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Synthesis of acylphosphine complexes by controllable migration of acyl groups from molybdenum to phosphido ligands†

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The acyl complexes $[Mo(COR^1)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ (R^1 = Me or Et) have been prepared in high yield by the reaction of $[MoR^1(CO)_3(\eta\text{-}C_5H_5)]$ with PPh_2H. Deprotonation of the diphenylphosphine ligand with 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) at −78 °C produced a phosphorus-centred anion which can be alkylated by treatment with R^2I (R^2 = Me or Et) to give the substituted phosphine acyl complexes $[Mo(COR^1)(CO)_2(PPh_2R^2)(\eta\text{-}C_5H_5)]$, or acylated with R^2COCl to produce acylphosphine acyl complexes $[Mo(COR^1)(CO)_2(PPh_2COR^2)(\eta\text{-}C_5H_5)]$. If the deprotonation is carried out at room temperature, however, migration of the metal acyl group to the phosphorus atom occurs to give the molybdenum-centred anion $[Mo(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]^-$, which can in turn be alkylated with R^2I to give the acylphosphine alkyl complexes $[MoR^2(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$. The metal-centred anion also undergoes typical reactions with H^+ and chlorinated solvents to give $[MoX(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$ (X = H or Cl). Mechanistic studies showed that (i) on deprotonation of the related complex $[MoMe(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ the methyl group does not undergo migration to phosphorus, and (ii) the reaction is largely intramolecular but with a measurable intermolecular component. A mechanism is therefore proposed involving nucleophilic attack on the acyl carbon atom by the anionic phosphido ligand. Full spectroscopic data for the new complexes are reported and interpreted, and the crystal structure of $[Mo(COMe)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$ has been determined.

The migratory insertion reaction of a metal-bound alkyl group with a CO ligand to form a metal acyl is one of the fundamental reactions of organometallic chemistry, and plays a major role in important catalytic processes such as hydroformylation and acetic acid carbonylation.[1] On the other hand, further migration reactions involving the acyl ligand itself, *e.g.* with CO to give a ketoacyl ligand, are relatively rare, at least in part because of the increased metal–carbon bond strength of $M-C(sp^2)$ bonds. In this paper we report the unprecedented migration of acyl ligands from a metal centre to a co-ordinated phosphido group to form acylphosphine complexes. Part of this work has previously appeared as a communication.[2]

Results and Discussion

We are interested in the processes of P−C bond cleavage and formation in phosphido complexes because of their involvement in the deactivation of industrially important catalyst systems, *e.g.* in hydroformylation.[3] It has been known for a long time that co-ordinated secondary phosphines can be readily deprotonated to give anionic terminal phosphido species which can subsequently be treated with a range of electrophiles.[4] During our previous work, we showed that a simple deprotonation–alkylation sequence could be successfully effected on the iron acyl complexes $[Fe(COR^1)(CO)(PPh_2H)(\eta\text{-}C_5H_5)]$ to give $[Fe(COR^1)(CO)(PPh_2R^2)(\eta\text{-}C_5H_5)]$ (R^1, R^2 = Me or Et).[5] On extension of the study to the analogous molybdenum acyl complexes, however, the unexpected results described below were obtained.

The appropriate starting materials $[Mo(COR^1)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ (R^1 = Me **1a** or Et **1b**) were readily prepared by stirring $[MoR^1(CO)_3(\eta\text{-}C_5H_5)]$ with PPh_2H at room temperature in acetonitrile overnight, as already established for the PPh_3 analogues (Scheme 1).[6] Their spectroscopic properties (Tables 1–3) are in complete accord with the proposed structures, with the characteristic doublet (J = 360 Hz) due to the P−H moiety present in their ^1H NMR spectra. The complexes exist, like the PPh_3 analogues, exclusively as the *trans* isomers, as shown by the intensities of the two peaks in the IR spectrum and by the observation of one resonance for the two CO ligands in the ^{13}C NMR spectrum.[7]

Low-temperature deprotonation–alkylation reactions

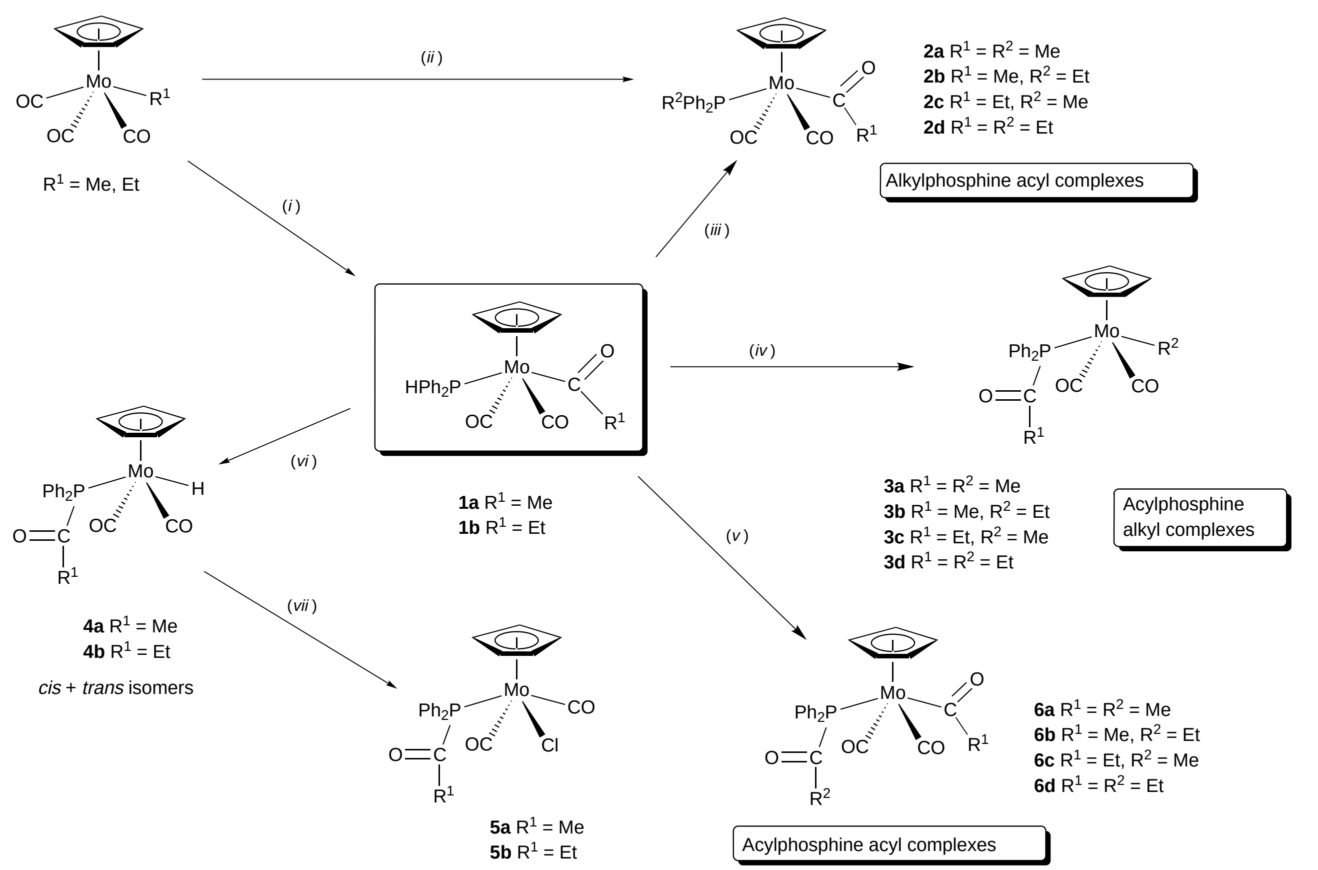
Deprotonation of the phosphine ligand of complex **1** proceeds smoothly with the organic base dbu (1,8-diazabicyclo[5.4.0]-undec-7-ene) at −78 °C in tetrahydrofuran (thf) to give an anionic species which is assumed to be the phosphido complex $[Mo(COR^1)(CO)_2(PPh_2)(\eta\text{-}C_5H_5)]^-$. The choice of base is however quite important. Previous attempts to deprotonate the acetyl ligand of $[Mo(COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ with $LiBu^n$ or the Wittig reagent $PPh_3{=}CH_2$ resulted only in loss of the acyl ligand and formation of the $[Mo(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^-$ anion.[8,9] In contrast to $[Fe(COMe)(CO)(PPh_2H)(\eta\text{-}C_5H_5)]$, which can be successfully deprotonated with either of these reagents, their use in the current reaction led to mixtures of products arising from competing phosphine deprotonation and acyl loss in both cases.

Addition of R^2I (R^2 = Me or Et) to the anion solution at low temperature produced excellent yields (>80%) of the alkylphosphine acyl complexes $[Mo(COR^1)(CO)_2(PPh_2R^2)(\eta\text{-}C_5H_5)]$ **2a**–**2d** (Scheme 1). This reaction therefore parallels the deprotonation–alkylation sequence previously observed for the iron acyl complexes. The products are known compounds, but their full characterising data, including ^{13}C NMR spectra, have not been previously reported and so are included here for ease of comparison (Tables 1–3). The identities of **2a**–**2d** were also confirmed by independent synthesis from $[MoR^1(CO)_3(\eta\text{-}C_5H_5)]$ and PPh_2R^2 in MeCN.

Room-temperature deprotonation–alkylation reactions

When the deprotonation reaction was carried out at room temperature (or if the low-temperature anion solution produced above was stirred at room temperature for a while before alkylation) the addition of R^2X (R^2 = Me or Et) gave different

† *Supplementary data available* (No. SUP 57273,7 pp): characterisation data for complexes **11**–**13**. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.



