Synthesis and Crystal Structures of Chloro(trimethylphosphine)tris(trimethylsilylmethyl)molybdenum(IV) and Di-μ-chloro-bis[bis(carbonyl)trimethylphosphine(1—2-η-trimethylsilylmethylcarbonyl)molybdenum(II)] †

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Tetrachlorobis(tetrahydrofuran)molybdenum and bis(trimethylsilylmethyl)magnesium react in the presence of trimethylphosphine to give a five-co-ordinate molybdenum(IV) alkyl $MoCl(CH_2SiMe_3)_3(PMe_3)$, which upon carbonylation at room temperature and pressure yields $[MoCl(1-2\text{-}\eta\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$. I.r. and ^1H n.m.r. data for the latter complex suggest the presence of an η^2-acyl linkage, a result later confirmed by an *X*-ray crystal-structure determination. The crystal structures of $MoCl(CH_2SiMe_3)_3(PMe_3)$ and $[MoCl(COR)(CO)_2(PMe_3)]_2$ have been determined from three-dimensional *X*-ray diffraction data collected by counter methods. The former crystallizes in the monoclinic space group $P2_1/n$ with a = 10.400(5), b = 19.029(7), c = 12.849(5) Å, β = 91.74(4)°, and Z = 4 for D_c = 1.23 g cm^{-3}. The final R value was 0.033 for 2 198 independent observed reflections. Electron deficiency at the metal centre of this five-co-ordinate molybdenum compound is the apparent cause of the very short molybdenum–carbon σ-bond length of 2.110(16) Å. $[MoCl(COR)(CO)_2(PMe_3)]_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 8.415(3), b = 10.484(3), c = 19.229(5) Å, β = 90.62(2)°, and Z = 2 for D_c = 1.48 g cm^{-3}. A final R value of 0.020 was obtained based on 2 579 independent observed reflections. The molecule exists as a chlorine-bridged dimer with an η^2-acyl linkage. The molybdenum–carbon(acyl) bond length is 2.023(3) Å and the molybdenum–oxygen(acyl) distance is 2.292(2) Å.

MOLYBDENUM(IV) compounds containing metal to carbon bonds other than those with η-C_5H_5 groups are rather uncommon, the only examples being the tetrabenzylmolybdenum,[1] $Mo(CH_2Ph)_4$, and the poorly characterised $MoMeCl_3(OEt_2)_2$.[2] Compounds of this type are of interest as they can provide information regarding the nature of the metal to carbon bonds. For a wide range of organometallic derivatives of molybdenum, the metal–carbon σ bond lengths have been found to vary from 2.244(9) [3] to 2.414(4) Å [4] for 18-electron systems. For the 12-electron case, $Mo_2(CH_2SiMe_3)_6$,[5] the molybdenum–carbon lengths average 2.131 Å. In order to better establish the cause of this marked contraction in bond length associated with the electron deficiency of the central molybdenum atom we have determined the structure of the molybdenum(IV) alkyl, $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1). In addition we report the preparation and structural properties of the carbonyl $[MoCl(COR)(CO)_2(PMe_3)]_2$ (2). The latter contains a η^2-acyl linkage and is the first fully characterised CO insertion product from an $M\text{-}CH_2SiMe_3$ group. The ' side-on ' arrangement of the acyl ligand has already been encountered for $Zr(\eta^5\text{-}C_5H_5)_2(COMe)Me$ [6] and $Ti(\eta^5\text{-}C_5H_5)_2(COMe)Cl$,[7] and seems to occur fairly commonly among the early transition metals,[8] as well as in later elements such as ruthenium.[9]

RESULTS AND DISCUSSION

When a suspension of $MoCl_4(thf)_2$ (thf = tetrahydrofuran) in diethyl ether is treated with $Mg(CH_2SiMe_3)_2$ in the presence of a slight excess of trimethylphosphine, a deep purple solution is obtained from which, following work-up the compound $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1) can be isolated as a purple crystalline solid. When the reaction between $MoCl_4(thf)_2$ and $Mg(CH_2SiMe_3)_2$ is carried out in the presence of a large excess of phosphine, yellow $MoCl_3(PMe_3)_3$ [10] is also formed. This compound is almost insoluble in light petroleum and can be easily separated from $MoCl(CH_2SiMe_3)_3(PMe_3)$ by crystallization. Compound (1) is very air and moisture sensitive both in the solid state and in solution, decomposing immediately upon exposure to air. It is very volatile, subliming at *ca.* 55 °C (10^{-2} mmHg ‡) but it does not give a molecular ion when studied by mass spectroscopy. The compound is very soluble in non-polar solvents in which it exists as a monomer. The i.r. spectrum (see Experimental section) shows absorptions characteristic of trimethylsilylmethyl and trimethylphosphine groups.

