Pergamon

Polyhedron Vol. 14, No. 20–21, pp. 3077–3085, 1995

0277–5387/95 $9.50+0.00

0277–5387(95)00096–8

COMPLEXES OF MOLYBDENUM(III) AND -(IV) WITH CHLORIDE AND TERTIARY PHOSPHINE LIGANDS; AN OMNIUMGATHERUM OF NEW AND OLD RESULTS

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(*Received* 4 *November* 1994; *accepted* 15 *February* 1995)

Abstract—The preparations and structures of four new mixed chloro-tertiary phosphine complexes **1**, **3–5** of molybdenum(III) are reported, as well as the structure of two previously known Mo^{III} complexes **2**, **6** and the structure of an $[MoCl_6]^{2-}$ compound **7**. These results are discussed along with data for other such compounds.

Relatively few complexes of molybdenum(III) containing chloride ions and tertiary phosphines have been structurally characterized. In the course of a synthetic program having other goals, we have chanced to make and identify by X-ray crystallography several such compounds. In this paper we report the syntheses and structures, as well as comparisons with other structural data on compounds of this type. Also included is one Mo^{IV} compound, namely, $[PClMe_2Ph]_2[MoCl_6]$.

EXPERIMENTAL

The compounds $MoCl_4(CH_3CN_2)$,[1] $MoCl_4(THF)_2$,[1] $[PPh_4][MoCl_4(THF)_2]$[2] and $[PPh_4][MoCl_4(PMe_2Ph)_2]$[2] were prepared according to literature procedures. All manipulations were carried out in an argon atmosphere.

Preparation of $[PPh_4][MoCl_4(PMePh_2)_2]$ (1)

The method is similar to that used to prepare the PMe_2Ph analogue.[2] To a solution of $[PPh_4][MoCl_4(THF)_2]$ (0.2 g, 0.28 mmol) in dichloromethane (15 cm^3) was added $PMePh_2$ (0.26 cm^3, 1.4 mmol) and the mixture was refluxed for 12 h. After cooling to room temperature, the mixture was concentrated *in vacuo* to *ca* 8 cm^3 and then 30 cm^3 of ether was added to give a yellow solid, $[PPh_4][MoCl_4(PMePh_2)_2]$. The compound was washed with ether, filtered, vacuum dried and then recrystallized from CH_2Cl_2 with ether. Yield 0.19 g, 69%.

Preparation of $[PPh_4][MoCl_4(PEt_3)_2]$ (3)

To a slurry of $MoCl_4(THF)_2$ (0.58 g, 1.52 mmol) in dichloromethane (10 cm^3) was added (0.7 cm^3, 4.74 mmol) PEt_3 and the mixture stirred for 1 h. The red homogeneous solution thus obtained was filtered and then treated with PPh_4Br (0.96 g, 2.26 mmol). The solution turned dark brown. It was reduced to half its volume and then treated with 20 cm^3 of ether to give the bright yellow powder of **3**. This was washed with 4 × 20 cm^3 of ether, vacuum dried and recrystallized from CH_2Cl_2/hexane. Yield 1.05 g, 85%.

Preparation of $[PHEt_2Ph][MoCl_4(PEt_2Ph)_2] \cdot C_6H_{14}$ (4)

To a slurry of $MoCl_4(THF)_2$ (0.3 g, 0.79 mmol) in dichloromethane (10 cm^3) was added PEt_2Ph (0.31 cm^3, 1.57 mmol) and the mixture stirred at room temperature for 1 h to give a red homogeneous solution. The red solution was filtered and layered with hexane. As this did not lead to the formation of any crystals, the solvents were removed *in vacuo* to leave behind an oily residue. This was dissolved in benzene (25 cm^3) and layered

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with hexane, which led to the formation of a few crystals of compound **4**. Yield <5%.

Preparation of $[PHMe_2Ph]_2[MoCl_5PMe_2Ph]$ (**5**)

A mixture of $MoCl_4(THF)_2$ (0.25 g, 0.65 mmol), PMe_2Ph (0.18 g, 1.3 mmol) and CH_2Cl_2 (30 cm^3) was stirred at room temperature, filtered and then layered with hexane. After complete diffusion of solvents an oily residue was obtained. The Schlenk tube was placed in the refrigerator. After 1 month, a few needle-like crystals of **5** were obtained.

Preparation of $MoCl_3(CH_3CN)(PEtPh_2)_2 \cdot C_6H_6$ (**6**)

To a slurry of $MoCl_4(CH_3CN)_2$ (0.5 g, 1.3 mmol) in dichloromethane (10 cm^3) was added $PEtPh_2$ (0.6 cm^3, 2.6 mmol) and the mixture stirred at room temperature for *ca* 2 h. The resulting red solution was filtered and then evaporated *in vacuo*. The residue was redissolved in benzene and this solution layered with hexane. A few crystals of **6** were obtained.

Preparation of $[PClMe_2Ph]_2[MoCl_6]$ (**7**)

Our attempts to synthesize $MoCl_4(PMe_2Ph)_2$ by oxidizing $Mo(CO)_4(PMe_2Ph)_2$ with chlorine, as reported in the literature,[3] have led to the formation of red solid **7**. $Mo(CO)_4(PMe_2Ph)_2$ was obtained as a white powder by refluxing a mixture of $Mo(CO)_6$ (1 g), $NaBH_4$ (0.39 g), PMe_2Ph (1.1 cm^3) and EtOH (20 cm^3) for 5 h and then allowing it to cool to room temperature.[4] The white powder was washed with water and EtOH.

