt$_2$ or SMe$_2$ and SiMe$_3$Cl in thf at r.t. for 2 h, >80%; (*viii*) dppm or dppe and SiMe$_3$Cl in thf at r.t., >90%; (*ix*) PEt$_3$ and SiMe$_3$Cl (excess over 2 equivalents) in thf at r.t. for 24 h, 79%; (*x*) dppm in thf at 80 °C for 4 h, 70%

The structures of the new compounds (2)—(6) are based primarily on the spectroscopic data given in Table 1 and the Experimental section. The data show that many of the compounds occur as isomers but do not allow distinction between them. Possible structural isomers for a compound of stoicheiometry [LXMo(μ-OCOMe)$_2$MoXL] are shown in Scheme 1 and the synthetic pathways are shown in Scheme 2. The hydrogen-1 n.m.r. spectra were particularly revealing, especially of the presence of isomers *via* the bands assignable to the equivalent hydrogens of the methyl groups of differing μ-OCOMe groups. Also, the i.r. spectra in the regions 1 400—1 450 and 1 590—1 620 cm^{-1}, where bands due to the μ-acetato-groups occur, can provide useful structural information, as outlined below.

The compound [{MoCl(μ-OCOMe)(thf)}$_2$] (2) is highly reactive. Attempts to recrystallise it from tetrahydrofuran gave only microcrystals, and on standing these solutions turned red. The hydrogen-1 n.m.r. spectrum in acetonitrile solution showed two main and two or more minor bands assignable to the methyl hydrogens of μ-OCOMe groups. The total intensity of all the bands assignable to the methyl groups, when compared to that of the bands due to the thf, showed that the ratio of tetrahydrofuran to acetato-groups was 1 : 1. However, the relative intensity of the individual methyl resonances was never 1 : 1 and so each band must be assigned to a different isomer. The i.r. spectrum of (2) when compared to that of (3) or (5) showed approximately twice the number of bands due to μ-OCOMe groups. We conclude that (2) is present as at least two isomers, both in the solid and in solution. The complexity of the hydrogen-1 n.m.r. may be due in part to substitution of the tetrahydrofuran ligands by acetonitrile. The ease of replacement of these ligands by tertiary phosphines has been demonstrated above. Also, (2) reacts very rapidly with acetic acid giving [{Mo(μ-OCOMe)$_2$}$_2$], and with carbon tetrachloride in the presence of tetraethylammonium chloride giving good yields of the known compound [NEt$_4$]$_3$[Cl$_3$Mo(μ-Cl)$_3$MoCl$_3$]. These reactions show that a Mo$_2$ unit is present in (2).

Table 1. Analytical and spectroscopic data

Compound	Colour	Analysis (%) [a] C	H	Cl	Hydrogen-1 n.m.r. data [b]
(2) $[\{MoCl(\mu\text{-}OCOMe)(thf)\}_2]$	Bright orange	27.8 (27.4)	4.1 (4.1)	14.2 [c] (13.5)	3.64, **8**, 2 $O(CH_2)_2$; 2.79—2.73, **3** (total), *several s*,[d] 2 Me; 1.80, **8**, thf [e]
(3) $[\{MoCl(PPh_3)(\mu\text{-}OCOMe)\}_2]$	Red-pink	52.7 (53.1)	4.1 (4.0)	7.8 (7.8)	7.0—7.5, *c*, Ph; 2.5—2.8, *several s*, CMe [f,g]
(4) α-$[\{MoCl(PEt_3)(\mu\text{-}OCOMe)\}_2]$	Red	31.6 (31.1)	5.8 (5.8)	11.3 (11.5)	2.74, **6**, *s*, 2 Me; 2.07, **12**, *m*, 6 PCH_2; 0.97, **18**, *m*, 6 CMe [g,h]
(5) *trans*-$[\{MoCl(PBu^n_3)(\mu\text{-}OCOMe)\}_2]$	Red-orange	43.0 (42.8)	7.7 (7.7)	9.0 [i] (9.0)	2.87, **6**, *s*, 2 O_2CMe; 1.89, **12**, *m*, 6 PCH_2; 1.29, **12**, *q*, 6 β-CH_2; 1.15, **12**, *m*, 6 γ-CH_2; 0.85, **18**, *t*, 6 Me of PBu^n_3 [g,j]
(6) β-$[\{MoCl(PEt_3)(\mu\text{-}OCOMe)\}_2]$	Orange	31.4 (31.1)	6.2 (5.8)	11.5 (11.5)	2.90, **6**, *s*, 2 O_2CMe; 1.95, **12**, *q* $^4J(P\text{-}H) = J(H\text{-}H) = 0.8$, 6 PCH_2; 0.92, **18**, *m five lines*, 6 Me of PEt_3 [g,k]
(13) $[Mo_2Cl_2(OCOMe)_2(dppm)]\cdot thf$	Red-violet	47.0 (47.3)	3.5 (4.3)	8.2 [l] (8.5)	7.7—7.0, *several c*, Ph; 4.0—5.0, *two d of t* (*overlapping*), 2 pairs of CH_2 of dppm; 2.98 (α), 2.8 (β), 2.71 (β), 2.59 (α), *four s*, 2 different Me of α and β isomers [e,m]