When carbon monoxide is bubbled through a light petroleum solution of $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1) a rapid, essentially quantitative reaction takes place with deposition of a yellow solid. This can be identified as the chlorine-bridged dimer $[MoCl(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2). It is more stable towards air and moisture than the parent alkyl. The i.r. spectrum (KBr disc) shows two very strong absorptions at 1 930 and 1 835 cm^{-1} that can be assigned to terminal CO groups and a somewhat weaker band at 1 585 cm^{-1} which strongly suggests the presence of a ' side-on,' three-electron donor acyl group. The same bands can be observed in the solution spectrum ($CDCl_3$).

The ^1H n.m.r. spectrum of $[MoCl(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ ($CDCl_3$ solution) shows two singlets at τ 6.75 and 9.8 respectively due to the methylene and methyl protons of the acyl ligand. In addition, there is a doublet centred at *ca.* τ 8.2 [*J*(P–H) 10 Hz] which corresponds to the methyl phosphine protons. The

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† No reprints available. Preliminary note: E. Carmona Guzman, G. Wilkinson, J. L. Atwood, R. D. Rogers, W. E. Hunter, and M. J. Zaworotko, *J.C.S. Chem. Comm.*, 1978, 465.

‡ Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

areas of these resonances are in good agreement with the expected values. The ^{31}P n.m.r. spectrum is not very informative consisting of a single resonance at 10.6 p.p.m.*

The molecular structure and atom-numbering scheme for $MoCl(CH_2SiMe_3)_2(PMe_3)$ (1) is shown in Figure 1. The most remarkable features are the molybdenum–carbon σ-bond distances which range from 2.091(5) to 2.126(6) Å (Table 1) and average 2.110(16) Å. In the structure of $Mo_2(CH_2SiMe_3)_6$ where there is a molybdenum–molybdenum triple bond, the Mo–Cl lengths average 2.131 Å. These two compounds are quite dissimilar from many points of view, but the Mo–C bond lengths are not significantly different. It has previously been established that metal–carbon bond distances vary only slightly and irregularly with oxidation state. It would seem, therefore, that the most important correlation between these two compounds is the fact that formally both have 12 electrons. In the wide range of 18-electron structures, the bond distances are from 0.1 to 0.3 Å longer.[3,4] Although additional structures need to be studied in order to assess relative effects on coordination number and ligand size, it would seem that the dominant effect in the determination of the molybdenum–carbon σ-bond length is the electron deficiency of the metal atom. In both cases this is caused by the use of bulky alkyl ligands.

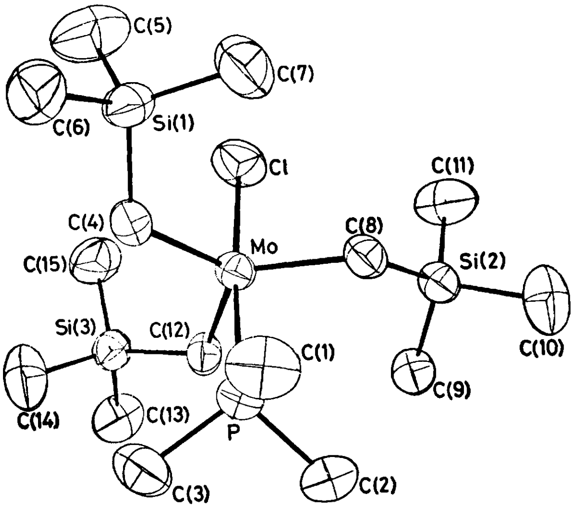

FIGURE 1 The molecular structure of chloro(trimethylphosphine)tris(trimethylsilylmethyl)molybdenum(IV) (1) with the atoms represented by their 40% probability ellipsoids for thermal motion

Of particular significance in the assessment of the bonding of the alkyl group to the molybdenum atom are the positions of the hydrogen atoms of the trimethylsilylmethyl ligand. Firstly the two hydrogen atoms were clearly observed in the difference-Fourier maps and the bond angles and distances associated with them appeared to be as expected. Even more to the point is the fact that the Mo–C–Si bond angles range from 121.2(3) to 122.8(3)°. With two hydrogen atoms on the carbon atom one would expect the angle at the carbon atom to be ideally 109.5°. Clearly, because of the bulky alkyl group, this angle must be considerably expanded over the normal value. Thus the angle goes from 109.5 to 122°, a 13° increase.

