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The structure of two analogous 16-electron piano stool molybdenum(IV) complexes, $[YMoI_2(PMe_3)_2]^+$ (Y=Cp, Cp*)

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Abstract

The title complexes have been obtained by oxidation from the corresponding neutral Mo(III) species and have been crystallized as the I^- and BF_4^- salts, respectively. Crystal data: $[CpMoI_2(PMe_3)_2]^+I^-$, monoclinic, space group $P2_1/n$, $a=9.273(2)$, $b=8.439(2)$, $c=25.406(7)$ Å, $\beta=90.62(2)°$, $V=1988.0(8)$ Å^3, $Z=4$, $R=0.0661$, $R_w=0.0703$; $[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]^+BF_4^-$, orthorhombic, space group *Pnma*, $a=15.596(4)$, $b=11.226(3)$, $c=13.816(5)$ Å, $V=2418.9(13)$ Å^3, $Z=4$, $R=0.0706$, $R_w=0.0851$. The structural changes observed on going from the previously reported Mo(III) neutral complex, $CpMoI_2(PMe_3)_2$, to the corresponding cation of Mo(IV), as well as those observed on going from the Cp to the Cp* Mo(IV) complex, are discussed.

Introduction

We have reported earlier the synthesis and characterization of the class of 17-electron complexes of Mo(III), $CpMoX_2(PMe_3)_2$ (X=Cl, Br, I) [1], which included the observation of a reversible one-electron oxidation by cyclic voltammetry. The chloride compound was also oxidized chemically and the salt $[CpMoCl_2(PMe_3)_2]^+PF_6^-$ was characterized crystallographically together with its parent neutral precursor. Since then, we have obtained products of one-electron oxidation also for the iodide complex in the form of I^-, I_3^- and PF_6^- salts [2]. Furthermore, as part of a kinetic study of the halide substitution reaction in this class of compounds, we found it necessary to synthesize the analogous materials where the Cp ring had been replaced with the fully methyl-substituted analogue, Cp* [3]. During these investigations, we have isolated the product of one-electron oxidation for the diiodide compound in crystalline form as the BF_4^- salt, which shows partial disorder with chlorine ligands that were present as contaminants in the starting material. We report and compare here the structures of the two compounds $[CpMoI_2(PMe_3)_2]^+I^-$ and $[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]^+$-$BF_4^-$ with themselves and with those of the similar compounds reported previously.

Experimental

All operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line and glove-box techniques. Solvents were dried by conventional methods and distilled under dinitrogen prior to use. Elemental analyses were by M-H-W, Phoenix, AZ. Compounds $[CpMoI_2(PMe_3)_2]^+I^-$ and $Cp^*MoI_2(PMe_3)_2$ were prepared as described in the literature [2, 3].

Preparation of $[Cp^*MoI_2(PMe_3)_2]BF_4$

$Cp^*MoI_2(PMe_3)_2$ (112 mg, 0.176 mmol) was dissolved in toluene (10 ml) and BF_3 was passed through the magnetically stirred solution at room temperature. The immediate formation of a red oily material was observed. Monitoring by EPR spectroscopy indicated that all the starting material was consumed after about 1/2 h. The oil was separated from the mother liquor by gently decanting the latter away and then, after drying *in vacuo*, it was redissolved in dichloromethane (3 ml). After filtration, the red solution was layered with heptane (10 ml) and slow diffusion was allowed to occur at −20 °C to produce 28 mg of product as red crystals. *Anal.* Calc. for $C_{16}H_{33}BF_4I_2MoP_2$: C, 26.6; H, 4.6. Found: C, 27.0; H, 4.8%. Single crystals for the X-ray analysis were obtained from a similar reaction by crystallization from CH_2Cl_2/Et_2O. The compound is soluble in THF, acetone and methylene chloride, and the solutions do not change color upon treatment with

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excess I^- ions. The ^1H NMR (acetone-d^6) shows very broad features at δ *c.* 2 and -30 ppm.

X-ray crystallography

[CpMoI$_2$(PMe$_3$)$_2$]$^+$I$^-$

Crystal data, collection and refinement parameters are collected in Table 1. A dark red crystal, suitable for X-ray diffraction, was mounted on a fine glass fiber with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of 25 reflections ($20 \leqslant 2\theta \leqslant 25°$). Preliminary photographic characterization showed $2/m$ Laue symmetry. Systematic absences in the diffraction data uniquely established the space group as $P2_1/n$. A semi-empirical absorption correction was applied to the diffraction data ($T_{max}/T_{min} = 1.447$) [4].

The structure was solved by direct methods which located the three iodine atoms and the Mo atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier and least-squares syntheses. All non-hydrogen atoms, except for C(4), were refined with anisotropic thermal parameters. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, $U = 1.2U$ for attached C). All computer programs and the sources of the scattering factors are contained in the SHELXTL-PLUS(4.2) program library [4]. Positional and equivalent isotropic thermal parameters are listed in Table 2 and selected bond distances and bond angles are contained in Table 3.