Scheme 1 Synthesis and deprotonation reactions of complexes **1a** and **1b**. Reagents and conditions: (*i*) PPh_2H in MeCN, room temperature (r.t.), 18 h; (*ii*) PPh_2R^2 in MeCN, r.t., 18 h; (*iii*) dbu, thf, −78 °C, 30 min, then R^2I, warm to r.t., stir for 18 h; (*iv*) dbu, thf, r.t., 30 min, then R^2I, stir for 18 h; (*v*) dbu, thf, −78 °C, 30 min, then R^2COCl at −78 °C, stir cold for 2 h; (*vi*) dbu, thf, r.t., 30 min, then $MeCO_2H$; (*vii*) $CHCl_3$

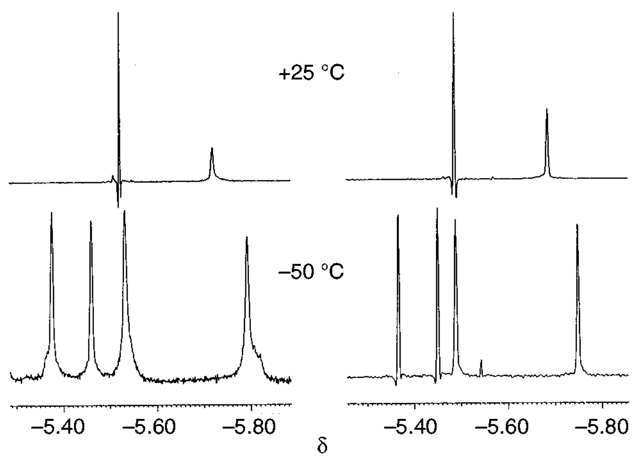


Fig. 1 Proton NMR spectra of $[MoH(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$ in $[^2H_8]$toluene at 25 °C and −50 °C: left, **4a** (R^1 = Me), right **4b** (R^1 = Et)

products, again in excellent yield. These four compounds **3a**–**3d** were identified as the novel acylphosphine alkyl complexes $[MoR^2(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$ on the basis of their spectroscopic data (Scheme 1). Examination of the data (Tables 1–3) shows that the acylphosphine alkyl complexes **3** can be distinguished from their isomeric alkylphosphine acyl counterparts **2** in several ways. First, in the IR spectrum in CH_2Cl_2, although there is little change in the two strong terminal CO absorptions (indicative of a *trans* configuration of the CO ligands), the rather weak ketonic carbonyl peak appears at *ca.* 1685 cm^{-1} for **3** compared to *ca.* 1600 cm^{-1} for **2**. Secondly, the ^{31}P NMR spectrum of **3** comprises a singlet at around δ 80, a difference in chemical shift of approximately 30 ppm compared to **2**. Thirdly, the presence of the acylphosphine ligand is confirmed by the ^{13}C NMR spectrum which contains a doublet at about δ 212 (J = *ca.* 15 Hz) due to the acyl carbon, whereas acyl ligands bound to molybdenum such as in **2** resonate at much lower field, *ca.* δ 270. The ^1H NMR spectra of the methyl complexes **3a** and **3c** reveal the presence of small amounts (<5%) of *cis* isomers, whereas in the ethyl complexes **3b** and **3d** only the *trans* isomers could be distinguished.

From the exclusive formation of these products and the distribution of R^1 and R^2 in them, we concluded that at room temperature a rapid migration of the acyl ligand to the phosphido group occurs, giving the molybdenum-centred anion $[Mo(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]^-$. Complexes containing acylphosphine ligands are not common and have previously been prepared by the reaction of suitably labile precursors with free acylphosphines[10] or by acetylation of anionic phosphido ligands with acetyl chloride.[11] There are no prior reports of migration of an acyl ligand to a phosphido group, though it has been reported that at 120 °C acylphosphines are decarbonylated to alkylphosphines by Wilkinson's catalyst, a reaction which presumably involves the reverse process.[12] There are, however, examples of the attack of cyclopentadienylphosphine ligands on η^2-acyl groups bound to zirconium.[13]

The presence of $[Mo(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]^-$ is also indicated by the fact that the solution undergoes the typical reactions expected of such an anion (Scheme 1); thus protonation with acetic acid afforded the hydride complexes $[MoH(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$ **4a**, **4b** and dissolution of these in chlorinated solvents produced $[MoCl(CO)_2(PPh_2COR^1)(\eta\text{-}C_5H_5)]$ **5a**, **5b**, which were characterised spectroscopically. All showed IR and NMR peaks for the acylphosphine ligand similar to those observed for **3**.

The hydride complexes **4a** and **4b** both give rise to asymmetric doublets at δ −5.62 and −5.59 respectively in their room-temperature ^1H NMR spectra in $[^2H_8]$toluene because they exist as rapidly interconverting *cis* and *trans* isomers.[14] At −50 °C this isomerisation can be frozen out (Fig. 1) and the separate signals for the two isomers resolved. In keeping with

Table 1 Infrared, mass spectra and analytical data for the complexes

	Compound	IR ν(CO)[a]/cm^{-1}	Mass spectrum *m/z*	Microanalysis (%)[b]
1a	$[Mo(COMe)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$	1940m, 1856s, 1618 (br)	448 (M^+)	C 56.43 (56.52); H 4.14 (4.29)
1b	$[Mo(COEt)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$	1938m, 1853s, 1614mw	463 (M + H)$^+$	C 57.36 (57.40); H 4.75 (4.60)
2a	$[Mo(COMe)(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)]$	1934m, 1849s, 1601 (br)	462 (M^+)	C 57.15 (57.40); H 4.35 (4.60)
2b	$[Mo(COMe)(CO)_2(PPh_2Et)(\eta\text{-}C_5H_5)]$	1933m, 1847s, 1603 (br)	477 (M + H)$^+$	C 58.18 (58.24); H 4.80 (4.89)
2c	$[Mo(COEt)(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)]$	1931m, 1845s, 1610mw	477 (M + H)$^+$	C 58.01 (58.24); H 4.72 (4.89)
2d	$[Mo(COEt)(CO)_2(PPh_2Et)(\eta\text{-}C_5H_5)]$	1930m, 1845s, 1611w	491 (M + H)$^+$	C 58.87 (59.03); H 4.91 (5.16)
3a	$[MoMe(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1937m, 1855s, 1686vw	462 (M^+)	C 57.14 (57.40); H 4.74 (4.60)
3b	$[MoEt(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1931m, 1850s, 1686vw	476 (M^+)	C 58.10 (58.24); H 4.79 (4.89)
3c	$[MoMe(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1936m, 1854s, 1690w	476 (M^+)	C 58.19 (58.24); H 4.78 (4.89)
3d	$[MoEt(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1930m, 1849s, 1689w	490 (M^+)	C 58.83 (59.03); H 5.24 (5.16)
4a	$[MoH(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1941s, 1861s, 1685w	448 (M^+)	C 56.07 (56.52); H 4.18 (4.29)
4b	$[MoH(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1940s, 1860s, 1684w	463 (M + H)$^+$	C 57.54 (57.40); H 4.57 (4.60)
5a	$[MoCl(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1972s, 1881ms, 1686w	484 (M + H)$^+$	C 52.33 (52.47); H 3.81 (3.77)[c]
5b	$[MoCl(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1971s, 1879ms, 1687w	498 (M + H)$^+$	C 53.74 (53.41); H 4.22 (4.07)[d]
6a	$[Mo(COMe)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1939m, 1858s, 1690vw, 1623w	491 (M + H)$^+$	C 56.57 (56.57); H 4.15 (4.33)
6b	$[Mo(COMe)(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1939m, 1857s, 1693w, 1622w	505 (M + H)$^+$	C 57.13 (57.38); H 4.65 (4.62)
6c	$[Mo(COEt)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1937m, 1855s, 1690w, 1619mw	504 (M^+)	C 57.23 (57.38); H 4.88 (4.62)
6d	$[Mo(COEt)(CO)_2(PPh_2COEt)(\eta\text{-}C_5H_5)]$	1936m, 1854s, 1692w, 1619m	519 (M + H)$^+$	C 57.90 (58.19); H 4.77 (4.88)
7	$[\{Mo(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)\}_2]$	1856m, 1835s	807 (M + H)$^+$	C 56.39 (56.59); H 4.20 (4.00)
8	$[MoMe(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$	1935m, 1851s	420 (M^+)	C 57.90 (57.43); H 4.79 (4.58)
9a	$[\{Mo(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)\}_2]$	1846m, 1825s	834 (M^+)	C 57.54 (57.57); H 4.53 (4.35)
9b	$[\{Mo(CO)_2(PPh_2Et)(\eta\text{-}C_5H_5)\}_2]$	1844m, 1824s	863 (M + H)$^+$	C 58.18 (58.48); H 4.86 (4.67)
10a	$[MoMe(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)]$	1929m, 1842s	434 (M^+)	C 58.12 (58.34); H 4.95 (4.90)
10b	$[MoEt(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)]$	1924m, 1838s	448 (M^+)	C 58.74 (59.20); H 5.14 (5.19)
10c	$[MoMe(CO)_2(PPh_2Et)(\eta\text{-}C_5H_5)]$	1929m, 1842s	448 (M^+)	C 58.95 (59.20); H 5.00 (5.19)
10d	$[MoEt(CO)_2(PPh_2Et)(\eta\text{-}C_5H_5)]$	1923m, 1837s	462 (M^+)	C 59.91 (60.01); H 5.57 (5.57)

[a] In CH_2Cl_2 solution. [b] Found (Calc.). [c] Cl 7.64 (7.37). [d] Cl 6.98 (7.17).

other complexes of this type, the hydride signal of the *cis* isomer occurs at slightly higher field and has a much larger J(PH) value (*ca.* 65 Hz) than the *trans* isomer (*ca.* 20 Hz).[15] The ratio of the *cis*:*trans* isomers at this temperature was approximately 57:43 for both compounds.