In Figure 1, the phosphine ligand is *trans* to the chlorine atom in a nearly trigonal-bipyramidal arrangement. The P–Mo–C bond angle is 175.1(1)°. The C–Mo–C bond angles range from 115.4(2) to 123.5(2)°. The effects of the phosphine ligand on the trigonal-bipyramidal arrangement is not what might be expected. The C–Mo–P bond angles are all less than 90°. This may be attributed to a non-bonded repulsion between the chlorine atom and the trimethylsilyl unit, which in turn increases the Cl–Mo–C bond angle at the expense of the C–Mo–P angle.

Molybdenum–phosphorus bond lengths have been found to cluster around 2.49 Å.[11] The 2.504(2) Å length found in (1) is therefore very close to the expected value; the same is true for the molybdenum–chlorine bond length, 2.368(2) Å.[12]

TABLE 1

Interatomic bond distances (Å) and angles (°) for $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1) with estimated standard deviations in parentheses

Mo–Cl	2.367(2)	Mo–C(4)	2.091(5)
Mo–P	2.504(2)	Mo–C(8)	2.108(6)
P–C(1)	1.798(7)	Mo–C(12)	2.126(6)
P–C(2)	1.810(6)	C(8)–Si(2)	1.858(6)
P–C(3)	1.813(6)	Si(2)–C(9)	1.856(7)
C(4)–Si(1)	1.873(5)	Si(2)–C(10)	1.855(7)
Si(1)–C(5)	1.851(7)	Si(2)–C(11)	1.838(9)
Si(1)–C(6)	1.856(8)	C(12)–Si(3)	1.867(6)
Si(1)–C(7)	1.830(8)	Si(3)–C(13)	1.849(7)
Si(3)–C(14)	1.842(6)	Si(3)–C(15)	1.831(7)
Cl–Mo–P	175.1(1)	P–Mo–C(4)	87.8(2)
Cl–Mo–C(4)	96.5(2)	P–Mo–C(8)	84.9(2)
Cl–Mo–C(8)	95.3(2)	P–Mo–C(12)	83.6(2)
Cl–Mo–C(12)	92.3(2)	C(4)–Mo–C(8)	115.4(2)
C(4)–Mo–C(12)	119.2(2)	C(8)–Mo–C(12)	123.5(2)
Mo–C(4)–Si(1)	122.2(3)	Mo–P–C(1)	118.2(2)
Mo–C(8)–Si(2)	122.8(3)	Mo–P–C(2)	113.2(2)
Mo–C(12)–Si(3)	121.2(3)	Mo–P–C(3)	116.8(2)
C(4)–Si(1)–C(5)	107.7(3)	C(1)–P–C(2)	102.9(3)
C(4)–Si(1)–C(6)	111.3(3)	C(1)–P–C(3)	102.1(3)
C(4)–Si(1)–C(7)	112.5(3)	C(2)–P–C(3)	101.4(3)
C(5)–Si(1)–C(6)	107.3(4)	C(8)–Si(2)–C(9)	108.8(3)
C(5)–Si(1)–C(7)	109.1(4)	C(8)–Si(2)–C(10)	111.7(3)
C(6)–Si(1)–C(7)	108.8(4)	C(8)–Si(2)–C(11)	109.3(4)
C(12)–Si(3)–C(13)	107.7(3)	C(9)–Si(2)–C(10)	107.6(3)
C(12)–Si(3)–C(14)	113.4(3)	C(9)–Si(2)–C(11)	106.8(4)
C(12)–Si(3)–C(15)	110.6(3)	C(10)–Si(2)–C(11)	112.3(4)
C(13)–Si(3)–C(14)	106.5(3)	C(14)–Si(3)–C(15)	110.3(3)
C(13)–Si(3)–C(15)	108.1(4)		

The carbonyl complex, whose molecular structure and atom-numbering scheme is shown in Figure 2, has an 18-electron configuration for Mo with the acyl group acting as a three-electron donor. There are two points concerning the acyl linkage. The first concerns the extremely short molybdenum–carbon bond length. The observed value, 2.023(3) Å (Table 2), is in fact 0.1 Å shorter than the shortest known alkyl distance, and is only 0.08 Å longer than the metal–carbonyl bond lengths. The molybdenum–oxygen distance, 2.292(2) Å,

