



HAL
open science

[CpMoCl(PMe₃)₃][BF₄] and [Cp*MoCl(PMe₃)₃][PF₆]

James C Fettinger, Heinz-Bernhard Kraatz, Rinaldo Poli, Arnold L. Rheingold

► **To cite this version:**

James C Fettinger, Heinz-Bernhard Kraatz, Rinaldo Poli, Arnold L. Rheingold. [Cp-MoCl(PMe₃)₃][BF₄] and [Cp*MoCl(PMe₃)₃][PF₆]. Acta Crystallographica Section C : Crystal Structure Communications [1968-2013], 1995, 51 (3), pp.364-367. 10.1107/S010827019400898X . hal-03531376

HAL Id: hal-03531376

<https://hal.science/hal-03531376>

Submitted on 18 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**[CpMoCl(PMe₃)₃][BF₄] and
[Cp*MoCl(PMe₃)₃][PF₆]**

JAMES C. FETTINGER, HEINZ-BERNHARD KRAATZ AND
RINALDO POLI*

*Department of Chemistry and Biochemistry,
University of Maryland, College Park,
Maryland 20742, USA*

ARNOLD L. RHEINGOLD

*Department of Chemistry, University of Delaware,
Newark, DE 19719, USA*

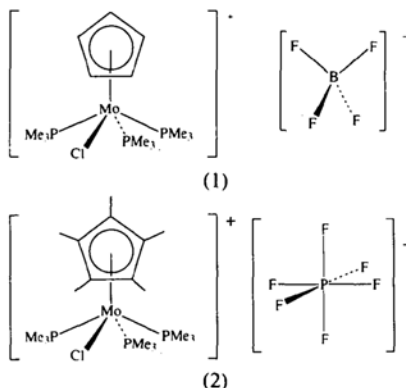
(Received 18 January 1994; accepted 2 August 1994)

Abstract

Chloro(η^5 -cyclopentadienyl)tris(trimethylphosphine)-molybdenum(III) tetrafluoroborate, [MoCl(C₅H₅)(C₃H₉P)₃][BF₄], was obtained from the oxidation of [MoH(C₅H₅)(PMe₃)₃] by AgBF₄, followed by crystallization from dichloromethane. Chloro(η^5 -pentamethylcyclopentadienyl)tris(trimethylphosphine)molybdenum(III) hexafluorophosphate, [MoCl(C₁₀H₁₅)(C₃H₉P)₃][PF₆], was obtained from the reaction of [MoCl₂(C₁₀H₁₅)(C₃H₉P)₂] with TlPF₆ and PMe₃ in dichloromethane. Both cations adopt a four-legged piano-stool arrangement.

Comment

Odd-electron complexes having the general formula $[(\text{ring})\text{MX}_{2-n}\text{L}_{2+n}]^{n+}$ (ring = cyclopentadienide or substituted analogue; $X = \text{Cl}, \text{Br}, \text{I}; L = \text{PR}_3; n = 0$ or 1) and possessing a four-legged piano-stool configuration are now well established (Poli, 1992). As part of our ongoing investigation of CpMo^{III} complexes, we now report the crystal structures of $[\text{CpMoCl}(\text{PMe}_3)_3][\text{BF}_4]$ (1) and $[\text{Cp}^*\text{MoCl}(\text{PMe}_3)_3][\text{PF}_6]$ (2), where Cp and Cp* are η^5 -cyclopentadienyl and η^5 -pentamethylcyclopentadienyl ligands, respectively.

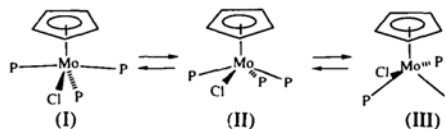


A different salt of the $[\text{CpMoCl}(\text{PMe}_3)_3]^+$ cation [with the PF_6^- anion, compound (3)] was prepared previously by one-electron oxidation of $[\text{CpMoCl}(\text{PMe}_3)_3]$ and characterized crystallographically (Abugideiri, Kelland, Poli & Rheingold, 1992). However, while compound (3) crystallizes in the orthorhombic space group $P2_12_12_1$, compounds (1) and (2) crystallize under the same conditions in the monoclinic space group $P2_1/c$.