The chloride complexes **5a** and **5b** could be obtained either by treatment of the hydrides **4** with chloroform, or directly from the anion by dissolution in CH_2Cl_2 or $CHCl_3$. They exist exclusively as the *cis* isomers, as shown by the IR spectrum and the appearance of two terminal CO resonances in the ^{13}C NMR spectrum. In a seminal study of the *cis*:*trans* ratios in complexes of the type $[MoR(CO)_2L(\eta\text{-}C_5H_5)]$, Faller and Anderson[14] showed that the steric and electronic properties of R and L were both important factors, but for a constant L the *cis*:*trans* ratio increased in the order R = CH_2Ph < Me < H < I < Br < Cl. The observation of small amounts of *cis* isomers for the methyl complexes **3a** and **3c**, an approximate 6:4 ratio for the hydride complexes **4a** and **4b**, and exclusively *cis* for the chlorides **5a** and **5b** is entirely consistent with these findings.

Deprotonation–acylation reactions

The phosphorus-centred anions derived from low-temperature deprotonation of complex **1** reacted cleanly with the acyl chlorides R^2COCl to give the acylphosphine acyl complexes $[Mo(COR^1)(CO)_2(PPh_2COR^2)(\eta\text{-}C_5H_5)]$ **6a**–**6d** in yields of over 80% (Scheme 1). Attempts to obtain the same products from the molybdenum-centred anions derived by room-temperature deprotonation of **1** led instead to a mixture of products, including the hydride complexes **4**. As expected these four compounds show NMR signals characteristics of both molybdenum–acyl and phosphorus–acyl functionalities which can be readily assigned by comparison with the spectra of **2** and **3**.

The structure of complex **6a** was determined by X-ray diffraction and is shown in Fig. 2. Selected bond lengths and angles are given in Table 4. As expected the acylphosphine and acyl ligands occupy the *trans* positions in a typical four-legged piano-stool structure. The Mo–P and Mo–C(21) distances are virtually identical to those found in the triphenylphosphine analogue $[Mo(COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$, as are

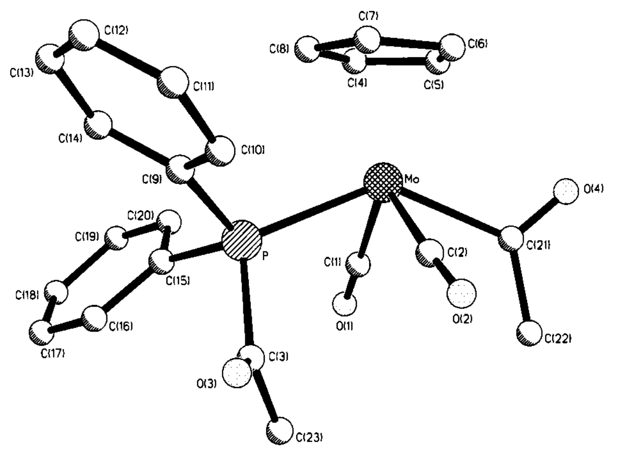


Fig. 2 Molecular structure of $[Mo(COMe)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **6a** in the crystal

the bond angles around the basal ligands except for a very slight opening up of the C(21)–Mo–P angle.[16] The two acetyl groups are orientated almost perpendicular to each other; the C(3)–O(3) distance in the acylphosphine unit is slightly shorter than the C(21)–O(4) length of the metal acyl, but not significantly so.

Synthesis of alkylphosphine alkyl complexes

In order to study the mechanism of the migration reaction (see below) we required a route to the complex $[MoMe(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$. Attempts to prepare it by thermal decarbonylation of the acyl complex **1a** led instead to loss of the phosphine ligand and formation of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ among other products. A different method was therefore employed (Scheme 2). The substituted dimer $[\{Mo(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)\}_2]$ **7** was prepared by the reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with 2 equivalents of PPh_2H. Cleavage of this dimer with sodium amalgam and alkylation of the resulting anion with MeI gave the desired complex **8** in moderate yield (46%). The ^{1}H NMR spectrum of the product showed that it exists mainly as the *cis* isomer (*cis*:*trans* ratio 1.66:1).