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* Chemical shift to high frequency of external 85% H_3PO_4.

is clearly well within the range of molybdenum–oxygen single-bond lengths.[12,13] It has been found for a related molybdenum carbonyl compound, Mo(η-C_5H_5)(COMe)-$(CO)_2(PMe_3)$ that the metal–carbon(acyl) distance was 2.264 Å while the metal–oxygen separation was 3.068 Å and the Mo–C(acyl)–O bond angle was 121°. This clearly indicates no Mo–O interaction. In [MoCl-$(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2) the short Mo–C(acyl) and Mo–O bond lengths along with the Mo–C(acyl)–O bond angle of 86.1(2)° is indicative of an η^2 interaction. In the previously reported metal–(η^2-acyl) structures similar distances and angles were found, namely, Zr–C(acyl) = 2.197 Å and Zr–O(acyl) = 2.206 Å in Zr(η-$C_5H_5)_2$(COMe)Me [6] and Ti–C(acyl) = 2.07(2) Å and Ti–O(acyl) = 2.194(14) Å in TiCl(η-$C_5H_5)_2$(COMe).[7] In the molybdenum–(η^2-acyl) structure $\Delta_{M=Mo}$ = (M–O) − (M–C) = 0.27 Å, while $\Delta_{M=Zr}$ = 0.09 Å and $\Delta_{M=Ti}$ = 0.12 Å, showing a weaker metal–oxygen interaction for M = Mo. This can also be seen in the M–C(acyl)–O angles: 79.7 (Zr), 78.6 (Ti), and 86.1(2)° (Mo). Since the Zr–C(acyl), Ti–C(acyl), and the Mo–C(acyl) bond lengths all compare quite favourably with the corresponding metal–carbonyl distances, one may conclude that there is a close similarity among the groups and that there is appreciable metal–carbon π bonding involved in the acyl linkage.

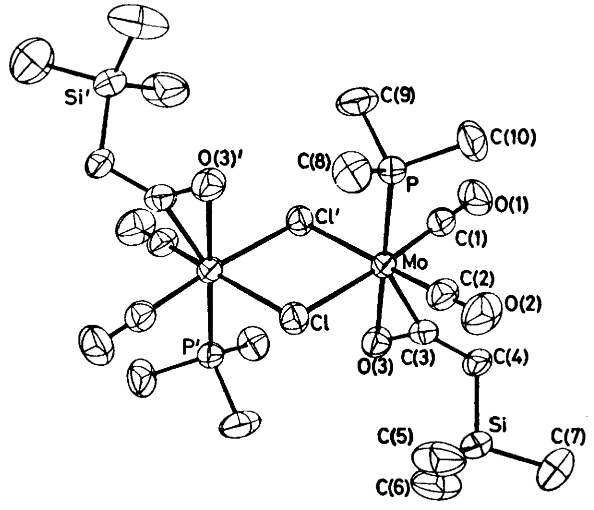

FIGURE 2 The molecular structure of di-μ-chloro-bis[bis-(carbonyl)trimethylphosphine(η^2-trimethylsilylmethylcarbonyl)molybdenum(II)] (2)

TABLE 2

Interatomic bond distances (Å) and angles (°) for [MoCl-(η^2-$COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2) with estimated standard deviations in parentheses