[a] Calculated values given in parentheses. [b] Given as: chemical shift (δ), **relative intensity**, *multiplicity* (*J* in Hz), assignment. [c] Mo 36.4(36.6)%. [d] See the text. [e] In CD_3CN. [f] ^{31}P N.m.r. (p.p.m.): 32.0, s; 26.0, s; 23.0, s; relative intensity 1 : 0.1 : 0.05. Both ^1H and ^{31}P n.m.r. of very dilute solutions. [g] In CD_2Cl_2. [h] Also a small band at δ 2.87 assignable to the presence of a small amount of the isomer (6). [i] P 8.1(7.9), Mo 24.7 (24.4)%. [j] Also a small band at δ 2.72 due to the presence of an isomer: since only one band is observed this suggests a structure of type (A) or (D) (Scheme 1). [k] The spectrum changes slowly and after 2 d there is a band at δ 2.74 assignable to the isomer (4). Another small band is assignable to a μ-OCOMe group. [l] Data for the unsolvated compound: C 45.4(45.5); H 4.4(3.7)%. [m] The main features of the initial spectrum (20 min after preparation of the solution); after 12 h new bands appear at δ 2.933, 2.793, 2.653, and 2.579.

Table 2. Fractional atomic co-ordinates (× 10^4) for compound (5)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	4 918.5(5)	648.8(5)	355.6(8)	C(21)	2 274(14)	687(18)	−583(33)
Cl(1)	6 208(2)	1 364(2)	2 170(3)	C(121)	2 301(14)	225(17)	−1 456(31)
O(1)	5 344(4)	1 168(4)	−1 540(6)	C(22)	2 220(13)	−259(13)	−92(32)
O(2)	5 554(4)	−209(4)	−2 246(6)	C(23)	1 210(13)	−482(13)	−65(27)
P(1)	3 302(2)	981(2)	−1 184(3)	C(24)	1 114(15)	−1 446(13)	−346(23)
C(1)	5 570(7)	618(7)	−2 470(10)	C(31)	2 922(12)	1 984(11)	−349(27)
C(2)	5 879(9)	976(8)	−3 858(11)	C(131)	3 337(23)	2 218(12)	−982(23)
C(11)	3 172(8)	997(9)	−3 309(11)	C(32)	3 733(15)	2 644(11)	−289(29)
C(12)	2 248(9)	1 313(9)	−4 265(13)	C(132)	3 435(23)	2 511(15)	746(24)
C(13)	2 257(11)	1 326(11)	−5 999(14)	C(33)	3 581(12)	3 495(12)	569(22)
C(14)	1 347(12)	1 683(12)	−6 977(17)	C(34)	4 500(14)	3 959(15)	826(25)

Fractional occupancies: C(21) 0.427, C(31) 0.644, C(32) 0.665, C(121) 0.573, C(131) 0.356, C(132) 0.335.

The crystal structure of *trans*-$[\{MoCl(PBu^n_3)(\mu\text{-}OCOMe)\}_2]$ (5) has been determined and is shown in the Figure. The atomic positional parameters are given in Table 2 and selected bond lengths and angles in Table 2.