Table 2 Proton and ^{31}P NMR spectra of the complexes

Compound	^{1}H NMR [a] (δ)	^{31}P NMR [a] (δ)
1a	7.75–7.30 (m, 10 H, Ph), 7.08 (d, J_{PH} 361, 1 H, PH), 5.08 (d, J_{PH} 1.6, 5 H, η-C_5H_5), 2.60 (s, 3 H, Me)	41.3
1b	7.61–7.37 (m, 10 H, Ph), 7.07 (d, J_{PH} 360, 1 H, PH), 5.07 (d, J_{PH} 1.2, 5 H, η-C_5H_5), 2.98 (q, J_{HH} 7.4, 2 H, CH_2), 0.88 (t, J_{HH} 7.4, 3 H, CH_3)	42.3
2a	7.58–7.42 (m, 10 H, Ph), 5.00 (d, J_{PH} 1.0, 5 H, η-C_5H_5), 2.59 (s, 3 H, COMe), 2.20 (d, J_{PH} 8.5, 3 H, PMe)	49.5
2b	7.51–7.41 (m, 10 H, Ph), 4.92 (d, J_{PH} 1.0, 5 H, η-C_5H_5), 2.67 (dq, J_{PH} 8.5, J_{HH} 7.8, 2 H, CH_2 of Et), 2.61 (s, 3 H, COMe), 1.16 (dt, J_{PH} 19, J_{HH} 7.8, 3 H, CH_3 of Et)	60.2
2c	7.56–7.41 (m, 10 H, Ph), 4.99 (d, J_{PH} 1.2, 5 H, η-C_5H_5), 3.00 (q, J_{HH} 7.1, 2 H, CH_2 of Et), 2.19 (d, J_{PH} 8.1, 3 H, PMe), 0.89 (t, J_{HH} 7.1, 3 H, CH_3 of Et)	50.0
2d	7.53–7.38 (m, 10 H, Ph), 4.92 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 3.07 (q, J_{HH} 7.0, 2 H, CH_2 of COEt), 2.67 (dq, J_{HH} 7.5, J_{PH} 0.5, 2 H, CH_2 of PEt), 1.16 (dt, J_{PH} 18.0, J_{HH} 7.5, 3 H, CH_3 of PEt), 0.92 (t, J_{HH} 7.0, 3 H, CH_3 of COEt)	60.6
3a	*trans* isomer: 7.58–7.42 (m, 10 H, Ph), 4.77 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.27 (d, J_{PH} 4.0, 3 H, COMe), 0.44 (d, J_{PH} 2.5, 3 H, MoMe) *cis* isomer: 5.12 (s, η-C_5H_5), 2.18 (d, J_{PH} 3.1, COMe), −0.20 (d, J_{PH} 11.8, MoMe)	*trans* 83.0, *cis* 77.9
3b	7.55–7.41 (m, 10 H, Ph), 4.75 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.27 (d, J_{PH} 4.5, 3 H, COMe), 1.73 (m, 2 H, CH_2 of Et), 1.53 (dt, J_{HH} 7.5, J_{PH} 1.0, 3 H, CH_3 of Et)	84.1
3c	*trans* isomer: 7.56–7.38 (m, 10 H, Ph), 4.76 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.58 (q, J_{HH} 7.0, J_{PH} 0.8, 2 H, CH_2 of Et), 1.02 (dt, J_{HH} 7.0, J_{PH} 0.5, 3 H, CH_3 of Et), 0.42 (d, J_{PH} 2.1, 3 H, MoMe) *cis* isomer: 5.10 (s, η-C_5H_5), 2.43 (m, CH_2 of Et), 0.88 (m, CH_3 of Et), −0.21 (d, J_{PH} 11.5, MoMe)	*trans* 81.0, *cis* 76.8
3d	7.54–7.37 (m, 10 H, Ph), 4.73 (d, J_{PH} 1.4, 5 H, η-C_5H_5), 2.59 (dq, J_{HH} 7.5, J_{PH} 0.8, 2 H, CH_2 of COEt), 1.71 (m, 2 H, CH_2 of MoEt), 1.53 (t, J_{HH} 7.5, CH_3 of MoEt), 1.01 (dt, J_{HH} 7.0, J_{PH} 0.8, 3 H, CH_3 of COEt)	82.1
4a	+25 °C:[b] 7.58–6.92 (m, 10 H, Ph), 4.66 (d, J_{PH} 0.8, 5 H, η-C_5H_5), 2.01 (d, J_{PH} 4.3, 3 H, Me), −5.62 (d, J_{PH} 50.4, 1 H, MoH) *cis* isomer, −50 °C:[b] 7.48–6.85 (m, 10 H, Ph), 4.54 (s, 5 H, η-C_5H_5), 2.02 (m, 3 H, Me), −5.65 (d, J_{PH} 65.1, MoH) *trans* isomer, −50 °C:[b] 7.48–6.85 (m, 10 H, Ph), 4.43 (s br, 5 H, η-C_5H_5), 1.81 (d, J_{PH} 6.0, 3 H, Me), −5.42 (d, J_{PH} 20.7, MoH)	81.5
4b	+25 °C:[b] 7.52–6.92 (m, 10 H, Ph), 4.65 (s, 5 H, η-C_5H_5), 2.44 (q, J_{HH} 6.8, 2 H, CH_2), 0.87 (t, J_{PH} 6.8, 3 H, CH_3), −5.59 (d, J_{PH} 50.5, 1 H, MoH) *cis* isomer, −50 °C:[b] 7.51–6.89 (m, 10 H, Ph), 4.56 (s, 5 H, η-C_5H_5), 2.45 (m, 2 H, CH_2), 0.86 (m, 3 H, CH_3), −5.63 (d, J_{PH} 65.5, MoH) *trans* isomer, −50 °C:[b] 7.51–6.89 (m, 10 H, Ph), 4.45 (s br, 5 H, η-C_5H_5), 2.45 (m, 2 H, CH_2), 0.86 (m, 3 H, CH_3), −5.42 (d, J_{PH} 20.8, MoH)	79.6
5a	7.66–7.38 (m, 10 H, Ph), 5.44 (s, η-C_5H_5), 2.24 (d, J_{PH} 2.7, 3 H, Me)	59.1
5b	7.67–7.36 (m, 10 H, Ph), 5.39 (s, η-C_5H_5), 2.44 (ddq, J_{HH} 7.0, J_{PH} 2.1, 2 H, CH_2), 0.95 (dt, J_{HH} 7.0, J_{PH} 1.0, 3 H, CH_3)	58.0
6a	7.55–7.45 (m, 10 H, Ph), 5.00 (d, J_{PH} 1.3, 5 H, η-C_5H_5), 2.66 (s, 3 H, MoCOMe), 2.43 (d, J_{PH} 4.5, 3 H, PCOMe)	77.0
6b	7.51–7.41 (m, 10 H, Ph), 4.97 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.72 (dq, J_{HH} 7.0, J_{PH} 1.0, 2 H, CH_2 of Et), 2.64 (s, 3 H, COMe), 1.09 (dt, J_{HH} 7.0, J_{PH} 0.8, 3 H, CH_3 of Et)	75.0
6c	7.51–7.41 (m, 10 H, Ph), 4.98 (d, J_{PH} 1.1, 5 H, η-C_5H_5), 3.05 (q, J_{HH} 7.2, 2 H, CH_2 of Et), 2.41 (d, J_{PH} 4.0, 3 H, COMe), 0.92 (t, J_{HH} 7.2, 3 H, CH_3 of Et)	77.4
6d	7.62–7.40 (m, 10 H, Ph), 4.99 (d, J_{PH} 1.2, 5 H, η-C_5H_5), 3.06 (q, J_{HH} 7.0, 2 H, CH_2 of MoCOEt), 2.73 (dq, J_{HH} 7.0, J_{PH} 1.2, 2 H, CH_2 of PCOEt), 1.10 (dt, J_{HH} 7.0, J_{PH} 0.8, 3 H, CH_3 of PCOEt), 0.94 (t, J_{HH} 7.0, 3 H, CH_3 of MoCOEt)	75.5
7	7.71–7.28 (m, 20 H, Ph), 7.26 (d, J_{PH} 353, 2 H, PH), 4.61 (d, J_{PH} 2.2, 10 H, η-C_5H_5)	57.8
8	*cis* isomer: 7.59–7.30 (m, 10 H, Ph), 6.36 (d, J_{PH} 346, 1 H, PH), 5.06 (s, 5 H, η-C_5H_5), −0.08 (d, J_{PH} 15.0, 3 H, Me) *trans* isomer: 7.10 (d, J_{PH} 355, 1 H, PH), 4.84 (d, J_{PH} 1.9, 5 H, η-C_5H_5), 0.34 (d, J_{PH} 2.5, 3 H, Me)	*cis* 58.4, *trans* 45.7
9a	*trans* isomer: 7.64–7.38 (m, 20 H, Ph), 4.63 (d, J_{PH} 1.8, 10 H, η-C_5H_5), 2.16 (d, J_{PH} 8.3, 6 H, Me) *cis* isomer: 4.81 (d, J_{PH} 1.4, 10 H, η-C_5H_5), 2.17 (m, 6 H, Me)	*trans* 60.7, *cis* 62.7
9b	*trans* isomer: 7.77–7.38 (m, 20 H, Ph), 4.66 (d, J_{PH} 1.8, 10 H, η-C_5H_5), 2.58 (dq, J_{PH} 7.0, J_{HH} 7.0, 4 H, CH_2), 1.10 (m, 6 H, CH_3) *cis* isomer: 4.72 (d, J_{PH} 1.5, 10 H, η-C_5H_5), 2.68 (dq, J_{PH} 7.0, J_{HH} 7.0, 4 H, CH_2), 1.10 (m, 6 H, CH_3)	*trans* 70.8, *cis* 71.2
10a	*trans* isomer: 7.59–7.30 (m, 10 H, Ph), 4.74 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.11 (d, J_{PH} 8.0, 3 H, PMe), 0.34 (d, J_{PH} 2.6, 3 H, MoMe) *cis* isomer: 5.08 (s, 5 H, η-C_5H_5), 1.95 (d, J_{PH} 8.0, 3 H, PMe), −0.20 (d, J_{PH} 11.5, 3 H, MoMe)	*trans* 53.7, *cis* 49.8
10b	7.58–7.38 (m, 10 H, Ph), 4.72 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.15 (d, J_{PH} 8.0, 3 H, PMe), 1.69–1.58 (m, 2 H, CH_2 of Et), 1.54–1.47 (m, 3 H, CH_3 of Et)	54.9
10c	*trans* isomer: 7.56–7.36 (m, 10 H, Ph), 4.66 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.70 (dq, J_{HH} 7.0, J_{PH} 7.5, 2 H, CH_2 of Et), 1.00 (dt, J_{HH} 7.0, J_{PH} 17.5, 3 H, CH_3 of Et), 0.37 (d, J_{PH} 2.5, 3 H, MoMe) *cis* isomer: 5.10 (s, 5 H, η-C_5H_5), 2.33 (m, 2 H, CH_2 of Et), 0.98 (dt, J_{HH} 7.5, J_{PH} 16.5, 3 H, CH_3 of Et), −0.2 (d, J_{PH} 1.5, MoMe)	*trans* 65.3, *cis* 60.5
10d	7.56–7.30 (m, 10 H, Ph), 4.65 (d, J_{PH} 1.5, 5 H, η-C_5H_5), 2.58 (dq, J_{HH} 7.5, J_{PH} 7.5, 2 H, CH_2 of PEt), 1.66–1.59 (m, 2 H, CH_2 of MoEt), 1.55–1.48 (m, 3 H, CH_3 of MoEt), 1.00 (dt, J_{HH} 7.5, J_{PH} 18.0, 3 H, CH_3 of PEt)	65.9

[a] In $CDCl_3$ solution unless otherwise stated; *J* in Hz. [b] In [$^2H_8$]toluene solution.

Sequential addition of dbu and EtI to a thf solution of complex **8** at room temperature afforded a single product which was characterised as [MoMe(CO)$_2$(PPh$_2$Et)(η-C_5H_5)] **10c**. It is therefore possible to say that there is no migration of the methyl ligand to the phosphido group in the intermediate anion, and this remained so even when the reaction was repeated in refluxing thf.

To complete a series of related complexes and provide a sample of complex **10c** independently for comparison purposes, we then prepared the alkylphosphine alkyl species [MoR^2(CO)$_2$(PPh$_2$R^1)(η-C_5H_5)] **10a**–**10d** by the same synthetic route as used for **8** (Scheme 2). The substituted dimers **9a** and **9b** were made from [Mo$_2$(CO)$_4$(η-C_5H_5)$_2$] and PPh$_2$Me or PPh$_2$Et; they display similar spectroscopic properties to those of the PPh$_3$ analogue, though their relative insolubility prevented the acquisition of useful ^{13}C NMR spectra.[17] Reduction with Na/Hg and alkylation with R^{2}X gave good yields of **10a**–**10d**. Of these, **10a** has been previously made by the thermal decarbonylation of