Mo–Cl	2.577(1)	P–C(8)	1.810(4)
Mo–Cl′	2.544(1)	P–C(9)	1.814(4)
Mo–P	2.474(1)	P–C(10)	1.812(4)
Mo–C(1)	1.940(4)	C(1)–O(1)	1.160(4)
Mo–C(2)	1.941(4)	C(2)–O(2)	1.160(4)
Mo–C(3)	2.023(3)	C(3)–O(3)	1.225(4)
Mo–O(3)	2.292(2)	C(3)–C(4)	1.468(5)
C(4)–Si	1.910(4)	Si–C(6)	1.848(5)
Si–C(5)	1.839(5)	Si–C(7)	1.844(6)
Cl–Mo–P	96.1(1)	Cl′–Mo–P	92.0(1)
Cl–Mo–C(1)	175.0(1)	Cl′–Mo–C(1)	94.7(1)
Cl–Mo–C(2)	90.4(1)	Cl′–Mo–C(2)	166.5(1)
Cl–Mo–C(3)	104.2(1)	Cl′–Mo–C(3)	115.1(1)
Cl–Mo–C(3)	85.2(1)	Cl′–Mo–O(3)	86.9(1)
		Cl′–Mo–Cl	81.0(1)
P–Mo–C(1)	81.4(1)	C(1)–Mo–C(2)	93.2(2)
P–Mo–C(2)	78.5(1)	C(1)–Mo–C(3)	79.9(1)
P–Mo–C(3)	148.0(1)	C(1)–Mo–O(3)	97.2(1)
P–Mo–O(3)	178.2(1)		
Mo–Cl–Mo′	99.0(1)	C(2)–Mo–C(3)	77.0(1)
Mo–C(3)–O(3)	86.1(2)	C(2)–Mo–O(3)	102.8(1)
		C(3)–Mo–O(3)	32.2(1)
Mo–O(3)–C(3)	61.7(2)	Mo–C(1)–O(1)	178.0(3)
O(3)–C(3)–C(4)	127.2(3)	Mo–C(2)–O(2)	179.4(4)
C(3)–C(4)–Si	112.9(2)	Mo–P–C(8)	115.7(1)
C(4)–Si–C(5)	108.7(2)	Mo–P–C(9)	113.5(1)
C(4)–Si–C(6)	111.5(2)	Mo–P–C(10)	117.1(1)
C(4)–Si–C(7)	105.7(2)	C(8)–P–C(9)	102.9(2)
C(5)–Si–C(6)	109.7(3)	C(8)–P–C(10)	103.0(2)
C(5)–Si–C(7)	110.2(3)	C(9)–P–C(10)	102.7(2)
C(6)–Si–C(7)	110.9(3)		

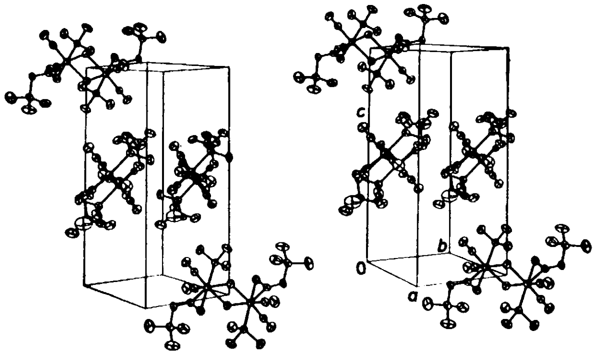

FIGURE 3 Stereoscopic view of the unit-cell packing for $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1)

The molybdenum–chlorine bridge bond lengths of 2.544(1) and 2.577(1) Å agree quite well with those found in other bridging situations such as the 2.55 Å value for the triply chloro-bridged molecule $Mo_2Cl_3(CO)_4$-$(POMe_3)_4$.[14] The molybdenum–phosphorus bond lengths and molybdenum–carbonyl bond distances appear normal.

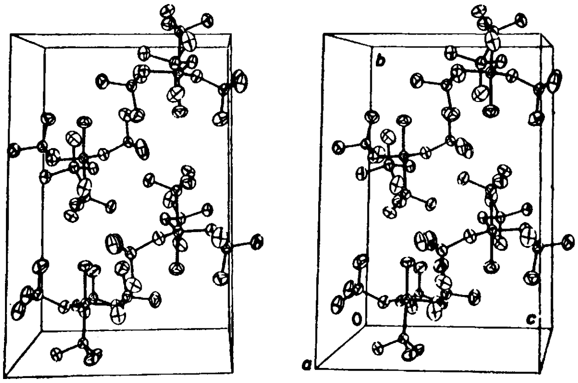

FIGURE 4 Stereoscopic view of the packing for [MoCl(η^2-$COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2)

Figures 3 and 4 show stereoscopic views of the unit-cell packing in these molecules. No abnormally short intermolecular separations are noted.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn) Microanalytical Laboratories. Molecular weights were measured cryoscopically in benzene under an N_2 atmosphere. The spectroscopic instruments used were Perkin-Elmer models 457 and 257 for i.r. spectra, a Perkin-Elmer R12A for ^1H n.m.r. spectra, and a Varian XL–100–12 for ^{31}P n.m.r. spectra.