X-ray crystallography

A crystal of each of the compounds **1**–**7** was mounted on the end of a glass fiber and covered with epoxy glue. Pertinent crystallographic data are given in Table 1. Geometric and intensity data were gathered with an automated diffractometer (as given in Table 1) by following procedures described previously.[5] Lattice dimensions and Laue symmetry were verified by axial photography. Intensity data, gathered by the 2θ–ω method, were reduced by routine procedures.[6] Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90°.[7] In the case of compound **3**, an additional correction was applied for the average decay of 11% observed in the three periodically monitored standard reflections during the 106 h of data collection. The choice of space group from systematic absences, for each compound except **2**, was unambiguous. For **2**, successful refinement justified *C*2/*c* rather than *Cc*.

The molybdenum, chlorine and phosphorus atoms were located via Patterson maps for almost all the seven compounds. In some cases, the entire structure was found from Patterson maps. The total structure (if not found) was developed by an altering sequence of least-square refinements and difference Fourier maps. Selected bond distances and bond angles are given in Tables 2–8. Tables of positional parameters have been deposited with the Editor as supplementary material.

$[PPh_4][MoCl_4(PMePh_2)_2]$ (**1**). Two independent *trans* anions, $[MoCl_4P_2]^-$, residing on inversion centres were found in the asymmetric unit. The hydrogen atoms, found from the difference Fourier maps, were refined isotropically but with fixed *B* values. The principal bond lengths and angles are given in Table 2 and a drawing of the anion in Fig. 1.

$[PPh_4][MoCl_4(PMe_2Ph)_2]$ (**2**). The *trans* anion was found to reside on a crystallographic twofold axis. The hydrogen atoms were refined isotropically with their thermal displacement parameters constrained to the same value. The principal bond lengths and angles are given in Table 3, and a drawing of the anion in Fig. 1.

$[PPh_4][MoCl_4(PEt_3)_2]$ (**3**). The *trans* anion sits on a general position. Terminal carbons of the PEt_3 groups have large thermal parameters, indicating a large freedom of motion. In fact, one terminal carbon is disordered over two sites, C(6) and C(6)′. The restraints imposed on the thermal parameters of hydrogen atoms in the refinement are similar to those for compound **2**. The principal bond lengths and angles are given in Table 4, and a drawing of the anion in Fig. 1.

$[PHEt_2Ph][MoCl_4(PEt_2Ph)_2] \cdot C_6H_{14}$ (**4**). The *cis* anion sits on a general position. The solvent molecule, n-hexane, was found on an inversion centre with the carbon atom C(32) disordered over two sites. The principal bond lengths and angles are given in Table 5, and a drawing of the anion in Fig. 1.

$[PHMe_2Ph]_2[MoCl_5PMe_2Ph]$ (**5**). The anion sits on a general position. The constraints used on the *B* values of hydrogen atoms are similar to those for **2**. The principal bond lengths and angles are given in Table 6, and a drawing of the anion in Fig. 2.

$MoCl_3(CH_3CN)(PEtPh_2)_2 \cdot C_6H_6$ (**6**). The molecule sits on a general position and the solvent molecule, benzene, on an inversion centre. Constraints on the *B* values of hydrogen atoms are similar to those for **2**. The principal bond lengths and angles are given in Table 7, and a drawing of the anion in Fig. 3.

Table 1. Crystal data for $[PPh_4][MoCl_4(PMePh_2)_2]$ (**1**), $[PPh_4][MoCl_4(PMe_2Ph)_2]$ (**2**), $[PPh_4][MoCl_4(PEt_3)_2]$ (**3**), $[PHEt_2Ph][MoCl_4(PEt_2Ph)_2] \cdot n\text{-}C_6H_{14}$ (**4**), $[PHMe_2Ph]_2[MoCl_5PMe_2Ph]$ (**5**), $MoCl_3(CH_3CN)(PEtPh_2)_2 \cdot C_6H_6$ (**6**) and $[PClMe_2Ph]_2[MoCl_6]$ (**7**)