The structure consists of discrete organometallic dimers, which possess crystallographic centres of symmetry. The molybdenum atoms are separated by 2.099(1) Å, and are linked by two coplanar, bridging acetato-ligands. Perpendicular to the plane of the bridging ligands is the $Mo_2P_2Cl_2$ plane, which has a *trans* disposition of ligands. The Mo(1)–P(1) distance is 2.501(3) Å, and Mo(1)–Cl(1) is 2.427(2) Å.

Two of the butyl chains of the PBu^n_3 ligand suffer from a combination of high thermal motion and disorder, and their dimensions were initially poor. Slack constraints [8] were applied to the affected P–C and C–C distances, restraining them to chemically reasonable values. The P–C bonds were constrained to their mean [including P(1)–C(11)], which was recalculated after each cycle of refinement, and the C–C distances [excluding C(11) to C(14)] were constrained to 1.54 Å. An estimated standard deviation (e.s.d.) of 0.02 Å was used to weight these constraints. For C(21), C(31), and C(32), alternative sites were resolved, labelled C(121), C(131), and C(132) respectively, and the site occupancies are given in Table 2. A typical tetrahedral group about P(1) is Mo(1), C(11), C(21), and C(131). All other disorder of the n-butyl groups was absorbed into the anisotropic thermal parameters, some of which are very large (U_{11} in the range 0.05—0.38 Å^2).

The molecular arrangement of (5) is very similar to that found [9] for $[\{MoBr(PBu^n_3)(O_2CPh)\}_2]$ which has a metal–metal bond length of 2.091(3) Å. However, the Mo–P bond length in the benzoate derivative is significantly longer [2.526(5) Å] than for (5). The n-butyl groups of the benzoato-dimer showed a similar disorder to that found with (5). The hydrogen-1 n.m.r. spectrum of (5) (Table 1) is consistent with a solution structure which is the same as that in the crystal. We note that the bands assignable to the three methylene groups of the six equivalent n-butyl groups are both well separated and shifted downfield compared to those in the unco-ordinated PBu^n_3 ligand. We attribute this behaviour to the diamagnetic anisotropy of the quadruple bond.*

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* *Note added in proof.* The crystal structure of $[Mo_2Cl_2(PEt_3)_2(O_2CCMe_3)_2]$ has been described (J. D. Arenivar, V. V. Mainz, H. Ruben, R. A. Andersen, and A. Zalkin, *Inorg. Chem.*, 1982, **21**, 2649).

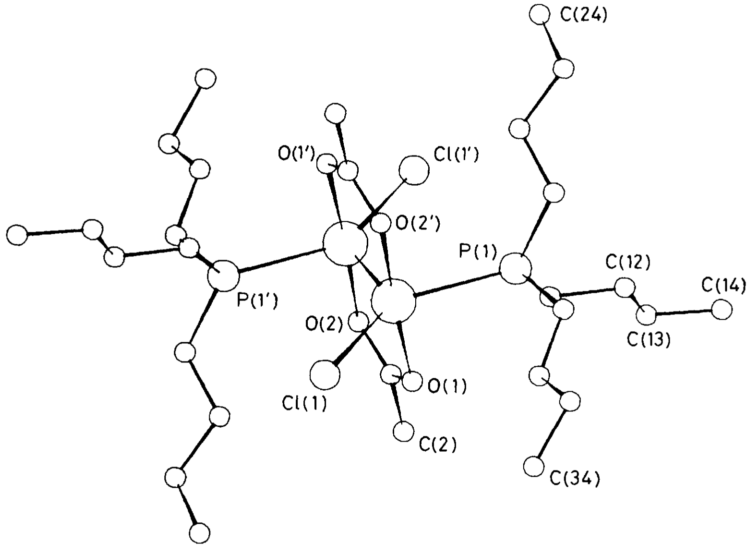

Figure. Crystal structure of compound (5) showing only one configuration of the disordered n-butyl chains and with the principal atoms labelled

Table 3. Selected bond lengths (Å) and angles (°) for compound (5); primes refer to the symmetry operation 1 − *x*, −*y*, −*z*