$(Me_3SiCH_2)_2Mg$ was prepared from Me_3SiCH_2MgCl and dioxan; $MoCl_4(thf)_2$ was made as described.[15] Solvents were dried using conventional procedures and distilled under N_2 before use. All preparations and other operations were carried out under N_2.

Chloro(trimethylphosphine)tris(trimethylsilylmethyl)molybdenum(IV) (1).—To a suspension of $MoCl_4{\cdot}2thf$ (0.42 g, *ca.* 1.1 mmol) in ether (50 cm^3), trimethylphosphine (0.2 cm^3, *ca.* 2 mmol) and $(Me_3SiCH_2)_2Mg$ (3 mg) were successively added. The mixture was stirred at room temperature for 4—6 h and the solvent removed *in vacuo*. The residue was dissolved in light petroleum (60—70 cm^3) and centrifuged. The resulting deep purple solution was concentrated and cooled at −30 °C overnight, when a purple crystalline solid precipitated. The solid was collected and recrystallised twice from ether–light petroleum to give purple crystals in *ca.* 50% yield (Found: C, 38.0; H, 9.0; Cl, 7.5; P, 6.7; *M*, 490. $C_{15}H_{42}ClMoPSi_3$ requires C, 38.4; H, 9.0; Cl, 7.6; P, 6.6%; *M*, 469).

Infrared (Nujol mull) bands at: 1 420, 1 315, 1 305, 1 280, 1 250, 1 240, 955, 935, 890, 830, 745, 730, 695, 680, 610, 565, 545, and 490 cm^{-1}. The complex is paramagnetic as expected for Mo^{IV}.

Di-μ-chloro-bis[bis(carbonyl)trimethylphosphine(η^2-trimethylsilylmethylcarbonyl)molybdenum(II)] (2).—The crude purple solid resulting from cooling the light petroleum solution at −30 °C overnight (see above) was redissolved in light petroleum and treated with CO at room temperature and pressure. A light yellow solid was obtained which was insoluble in light petroleum and diethyl ether, and moderately soluble in benzene, dichloromethane, tetrahydrofuran, *etc.* The yellow-orange compound was best recrystallised by slowly cooling to room temperature over a period of 8—12 h from a hot (*ca.* 50—60 °C) concentrated benzene solution (Found: C, 31.9; H, 5.5; Cl, 9.5; P, 8.3; *M*, 730. $C_{20}H_{40}Cl_2Mo_2O_6P_2Si_2$ requires C, 31.7; H, 5.3; Cl, 9.4; P, 8.2%; *M*, 757).

Infrared (KBr disc) bands at: 2 950, 2 900, 2 890, 1 930, 1 835, 1 575, 1 430, 1 420, 1 390, 1 305, 1 290, 1 285, 1 260, 1 245, 1 170, 1 120, 1 020, 955, 855, 840, 805, 770, 740, 715, 700, 675, 630, 590, 565, 555, 495, 440, and 335 cm^{-1}.

X-Ray Data Collection, Structure Determination and Refinement for $[MoCl(CH_2SiMe_3)_3(PMe_3)]$ (1).—*Crystal data.* $C_{15}H_{42}ClMoPSi_3$, $M = 469.1$, Monoclinic, $a = 10.400(5)$, $b = 19.029(7)$, $c = 12.849(5)$ Å, $\beta = 91.74(4)°$, $U = 2\,541.7$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 8.09$ cm^{-1}, space group $P2_1/n$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta \geqslant 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.50 × 0.50 × 0.60 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were measured by the w—2θ scan technique in a manner similar to that described previously.[16] All reflections in one independent quadrant out to $2\theta \leqslant 50°$ were measured; 2 302 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Full-matrix least-squares refinement was carried out using the Busing and Levy ORFLS program.* The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Mo, Cl, P, Si, and C were taken from Cromer and Waber;[17] those for H were taken from ref. 18. The scattering for molybdenum was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[19]

The position of the molybdenum atom was deduced by the inspection of a Patterson map, and the subsequent calculation of Fourier maps afforded the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.071$. Conversion to anisotropic thermal parameters and further refinement led to $R = 0.050$. The hydrogen atoms were located on a difference-Fourier map, and their co-ordinates and thermal parameters were varied for two cycles at a damping factor of 0.2. Additional cycles of refinement of the non-hydrogen atoms led to final values of $R = 0.033$ and $R' = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{\frac{1}{2}} = 0.034$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.2 e Å^{-3}. The standard deviation of an observation of unit weight was 1.67. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 3. The thermal parameters and the observed and calculated structure factor amplitudes are given in Supplementary Publications No. SUP 22678 (40 pp.).†