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$MoCl_4P_3C_{50}H_{46}$	$MoCl_4P_3C_{40}H_{42}$	$MoCl_4P_3C_{36}H_{45}$	$MoCl_4P_3C_{44}H_{50}$	$MoCl_5P_3C_{24}H_{35}$	$MoCl_3P_2NC_{33}H_{35}$	$MoCl_8P_2C_{16}H_{22}$
Formula weight	977.6	853.45	813.47	909.56	782.59	709.9	655.86
Space group	$P2_1/a$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Systematic absences	$(0k0)$, $k \neq 2n$; $(h0l)$, $h \neq 2n$	(hkl), $h+k \neq 2n$; $(h0l)$, $h,l \neq 2n$	$(0k0)$, $k \neq 2n$; $(h0l)$, $h+l \neq 2n$	$(0k0)$, $k \neq 2n$; $(h0l)$, $l \neq 2n$	$(0k0)$, $k \neq 2n$; $(h0l)$, $h+l \neq 2n$	$(0k0)$, $k \neq 2n$; $(h0l)$, $h+l \neq 2n$	$(0k0)$, $k \neq 2n$ $(h0l)$, $l \neq 2n$
a (Å)	16.595 (1)	14.485 (1)	12.238 (6)	12.517 (4)	10.722 (1)	9.763 (2)	9.469 (1)
b (Å)	12.074 (1)	12.663 (1)	18.047 (6)	14.071 (4)	10.248 (1)	16.058 (3)	12.244 (1)
c (Å)	24.209 (3)	22.95 (3)	18.667 (4)	22.124 (9)	28.163 (2)	21.777 (3)	11.059 (1)
α (°)	90	90	90	90	90	91.16 (3)	90
β (°)	109.1 (1)	106.61 (1)	102.70 (2)	96.11 (3)	95.62 (1)	92.7 (1)	93.13 (1)
γ (°)	90	90	90	90	90	90	90
V (Å^3)	4588 (2)	4034 (2)	4022 (2)	3875 (3)	3080 (2)	3411 (2)	1280 (3)
Z	4	4	4	4	4	4	2
d_{calc} (g cm^{-3})	1.419	1.408	1.343	1.383	1.016	1.382	1.025
Crystal size (mm)	0.40 × 0.30 × 0.10	0.30 × 0.30 × 0.15	0.40 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.50 × 0.40 × 0.25	0.25 × 0.20 × 0.10
μ(Mo-K_α) (cm^{-1})	6.518	7.296	7.268	7.527			
Data collection instrument	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Rigaku AFIC5R	Syntex Pl			
Radiation monochromated in incident beam (λ, Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)			
Orientation reflections: number, range (2θ) (°)	25, $21.82 \leqslant 2\theta \leqslant 32.50$	25, $21.56 \leqslant 2\theta \leqslant 26.26$	25, $19.00 \leqslant 2\theta \leqslant 226.5$	25, $20.07 \leqslant 2\theta \leqslant 28.00$	25, $19.04 \leqslant 2\theta \leqslant 44.66$	25, $19.07 \leqslant 2\theta \leqslant 25.22$	25, $21.34 \leqslant 2\theta \leqslant 41.51$
Temperature (°C)	20 + 1	20 + 1	20 + 1	20 + 1	$2\theta + 1$	$2\theta + 1$	$2\theta + 1$
Scan method	2θ–ω	2θ–ω	2θ–ω	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Data collection range, 2θ (°)	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 45$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6038, 3812	2647, 2340	6711, 4176	5079, 2555	4017, 2708	4347, 3798	1559, 1302
No. parameters refined	665	283	429	362	376	407	124
Transmission factors, %: maximum, minimum	99.9, 93.1	99.9, 87.7	99.9, 84.1	99.6, 94.3	99.9, 97.4	99.9, 95.2	99.9, 92.3
R^a	33	31	63	67	37	35	28
R_w	0.041^b	0.040^b	0.098^c	0.070^c	0.055^b	0.058^b	0.035^c
Quality-of-fit indicator^d	1145	1272	2102	1771	1541	1463	1031
Largest shift/e.s.d., final cycle	0.37	0.25	0.81	0.76	0.38	0.86	0.44
Largest peak (e Å^{-3})	0.46	0.53	0.98	0.68	0.75	0.64	0.35

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [1/\sigma^2\{|F_o|\} + 0.001|F_o|^2]^{1/2}$.

[d] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{para})]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for $[PPh_4][MoCl_4(PMePh_2)_2]$ (**1**)

Mo(1)—Cl(1)	2.434(1)	P(1)—C(1)	1.824(5)	P(3)—C(27)	1.786(5)
Mo(1)—Cl(2)	2.429(1)	P(1)—C(7)	1.834(4)	P(3)—C(33)	1.798(5)
Mo(1)—P(1)	2.591(1)	P(1)—C(13)	1.821(5)	P(3)—C(39)	1.798(5)
Mo(2)—Cl(3)	2.421(1)	P(2)—C(14)	1.826(6)	P(3)—C(45)	1.798(4)
Mo(2)—Cl(4)	2.438(1)	P(2)—C(20)	1.825(4)		
Mo(2)—P(2)	2.589(1)	P(2)—C(26)	1.815(6)		
Cl(1)—Mo(1)—Cl(2)	89.90(5)	Mo(1)—P(1)—C(13)	111.0(2)	C(14)—P(2)—C(26)	103.5(3)
Cl(1)—Mo(1)—P(1)	87.32(4)	C(1)—P(1)—C(7)	101.4(2)	C(20)—P(2)—C(26)	104.0(2)
Cl(2)—Mo(1)—P(1)	88.19(4)	C(1)—P(1)—C(13)	104.9(2)	C(27)—P(3)—C(33)	107.1(2)
Cl(3)—Mo(2)—Cl(4)	90.90(5)	C(7)—P(1)—C(13)	99.7(2)	C(27)—P(3)—C(39)	112.0(2)
Cl(3)—Mo(2)—P(2)	93.94(4)	Mo(2)—P(2)—C(14)	116.5(2)	C(27)—P(3)—C(45)	110.8(2)
Cl(4)—Mo(2)—P(2)	90.08(4)	Mo(2)—P(2)—C(20)	118.3(2)	C(33)—P(3)—C(39)	109.7(2)
Mo(1)—P(1)—C(1)	117.7(1)	Mo(2)—P(2)—C(26)	112.1(2)	C(33)—P(3)—C(45)	111.0(2)
Mo(1)—P(1)—C(7)	119.7(2)	C(14)—P(2)—C(20)	100.4(2)	C(39)—P(3)—C(45)	106.4(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Selected bond distances (Å) and angles (°) for $[PPh_4][MoCl_4(PMe_2Ph)_2]$ (**2**)

Mo—Cl(1)	2.440(1)	P(1)—C(1)	1.818(3)	P(2)—C(9)	1.802(3)
Mo—Cl(2)	2.420(1)	P(1)—C(7)	1.820(4)	P(2)—C(15)	1.805(3)
Mo—P(1)	2.542(1)	P(1)—C(8)	1.819(4)		
Cl(1)—Mo—Cl(2)	89.16(3)	Mo—P(1)—C(7)	114.4(1)	C(7)—P(1)—C(8)	102.7(2)
Cl(1)—Mo—P(1)	87.77(3)	Mo—P(1)—C(8)	112.3(1)	C(9)—P(2)—C(15)	109.3(1)
Cl(2)—Mo—P(1)	94.06(3)	C(1)—P(1)—C(7)	104.7(2)		
Mo—P(1)—C(1)	117.1(1)	C(1)—P(1)—C(8)	104.1(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

$[PClMe_2Ph]_2[MoCl_6]$ (**7**). The anion sits on an inversion centre. Hydrogen atoms at idealized positions were included in the final structure factor calculations. The principal bond lengths and angles are given in Table 8, and a drawing of the anion in Fig. 4.