Table 3 Carbon-13 NMR data for the complexes

Compound	δ (J/Hz)[a]
1a	265.6 (d, *J* 11, *C*OMe), 235.8 (d, *J* 25, CO), 133.5 (d, *J* 40, C_{ipso}), 133.8–128.4 (m, Ph), 95.8 (s, η-C_5H_5), 51.4 (s, Me)
1b	267.3 (d, *J* 12, *C*OEt), 236.2 (d, *J* 16, CO), 133.2 (apparent s, C_{ipso}), 132.3–128.9 (m, Ph), 95.7 (s, η-C_5H_5), 58.2 (s, CH_2), 9.9 (s, CH_3)
2a	266.7 (d, *J* 11, *C*OMe), 237.5 (d, *J* 24, CO), 137.1 (d, *J* 44, C_{ipso}), 131.4–128.4 (m, Ph), 96.0 (s, η-C_5H_5), 51.3 (s, CO*Me*), 20.5 (d, *J* 34, PMe)
2b	265.9 (d, *J* 11, *C*OMe), 238.3 (d, *J* 23, CO), 135.8 (d, *J* 40, C_{ipso}), 131.9–128.5 (m, Ph), 96.3 (s, η-C_5H_5), 50.7 (s, CO*Me*), 26.3 (d, *J* 32, CH_2 of Et), 8.8 (s, CH_3 of Et)
2c	268.2 (d, *J* 11, *C*OEt), 237.9 (d, *J* 24, CO), 137.4 (d, *J* 40, C_{ipso}), 131.4–128.5 (m, Ph), 96.1 (s, η-C_5H_5), 57.9 (s, CH_2 of Et), 20.3 (d, *J* 34, PMe), 9.9 (s, CH_3 of Et)
2d	267.9 (d, *J* 11, *C*OEt), 238.5 (d, *J* 23, CO), 135.8 (d, *J* 40, C_{ipso}), 131.9–128.5 (m, Ph), 96.2 (s, η-C_5H_5), 57.4 (s, CH_2 of COEt), 26.1 (d, *J* 32, CH_2 of PEt), 10.0 (s, CH_3 of COEt), 8.8 (s, CH_3 of PEt)
3a	*trans* isomer: 235.5 (d, *J* 21, CO), 212.9 (d, *J* 15, *C*OMe), 133.6 (d, *J* 40, C_{ipso}), 133.7–128.5 (m, Ph), 92.3 (s, η-C_5H_5), 30.3 (d, *J* 43, CO*Me*), −18.8 (d, *J* 9, MoMe) *cis* isomer: 92.2 (s, η-C_5H_5)
3b	236.0 (d, *J* 21, CO), 213.0 (d, *J* 15, *C*OMe), 133.3 (apparent s, C_{ipso}), 133.7–128.5 (m, Ph), 92.6 (s, η-C_5H_5), 30.2 (d, *J* 44, CO*Me*), 19.6 (s, CH_3 of Et), −2.5 (d, *J* 9, CH_2 of Et)
3c	*trans* isomer: 234.7 (d, *J* 21, CO), 215.9 (d, *J* 13, *C*OMe), 133.7 (d, *J* 39, C_{ipso}), 133.7–128.5 (m, Ph), 92.3 (s, η-C_5H_5), 36.1 (d, *J* 41, CH_2 of Et), 8.3 (d, *J* 2, CH_3 of Et), −18.8 (d, *J* 9, MoMe) *cis* isomer: 92.2 (s, η-C_5H_5)
3d	236.2 (d, *J* 21, CO), 216.0 (d, *J* 13, *C*OMe), 133.7 (d, *J* 39, C_{ipso}), 133.7–128.4 (m, Ph), 92.6 (s, η-C_5H_5), 36.0 (d, *J* 40, CH_2 of COEt), 19.55 (s, CH_3 of MoEt), 8.2 (d, *J* 2, CH_3 of COEt), −2.3 (d, *J* 9, CH_2 of MoEt)
4a	236.1 (s br, CO), 213.5 (d, *J* 16, *C*OMe), 135.4 (d, *J* 42, C_{ipso}), 133.9–128.5 (m, Ph), 89.9 (s, η-C_5H_5), 29.5 (d, *J* 46, CO*Me*)[b]
4b	236.5 (s br, CO), 216.7 (d, *J* 13, *C*OEt), 135.4 (d, *J* 40, C_{ipso}), 133.9–128.6 (m, Ph), 89.9 (s, η-C_5H_5), 35.8 (d, *J* 43, CH_2 of Et), 8.3 (d, *J* 2, CH_3 of Et)[b]
5a	255.4 (d, *J* 28, *cis* CO), 242.6 (d, *J* 6, *trans* CO), 218.5 (d, *J* 11, *C*OMe), 135.4–128.7 (m, Ph), 132.6 (d, *J* 38, C_{ipso}), 129.3 (d, *J* 38, C_{ipso}), 95.0 (s, η-C_5H_5), 36.9 (d, *J* 35, CO*Me*)
5b	255.9 (d, *J* 29, *cis* CO), 242.9 (d, *J* 6, *trans* CO), 220.9 (d, *J* 9, *C*OEt), 135.5–128.7 (m, Ph), 132.8 (d, *J* 37, C_{ipso}), 129.4 (d, *J* 36, C_{ipso}), 95.0 (s, η-C_5H_5), 43.0 (d, *J* 32, CH_2), 6.9 (s, CH_3)
6a	263.3 (d, *J* 10, Mo*C*OMe), 236.6 (d, *J* 22, CO), 212.0 (d, *J* 15, P*C*OMe), 133.6–128.8 (m, Ph), 132.0 (d, *J* 41, C_{ipso}), 96.5 (s, η-C_5H_5), 51.3 (s, MoCO*Me*), 30.9 (d, *J* 44, PCO*Me*)
6b	263.5 (d, *J* 9, *C*OMe), 236.8 (d, *J* 22, CO), 215.3 (d, *J* 12, *C*OEt), 133.6–128.7 (m, Ph), 132.2 (d, *J* 40, C_{ipso}), 96.5 (s, η-C_5H_5), 51.2 (s, CO*Me*), 37.1 (d, *J* 41, CH_2 of Et), 8.0 (d, *J* 3, CH_3 of Et)
6c	264.6 (d, *J* 10, *C*OEt), 236.8 (d, *J* 22, CO), 212.1 (d, *J* 15, *C*OMe), 133.6–128.8 (m, Ph), 132.2 (d, *J* 41, C_{ipso}), 96.4 (s, η-C_5H_5), 58.2 (s, CH_2 of Et), 30.9 (d, *J* 44, CO*Me*), 10.1 (s, CH_3 of Et)
6d	265.2 (d, *J* 10, Mo*C*OEt), 236.9 (d, *J* 22, CO), 215.3 (d, *J* 12, P*C*OEt), 133.5–128.7 (m, Ph), 132.1 (d, *J* 41, C_{ipso}), 96.3 (s, η-C_5H_5), 58.1 (s, CH_2 of MoCOEt), 36.9 (d, *J* 41, CH_2 of PCOEt), 10.1 (s, CH_3 of MoCOEt), 8.0 (d, *J* 3, CH_3 of PCOEt)
8	*cis* isomer: 253.5 (d, *J* 28, *cis* CO), 239.7 (s, *trans* CO), 137.5 (d, *J* 41, C_{ipso}), 134.7 (d, *J* 43, C_{ipso}), 133.7–128.5 (m, Ph), 92.0 (s, η-C_5H_5), −16.6 (d, *J* 20, Me), *trans* isomer: 233.9 (d, *J* 23, CO), 91.6 (s, η-C_5H_5), 20.0 (d, *J* 10, Me)
10a	*trans* isomer: 235.5 (d, *J* 23, CO), 139.2 (d, *J* 40, C_{ipso}), 132.4–128.1 (m, Ph), 92.0 (s, η-C_5H_5), 21.5 (d, *J* 34, PMe), −19.6 (d, *J* 10, MoMe) *cis* isomer: 91.9 (s, η-C_5H_5)
10b	236.6 (apparent s, CO), 139.3 (d, *J* 40, C_{ipso}), 133.0–127.8 (m, Ph), 92.3 (s, η-C_5H_5), 21.5 (d, *J* 33, PMe), 20.0 (s, CH_3 of Et), −3.4 (d, *J* 11, CH_2 of Et)
10c	*trans* isomer: 236.4 (d, *J* 22, CO), 137.7 (d, *J* 37, C_{ipso}), 132.1–128.3 (m, Ph), 92.0 (s, η-C_5H_5), 27.1 (d, *J* 33, CH_2 of Et), 8.7 (s, CH_3 of Et), −18.8 (d, *J* 11, MoMe) *cis* isomer: 91.7 (s, η-C_5H_5)
10d	237.9 (d, *J* 22, CO), 137.8 (d, *J* 37, C_{ipso}), 132.2–128.2 (m, Ph), 92.4 (s, η-C_5H_5), 26.7 (d, *J* 33, CH_2 of PEt), 19.6 (s, CH_3 of MoEt), 8.7 (s, CH_3 of PEt), −2.9 (d, *J* 10, CH_2 of MoEt)

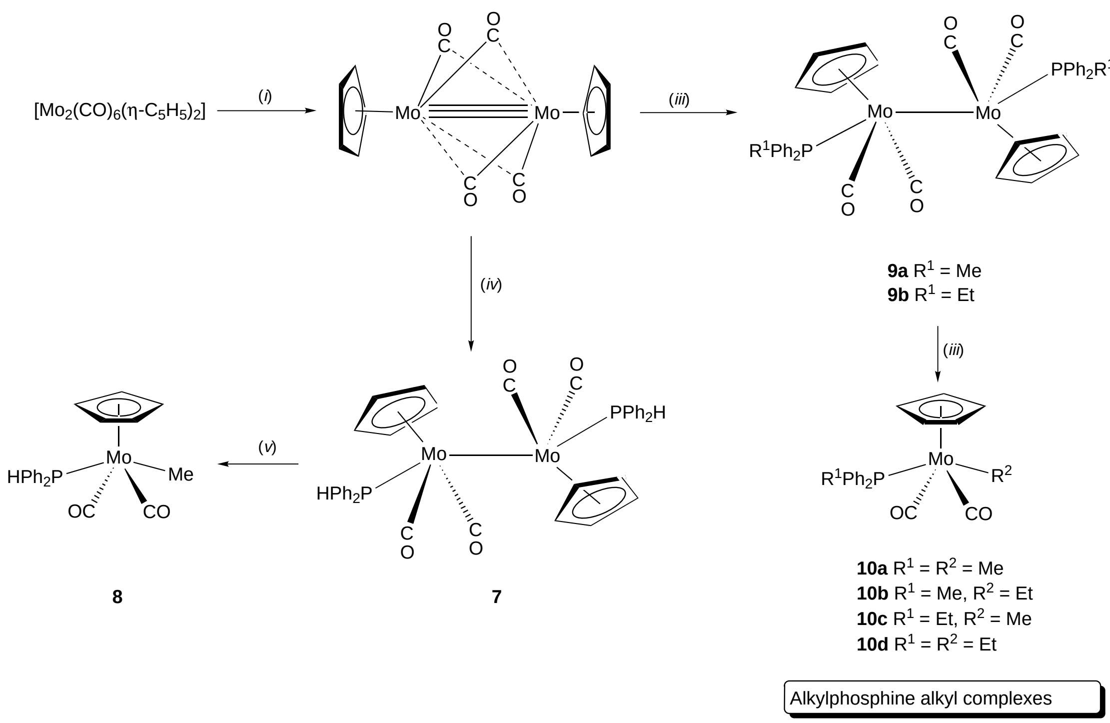
[a] In $CDCl_3$ solution unless otherwise stated, all couplings are J_{PC}. [b] In C_6D_6 with added $[Cr(acac)_3]$ (acac = acetylacetonate).

2a, but the others appear to be new compounds.[6] Their spectroscopic data are as expected; in the cases where R^2 = Me, significant amounts of *cis* isomers were observed in the ^1H NMR spectra whereas the signals for a *cis* isomer could not be unambiguously identified for **10b** and **10d**.