Mo(1)-Mo(1′)	2.099(1)	C(11)-C(12)	1.500(15)
Mo(1)-Cl(1)	2.427(2)	C(12)-C(13)	1.550(15)
Mo(1)-O(1)	2.109(5)	C(13)-C(14)	1.513(19)
Mo(1)-O(2′)	2.100(6)	C(21)-C(22)	1.506(19)
Mo(1)-P(1)	2.501(3)	C(121)-C(22)	1.453(17)
O(1)-C(1)	1.282(10)	C(22)-C(23)	1.556(16)
O(2)-C(1)	1.269(11)	C(23)-C(24)	1.482(16)
P(1)-C(11)	1.855(10)	C(31)-C(32)	1.563(16)
P(1)-C(21)	1.813(15)	C(131)-C(132)	1.574(17)
P(1)-C(121)	1.850(17)	C(32)-C(33)	1.546(16)
P(1)-C(31)	1.847(14)	C(132)-C(33)	1.520(18)
P(1)-C(131)	1.882(17)	C(33)-C(34)	1.508(15)
C(1)-C(2)	1.531(12)		
Mo(1′)-Mo(1)-Cl(1)	119.00(8)	O(1)-C(1)-O(2)	121.4(8)
Mo(1′)-Mo(1)-P(1)	101.21(8)	O(1)-C(1)-C(2)	118.6(9)
Cl(1)-Mo(1)-P(1)	139.8(1)	O(2)-C(1)-C(2)	120.0(9)
O(1)-Mo(1)-O(2′)	176.2(2)		

The hydrogen-1 n.m.r. spectrum of (5) also showed bands assignable to an isomer which was present in *ca.* 12% concentration.

The appearance of the bands in the region 1 524—1 342 cm^{-1} in the i.r. spectrum of (5), which are assignable to bridging acetato-ligands, is very similar to that of the related bands of [{MoCl(PPh$_3$)(μ-OCOMe)}$_2$] (3). The Mo≡Mo stretching frequency appears in the Raman spectrum at 383 cm^{-1}.

When (5) is treated with acetic acid then (1) is formed rapidly. We note that it has been reported that the treatment of [{MoCl$_2$(PBu$^n_3$)$_2$}$_2$] with acetic acid did not give (5).[10] This is presumably because any *trans*-[{MoCl(PBu$^n_3$)(μ-OCOMe)}$_2$] formed as an intermediate reacts further and rapidly with excess of acetic acid.

The red compound α-[{MoCl(PEt$_3$)(μ-OCOMe)}$_2$] (4) is spectroscopically distinct from the orange β-[{MoCl(PEt$_3$)(μ-OCOMe)}$_2$] (6). The hydrogen-1 n.m.r. spectrum of (4) shows the presence of a small quantity of (6). Also, the spectrum of (6) changes slowly with time and, amongst others, bands assignable to (4) appear and increase in intensity. The hydrogen-1 n.m.r. and i.r. spectra of β-[{MoCl(PEt$_3$)(μ-OCOMe)}$_2$] (6) are very similar to those of *trans*-[{MoCl(PBu$^n_3$)(μ-OCOMe)}$_2$], and on this basis we assign (6) the same isomer type (B) (Scheme 1). The data do not allow the preferential allocation of any one of the other isomeric structures (A), (C), or (D) to α-[{MoCl(PEt$_3$)(μ-OCOMe)}$_2$]. The hydrogen-1 n.m.r. spectrum of (6) was monitored over a period of several days and it showed changes corresponding to the appearance of bands assignable to α-[{MoCl(PEt$_3$)(μ-OCOMe)}$_2$] (4), together with traces of further bands assignable to another isomer different from (4) or (6).