RESULTS AND DISCUSSION

Even though a number of workers have reported various methods[8–11] of synthesizing some $MoCl_4(PR_3)_2$ compounds from a variety of starting materials such as $MoCl_4(CH_3CN)_2$, $MoCl_4(THF)_2$ and $Mo(CO)_4(PR_3)$, no structural characterization of these compounds has been reported in the literature. This is probably due to the difficulty of obtaining crystals suitable for X-ray crystallographic studies. Synthesis of $[MoCl_4(PMe_2Ph)_2]^-$ has been somewhat recently reported.[2]

Our attempts to crystallize the known compounds $MoCl_4(PMe_2Ph)_2$,[3] $MoCl_4(PMePh_2)_2$[12] and $MoCl_4(PPh_3)_2$[13] were not successful. When we attempted to make $MoCl_4(PEt_3)_2$ and $MoCl_4(PEt_2Ph)_2$, it quickly became apparent that these two phosphines react with $MoCl_4(THF)_2$ to reduce the molybdenum from IV to III, thereby forming compounds containing the $[MoCl_4(PR_3)_2]^-$ ions. For this reason we introduced PPh_4^+ rather than relying on the autogenous formation of $PHEt_3^+$ and thus obtained a better yield of $[MoCl_4(PEt_3)_2]^-$.

Synthesis of $[PPh_4][MoCl_4(PR_3)_2]$ compounds from $[PPh_4][MoCl_4(THF)_2]$ by the method of Hills *et al.*[2] works well for $PR_3 = PMe_2Ph$, $PMePh_2$ but not for PEt_3. The reaction of $[PPh_4][MoCl_4(THF)_2]$ with PEt_3 gives $[Mo_2Cl_8PR_3]^{2-}$, as reported elsewhere.[14] As the reaction between PEt_2Ph and $[PPh_4][MoCl_4(THF)_2]$ showed indications of proceeding in the same way, we did not bother to characterize the reaction products.

The compounds **5** and **6** were only minor products of the reactions we used. A better method of synthesis of **6** is available in the literature.[15]

The structures of compounds **1**–**4** are interesting chiefly because while the first three have *trans*-$[MoCl_4(PR_3)_2]^-$ anions, the fourth has a *cis* structure. There is no apparent internal reason for this,

Table 4. Selected bond distances (Å) and angles (°) for $[PPh_4][MoCl_4(PEt_3)_2]$ (**3**)

Mo—Cl(1)	2.452(2)	P(1)—C(5)	1.859(13)	C(1)—C(2)	1.58(2)
Mo—Cl(2)	2.441(3)	P(2)—C(7)	1.850(12)	C(3)—C(4)	1.50(2)
Mo—Cl(3)	2.434(2)	P(2)—C(9)	1.780(15)	C(5)—C(6)	1.36(3)
Mo—Cl(4)	2.421(3)	P(2)—C(11)	1.844(13)	C(5)—C(6)″	1.47(6)
Mo—P(1)	2.574(3)	P(3)—C(13)	1.807(8)	C(7)—C(8)	1.48(2)
Mo—P(2)	2.560(3)	P(3)—C(19)	1.785(8)	C(9)—C(10)	1.49(3)
P(1)—C(1)	1.851(13)	P(3)—C(25)	1.796(7)	C(11)—C(12)	1.57(3)
P(1)—C(3)	1.838(12)	P(3)—C(31)	1.799(7)		

Cl(1)—Mo—Cl(2)	177.55(9)	P(1)—Mo—P(2)	178.48(9)	C(13)—P(3)—C(25)	112.1(4)
Cl(1)—Mo—Cl(3)	91.25(8)	Mo—P(1)—C(1)	111.0(4)	C(13)—P(3)—C(31)	111.3(4)
Cl(1)—Mo—Cl(4)	89.0(1)	Mo—P(1)—C(3)	116.2(4)	C(19)—P(3)—C(25)	109.2(4)
Cl(1)—Mo—P(1)	88.95(9)	Mo—P(1)—C(5)	116.5(6)	C(19)—P(3)—C(31)	109.1(4)
Cl(1)—Mo—P(2)	90.9(1)	C(1)—P(1)—C(3)	107.1(7)	C(25)—P(3)—C(31)	108.6(4)
Cl(2)—Mo—Cl(3)	90.64(9)	C(1)—P(1)—C(5)	103.4(8)	P(1)—C(1)—C(2)	115.0(1)
Cl(2)—Mo—Cl(4)	89.1(1)	C(3)—P(1)—C(5)	101.4(7)	P(1)—C(3)—C(4)	110.0(1)
Cl(2)—Mo—P(1)	92.52(9)	Mo—P(2)—C(7)	115.8(4)	P(1)—C(5)—C(6)	119.0(1)
Cl(2)—Mo—P(2)	87.6(1)	Mo—P(2)—C(9)	111.6(6)	P(1)—C(5)—C(6)″	117.0(2)
Cl(3)—Mo—Cl(4)	178.7(1)	Mo—P(2)—C(11)	113.9(5)	C(6)—C(5)—C(6)″	94.0(3)
Cl(3)—Mo—P(1)	92.39(9)	C(7)—P(2)—C(9)	106.8(7)	P(2)—C(7)—C(8)	114.2(8)
Cl(3)—Mo—P(2)	89.13(9)	C(7)—P(2)—C(11)	100.7(6)	P(2)—C(9)—C(10)	118.0(2)
Cl(4)—Mo—P(1)	86.4(1)	C(9)—P(2)—C(11)	107.1(9)	P(2)—C(11)—C(12)	118.0(1)
Cl(4)—Mo—P(2)	92.1(1)	C(13)—P(3)—C(19)	106.5(4)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. Selected bond distances (Å) and angles (°) for $[PHEt_2Ph][MoCl_4(PEt_2Ph)_2]\cdot n\text{-}C_6H_{14}$ (**4**)