X-Ray Data Collection, Structure Determination and Refinement for $[MoCl(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2).—*Crystal data.* $C_{20}H_{40}Cl_2Mo_2O_6P_2Si_2$, $M = 757.4$, Monoclinic, $a = 8.415(3)$, $b = 10.484(3)$, $c = 19.229(5)$ Å, $\beta = 90.62(2)°$, $U = 1\,696.3$ Å^3, $Z = 2$, $Dc = 1.48$ g cm^{-3}; $\mu(Mo\text{-}K_\alpha) = 10.71$ cm^{-1}, space group $P2_1/c$. The lattice parameters were determined as above based on 15 reflections with $2\theta \geqslant 30°$.

The crystal of dimensions 0.40 × 0.50 × 0.80 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. The data collection procedure was the same as given above. All reflections in one independent quadrant out to $2\theta \leqslant 50°$ were measured; 2 579 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the methods described above. Refinement with isotropic temperature factors gave $R = 0.060$. The employment of anisotropic thermal parameters led to $R = 0.040$, and addition of the hydrogen

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* Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distance and angle with estimated standard deviations by W. R. Busing, K. O. Martin, and H. A. Levy), ORABS (absorption correction, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), BPL (least-squares planes, by W. E. Hunter), and FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program).

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

atoms followed by further refinement of the non-hydrogen atoms gave final values of $R = 0.020$ and $R' = 0.026$. The standard deviation of an observation of unit weight was 1.07. A final difference Fourier showed no feature greater than 0.2 e Å^{-3}. Unit weights were used, and no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin \theta)/\lambda$ was observed. The final values of the positional parameters are given in Table 4. The thermal parameters and the observed and calculated structure factor amplitudes are given in the Supplementary Publication.

TABLE 3

Final fractional co-ordinates for $MoCl(CH_2SiMe_3)_3(PMe_3)$ (1) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.148 4(1)	0.112 5(1)	0.245 5(1)
Cl	0.099 4(2)	0.233 9(1)	0.237 7(2)
P	0.188 8(1)	−0.017 2(1)	0.239 8(1)
Si(1)	0.313 9(2)	0.150 2(1)	0.477 6(1)
Si(2)	0.323 5(2)	0.162 6(1)	0.030 8(1)
Si(3)	−0.184 2(2)	0.093 2(1)	0.250 7(1)
C(1)	0.334 6(7)	−0.050 3(4)	0.300 5(6)
C(2)	0.195 2(7)	−0.051 6(4)	0.108 7(5)
C(3)	0.067 8(6)	−0.073 4(3)	0.295 0(5)
C(4)	0.174 9(5)	0.106 8(3)	0.407 3(4)
C(5)	0.294 1(8)	0.136 6(4)	0.618 9(5)
C(6)	0.468 8(6)	0.109 0(5)	0.443 4(6)
C(7)	0.322 4(8)	0.244 5(4)	0.451 1(6)
C(8)	0.318 4(5)	0.120 3(3)	0.161 0(4)
C(9)	0.460 3(7)	0.125 4(5)	−0.040 5(5)
C(10)	0.174 5(7)	0.145 5(5)	−0.048 1(5)
C(11)	0.355 6(10)	0.257 0(4)	0.047 0(7)
C(12)	−0.033 1(5)	0.084 5(3)	0.177 0(4)
C(13)	−0.306 5(6)	0.035 3(4)	0.187 8(6)
C(14)	−0.166 9(6)	0.064 2(4)	0.387 2(4)
C(15)	−0.244 4(8)	0.183 5(4)	0.244 3(6)
H(1)[C(1)]	0.349	−0.036	0.378
H(2)[C(1)]	0.414	−0.032	0.281
H(3)[C(1)]	0.338	−0.097	0.296
H(4)[C(2)]	0.269	−0.043	0.085
H(5)[C(2)]	0.215	−0.094	0.112
H(6)[C(2)]	0.170	−0.031	0.066
H(7)[C(3)]	0.087	−0.124	0.284
H(8)[C(3)]	−0.011	−0.064	0.262
H(9)[C(3)]	0.083	−0.067	0.365
H(10)[C(4)]	0.180	0.058	0.426
H(11)[C(4)]	0.118	0.127	0.432
H(12)[C(5)]	0.295	0.083	0.632
H(13)[C(5)]	0.207	0.158	0.642
H(14)[C(5)]	0.342	0.152	0.648
H(15)[C(6)]	0.442	0.055	0.460
H(16)[C(6)]	0.483	0.117	0.372
H(17)[C(6)]	0.527	0.127	0.468
H(18)[C(7)]	0.347	0.250	0.385
H(19)[C(7)]	0.236	0.260	0.468
H(20)[C(7)]	0.389	0.266	0.479
H(21)[C(8)]	0.361	0.079	0.160
H(22)[C(8)]	0.359	0.145	0.204
H(23)[C(9)]	0.446	0.071	0.045
H(24)[C(9)]	0.543	0.133	0.002
H(25)[C(9)]	0.455	0.145	−0.105
H(26)[C(10)]	0.178	0.167	−0.102
H(27)[C(10)]	0.113	0.172	−0.023
H(28)[C(10)]	0.134	0.095	−0.053
H(29)[C(11)]	0.270	0.262	0.032
H(30)[C(11)]	0.379	0.270	0.118
H(31)[C(11)]	0.411	0.272	−0.005
H(32)[C(12)]	−0.032	0.036	0.150
H(33)[C(12)]	−0.040	0.117	0.122
H(34)[C(13)]	−0.321	0.030	0.116
H(35)[C(13)]	−0.379	0.040	0.213
H(36)[C(13)]	−0.264	−0.011	0.187
H(37)[C(14)]	−0.240	0.063	0.419
H(38)[C(14)]	−0.138	0.090	0.418
H(39)[C(14)]	−0.152	0.016	0.398
H(40)[C(15)]	−0.241	0.209	0.189
H(41)[C(15)]	−0.183	0.215	0.297
H(42)[C(15)]	−0.299	0.187	0.268

