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Structure of Chlorotriphenylphosphonium Hexachloromolybdate

BY RAYMOND L. RICHARDS AND CAROLINE SHORTMAN

AFRC Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ, England
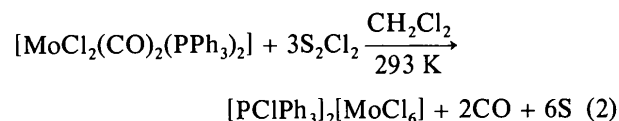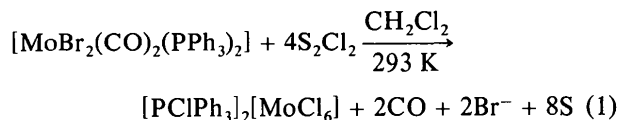
AND DAVID C. POVEY AND GALLIENUS W. SMITH

Department of Chemistry, University of Surrey, Guildford GU2 5XH, Surrey, England

Abstract. [PCl(C$_6$H$_5$)$_3$]$_2$[MoCl$_6$], $M_r = 904 \cdot 15$, trigonal rhombohedral, $R\bar{3}$, hexagonal cell $a = 13 \cdot 163$ (2), $c = 18 \cdot 876$ (7) Å, $V = 2832 \cdot 5$ (5) Å^3, $Z = 3$, $D_x = 1 \cdot 58$ Mg m^{-3}, D_m not measured, λ(Mo $K\alpha$) $= 0 \cdot 71069$ Å, $\mu = 10 \cdot 20$ cm^{-1}, $F(000) = 1362$, $T = 292$ K, $R = 0 \cdot 024$ for 1674 observed data with $I \geq 3\sigma(I)$. The complex contains an Mo atom at the centre of a regular octahedron of chloride ions and is the first accurately determined structure of this anion. The chlorophosphonium cations [PClPh$_3$]$^+$ have the expected tetrahedral symmetry with the P–Cl bonds directed towards opposite faces of the [MoCl$_6$]$^-$ octahedron.

Introduction. In a continuation of our studies of the reactions of molybdenum complexes with sulfur-containing reagents (Povey & Richards, 1984; Povey, Richards & Shortman, 1986), we have investigated the reactions of S$_2$Cl$_2$, widely used in organic chemistry for generating sulfur- and chloride-containing compounds (Kutney & Turnbull, 1982). In inorganic chemistry S$_2$Cl$_2$ is often used as a reactive solvent in the synthesis of thiohalide species, such as NbCl$_2$S$_2$ (Schäfer & Beckman, 1966), Mo$_3$Cl$_4$S$_7$ (Ul'ko & Kolesnicheno,

1980), and ReCl$_3$S (Marcole, Rabenau, Mootz & Wunderlich, 1974). The product of the reaction between [MoX$_2$(CO)$_2$(PPh$_3$)$_2$] (X = Br or Cl) and S$_2$Cl$_2$ does not, however, contain sulfur, but is the yellow complex [PClPh$_3$]$_2$[MoCl$_6$], which has been structurally characterized by X-ray crystallography.

$$[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2] + 4\text{S}_2\text{Cl}_2 \xrightarrow[293\text{ K}]{\text{CH}_2\text{Cl}_2}$$

$$[\text{PClPh}_3]_2[\text{MoCl}_6] + 2\text{CO} + 2\text{Br}^- + 8\text{S} \quad (1)$$

$$[\text{MoCl}_2(\text{CO})_2(\text{PPh}_3)_2] + 3\text{S}_2\text{Cl}_2 \xrightarrow[293\text{ K}]{\text{CH}_2\text{Cl}_2}$$

$$[\text{PClPh}_3]_2[\text{MoCl}_6] + 2\text{CO} + 6\text{S} \quad (2)$$

Experimental. Accurate unit-cell parameters were measured on a CAD-4 diffractometer using 25 accurately centred reflexions (θ range 19·5–25·7°) from a crystal of dimensions 0·2 × 0·25 × 0·25 mm mounted in a capillary because of instability. A full hemisphere of reciprocal space was measured ($-18 \leq h \leq 18$; $-18 \leq k \leq 18$; $0 \leq l \leq 26$), θ limit = 30°, $\omega/2\theta$ scan, scan speed 4° min^{-1}, with the 600 reflexion monitored

hourly. No decay was observed over the data collection period and a total of 5513 reflexions were measured of which 4869 had $I \geq 3\sigma(I)$.