Mo—Cl(1)	2.427(4)	P(1)—C(3)	1.841(15)	P(3)—C(25)	1.806(15)
Mo—Cl(2)	2.450(4)	P(1)—C(5)	1.842(14)	C(1)—C(2)	1.61(2)
Mo—Cl(3)	2.433(4)	P(2)—C(11)	1.850(8)	C(3)—C(4)	1.65(2)
Mo—Cl(4)	2.455(4)	P(2)—C(13)	1.850(10)	C(11)—C(12)	1.51(2)
Mo—P(1)	2.558(4)	P(2)—C(15)	1.856(12)	C(13)—C(14)	1.50(3)
Mo—P(2)	2.596(4)	P(3)—C(21)	1.813(13)	C(21)—C(22)	1.50(4)
P(1)—C(1)	1.85(2)	P(3)—C(23)	1.82(2)	C(23)—C(24)	1.51(4)

Cl(1)—Mo—Cl(2)	90.3(1)	Cl(4)—Mo—P(1)	176.8(2)	C(11)—P(2)—C(13)	108.6(8)
Cl(1)—Mo—Cl(3)	176.7(2)	Cl(4)—Mo—P(2)	86.3(1)	C(11)—P(2)—C(15)	105.4(7)
Cl(1)—Mo—Cl(4)	91.2(1)	P(1)—Mo—P(2)	94.3(1)	C(13)—P(2)—C(15)	105.3(6)
Cl(1)—Mo—P(1)	91.9(1)	Mo—P(1)—C(1)	110.7(5)	C(21)—P(3)—C(23)	106.5(9)
Cl(1)—Mo—P(2)	86.6(1)	Mo—P(1)—C(3)	116.1(6)	C(21)—P(3)—C(25)	109.7(7)
Cl(2)—Mo—Cl(3)	89.2(1)	Mo—P(1)—C(5)	117.0(5)	C(23)—P(3)—C(25)	109.0(1)
Cl(2)—Mo—Cl(4)	90.7(2)	C(1)—P(1)—C(3)	106.1(8)	P(1)—C(1)—C(2)	110.0(1)
Cl(2)—Mo—P(1)	88.9(1)	C(1)—P(1)—C(5)	102.2(7)	P(1)—C(3)—C(4)	109.0(1)
Cl(2)—Mo—P(2)	175.7(2)	C(3)—P(1)—C(5)	103.3(7)	P(2)—C(11)—C(12)	116.0(1)
Cl(3)—Mo—Cl(4)	92.1(1)	Mo—P(2)—C(11)	107.2(5)	P(2)—C(13)—C(14)	111.0(1)
Cl(3)—Mo—P(1)	84.8(1)	Mo—P(2)—C(13)	113.5(5)	P(3)—C(21)—C(22)	106.0(1)
Cl(3)—Mo—P(2)	94.1(1)	Mo—P(2)—C(15)	116.4(4)	P(3)—C(23)—C(24)	126.0(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

and it may well relate to the relative solubilities and/or packing forces. In these four compounds, there is no distinct indication of differing *trans* influences. All Mo—P distances are in the range 2.542–2.574 Å and the Mo—Cl distances range from 2.420 to 2.455 Å. Even for the Mo—Cl bonds in **4** which are *cis* and *trans* to the Mo—P bonds, there is little difference, namely *ca* 0.02 Å. There

Table 6. Selected bond distances (Å) and angles (°) for $[PHMe_2Ph]_2[MoCl_5PMe_2Ph]$ (**5**)

Mo—Cl(1)	2.456(2)	P(1)—C(1)	1.829(9)	P(2)—H(1)	1.29(9)
Mo—Cl(2)	2.433(2)	P(1)—C(2)	1.806(9)	P(3)—C(17)	1.781(10)
Mo—Cl(3)	2.436(2)	P(1)—C(3)	1.821(7)	P(3)—C(18)	1.775(10)
Mo—Cl(4)	2.438(2)	P(2)—C(9)	1.779(9)	P(3)—C(19)	1.798(7)
Mo—Cl(5)	2.477(2)	P(2)—C(10)	1.773(9)	P(3)—H(2)	1.39(8)
Mo—P(1)	2.538(2)	P(2)—C(11)	1.777(8)		