A comparison of selected bond distances and angles for the cations of compounds (1) and (2) is given in Table 3. In both structures, the ions are well separated from each other. The average B—F bond length in (1) is 1.317 (13) Å. The F—B—F angles are very close to the expected tetrahedral value, being in the range 106–114° with an average value of 109.1 (10)°. The PF_6^- anion in compound (2) is either highly thermally active or disordered among different orientations too close to each other to be distinguished in the E map. Therefore, it was restrained to adopt O_h symmetry with P—F bond lengths of 1.52 (1) Å.

Views of the cations of (1) and (2) are shown in Figs. 1 and 2, respectively. Both ions exhibit a typical four-legged piano-stool geometry. The metric parameters and angular distortions of the cation in compound (1) are significantly different from those of the same cation in the previously reported structure of (3). In particular, the cation in (3) has a shorter Mo—Cl distance [2.427 (9) versus 2.509 (3) Å in (1)] and longer Mo—P distances [2.504 (7) Å for the PMe_3 ligand *trans* to Cl and an average of 2.545 (12) Å for the other two PMe_3 ligands,

versus 2.455 (2) and 2.505 (2) Å, respectively, for (1)]. The Mo—C*nt* distance in (1), where C*nt* is the centroid of the cyclopentadienyl moiety, however, is statistically equivalent to that in compound (3) [1.986 (18) Å]. The C*nt*—Mo—L angles are more homogeneous in (1) (within the range 107–112°) than in (3) {larger for the Cl ligand [123.9 (8)°] and the PMe_3 ligand *trans* to Cl [113.3 (8)°], and smaller for the other two PMe_3 ligands [104.5 (8) and 104.0 (8)°]}. The angular changes of the four monodentate ligands on going from compound (1) to compound (3) can be viewed collectively as being analogous to a Berry pseudo-rotation for the interconversion of trigonal-bipyramidal and square-pyramidal structures (Huheey, 1983) (see scheme below). The fact that the nature of the anion (and therefore consequent minor differences in packing forces) causes such significant changes in the angular distortions for the $[\text{CpMoCl}(\text{PMe}_3)_3]^+$ cation, suggests that the pseudo-rotation illustrated below has a smooth potential-energy surface for this ion. The phenomenon of the correlation between the C*nt*—Mo—L angles for two ligands in relative *trans* positions in a four-legged piano-stool geometry has been termed 'angular *trans* influence' (Poli, 1990) and has been the subject of a recent theoretical analysis (Lin & Hall, 1993).



For the $[\text{Cp}^*\text{MoCl}(\text{PMe}_3)_3]^+$ cation of compound (2), the angular distortions are in the opposite direction compared with those of the cation in (3). The C*nt*—Mo—L angles are smaller for the Cl and the PMe_3 ligand *trans* to Cl [110.0 (3) and 109.3 (3)°], and larger for the other two PMe_3 ligands [120.2 (3) and 120.5 (3)°]. In other words, whereas the cation in (1) is the most symmetrical structure [like structure (II) in the scheme above] and the cation in (3) distorts towards structure (I), the cation in (2) distorts in the other direction, towards structure (III). The average C*nt*—Mo—L angle for the four ligands increases on going from compound (1) (109.7°) and (3) (111.4°) to compound (2) (115°); no doubt an effect of the greater steric bulk of the Cp* ligand in (2). Compound (2) has Mo—P distances similar to those in (3) and an Mo—Cl distance intermediate between those of compounds (1) and (3). The Mo—C*nt* distance in (2) is significantly longer than those of compounds (1) and (3); perhaps another result of the greater steric interactions in the Cp* complex.

One effect that is identical in both structures examined here [and also in the previously reported structure of (3)] is the shorter Mo—P bond *trans* to the Cl⁻ ligand and relative to the other two Mo—P distances (by *ca*

[MoCl(C₅H₅)(C₃H₉P)₃][BF₄] AND [MoCl(C₁₀H₁₅)(C₃H₉P)₃][PF₆]

0.050 Å in all cases). This can be rationalized in terms of the weaker *trans* influence of the Cl⁻ ligand relative to the PMe₃ ligand.

