Synthesis and Molecular Structures of Chloro(trimethylphosphine)tris(trimethylsilylmethyl)molybdenum(IV) and Di-μ-Chloro-bis[η_2-trimethylsilylmethylcarbonylbis(carbonyl)trimethylphosphinemolybdenum(II)]†

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Summary The interaction of bis(trimethylsilylmethyl)magnesium and molybdenum tetrachloridebis(tetrahydrofuran) in the presence of trimethylphosphine gives a 5-co-ordinate molybdenum(IV) alkyl $MoCl(CH_2SiMe_3)_3$-PMe_3 which reacts with carbon monoxide to give a molybdenum(II) chlorine-bridged dimer $[MoCl(\eta_2\text{-}COCH_2SiMe_3)(CO)_2PMe_3]_2$; the structures of both complexes have been determined by *X*-ray crystallography and the dimer shown to have a bidentate η_2-acyl group.

Apart from recently described tetrabenzylmolybdenum,[1] $Mo(CH_2Ph)_4$, and the poorly characterised methylmolybdenum compound $MoMeCl_3(OEt_2)_2$,[2] molybdenum(IV) alkyls other than those with η-C_5H_5 groups are unknown.[3] Although in the absence of trimethylphosphine the interaction of $MoCl_4(C_4H_8O)_2$ with $(Me_3SiCH_2)_2Mg$ gives a mixture of carbene and carbyne complexes similar to that obtained by interaction of $MoCl_5$ and $LiCH_2SiMe_3$,[4] in the presence of trimethylphosphine high yields of a purple, light petroleum soluble compound, $MoCl(CH_2SiMe_3)_3PMe_3$ (**A**), are obtained.

Interaction of solutions of (**A**) with carbon monoxide at room temperature and pressure yielded a diamagnetic molybdenum(II) complex (**B**) of stoicheiometry $[MoCl(\eta_2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ for which the low C–O stretching frequency (1585 cm^{-1}) in the i.r. spectrum suggested the presence of a η_2-acyl group; no CO insertion products from M–CH_2SiMe_3 groups have been previously fully characterised.

The structures of both compounds have been determined by *X*-ray diffraction study. Previously, structural data for η_2-acyls have been available only for $(\eta\text{-}C_5H_5)_2Zr(COMe)Me$[5] and $(\eta\text{-}C_5H_5)_2Ti(COMe)Cl$.[6]

Crystal data: $C_{15}H_{42}ClMoPSi_3$ (**A**), *M* 469·1, monoclinic, $a = 10{\cdot}400(5)$, $b = 19{\cdot}029(7)$, $c = 12{\cdot}849(5)$ Å, $\beta = 91{\cdot}74(4)°$, $U = 2541{\cdot}7$ Å^3, $Z = 4$, $D_c = 1{\cdot}22$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8{\cdot}02$ cm^{-1}, space group $P2_1/n$. $C_{20}H_{40}Cl_2Mo_2O_6P_2Si_2$ (**B**), *M* 757·4, monoclinic, $a = 8{\cdot}415(3)$, $b = 10{\cdot}484(3)$, $c = 19{\cdot}229(5)$ Å, $\beta = 90{\cdot}62(2)°$, $U = 1696{\cdot}2$ Å^3, $Z = 2$, $D_c = 1{\cdot}48$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 10{\cdot}71$ cm^{-1}, space group $P2_1/c$.

Intensity data for both compounds were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan technique. All reflections in one independent quadrant out to $2\theta = 50°$ were measured; 2302 reflections for (**A**) and 2579 reflections for (**B**) were considered observed $[I > 3\sigma(I)]$. The structures were solved by Patterson and difference Fourier techniques, and refined to a conventional *R* value of 0·034 for (**A**) and 0·020 for (**B**).‡

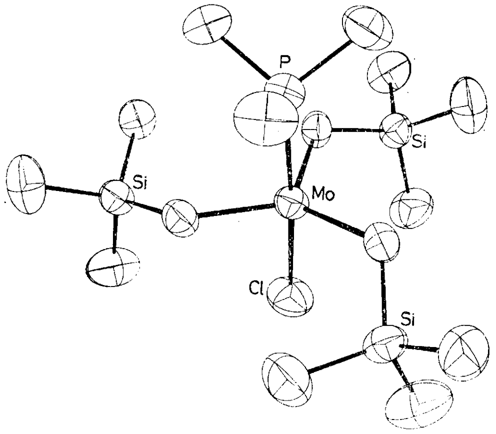

Figure 1. The structure of $MoCl(CH_2SiMe_3)_3PMe_3$.

The structure of $MoCl(CH_2SiMe_3)_3PMe_3$, Figure 1, shows that the molecule is essentially trigonal bipyramidal with equatorial alkyl groups. The Mo–C distances average 2·110(16) Å, and are the shortest yet reported for alkyl ligands. In $Mo_2(CH_2SiMe_3)_6$[7] the Mo–C lengths average 2·131 Å, but for situations which do not involve bulky alkyl groups the Mo–C distances are near 2·3 Å.[8]

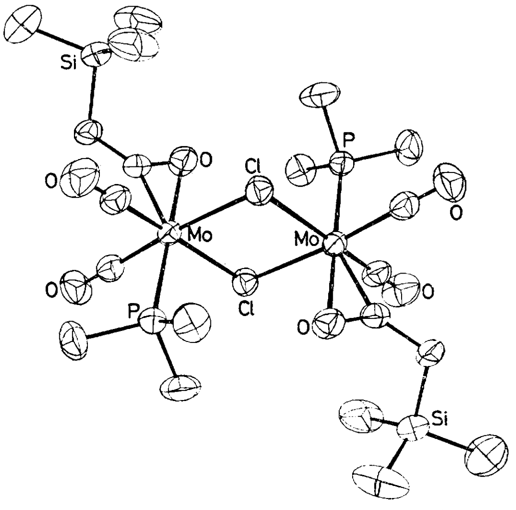

Figure 2. The structure of $[MoCl(COCH_2SiMe_3)(CO)_2PMe_3]_2$.

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† No reprints available.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

In $[MoCl(COCH_2SiMe_3)(CO)_2PMe_3]_2$, Figure 2, the Mo–$C_{acyl}$ length is 2·023(3) Å, and the oxygen atom of the carbonyl is strongly co-ordinated at a Mo–O separation of 2·292(2) Å. In this respect there exists a difference between the acyl linkage in (**B**) and that found in $(\eta\text{-}C_5H_5)_2Zr(COMe)Me$.[5] In (**B**), $\Delta_{M=Mo}$ = (M–O) – (M–C) = 0·27 Å, while $\Delta_{M=Zr}$ = 0·09 Å. The enhanced Zr–O interaction compared to the Mo–O distance in (**B**) is also reflected in a Zr–C_{acyl} bond length of 2·197 Å, 0·06 Å shorter than a normal Zr–C_{alkyl} bond,[9] while the Mo–C_{acyl} distance is 0·09 Å less than the shortest Mo–C_{alkyl} bond. The weaker binding of the acyl oxygen in the molybdenum compound probably reflects the lower electrophilicity of the metal atom in the more electron-rich system.

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