Cl(1)—Mo—Cl(2)	177.14(7)	Cl(3)—Mo—P(1)	88.67(7)	C(9)—P(2)—C(11)	110.3(4)
Cl(1)—Mo—Cl(3)	88.80(7)	Cl(4)—Mo—Cl(5)	92.01(7)	C(9)—P(2)—H(1)	107.0(4)
Cl(1)—Mo—Cl(4)	90.41(7)	Cl(4)—Mo—P(1)	87.54(7)	C(10)—P(2)—C(11)	110.8(4)
Cl(1)—Mo—Cl(5)	90.24(7)	Cl(5)—Mo—P(1)	175.25(7)	C(10)—P(2)—H(1)	112.0(4)
Cl(1)—Mo—P(1)	85.04(7)	Mo—P(1)—C(1)	113.2(3)	C(11)—P(2)—H(1)	108.0(4)
Cl(2)—Mo—Cl(3)	90.28(7)	Mo—P(1)—C(2)	114.8(3)	C(17)—P(3)—C(18)	110.9(4)
Cl(2)—Mo—Cl(4)	90.33(7)	Mo—P(1)—C(3)	118.6(3)	C(17)—P(3)—C(19)	110.2(4)
Cl(2)—Mo—Cl(5)	92.50(7)	C(1)—P(1)—C(2)	101.6(4)	C(17)—P(3)—H(2)	112.0(4)
Cl(2)—Mo—P(1)	92.23(7)	C(1)—P(1)—C(3)	104.5(4)	C(18)—P(3)—C(19)	110.0(4)
Cl(3)—Mo—Cl(4)	176.18(7)	C(2)—P(1)—C(3)	102.2(4)	C(18)—P(3)—H(2)	107.0(3)
Cl(3)—Mo—Cl(5)	91.72(7)	C(9)—P(2)—C(10)	109.4(4)	C(19)—P(3)—H(2)	106.0(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 7. Selected bond distances (Å) and angles (°) for $MoCl_3(CH_3CN)(PEtPh_2)_2 \cdot C_6H_6$ (**6**)

Mo—Cl(1)	2.413(1)	Mo—N	2.147(3)	P(2)—C(21)	1.824(4)
Mo—Cl(2)	2.387(1)	P(1)—C(1)	1.822(4)	P(2)—C(27)	1.838(5)
Mo—Cl(3)	2.404(1)	P(1)—C(7)	1.830(4)	N—C(29)	1.114(5)
Mo—P(1)	2.600(1)	P(1)—C(13)	1.846(4)	C(29)—C(30)	1.500(7)
Mo—P(2)	2.594(1)	P(2)—C(15)	1.836(4)		

Cl(1)—Mo—Cl(2)	94.74(4)	Cl(3)—Mo—P(2)	88.65(3)	C(7)—P(1)—C(13)	103.0(2)
Cl(1)—Mo—Cl(3)	171.06(4)	Cl(3)—Mo—N	84.98(9)	Mo—P(2)—C(15)	118.5(1)
Cl(1)—Mo—P(1)	86.63(3)	P(1)—Mo—P(2)	173.95(3)	Mo—P(2)—C(21)	111.0(1)
Cl(1)—Mo—P(2)	87.53(3)	P(1)—Mo—N	87.63(9)	Mo—P(2)—C(27)	115.6(2)
Cl(1)—Mo—N	86.98(9)	P(2)—Mo—N	90.52(9)	C(15)—P(2)—C(21)	102.7(2)
Cl(2)—Mo—Cl(3)	93.52(4)	Mo—P(1)—C(1)	110.7(1)	C(15)—P(2)—C(27)	103.3(2)
Cl(2)—Mo—P(1)	89.04(4)	Mo—P(1)—C(7)	120.6(1)	C(21)—P(2)—C(27)	104.2(2)
Cl(2)—Mo—P(2)	93.00(4)	Mo—P(1)—C(13)	113.6(2)	Mo—N—C(29)	175.0(3)
Cl(2)—Mo—N	176.15(9)	C(1)—P(1)—C(7)	104.2(2)	N—C(29)—C(30)	177.8(5)
Cl(3)—Mo—P(1)	96.91(4)	C(1)—P(1)—C(13)	103.0(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 8. Selected bond distances (Å) and angles (°) for $[PClMe_2Ph]_2\ [MoCl_6]$ (**7**)

Mo—Cl(1)	2.358(1)	Cl(4)—P	1.989(2)	P—C(8)	1.763(5)
Mo—Cl(2)	2.374(1)	P—C(1)	1.780(4)		
Mo—Cl(3)	2.398(1)	P—C(7)	1.769(5)		

Cl(1)—Mo—Cl(2)	90.54(4)	Cl(4)—P—C(1)	107.5(2)	C(1)—P—C(7)	111.4(2)
Cl(1)—Mo—Cl(3)	90.22(4)	Cl(4)—P—C(7)	106.9(2)	C(1)—P—C(8)	111.2(2)
Cl(2)—Mo—Cl(3)	89.98(5)	Cl(4)—P—C(8)	107.1(2)	C(7)—P—C(8)	112.4(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