Treatment of (2) with bis(diphenylphosphino)methane, dppm, gives red-violet plate-like crystals of [Mo$_2$Cl$_2$(OCOMe)$_2$(dppm)] (13) together with green microcrystalline [{MoCl$_2$(μ-dppm)}$_2$]. Crystallisation from thf gives the compound containing tetrahydrofuran of crystallisation which can be removed *in vacuo*. The i.r. spectrum of (13) shows bands assignable to a μ-OCOMe group and a band at 1 710 cm^{-1} assignable to a unidentate acetato-group. The hydrogen-1 n.m.r. spectrum of freshly prepared solutions of (13) show the presence of two isomers α-(13) and β-(13), each of which has two distinct dppm groups and two distinct acetato-groups. The solutions rapidly change so that after 1 d there are bands assignable to *ten* different methyl groups. After several days, green crystals of [{MoCl$_2$(μ-dppm)}$_2$] separate from solution. During the decompositon of the solutions the ratio of the bands assigned to α-(13) and β-(13) (2 : 1 within experimental error) remains unchanged. This suggests that α-(13) and β-(13) may be in equilibrium in solution. Treatment of (13) with acetic acid rapidly gives (1). Addition of dppm to solutions of (13) does not substantially increase the rate of deposition of [{MoCl$_2$(μ-dppm)}$_2$]. The data do not permit assignment of structures for the isomers α-(13) and β-(13) but are consistent with any of the possible isomers of which one is shown in Scheme 2. In this structure the ligand marked as S is incorporated so that both molybdenum atoms achieve an 18-electron configuration; S may represent a solvent molecule or possibly there may be a μ-chloro-ligand in the molecule. The compound [Mo$_2$Cl$_2$(OCOMe)$_2$(dppm)] can be seen to be an intermediate in the formation of [{MoCl$_2$(μ-dppm)}$_2$] and illustrates the conversion of a μ-OCOMe group into a unidentate acetato-ligand. We note that, even in the solid state, (13) decomposes slowly giving [{$MoCl_2$(μ-dppm)}$_2$].

The hydrogen-1 n.m.r. spectra of [{MoCl(PPh_3)(μ-OCOMe)}$_2$] (3), which were of poor quality due to low solubility, showed the presence of several bands assignable to hydrogens of different methyl groups and bands assignable to the phenyl groups of triphenylphosphine(s). The i.r. spectrum showed bands in the region 1 350—1 520 cm^{-1} assignable to bridging acetato-group(s). Involatility and low solubility precluded determination of the mass spectrum and molecular weight. The Raman spectrum showed a strong band at 384 cm^{-1} assignable to a quadruply bonded Mo_2 unit. Treatment of (3) with acetic acid reforms the parent compound (1). The crystals of (3) slowly deteriorated when removed from the mother-liquors and were found to be unsuitable for determination of the crystal structure. We conclude that (3) has two acetato-groups bridging an Mo_2 unit, but the evidence does not permit distinction between the possible isomers shown in Scheme 1 although the similarity of the i.r. spectrum in the region assignable to μ-OCOMe groups to that of the compound *trans*-[{MoCl(PBu^n_3)(μ-OCOMe)}$_2$] suggests a *trans* distribution of the μ-OCOMe groups to be most likely.

Discussion

The synthetic routes and proposed structures are shown in Scheme 2. The main purpose of the work has been to demonstrate the simplicity and mild conditions required for the syntheses. The formation of the silicon–oxygen bond in the compound $Me_3SiOCOMe$ must provide an important contribution to driving the equilibrium in equation (i) to the right-hand side.

$$[Mo]\text{-}OCOMe + Me_3SiCl \rightleftharpoons [Mo]\text{-}Cl + Me_3SiOCOMe \quad (i)$$

The literature preparations of most compounds of the class [{$MoCl_2L_2$}$_2$] proceed *via* the reaction between the donor ligand L and the anion $[Mo_2Cl_8]^{4-}$. The latter is prepared under carefully controlled conditions from (1). The syntheses described here for the known compounds (7)—(11) are more straightforward and proceed in higher yields than those described previously. The reactions are carried out in non-aqueous media and the residual $SiMe_3Cl$ and the product $SiMe_3(OCOMe)$ are readily separated from the molybdenum products.

It is clear from the reactions described above and changes occurring with time in the hydrogen-1 n.m.r. spectra that many of the compounds described are labile and can rearrange or undergo ligand substitution. We have not attempted to analyse these processes in detail nor have we investigated the possible factors, such as *trans* effects, which may determine the formation of the different structural isomers, for example, (4) and (6).

Experimental

All reactions and manipulations were carried out under dinitrogen or *in vacuo* unless otherwise stated. All solvents were thoroughly dried by standard methods and were distilled immediately before use. Hydrogen-1 n.m.r. spectra were determined using a Bruker (300 MHz) or a JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin-Elmer SP 2000 instrument.