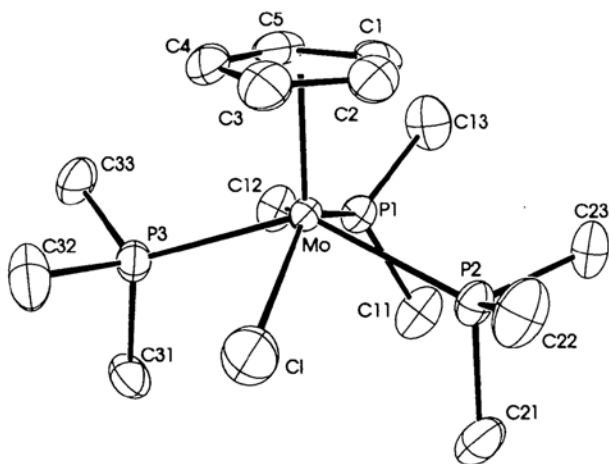


Fig. 1. The molecular configuration and atom-labelling scheme for the [CpMoCl(PMe₃)₃]⁺ cation. Ellipsoids are drawn at the 40% probability level.

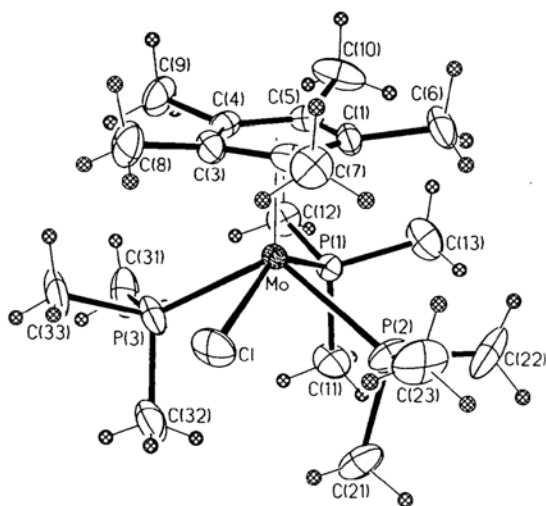


Fig. 2. The molecular configuration and atom-labelling scheme for the [Cp*MoCl(PMe₃)₃]⁺ cation. Ellipsoids are drawn at the 40% probability level.

Experimental

Compound (1) was obtained by recrystallizing the mixture of products that results from the oxidation of [CpMoH(PMe₃)₃] by AgBF₄ in tetrahydrofuran from an *n*-heptane-layered CH₂Cl₂ solution. Dark red crystals of (2) were obtained by exchanging a Cl⁻ ligand in [Cp*MoCl₂(PMe₃)₂] with PMe₃, a reaction that is assisted by TlPF₆ which precipitates Cl⁻ as insoluble TlCl, followed by diffusion of *n*-heptane into a CH₂Cl₂ solution.

Compound (1)

Crystal data

[MoCl(C₅H₅)(C₃H₉P)₃][BF₄]

M_r = 511.52

Monoclinic

*P*2₁/*c*

a = 13.364 (2) Å

b = 12.991 (2) Å

c = 13.548 (2) Å

β = 108.350 (12)°

V = 2232.4 (6) Å³

Z = 4

D_x = 1.522 Mg m⁻³

Data collection

Enraf-Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

empirical (ψ scans,

4 reflections)

T_{min} = 0.672, *T_{max}* =

0.997

3044 measured reflections

2901 independent reflections

Refinement

Refinement on *F*

R = 0.052

wR = 0.056

S = 1.051

2196 reflections

217 parameters

w = 1/[σ²(*F*) + 0.0005*F*²]

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10.0–16.9°

μ = 0.93 mm⁻¹

T = 293 K

Block

0.5 × 0.5 × 0.2 mm

Orange-red

2196 observed reflections

[*I* > 1.5σ(*I*)]

R_{int} = 0.040

θ_{max} = 22.43°

h = -14 → 13

k = 0 → 13

l = 0 → 14

3 standard reflections

frequency: 60 min

intensity decay: none

(Δ/σ)_{max} = 0.004

Δρ_{max} = 0.76 e Å⁻³

Δρ_{min} = -0.75 e Å⁻³

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Compound (2)

Crystal data

[MoCl(C₁₀H₁₅)(C₃H₉P)₃]-[PF₆]

M_r = 639.8

Monoclinic

*P*2₁/*c*

a = 12.369 (6) Å

b = 14.664 (5) Å

c = 15.769 (5) Å

β = 90.96 (3)°

V = 2859.8 (20) Å³

Z = 4

D_x = 1.486 Mg m⁻³

Data collection

Siemens P4 diffractometer

θ/2θ scans

Absorption correction:

empirical (ψ scan)

T_{min} = 0.992, *T_{max}* =

1.000

4749 measured reflections

4349 independent reflections

3516 observed reflections

[*F* > 4σ(*F*)]