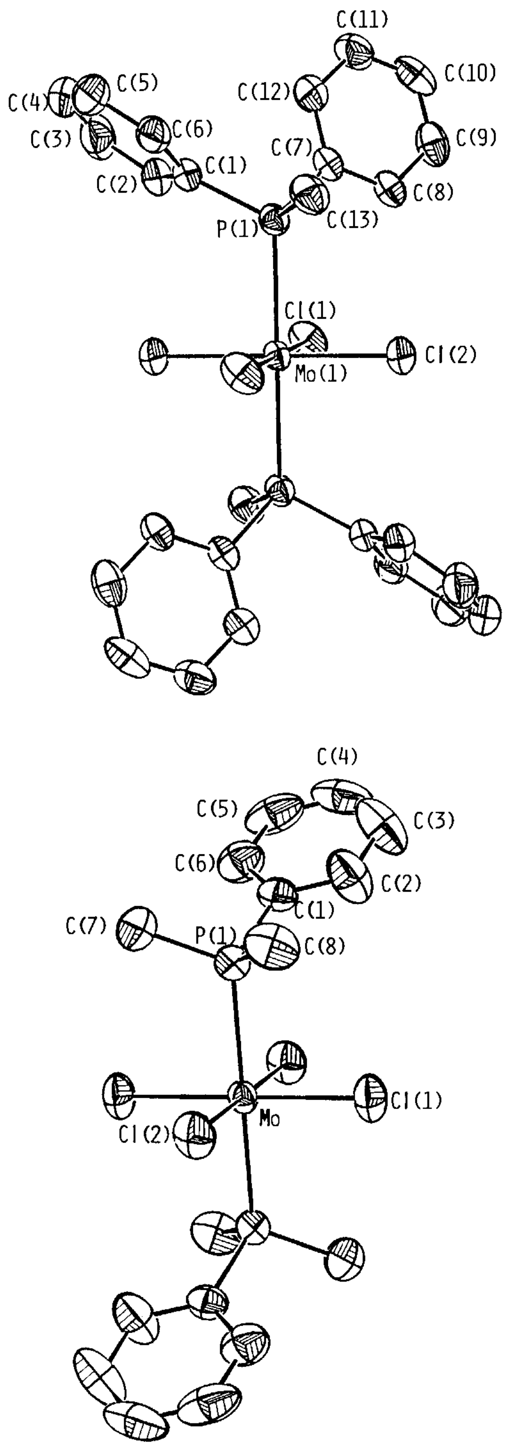

Fig. 1. ORTEP drawings of $[MoCl_4(PR_3)]^-$ ions. PR_3 = (a) $PMePh_2$, (b) PMe_2Ph, (c) PEt_3 and (d) PEt_2Ph. In the case of PEt_3, the sizes of the carbon atoms have been arbitrarily reduced.

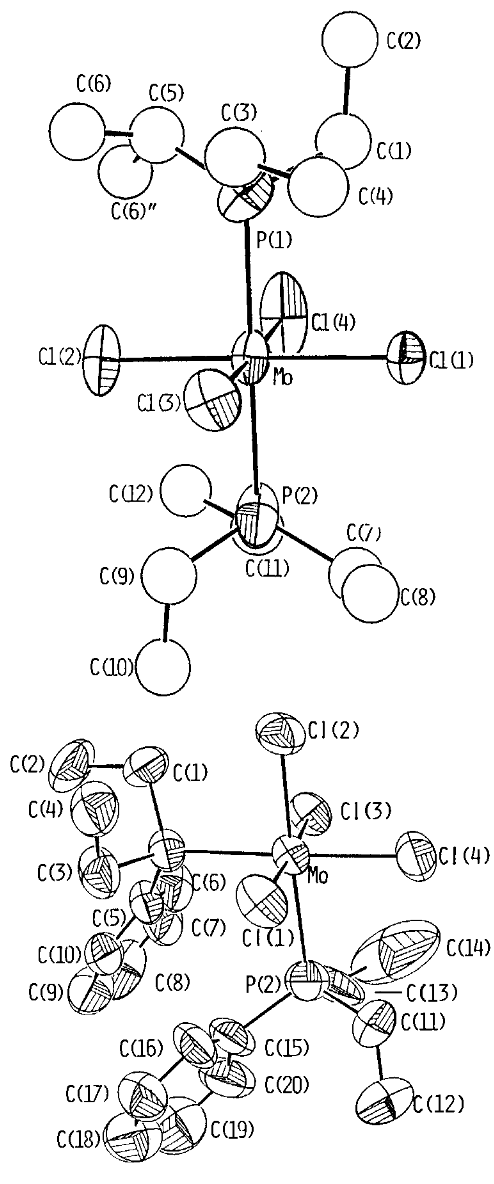

Fig. 1. *Continued.*

has been a previous report of the ^{31}P NMR spectra of the anions in **1**–**4**.[16]

In the $[MoCl_5(PEtPh_2)]^-$ ion the Mo—Cl bond *trans* to the Mo—P bond is 0.036 Å longer than the mean of the four *cis* Mo—Cl bonds. Again, the *trans* influence is very small.

There are several previous compounds containing the $[MoCl_6]^{2-}$ ion with which the structure of compound **7** can be compared. In one the counter cation is quite similar, namely PPh_3Cl^+.[17] The two cations are very similar, having P—Cl and mean P—C distances of 1.989(2) and 1.771(5) Å in the present case and 1.998(1) and 1.784(1) Å in the PPh_3Cl^+ compound. The previously reported Mo—Cl distance is 2.3825(5) Å,[17] while in this work we find 2.377(12) Å. The mean of these two results, 2.38 Å, can be compared with the Mo—Br distance, 2.532(4) Å, found in $[PPh_3Me]_2[MoBr_6]$.[18] The