The compound [{Mo(μ-OCOMe)$_2$}$_2$] was prepared as described.[11]

Di-μ-acetato-bis[chloro(tetrahydrofuran)molybdenum] (2).—A suspension of [{Mo(μ-OCOMe)$_2$}$_2$] (1.3 g, 3.0 mmol) in tetrahydrofuran (40 cm^3) was treated with chlorotrimethylsilane (4.0 cm^3, 31.6 mmol) and the mixture was stirred at 50 °C for 30 min. The solution turned orange and then red. The mixture was allowed to cool to room temperature (r.t.) and was stirred for a further 12 h. All the crystals of (1) had dissolved and there was a flocculent orange precipitate in the red solution. The precipitate was collected, washed with thf (2 × 10 cm^3) and then light petroleum (b.p. 30—40 °C), and dried *in vacuo*. Yield 1.19 g, 75%.

Di-μ-acetato-bis[chloro(triphenylphosphine)molybdenum] (3).—*Method A*. The compound [{Mo(μ-OCOMe)$_2$}$_2$] (5.05 g, 11.8 mmol) and triphenylphosphine (10 g, 38.2 mmol) in thf were treated with $SiMe_3Cl$ (9 cm^3, 71 mmol) and the mixture was stirred at r.t. The solution became orange, then red, and after 1 h pink crystals separated. These were collected, washed with thf (3 × 20 cm^3) and then light petroleum (20 cm^3), and finally dried *in vacuo*. Yield 10.5 g, 98%.

Method B. A suspension of [$Mo_2Cl_2(OCOMe)_2(thf)_2$] (0.05 g) in thf (10 cm^3) was treated with PPh_3 (0.1 g) and the mixture was stirred at r.t. for 1 h. On standing, red crystals separated from the resulting red solution. These were collected, washed with thf (10 cm^3) and light petroleum, and dried *in vacuo*. Yield >90%.

α-*Di-μ-acetato-bis[chloro(triethylphosphine)molybdenum]* (4).—The compound (2) (0.2 g) in thf (20 cm^3) was treated with triethylphosphine (0.5 cm^3). The orange crystals of (2) dissolved giving a red solution. This was concentrated under reduced pressure giving red crystals which were collected, washed with light petroleum, and dried *in vacuo*. Yield 0.20 g, 85%.

trans-*Di-μ-acetato-bis[chloro(tri-n-butylphosphine)molybdenum]* (5).—The compound [{MoCl(PPh_3)(μ-OCOMe)}$_2$] (1.0 g, 1.2 mmol) in thf (20 cm^3) was treated with tri-n-butylphosphine (1 cm^3). After stirring for 10 min the solution was concentrated under reduced pressure giving red-orange crystals. These were washed with cold thf and dried *in vacuo*. Yield 0.79 g, 91%.

β-*Di-μ-acetato-bis[chloro(triethylphosphine)molybdenum]* (6).—*Method A*. The compound [{Mo(μ-OCOMe)$_2$}$_2$] (0.7 g, 1.6 mmol) and PEt_3 (1 cm^3) in thf (20 cm^3) were treated, at r.t., with $SiMe_3Cl$ (2 cm^3, 15.8 mmol). The solution immediately became orange and after 15 min all the crystals of [{Mo(μ-OCOMe)$_2$}$_2$] had dissolved. The solvent was rapidly removed under reduced pressure and the resulting orange crystals were washed with cold thf (10 cm^3, −20 °C) and dried *in vacuo*. Yield 0.66 g, 92%.

Method B. A suspension of [{MoCl(PPh_3)(μ-OCOMe)}$_2$] (0.5 g, 0.6 mmol) in thf (40 cm^3) was treated with PEt_3 (1.0 cm^3) and the solution was stirred for 10 min giving a red-orange solution. Concentration under reduced pressure (to *ca*. 20 cm^3) and cooling at 0 °C for several hours gave orange crystals. These were collected and washed with light petroleum (b.p. 60—80 °C) and dried *in vacuo*. Yield 0.45 g, 94%.