No systematic absences were noted (other than those due to a rhombohedral lattice) and inspection of the data indicated Laue group $\bar{3}$ rather than $\bar{3}m$. After averaging, the data set contained 1895 reflexions, $R_m = 0.016$ and 0.023 for observed and all reflexions respectively. The $N(z)$ test yielded a distribution between the centrosymmetric and noncentrosymmetric curves so that initially all calculations were performed in space group $R3$ until it was shown later to be $R\bar{3}$.

A combination of direct methods and Patterson interpretation was used to solve the structure. The lack of a proper analysis resulted in considerable effort to establish that the coordinating octahedral atoms around the Mo atom, which was sited on the triad at $00\frac{1}{2}$ for origin selection, were not Br but either S or Cl. Two independent P atoms on the triad and their associated independent phenyl groups were located but the identities of their coordinating atoms also on the triad were uncertain. Trial refinements using S and Cl in octahedral positions and axial positions separately, together with refinement of occupational factors, served to show that S was not present in the structure. Criteria used were the standard deviation of the occupation factors, $\sum w\Delta^2$ and the estimated standard deviation of unit weight, S. The isotropic refinement of structure amplitudes, using calculated hydrogen positions (d_H set to 1.0 Å) converged at $R = 0.081$. An absorption correction by DIFABS (Walker & Stuart, 1983) on the original unaveraged data set yielded maximum and minimum corrections of 1.097 and 0.778 respectively and reduced R to 0.068. Although a full-matrix anisotropic refinement in $R3$ converged at $R = 0.022$, $wR = 0.033$, $S = 1.192$, one bond distance in each phenyl group lay outside accepted values. A full anisotropic refinement in $R\bar{3}$ converged at $R = 0.024$, $wR = 0.035$, $S = 1.226$ and resulted in a more satisfactory phenyl-ring geometry. $R\bar{3}$ was taken to be the

Fig. 1. Structure of [PClPh₃]₂[MoCl₆] showing the numbering scheme used.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å²)

The B_{eq} values are calculated according to the equation
$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo	0.000†	0.000†	0.500†	2.617 (3)
Cl	0.15841 (3)	0.02964 (4)	0.57473 (2)	4.341 (8)
Cl(1)	0.000†	0.000†	0.74518 (3)	4.271 (8)
P(1)	0.000†	0.000†	0.85105 (3)	3.004 (7)
C(1)	0.1081 (1)	0.1429 (1)	0.87977 (8)	3.10 (3)
C(2)	0.2243 (1)	0.1875 (1)	0.85879 (9)	3.90 (3)
C(3)	0.3100 (1)	0.2946 (1)	0.8842 (1)	4.29 (4)
C(4)	0.2810 (1)	0.3583 (1)	0.92966 (9)	4.06 (3)
C(5)	0.1658 (1)	0.3165 (1)	0.94879 (9)	4.02 (3)
C(6)	0.0786 (1)	0.2080 (1)	0.92452 (8)	3.53 (3)
H(2)	0.242 (1)	0.144 (1)	0.827 (1)	4.1 (4)*
H(3)	0.394 (2)	0.327 (1)	0.868 (1)	4.5 (4)*
H(4)	0.345 (1)	0.437 (1)	0.948 (1)	4.5 (4)*
H(5)	0.144 (1)	0.360 (1)	0.980 (1)	4.7 (4)*
H(6)	-0.005 (1)	0.178 (1)	0.939 (1)	4.3 (4)*

* Starred atoms were refined isotropically.
† Fixed coordinate.

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Mo—Cl	2.3825 (5)	C(3)—C(4)	1.380 (2)
P(1)—Cl(1)	1.998 (1)	C(4)—C(5)	1.377 (2)
P(1)—C(1)	1.784 (1)	C(5)—C(6)	1.388 (2)
C(1)—C(2)	1.394 (2)	C(6)—C(1)	1.390 (2)
C(2)—C(3)	1.379 (2)		

Cl(1)—P(1)—C(1)	107.69 (5)	P(1)—C(1)—C(6)	120.9 (1)
P(1)—C(1)—C(2)	119.1 (1)		

true space group. The weighting scheme used was $w = [\sigma^2(I) + (0.043F^2)^2]^{-1/2}$. Three final cycles in which the H positions were refined showed no improvement in R, wR or S. C—H distances were in the range 0.95–1.0 Å, $\sigma = 0.02$ Å. The largest $(\Delta/\sigma) = 0.05$ and maximum residual electron density 0.2 e Å⁻³.

Atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974) and all computer programs used the *SDP-Plus* system (Frenz, 1983).