The mechanism

At low temperature the complexes **1** undergo a standard deprotonation–alkylation sequence at the secondary phosphine ligand to produce **2**, whereas at room temperature migration of the acyl group to phosphorus leads to the acylphosphine alkyl complexes **3**. The migration must occur from a *cis* position, whereas both reagent and product exist almost exclusively in the *trans* conformation. On the other hand the methyl complex **8** does not undergo any rearrangement on deprotonation, even when heated. If the rearrangement was a simple migratory insertion reaction the methyl group of **8** would be expected to migrate more readily than the acyl group of **1** because (*i*) Me has a much higher migratory aptitude than COMe and (*ii*) complex **8** exists predominantly as the *cis* isomer and so is correctly aligned for migration to occur. We therefore propose that the migration occurs by nucleophilic attack of the phosphido group on the acyl carbon as shown in Scheme 3. This pathway would not be available to the alkyl complex **8**.

This mechanism has precedent in the deprotonation of $[Fe(COMe)(CO)(PPh_2H)(\eta\text{-}C_5H_5)]$, which afforded $[Fe(CO)\{PPh_2CMe(OSiMe_3)\}(\eta\text{-}C_5H_5)]$ on addition of $SiMe_3Cl$;[18] a similar complex, $[Mn(CO)_4\{PPh_2CMe(OSiMe_3)\}]$, was prepared by addition of a silylphosphine ligand to a manganese acyl.[19] Both of these contain the silylated form of the ligand present in our postulated intermediate, but we were unable to intercept it in this form by conducting the deprotonation of **1a** in the presence of $SiMe_3Cl$. The formation of a three-membered MoPC ring during this mechanism is a known process; for example, we have recently observed that addition of PPh_2H to $[Mo(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ affords $[Mo(PPh_2\text{-}C{=}CHR)(CO)_2(\eta\text{-}C_5H_5)]$, which contains a similar MoPC ring with an exocyclic double bond,[20] and several other examples are known.[21]



Scheme 2 Synthesis of the alkylmolybdenum phosphine complexes **8** and **10**. Reagents and conditions: (*i*) refluxing toluene, argon purge, 24 h; (*ii*) PPh_2R^1, r.t.; (*iii*) Na/Hg, then R^2I; (*iv*) PPh_2H, r.t.; (*v*) Na/Hg, MeI

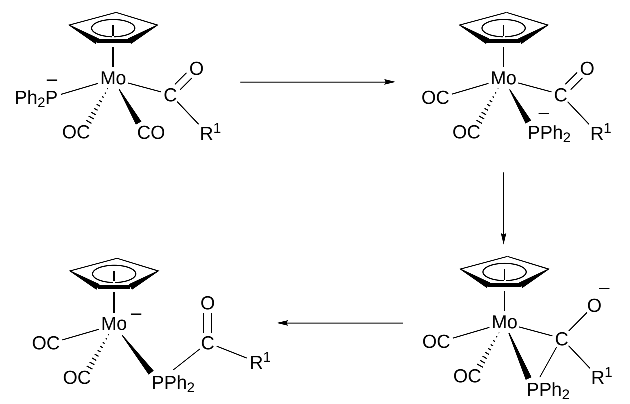
Table 4 Selected bond lengths (Å) and angles (°) for [Mo(COMe)-$(CO)_2(PPh_2COMe)(\eta$-$C_5H_5)$] **6a**

Mo–P	2.446(2)	Mo–C(1)	1.963(3)
Mo–C(2)	1.956(4)	Mo–C(4)	2.371(4)
Mo–C(5)	2.314(5)	Mo–C(6)	2.303(4)
Mo–C(7)	2.322(5)	Mo–C(8)	2.347(5)
Mo–C(21)	2.259(6)	P–C(3)	1.890(4)
P–C(9)	1.817(4)	P–C(15)	1.821(4)
O(1)–C(1)	1.154(4)	O(2)–C(2)	1.149(5)
O(3)–C(3)	1.185(5)	O(4)–C(21)	1.203(7)
C(3)–C(23)	1.487(7)	C(21)–C(22)	1.506(7)
P–Mo–C(1)	80.5(1)	P–Mo–C(2)	80.3(2)
C(1)–Mo–C(2)	106.4(2)	C(1)–Mo–C(21)	74.8(2)
P–Mo–C(21)	136.3(1)	C(2)–Mo–C(21)	73.1(2)
Mo–P–C(3)	112.6(2)	C(9)–P–C(15)	104.5(2)
C(3)–P–C(9)	103.0(2)	C(3)–P–C(15)	101.2(2)
Mo–C(2)–O(2)	175.8(3)	Mo–C(1)–O(1)	175.4(3)
P–C(3)–C(23)	116.6(3)	P–C(3)–O(3)	120.5(3)
O(3)–C(3)–C(23)	122.8(4)	Mo–C(21)–C(22)	123.6(4)
Mo–C(21)–O(4)	119.6(4)	O(4)–C(21)–C(22)	116.8(5)

Parallels can also be drawn between the anionic rearrangement observed here and that reported by Heah and Gladysz in [Re(COMe)(NO)$(PPh_3)(\eta$-$C_5H_5)$]. Deprotonation of this complex occurs at the C_5H_5 ligand and is followed by rapid intramolecular migration of the acyl group to the ring, whereas in the analogous methyl complex [ReMe(NO)$(PPh_3)(\eta$-$C_5H_5)$] no migration occurs.[22]

Although the intramolecular pathway shown in Scheme 3 accounts perfectly for the products observed, we realised that a second possibility existed: that the reaction could be intermolecular, as shown in Scheme 4 (upper pathway), with the phosphido group of one molecule attacking the acyl group of another. We therefore prepared and characterised complexes **11a**, **11b**, **12**, **13a** and **13b**, the η-C_5H_4Me analogues of **1a**, **1b**, **2a**, **3a** and **3c** respectively, and carried out some crossover reactions (the spectroscopic data for these compounds have been deposited as SUP 57273).

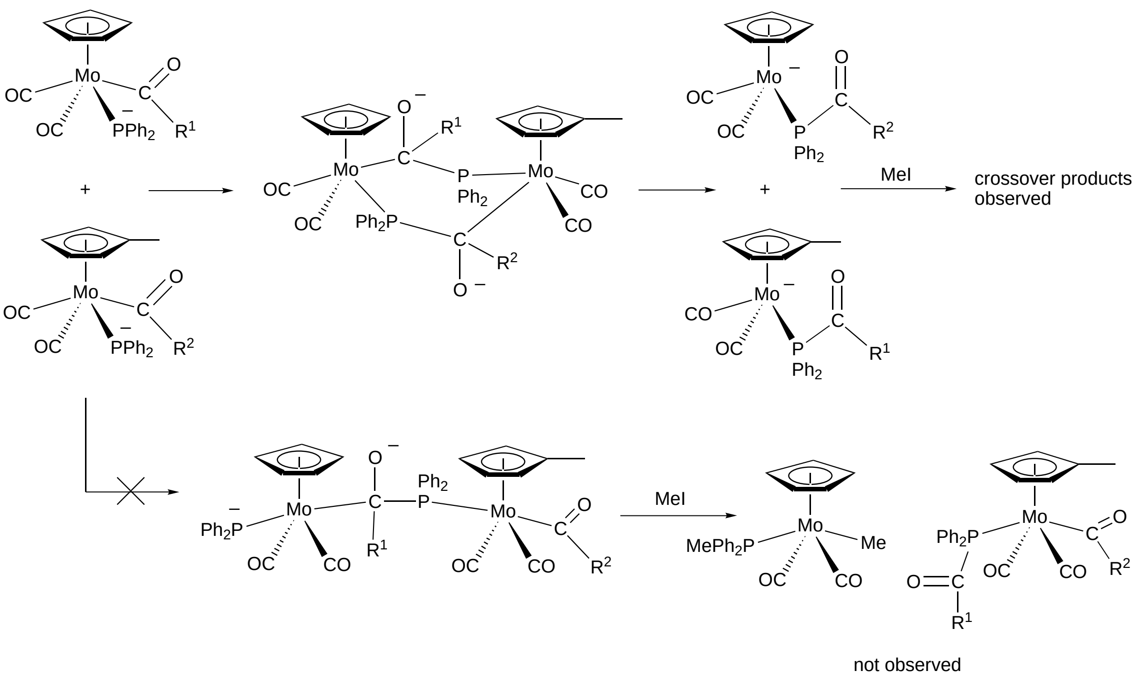
Deprotonation of an equimolar mixture of [Mo(COEt)-$(CO)_2(PPh_2H)(\eta$-$C_5H_5)$] **1b** and [Mo(COMe)$(CO)_2(PPh_2H)$-



Scheme 3 Intramolecular mechanism for the acyl migration reaction

$(\eta$-$C_5H_4Me)$] **11a** with dbu at −78 °C followed by addition of MeI gave exclusively [Mo(COEt)$(CO)_2(PPh_2Me)(\eta$-$C_5H_5)$] **2c** and [Mo(COMe)$(CO)_2(PPh_2Me)(\eta$-$C_5H_4Me)$] **12**, showing that the low-temperature reaction is, as expected, wholly intramolecular.