Bis[μ-bis(diphenylphosphino)methane]-bis(dichloro molybdenum)-Tetrahydrofuran (1/2), (7).—The compound (1) (0.4 g, 0.9 mmol) and dppm (0.9 g, 2.3 mmol) in thf (25 cm^3) were treated with $SiMe_3Cl$ (1.5 g, 11.9 mmol) and the mixture was stirred at r.t. for 20 min. A green powder separated which was collected, washed with thf (2 × 20 cm^3) and light petroleum (20 cm^3, b.p. 60—80 °C), and dried *in vacuo*. Yield 1.06 g, 91%. The product was identified by comparison of the i.r. spectrum with that of an authentic sample[10] (Found: C, 55.7; H, 4.9; Cl, 11.9. Calc. for $[\{MoCl_2(\mu\text{-}dppm)\}_2]\cdot 2thf$: C, 55.9; H, 4.8; Cl, 11.4%).

β-*Bis*[μ-1,2-*bis*(*diphenylphosphino*)*ethane*]-*bis*(*dichloromolybdenum*) (8).—The compound (1) (0.7 g, 1.6 mmol) and dppe (1.4 g, 3.5 mmol) in thf (30 cm^3) were treated with $SiMe_3Cl$ (3 cm^3, 23.7 mmol) and the mixture was stirred at r.t. for 30 min. Purple-pink crystals separated from a red-green dichroic solution. The precipitate was collected, washed with thf (3 × 15 cm^3) and light petroleum (b.p. 60—80 °C), and dried *in vacuo*. Yield 1.15 g. Concentration of the mother-liquor under reduced pressure gave a further 0.35 g of product. The product was identified as the β isomer by comparison of the i.r. spectrum with that of an authentic sample[4] (Found: Cl, 12.2. Calc. for $[\{MoCl_2(\mu\text{-}dppe)\}_2]$: Cl, 12.5%).

Bis[*dichlorobis*(*dimethyl sulphide*)*molybdenum*] (9).—A suspension of (1) (0.5 g, 1.2 mmol) in thf (20 cm^3) was treated with dimethyl sulphide (3.5 cm^3, 48 mmol) and $SiMe_3Cl$ (2 cm^3, 15.8 mmol). The mixture was stirred at r.t. for 2 h. The reaction mixture rapidly turned red. It was then warmed to 60 °C for 2 h when it became blue-red and small red crystals separated. These were collected, washed with cold thf (2 × 10 cm^3) and then light petroleum (b.p. 30—40 °C), and dried *in vacuo*. Yield 0.55 g, 81%. The compound was characterised by microanalysis and by comparison of the i.r. spectrum with the literature (Found: C, 16.8; H, 4.5. Calc. for $[\{MoCl_2(SMe_2)_2\}_2]$: C, 16.5; H, 4.1%).

Bis[*dichlorobis*(*diethyl sulphide*)*molybdenum*] (10).—The preparation was carried out as described for the dimethyl sulphide analogue except that diethyl sulphide (3.5 cm^3) was used. Yield 0.71 g, 88% (Found: C, 28.4; H, 6.1; Cl, 20.2; S, 17.8. Calc. for $[\{MoCl_2(SEt_2)_2\}_2]$: C, 27.7; H, 5.8; Cl, 20.5; S, 18.4%).

Bis[*dichlorobis*(*triethylphosphine*)*molybdenum*] (11).—The compound (1) (1.16 g, 2.7 mmol) in thf (30 cm^3) and PEt_3 (2 cm^3) were treated with $SiMe_3Cl$ (4 cm^3, 31.6 mmol). An immediate orange colour developed and after 30 min this had changed to purple-red. After stirring at r.t. for 24 h a purple precipitate had separated. The solution was concentrated and cooled to 0 °C and the precipitate was collected, washed with cold thf, and dried *in vacuo*. The product was recrystallised from thf giving purple crystals. Yield 1.73 g, 79% (Found: C, 36.1; H, 7.8; Cl, 17.5. Calc. for $[\{MoCl_2(PEt_3)_2\}_2]$: C, 35.7; H, 7.4; Cl, 17.6%).