Discussion. Yellow crystals of [PClPh₃]₂[MoCl₆] obtained by the reaction shown in (1) were found to have the structure shown in Fig. 1. Table 1 shows the final positional parameters whilst Table 2 lists selected bond distances and bond angles.*

The complex contains an Mo atom at the centre of a regular octahedron of Cl ions. The Mo—Cl bond distance is accurately refined at 2.3830 (1) Å which is
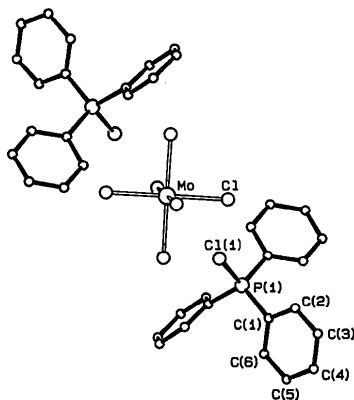
consistent with values found for other *trans*-Mo^{IV} chloride complexes such as *trans*-[MoCl$_2$(ttp)] (ttp = 5,10,15,20-tetra-*p*-tolylporphyrin), (MoCl)$_{av}$ = 2·311 Å, [MoOCl$_2$(dppe)$_2$] (dppe = Ph$_2$PCH$_2$-CH$_2$PPh$_2$), Mo–Cl = 2·46 Å and *trans*-[MoCl$_2$-{N(CH$_3$)CH$_3$C$_6$H$_4$O}$_2$], Mo–Cl = 2·388 (2) Å. While other complexes containing the [MoCl$_6$]$^{2-}$ anion have been prepared (Homer & Tyree, 1963; Davison, Howe & Shawl, 1967), this is the first accurately determined X-ray crystal structure of this anion. From unit-cell dimensions the Mo–Cl bond distances in K$_2$[MoCl$_6$] (Edwards, Peacock & Said, 1962) have been determined from Debye X-ray powder photographs. The Mo–Cl bond distance of 2·31 (5) Å is in agreement with that obtained for [ClPPh$_3$]$_2$[MoCl$_6$].

The chlorophosphonium cation [PClPh$_3$]$^+$ has the expected tetrahedral geometry, with the P–Cl(1) bonds directed towards the centre of opposite faces of the [MoCl$_6$]$^{2-}$ octahedron on a threefold axis of symmetry. This unusual cation has also been fortuitously prepared (Davison, Howe & Shawl, 1967; Enemark & Ibers, 1968) by reaction between S$_2$C$_2$(CF$_3$)$_2$ and [Ph$_3$PAu-Cl] to give [ClPPh$_3$][Au{S$_2$C$_2$(CF$_3$)$_2$}$_2$]. This complex has been structurally characterized and the bond angles and bond lengths of the chlorophosphonium cation are similar to those found in [ClPPh$_3$]$_2$[MoCl$_6$].

Analyses for C and H were made by Mr C. Macdonald, AFRC Unit of Nitrogen Fixation, while Cl analyses carried out by Mion Analysis Ltd, Devon.

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Structure of Bromo(trimethylsilylethynyl)bis(triphenylphosphine)palladium(II)–Chloroform–Dichloromethane (2/2/1) Solvate

BY ELLY VAN DER VOORT AND ANTHONY L. SPEK*

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND WIM DE GRAAF

Vakgroep Synthetisch Organische chemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Abstract. [PdBr{(C$_6$H$_5$)$_3$P}$_2$(C$_5$H$_9$Si)].CHCl$_3$.½CH$_2$-Cl$_2$, M_r = 969·94, triclinic, $P\bar{1}$, a = 11·603 (3), b = 11·909 (3), c = 16·811 (7) Å, α = 104·49 (3), β = 99·71 (3), γ = 93·20 (3)°, V = 2205 (1) Å^3, Z = 2, D_m = 1·49, D_x = 1·461 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 17·4 cm^{-1}, $F(000)$ = 978, T = 295 K, R = 0·0622 for 6899 observed reflections with $I > 2·5\sigma(I)$. The molecular structure consists of a central Pd atom, coordinated in a square-planar fashion by Br [Pd–Br = 2·481 (2) Å], a σ-bonded trimethylsilyl-ethynyl moiety [Pd–C(*sp*) = 1·974 (6) Å] and two *trans*-positioned triphenylphosphine groups [Pd–P = 2·327 (2) and 2·333 (2) Å].

Introduction. The generally accepted mechanism (Yamamoto, Yamamoto & Ozawa, 1985; Kumada,