TABLE 4

Final fractional co-ordinates for $[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (2) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.148 7(1)	0.369 1(1)	0.470 4(1)
Cl	−0.071 7(1)	0.403 0(1)	0.560 5(1)
P	−0.026 5(1)	0.281 1(1)	0.378 1(1)
Si	0.482 6(1)	0.211 2(1)	0.640 3(1)
O(1)	0.397 2(3)	0.340 3(3)	0.353 6(1)
O(2)	0.158 9(4)	0.080 2(3)	0.504 4(2)
O(3)	0.314 8(3)	0.454 8(2)	0.553 3(1)
C(1)	0.304 5(4)	0.353 5(4)	0.397 2(2)
C(2)	0.154 2(4)	0.188 3(4)	0.491 8(2)
C(3)	0.349 6(4)	0.351 2(3)	0.528 3(2)
C(4)	0.487 1(4)	0.271 1(4)	0.546 5(2)
C(5)	0.557 2(8)	0.338 2(6)	0.697 9(2)
C(6)	0.279 5(6)	0.165 3(6)	0.666 0(2)
C(7)	0.617 7(8)	0.072 7(6)	0.643 3(3)
C(8)	−0.220 5(5)	0.228 6(4)	0.406 0(2)
C(9)	−0.073 6(6)	0.394 6(4)	0.309 7(2)
C(10)	0.046 9(5)	0.145 1(4)	0.330 0(2)
H(1)[C(4)]	0.499	0.203	0.506
H(2)[C(4)]	0.584	0.314	0.538
H(3)[C(5)]	0.636	0.370	0.693
H(4)[C(5)]	0.459	0.406	0.693
H(5)[C(5)]	0.545	0.315	0.750
H(6)[C(6)]	0.277	0.136	0.711
H(7)[C(6)]	0.207	0.128	0.646
H(8)[C(6)]	0.254	0.241	0.673
H(9)[C(7)]	0.713	0.101	0.625
H(10)[C(7)]	0.557	0.012	0.616
H(11)[C(7)]	0.603	0.034	0.686
H(12)[C(8)]	−0.216	0.171	0.434
H(13)[C(8)]	−0.263	0.294	0.426
H(14)[C(8)]	−0.297	0.191	0.369
H(15)[C(9)]	−0.115	0.364	0.274
H(16)[C(9)]	0.016	0.437	0.284
H(17)[C(9)]	−0.123	0.460	0.324
H(18)[C(10)]	0.146	0.161	0.306
H(19)[C(10)]	−0.022	0.121	0.292
H(20)[C(10)]	0.045	0.071	0.356

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