Deprotonation of a mixture of the same two complexes at room temperature followed by addition of MeI gave a somewhat different result. The ^{31}P NMR spectrum of the mixture of products obtained after chromatography is shown in Fig. 3. The two major products are those formed by intramolecular reaction, *i.e.* [MoMe$(CO)_2(PPh_2COEt)(\eta$-$C_5H_5)$] **3c** and [Mo-Me$(CO)_2(PPh_2COMe)(\eta$-$C_5H_4Me)$] **13a**. However significant (and equal) amounts of the two crossover products arising from intermolecular reaction, *i.e.* [MoMe$(CO)_2(PPh_2COMe)$-$(\eta$-$C_5H_5)$] **3a** and [MoMe$(CO)_2(PPh_2COEt)(\eta$-$C_5H_4Me)$] **13b** are also present (identified by comparison with authentic samples). Separate experiments established that stirring a mixture of the starting complexes **1b** and **11a** in thf for 24 h did not result in ligand exchange; similarly a mixture of the major products remained intact under these conditions. Hence any crossover products must arise during the reaction. A second crossover reaction starting from [Mo(COMe)$(CO)_2(PPh_2H)$-$(\eta$-$C_5H_5)$] **1a** and [Mo(COEt)$(CO)_2(PPh_2H)(\eta$-$C_5H_4Me)$] **11b** produced a similar proportion of intramolecular (**3a** and **13b**)



Scheme 4 Possible intermolecular mechanism for the acyl migration reaction

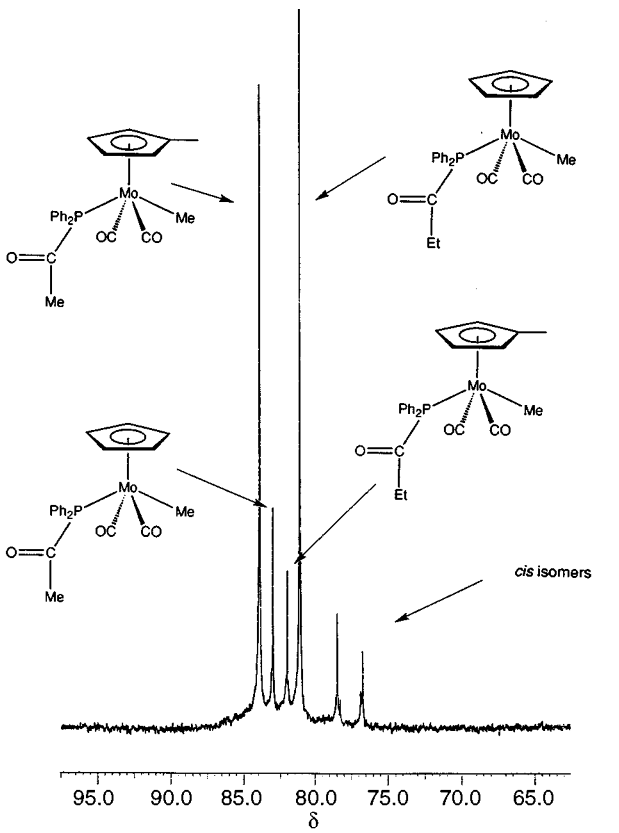


Fig. 3 The ^{31}P NMR spectrum of the mixture of products obtained from the reaction of equimolar quantities of complexes **1b** and **11a** with dbu and MeI at room temperature (see text)

and intermolecular (**3c** and **13a**) reaction products. It therefore appears that the reaction proceeds predominantly intramolecularly, as in Scheme 3, but with a measurable intermolecular component arising from the mechanism in Scheme 4. The fact that the two crossover products appear in approximately equal amounts supports the pairwise acyl exchange mechanism of the upper pathway of Scheme 4. If a random acyl transfer mechanism, such as that shown in the lower pathway of Scheme 4, were operating, additional products would include the alkylphosphine alkyl complexes and the acylphosphine acyl complexes, none of which is observed at all.

There are two possible reasons why the migration reaction does not occur at low temperature; first there might be a significant activation energy for the process, presumably associated with the Mo−C bond cleavage, or secondly the complex might be frozen into the *trans* configuration at low temperature, thus preventing migration by stopping the nucleophilic attack on the acyl ligand. In any event it seems likely that the phosphorus-centred anion is the kinetic product of deprotonation whereas the molybdenum-centred anion is the thermodynamic product.

In conclusion the reactions described in this paper demonstrate the unprecedented migration of an acyl ligand from a metal centre to a co-ordinated phosphido group, and serve as a further example of anionic rearrangement similar to those involving migration of acyl groups to deprotonated cyclopentadienyl rings.[8,22] The fact that this migration can easily be controlled provides a versatile and convenient method for the selective synthesis of a wide range of alkyl- and acylphosphine complexes, and we are currently exploring the scope of the reaction both with molybdenum and other metals.

Experimental

General experimental techniques were as detailed in recent papers from this laboratory.[23] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells, ^1H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or on AM250 (^1H, ^{13}C) or WP80SY (^{31}P) spectrometers. Chemical shifts are given on the δ scale relative to $SiMe_4$ (δ 0.0). The $^{13}C-\{^1H\}$ NMR spectra were recorded using an attached proton test technique (JMOD pulse sequence). The $^{31}P-\{^1H\}$ NMR spectra were referenced to 85% H_3PO_4 (δ 0.0) with downfield shifts reported as positive. Mass spectra were recorded on a Kratos MS 80 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

Literature methods were used to prepare $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[MoR^1(CO)_3(\eta\text{-}C_5H_5)]$.[24] Acyl halides were distilled and stored under argon before use. The phosphine ligands, alkyl and acyl halides and dbu were all obtained from Aldrich. Light petroleum refers to the fraction boiling in the range 60–80 °C.

Syntheses

[Mo(COR^1)(CO)$_2$(PPh$_2$H)(η-C$_5$H$_5$)] (R = Me 1a or Et 1b). A solution of [MoMe(CO)$_3$(η-C$_5$H$_5$)] (3.00 g, 11.54 mmol) and PPh$_2$H (2.1 cm^3, 12.07 mmol) in MeCN (170 cm^3) was stirred for 17 h. On removal of the solvent an orange oil was obtained which was dissolved in the minimum volume of CH$_2$Cl$_2$ and chromatographed on a silica column. A single yellow band was eluted with CH$_2$Cl$_2$ which gave complex **1a** as a yellow powder after washing with light petroleum. Yield 4.50 g, 87%. In an alternative work-up the orange oil was dissolved in a small volume of diethyl ether to which a large amount of light petroleum was then added. Decanting the supernatant, washing the residual solid with light petroleum and drying afforded **1a** as a yellow powder. M.p. 70 °C.

In a similar reaction, [MoEt(CO)$_3$(η-C$_5$H$_5$)] (1.00 g, 3.65 mmol) and PPh$_2$H (0.7 cm^3, 4.02 mmol) produced complex **1b** as a yellow solid (1.03 g, 58%). M.p. 135 °C.

Low-temperature deprotonation–alkylation of complexes 1a, 1b: synthesis of [Mo(COR^1)(CO)$_2$(PPh$_2$R^2)(η-C$_5$H$_5$)] (R^1 = R^2 = Me 2a; R^1 = Me, R^2 = Et 2b; R^1 = Et, R^2 = Me 2c; R^1 = R^2 = Et 2d). The complex **1a** (300 mg, 0.67 mmol) was dissolved in thf (20 cm^3) and cooled to −78 °C. Addition of dbu (0.11 cm^3, 0.73 mmol) caused a slight darkening of the solution to orange-red which was complete after 20 min of stirring. Methyl iodide (0.10 cm^3, 1.62 mmol) was added and the solution was allowed to warm to room temperature. Filtration of the yellow solution, removal of the solvent and washing with light petroleum yielded yellow solid **2a** (0.28 g, 91%). M.p. 108 °C.

Using the same method, complex **1a** (500 mg, 1.12 mmol) was deprotonated and quenched with EtI (0.09 cm^3, 1.13 mmol). Column chromatography gave 433 mg (81%) of **2b** as a yellow powdery solid on elution with CH$_2$Cl$_2$. M.p. 128 °C. The complexes **2c** (89%, m.p. 114 °C) and **2d** (90%, m.p. 157 °C) were prepared in the same way from complex **1b**.

[Mo(COR^1)(CO)$_2$(PPh$_2$R^2)(η-C$_5$H$_5$)] 2a–2d from [MoR^1(CO)$_3$(η-C$_5$H$_5$)] and PPh$_2$R^2. Following the same method as used for complex **1**, a solution of [MoMe(CO)$_3$(η-C$_5$H$_5$)] (2.95 g, 11.35 mmol) in MeCN (150 cm^3) was treated with a slight excess of PPh$_2$Me (2.2 cm^3, 11.82 mmol) and stirred for 17 h. Removal of the solvent yielded a yellow oil which was chromatographed to give a single yellow band on eluting with CH$_2$Cl$_2$. Trituration with light petroleum gave a pale yellow powder of **2a** (4.70 g, 90%). Complexes **2b** (88), **2c** (77) and **2d** (95%) were prepared in the same way from the appropriate starting materials.

Room-temperature deprotonation-alkylation of complexes 1a, 1b: synthesis of [MoR^2(CO)$_2$(PPh$_2$COR^1)(η-C$_5$H$_5$)] (R^1 = R^2 = Me 3a; R^1 = Me, R^2 = Et 3b; R^1 = Et, R^2 = Me 3c; R^1 = R^2 = Et 3d). A solution of **1a** (300 mg, 0.67 mmol) in thf (40 cm^3) was treated with dbu (0.11 cm^3, 0.74 mmol) at room temperature. A rapid change from yellow to deep red ensued. After stirring for 30 min, methyl iodide (0.05 cm^3, 0.80 mmol) was added, causing an instantaneous change to yellow-orange. After stirring for 17 h to ensure complete reaction, the solvent was removed and the resulting oil dissolved in a little diethyl ether. The yellow solution was decanted from a white precipitate (presumably the iodide salt of protonated dbu) to yield orange **3a** (270 mg, 87%) on removal of the solvent. M.p. 118 °C. A similar reaction in which EtBr (0.09 cm^3, 0.12 mmol) was used as the alkylating agent provided a yellow oil which was recrystallised from light petroleum to produce orange crystals of **3b** (200 mg, 38%). M.p. 104 °C.

Starting from **1b**, the complexes **3c** (85%, m.p. 134 °C) and **3d** (61%, m.p. 134 °C) were prepared in the same way.