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 20–25°

μ = 0.821 mm⁻¹

T = 299 K

Block

0.40 × 0.32 × 0.22 mm

Dark red

R_{int} = 0.012

θ_{max} = 27.50°

h = -14 → 13

k = 0 → 16

l = 0 → 18

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on F $R = 0.0694$ $wR = 0.1193$ $S = 1.89$

3516 reflections

281 parameters

 $w = 1/[\sigma^2(F) + 0.003F^2]$ $(\Delta/\sigma)_{\max} = 0.079$ $\Delta\rho_{\max} = 1.01 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.75 \text{ e } \text{\AA}^{-3}$

Atomic scattering factors

from *SHELXTL-Plus*

(Sheldrick, 1987)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Mo	0.25760 (5)	0.50387 (5)	0.24010 (5)	2.62 (3)
Cl	0.41551 (23)	0.60739 (23)	0.33992 (24)	6.86 (16)
P1	0.19591 (18)	0.32497 (17)	0.22955 (18)	3.46 (11)
P2	0.40076 (18)	0.44848 (18)	0.16863 (18)	3.65 (11)
P3	0.22845 (21)	0.53116 (19)	0.41194 (17)	3.97 (11)
B	0.8129 (8)	0.4387 (7)	0.2055 (8)	3.2 (5)
F1	0.8750 (6)	0.3650 (5)	0.1891 (6)	9.0 (5)
F2	0.8495 (8)	0.5270 (6)	0.1815 (9)	13.6 (9)
F3	0.7156 (6)	0.4257 (8)	0.1376 (7)	11.7 (6)
F4	0.8051 (9)	0.4393 (9)	0.2961 (6)	14.2 (8)
C1	0.1428 (8)	0.5172 (7)	0.0798 (6)	4.7 (5)
C2	0.2114 (8)	0.5997 (7)	0.0882 (7)	4.8 (5)
C3	0.2009 (9)	0.6644 (7)	0.1636 (8)	5.3 (6)
C4	0.1233 (9)	0.6269 (8)	0.2023 (7)	4.9 (5)
C5	0.0867 (7)	0.5350 (9)	0.1516 (8)	4.9 (5)
C11	0.2959 (8)	0.2267 (7)	0.2615 (9)	5.8 (6)
C12	0.1194 (8)	0.2837 (7)	0.3129 (8)	4.8 (5)
C13	0.1080 (9)	0.2787 (8)	0.1074 (8)	6.3 (6)
C21	0.5112 (8)	0.3819 (8)	0.2620 (9)	5.8 (6)
C22	0.4682 (9)	0.5522 (9)	0.1249 (9)	6.3 (6)
C23	0.3694 (8)	0.3669 (9)	0.0553 (7)	5.0 (5)
C31	0.3087 (9)	0.4504 (8)	0.5170 (7)	5.2 (5)
C32	0.2595 (11)	0.6572 (9)	0.4669 (8)	6.8 (7)
C33	0.0968 (9)	0.5146 (9)	0.4233 (8)	6.6 (8)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* \cdot a_j^*$$

	x	y	z	U_{eq}
Mo	0.7384 (1)	0.1594 (1)	0.8207 (1)	0.028 (1)
Cl	0.7094 (3)	0.2766 (2)	0.7084 (2)	0.068 (1)
P1	0.7524 (2)	-0.0091 (2)	0.8386 (2)	0.036 (1)
P2	0.5514 (3)	0.1270 (2)	0.7557 (2)	0.058 (1)
P3	0.9024 (3)	0.1439 (2)	0.7258 (2)	0.057 (1)
P4	0.2437 (2)	0.3464 (2)	0.0145 (2)	0.057 (1)
F1	0.1767 (7)	0.2784 (6)	0.0637 (6)	0.163 (6)
F2	0.3101 (8)	0.4157 (8)	-0.0336 (7)	0.232 (10)
F3	0.3471 (6)	0.2980 (6)	0.0421 (6)	0.148 (6)
F4	0.2535 (9)	0.4065 (7)	0.0938 (6)	0.176 (7)
F5	0.1410 (6)	0.3960 (7)	-0.0119 (8)	0.255 (12)
F6	0.2340 (10)	0.2864 (8)	-0.0627 (6)	0.247 (12)
C1	0.6646 (8)	0.1934 (7)	0.9539 (6)	0.041 (3)
C2	0.6874 (9)	0.2748 (7)	0.9098 (6)	0.045 (3)
C3	0.8010 (8)	0.2811 (7)	0.9015 (7)	0.044 (3)
C4	0.8463 (7)	0.2015 (7)	0.9379 (6)	0.042 (3)
C5	0.7625 (9)	0.1496 (6)	0.9726 (6)	0.041 (3)
C6	0.5556 (10)	0.1675 (8)	0.9910 (8)	0.064 (4)
C7	0.6070 (10)	0.3540 (8)	0.8950 (9)	0.063 (4)
C8	0.8590 (11)	0.3644 (8)	0.8736 (9)	0.070 (5)
C9	0.9684 (8)	0.1897 (9)	0.9537 (9)	0.068 (5)
C10	0.7803 (13)	0.0746 (9)	1.0396 (7)	0.082 (6)
C11	0.7414 (11)	-0.0763 (8)	0.7408 (8)	0.070 (5)
C12	0.8769 (9)	-0.0556 (8)	0.8833 (8)	0.057 (4)
C13	0.6526 (11)	-0.0679 (8)	0.9023 (9)	0.071 (5)
C21	0.5590 (11)	0.1009 (11)	0.6446 (9)	0.080 (5)
C22	0.4599 (10)	0.0381 (10)	0.7910 (12)	0.096 (7)
C23	0.4600 (10)	0.2241 (10)	0.7534 (9)	0.089 (6)