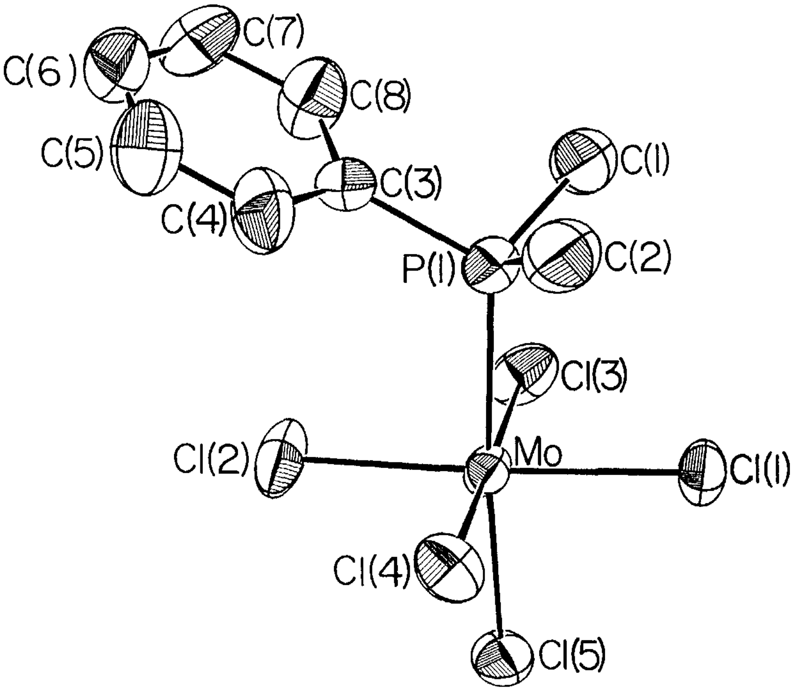

Fig. 2. An ORTEP drawing of the $[MoCl_5PMe_2Ph]^-$ ion.

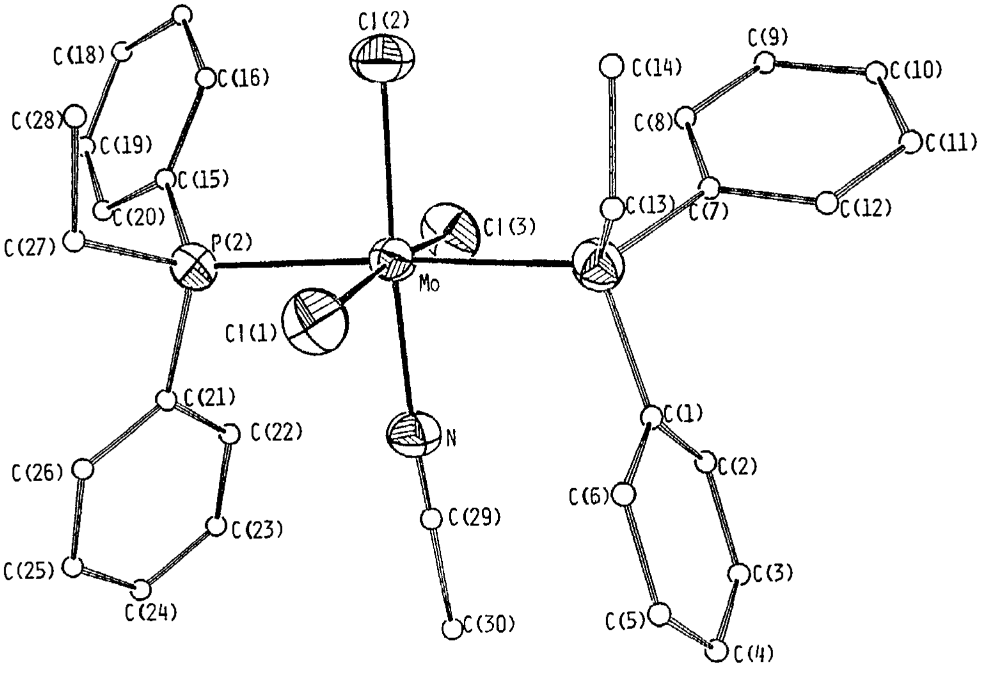

Fig. 3. An ORTEP drawing of the $MoCl_3(CH_3CN)(PEtPh_2)_2$ molecule. Carbon atoms have been arbitrarily reduced in size.

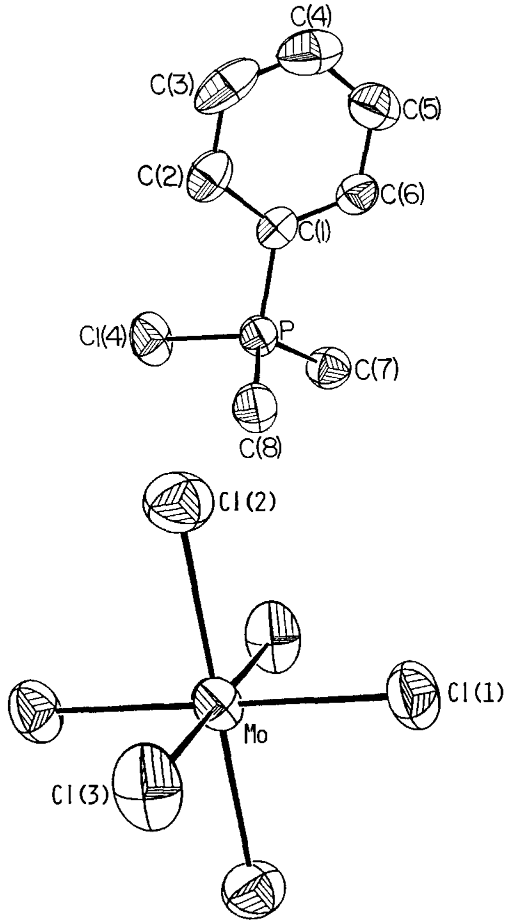

Fig. 4. ORTEP drawing of both (a) the cation and (b) the anion of the compound $[PClMe_2Ph]_2[MoCl_6]$.

difference, 0.15 Å, agrees exactly with the difference in the Br and Cl covalent radii, 0.15 Å. One other interesting comparison is with the mean Mo—Cl distance in the $[MoCl_6]^{3-}$ ion,[19] namely 2.452(7) Å. The observed difference, 0.075(14) Å, is appreciably greater than that expected, 0.04 Å, from tabulated radii for six-coordinate Mo^{3+} and Mo^{4+}.[20]

Acknowledgement—This research was supported by the National Science Foundation.

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