μ-σ:1—5-η-*Cyclopentadienediyl*-[*bis*(η-*cyclopentadienyl*)-*molybdenum*][(η-*cyclopentadienyl*)*hydridomolybdenum*] (12).—The compound (3) (0.72 g) in thf (35 cm^3) was treated with sodium cyclopentadienide in thf (4 cm^3 of a 2 mol dm^{-3} solution) and the mixture was stirred at r.t. for 4 h. A red-brown precipitate appeared. The mixture was filtered and the filtrate was concentrated under reduced pressure (to *ca.* 15 cm^3). Fine black crystals separated which were collected, washed with thf (3 × 10 cm^3), and dried *in vacuo*. Yield 0.25 g, 69%. The product was identified by comparison of the i.r. spectrum with that of an authentic sample.[2]

The Red-violet Compound $[Mo_2Cl_2(OCOMe)_2(dppm)]$ (13).—A suspension of $[\{MoCl(OCOMe)(thf)\}_2]$ (0.4 g, 0.8 mmol) in thf (20 cm^3) was treated with dppm (0.3 g, 0.8 mmol) in thf (6 cm^3). The mixture was stirred for 10 min and the suspension dissolved giving a deep red solution. Immediately the solution was concentrated under reduced pressure giving small red crystals which were collected, washed with light petroleum (b.p. 60—80 °C), and dried *in vacuo*. If the reaction mixture is allowed to stand then the compound $[\{MoCl_2(dppm)\}_2]$ separates. The yield of $[Mo_2Cl_2(OCOMe)_2(dppm)]$ was 0.48 g, 78%.

Selected I.R. Spectral Data.—Data (mulls) given as follows: compound number, wavenumbers (cm^{-1}) and intensities (w = weak, m = medium, s = strong, sh = shoulder, br = broad), assignments. [a] Characteristic of μ-OCOMe groups. [b] Mo–O and Mo–Cl stretching region. [c] ν(C=O) of a non-bridging, terminal Mo–O–COMe group.

(2): 1 528m, 1 499m, 1 430br s, 1 346w, 1 340w, 1 285vw;[a] 371m, 350m, 340m, 311m, 298m, 256w, Mo–O.[b]

(3): 1 520vw, 1 504vw, 1 481s, 1 434vs, 1 350w;[a] 357m, 316s, 294m, Mo-O[b]; ν(Mo≡Mo) 384 (Raman).

(4): 1 523m, 1 432s, 1 355w;[a] 389m, 347s, 299s, Mo–O.[b]

(5): 1 525vw, 1 510w, 1 475vs, 1 458vs, 1 342w;[a] 357m, 318s, 296s, Mo–O[b]; ν(Mo≡Mo) 383 (Raman).

(6): 1 515vw, 1 487m, 1 440vs, 1 410s, 1 380w, 1 341w;[a] 357m, 314s, 299s, Mo–O.[b]

(13): 1 710mw;[c] 1 523m, 1 487m, 1 460s, 1 410m, 1 365w, 1 353w;[a] 367m, 330s, 292m, Mo–O.[b]

Crystal Structure Determination.—*Crystal data.* $C_{28}H_{60}Cl_2Mo_2O_4P_2$, $M = 785.52$, Monoclinic, space group $P2_1/n$ (no. 14, non-standard setting: $x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$), $a = 14.969(2)$, $b = 15.146(2)$, $c = 8.920(2)$ Å, $\beta = 105.14(1)°$, $U = 1\,952$ Å^3, $Z = 2$, $D_c = 1.34$ g cm^{-3}, $F(000) = 816$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

Intensities of 5 417 reflections were measured on a CAD-4 diffractometer ($2\theta_{max.} = 52°$) using graphite-monochromated Mo-K_α radiation. 1 762 Independent reflections [$I > 3\sigma(I)$], not corrected for extinction or absorption [$\mu(\text{Mo-}K_\alpha) = 8.7$ cm^{-1}], were used in the refinement procedure.

The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All non-hydrogen atoms were allowed anisotropic thermal parameters; no hydrogens were located or included in the model. During the final stages of refinement, weights[12] were calculated from a three-term Chebyshev series, with parameters 21.3, 29.0, and 8.7. The final R value was 0.048 ($R' = 0.063$) for 1 776 observations, including 14 constraints as described in the Results section, and 199 least-squares parameters.

Data reduction, structure solution, and refinement were carried out with the Oxford CRYSTALS package[13] and the Oxford CHEMGRAF[14] system was used for the molecular diagram. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann;[15] the hydrogen scattering factor was taken from ref. 16.

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