[MoH(CO)$_2$(PPh$_2$COR^1)(η-C$_5$H$_5$)] (R^1 = Me 4a or Et 4b). A solution of complex **1a** (500 mg, 1.12 mmol) in thf (30 cm^3) was deprotonated at room temperature with dbu (0.18 cm^3, 1.20 mmol). After 30 min of stirring the ruby-red solution was treated with 2 equivalents of glacial acetic acid (0.12 cm^3, 2.1 mmol). After 1 h a change to orange-red had occurred. Evaporation to dryness gave a red oil which was dissolved in the minimum volume of CH$_2$Cl$_2$ and chromatographed. The major product was eluted as a yellow band with light petroleum–CH$_2$Cl$_2$ (4:1) and identified as **4a** (100 mg, 20%). M.p. 88 °C. An improved yield of 60% was obtained by using a four-fold excess of acetic acid.

The same method was followed for complex **1b** (500 mg, 1.09 mmol) except that a five-fold excess of MeCO$_2$H (0.30 cm^3, 5.24 mmol) was used. Chromatography gave a bright yellow band which was eluted as above. On removal of the solvent complex **4b** (230 mg, 46%) was obtained as an orange-brown powder by triturating with light petroleum. M.p. 106 °C.

[MoCl(CO)$_2$(PPh$_2$COR^1)(η-C$_5$H$_5$)] (R^1 = Me 5a or Et 5b). A solution of complex **1a** (500 mg, 1.12 mmol) in thf (30 cm^3) was deprotonated with dbu (0.18 cm^3, 1.20 mmol) at room temperature as above. The addition of a four-fold excess of glacial acetic acid (0.25 cm^3, 4.36 mmol) gave a bright yellow solution which was left to stir for 2 min before removing the solvent under reduced pressure. The resulting yellow oil was redissolved in CHCl$_3$ (30 cm^3) which gave an orange-red solution. The reaction was complete after 10 min (IR monitoring) at which point the solution was evaporated to dryness. The oily residue was then dissolved in the minimum volume of CH$_2$Cl$_2$ and chromatographed. A minor red zone was observed before elution of the major product as an orange-red band with light petroleum–CH$_2$Cl$_2$ (1:1). Removal of the solvent produced bright red powdery solid **5a** (300 mg, 56%). M.p. 170 °C. Analogous treatment of complex **1b** gave a 74% yield of **5b** as an orange powder. M.p. 140 °C.

Low-temperature deprotonation–acylation of complexes 1a, 1b: synthesis of [Mo(COR^1)(CO)$_2$(PPh$_2$COR^2)(η-C$_5$H$_5$)] (R^1 = R^2 = Me 6a; R^1 = Me, R^2 = Et 6b; R^1 = Et, R^2 = Me 6c; R^1 = R^2 = Et 6d). A solution of complex **1a** (500 mg, 1.12 mmol) in thf (30 cm^3) was cooled to −78 °C and treated with a slight excess of dbu (0.18 cm^3, 1.20 mmol), effecting a change to orange-red. After stirring for 30 min, acetyl chloride (0.09 cm^3, 1.27 mmol) was added. Stirring was continued for a further 10 min before removing the solvent under reduced pressure and chromatographing the resulting yellow solid. Eluting with CH$_2$Cl$_2$ afforded a bright yellow band which gave a yellow powdery solid of **6a** (430 mg, 79%) on triturating with light petroleum. M.p. 125 °C. Recrystallisation from toluene at −25 °C provided yellow crystals suitable for X-ray diffraction. Following the same method with EtCOCl (0.10 cm^3, 1.15 mmol) as the acylating agent led to the isolation of complex **6b** (460 mg, 82%) as a yellow powder. M.p. 132 °C.

Starting from **1b**, the complexes **6c** (82%, m.p. 148 °C) and **6d** (81%, m.p. 122 °C) were prepared in the same way.

[{Mo(CO)$_2$(PPh$_2$H)(η-C$_5$H$_5$)}$_2$] 7. A solution of [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (1.3 g, 3.06 mmol) in toluene (150 cm^3) was heated to reflux with an argon purge for 24 h to produce a solution of [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. The solution was allowed to cool to room temperature before dropwise addition of 2 equivalents of PPh$_2$H (1.10 cm^3, 6.32 mmol). The solution was stirred for 2 h. Column chromatography gave a weak orange band of [Mo$_2$-

(μ-H)(μ-PPh_2)$(CO)_4$(η-C_5H_5)$_2$],[25] eluted with light petroleum–CH_2Cl_2 (3:7) followed by a dark purple band of complex **7** (1.85 g, 75%), which was eluted with a 2:3 mixture of the same solvents. M.p. 146 °C. Like **9a** and **9b** (see below) the complex was found to have limited solubility.

[MoMe$(CO)_2$(PPh_2H)(η-C_5H_5)] 8. A solution of the dimeric complex [{Mo$(CO)_2$(PPh_2H)(η-C_5H_5)}$_2$] (500 mg, 0.62 mmol) in thf (40 cm^3) was shaken with sodium amalgam (29 mg, 1.26 mmol of Na in 0.5 cm^3 Hg) for 10 min causing the initially purple solution to turn olive green. The solution was transferred to a separate Schlenk tube by syringe and treated with MeI (0.08 cm^3, 1.29 mmol). After stirring overnight the green solution was evaporated to dryness, dissolved in the minimum volume of CH_2Cl_2 and chromatographed. A single yellow band was eluted with light petroleum–CH_2Cl_2 (9:1). Crystallisation of the resulting yellow oil from light petroleum at −25 °C gave 240 mg (46%) of complex **8** as yellow crystals. M.p. 99 °C. Ratio of *cis*:*trans* = 1.66:1.

Room-temperature deprotonation–alkylation of [MoMe$(CO)_2$(PPh_2H)(η-C_5H_5)] 8. A solution of complex **8** (50 mg, 0.12 mmol) in thf (20 cm^3) was treated with a small excess of dbu (0.02 cm^3, 0.13 mmol) at room temperature and stirred for 30 min, darkening slightly during this time. No colour change was observed on the addition of EtI (0.02 cm^3, 0.25 mmol). After 1 h the solvent was removed and the resulting yellow oil chromatographed. Elution with CH_2Cl_2 produced a yellow band of the PPh_2Et complex **10c**.

[{Mo$(CO)_2$(PPh_2R^1)(η-C_5H_5)}$_2$] (R^1 = Me 9a or Et 9b). The method used was the same as for complex **7**. A solution of [$Mo_2(CO)_4$(η-C_5H_5)$_2$] was generated from [$Mo_2(CO)_6$(η-C_5H_5)$_2$] (3.0 g, 6.12 mmol) and treated at room temperature with PPh_2Me (2.30 cm^3, 12.36 mmol) for 2 h. Column chromatography, eluting with light petroleum–CH_2Cl_2 (1:1), gave a broad red-purple band of **9a** (3.41 g, 66%). M.p. 160 °C. It was shown by NMR spectroscopy to exist as a mixture of *trans* and *cis* isomers in a ratio of 5:1.

A similar reaction with PPh_2Et (2.60 cm^3, 12.72 mmol) afforded a purple powder of complex **9b** (4.0 g, 76%) as a mixture of *trans* and *cis* isomers (2:1). M.p. 174 °C. Both compounds were only sparingly soluble in most solvents.

[Mo$R^2$$(CO)_2$($PPh_2R^1$)(η-$C_5H_5$)] ($R^1$ = R^2 = Me 10a; R^1 = Me, R^2 = Et 10b; R^1 = Et, R^2 = Me 10c; R^1 = R^2 = Et 10d). The method used was the same as that for complex **8**. A solution of [{Mo$(CO)_2$(PPh_2Me)(η-C_5H_5)}$_2$] (1.00 g, 1.19 mmol) in thf (100 cm^3) was shaken with an excess of sodium amalgam (0.45 g, 19.6 mmol Na in 7.5 cm^3 Hg). After 30 min the initially insoluble purple powder had dissolved to give a green solution which was then freed of excess of amalgam and treated with 2 molar equivalents of MeI (0.15 cm^3, 2.41 mmol). After stirring for 17 h the thf was removed under reduced pressure and the residue chromatographed. Elution with diethyl ether led to 0.70 g (71%) of [MoMe$(CO)_2$(PPh_2Me)(η-C_5H_5)] **10a** as a yellow-orange powder. M.p. 138 °C. By the same method, reduction of **9a** (1.00 g, 1.19 mmol) followed by alkylation with EtBr (0.18 cm^3, 2.41 mmol) gave orange powdery [MoEt$(CO)_2$(PPh_2Me)-(η-C_5H_5)] **10b** (0.700 g, 65%). M.p. 82 °C.

Starting from **9b**, the compounds **10c** (74%, m.p. 110 °C) and **10d** (66%, m.p. 86 °C) were prepared in the same way.

Crystallography

Crystal data for [Mo(COMe)$(CO)_2$(PPh_2COMe)(η-C_5H_5)] 6a. $C_{23}H_{21}Mo_2O_4P$ $M = 488.22$, crystallises from toluene as yellow oblongs, crystal dimensions 0.60 × 0.50 × 0.40 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 8.148(4)$, $b = 11.628(7)$, $c = 12.697(6)$ Å, $\alpha = 63.43(4)$, $\beta = 78.91(4)$, $\gamma = 86.41(4)°$, $U = 1055.5(9)$ Å^3, $Z = 2$, $D_c = 1.53$ g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 7.05 cm^{-1}, $F(000) = 495.87$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 3271 independent reflections (of 3762 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz-polarisation effects, and for absorption by analysis of eight azimuthal scans (minimum and maximum transmission coefficients 0.733 and 0.820). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement on F^2 converged at a final $R = 0.0389$ ($R' = 0.0386$, 262 parameters, mean and maximum δ/σ 0.002, 0.007), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density –0.86 and 0.34 e Å^{-3}. A weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,46F^2$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[26] as implemented on the Data General DG30 computer.

CCDC reference number 186/665. Tables of structure factors are available from the authors.

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