C31	1.0165 (10)	0.0616 (10)	0.7443 (11)	0.089 (6)
C32	0.8692 (12)	0.1203 (11)	0.6174 (8)	0.086 (6)
C33	0.9836 (13)	0.2474 (10)	0.7160 (10)	0.097 (6)

Table 3. Selected geometric parameters (\AA , $^\circ$)

Cnt is the centroid of the cyclopentadienyl moiety.

	(1)	(2)
Mo—Cl	2.509 (3)	2.489 (3)
Mo—P1	2.455 (2)	2.493 (2)
Mo—P2	2.506 (2)	2.559 (3)
Mo—P3	2.504 (2)	2.551 (3)
Mo— <i>Cnt</i>	1.971 (9)	2.017 (10)
Cl—Mo—P1	138.5 (1)	140.7 (1)
Cl—Mo—P2	75.36 (9)	74.0 (1)
Cl—Mo—P3	76.9 (1)	75.6 (1)
P1—Mo—P2	89.4 (1)	85.5 (1)
P1—Mo—P3	92.3 (1)	85.6 (1)
P2—Mo—P3	139.5 (1)	118.1 (1)
Cl—Mo— <i>Cnt</i>	111.9 (3)	110.0 (3)
P1—Mo— <i>Cnt</i>	109.7 (3)	109.3 (3)
P2—Mo— <i>Cnt</i>	110.1 (3)	120.2 (3)
P3—Mo— <i>Cnt</i>	107.2 (3)	120.5 (3)

The title structures (1) and (2) were solved by direct methods using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and the *SHELXTL-Plus* program library (Sheldrick, 1987), respectively, to locate the Mo atoms. The remaining non-H atoms were located in the subsequent difference Fourier syntheses. All H atoms were included in calculated positions [$C-H = 0.950$ for (1) and 0.960 \AA for (2)] with idealized U [$U(H) = 1.2(U$ of the attached C atom)]. All non-H atoms were refined with anisotropic displacement parameters. Due to disorder and/or high thermal motion within the PF_6 counterion in compound (2), the anion was restrained to adopt O_h symmetry by the use of *DFIX* instructions (Sheldrick, 1987) with P—F distances of 1.52 (1) \AA . Molecular graphics were obtained using *ORTEPII* (Johnson, 1976).

This work was supported by the DOE Office for Energy Research (92ER14230). Additional support from the NSF (PVI Award 1990–95, CHE-9058375) and the Alfred P. Sloan Foundation (Research Fellowship 1992–94) is also gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abugideiri, F., Kelland, M. A., Poli, R. & Rheingold, A. L. (1992). *Organometallics*, **11**, 1303–1311.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Huhey, J. E. (1983). In *Inorganic Chemistry*, 3rd ed. New York: Harper and Row.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lin, Z. & Hall, M. B. (1993). *Organometallics*, **12**, 19–23.
- Poli, R. (1990). *Organometallics*, **9**, 1892–1900.
- Poli, R. (1992). *J. Coord. Chem.* **29**, 121–173.
- Sheldrick, G. M. (1987). *SHELXTL-Plus*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.