*[Cp*MoCl$_{0.5}$I$_{1.5}$(PMe$_3$)$_2$]BF$_4$*

A crystal suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal, data collection and refinement parameters are collected in Table 1. The unit-cell parameters were obtained from the least-squares fit of 25 reflections ($20 \leqslant 2\theta \leqslant 25°$). The systematic absences in the diffraction data estab-

TABLE 1. Crystal data for compounds $[CpMoI_2(PMe_3)_2]^+I^-$ and $[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]^+BF_4^-$

Crystal parameters		
Compound	$[CpMoI_2(PMe_3)_2]^+I^-$	$[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]^+BF_4^-$
Formula	$C_{11}H_{23}I_3MoP_2$	$C_{16}H_{33}BCl_{0.5}F_4I_{1.5}MoP_2$
Formula weight	693.90	678.2
Space group	$P2_1/n$	*Pnma*
a (Å)	9.273(2)	15.596(3)
b (Å)	8.439(2)	11.226(3)
c (Å)	25.406(7)	13.816(4)
β (°)	90.62(2)	
V (Å^3)	1988.0(8)	2418.9(13)
Z	4	4
Crystal dimensions (mm)	0.40 × 0.32 × 0.06	0.21 × 0.24 × 0.52
Crystal color	dark red	dark red
D_{calc} (g/cm^3)	2.318	1.862
μ(Mo Kα) (cm^{-1})	54.00	32.57
Temperature (°C)	23	26
T_{max}/T_{min}	1.447	1.229
Data collection		
Diffractometer	Nicolet R3m	Siemens P4
Radiation (graphite-monochromated in incident beam)	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
2θ Scan range	4–48	4–52
Data collected (h, k, l)	±11, +10, +30	+19, +13, +17
Reflections collected	3453	2491
Independent reflections	3126	2491
Independent observed reflections $F_o \geqslant n\sigma(F_o)$	2053($n = 5$)	1676 ($n = 4$)
Standard reflections	3 std/197 rflns	3 std/197 rflns
Variation in standards (%)	<1	<2
Refinement		
$R(F)$[a]	0.0661	0.0706
$R_w(F)$[b]	0.0703	0.0851
Δ/σ(max)	0.006	0.517
$\Delta(\rho)$ (e Å^{-3})	1.418	3.09
N_{obs}/N_{param}	13.7	12.6
GOF[c]	1.239	1.01

[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] $GOF = [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\AA^2 \times 10^3$) for compound [CpMoI$_2$(PMe$_3$)$_2$]I

	x	y	z	U_{eq}[a]
Mo	4015.6(15)	7140.1(16)	1206.8(6)	28.4(4)
I(1)	2040(1)	6357(2)	1947(1)	50(1)
I(2)	5648(2)	9848(2)	1240(1)	64(1)
I(3)	8955(2)	3243(2)	801(1)	67(1)
P(1)	5730(5)	6426(6)	1958(2)	37(1)
P(2)	2066(6)	9135(6)	956(2)	43(2)
C(1)	3727(53)	4724(32)	844(15)	115(17)
C(2)	3117(32)	5767(63)	506(15)	122(18)
C(3)	4161(50)	6716(30)	319(10)	103(15)
C(4)	5306(32)	6234(36)	502(12)	79(7)
C(5)	5162(38)	5013(43)	836(11)	114(14)
C(6)	7657(18)	6512(25)	1823(9)	54(7)
C(7)	5523(25)	4415(24)	2214(9)	66(8)
C(8)	5486(21)	7650(23)	2542(7)	47(7)
C(9)	2482(26)	10367(25)	383(7)	61(8)
C(10)	355(20)	8288(27)	783(9)	63(8)
C(11)	1685(28)	10498(26)	1497(8)	73(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

lished the space group as either *Pnma* or *Pna*2_1. The E statistics suggested the centrosymmetric alternative, and the chemically sensible results of refinement established the space group as *Pnma*. The semi-empirical absorption correction program XABS was applied to the data set [5].

The structure was solved by direct methods which located the Mo and I atoms. Atom site I(1) contains about 50% of a lighter element presumed to be chlorine. The site occupancy was refined based on iodine to 0.66(3), which corresponds to a 50:50 halogen mixture ($s.o.f. = [x(17) + (1-x)(53)]/53$). No compositional disorder was seen in I(2). The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The highest peak in the final difference Fourier map was located at 0.128 Å from atom I(2). The value reported for the maximum Δ/σ is related to the boron atom. The maximum value for the Mo complex is 0.041. Positional and equivalent isotropic thermal parameters are listed in Table 4 and selected bond distances and angles are listed in Table 3. All computer programs and the sources of the scattering factors are contained in the SHELXTLPLUS(4.2) program library [4].

Results and discussion

The reaction between Cp*MoI$_2$(PMe$_3$)$_2$ and BF$_3$ was carried out in an attempt to abstract I$^-$ from the coordination sphere of Mo(III) and generate the hypothetical 15-electron [Cp*MoI(PMe$_3$)$_2$]$^+$ ion. The result of this reaction is quite different than expected,

TABLE 3. Selected bond distances and angles for compounds [CpMoI$_2$(PMe$_3$)$_2$]$^+$I$^-$ and [Cp*MoCl$_{0.5}$I$_{1.5}$(PMe$_3$)$_2$]$^+$BF$_4^-$

	[CpMoI$_2$(PMe$_3$)$_2$]$^+$I$^-$	[Cp*MoCl$_{0.5}$I$_{1.5}$(PMe$_3$)$_2$]$^+$BF$_4^-$
Bond distances (Å)		
Mo–I(1)	2.721(2)	2.573(3)
Mo–I(2)	2.742(2)	2.721(1)
Mo–P(1)	2.544(5)	2.574(3)
Mo–P(2)	2.546(5)	
Mo–C(1)	2.25(3)	2.402(12)
Mo–C(2)	2.28(4)	2.371(8)
Mo–C(3)	2.29(3)	2.352(8)
Mo–C(4)	2.30(3)	
Mo–C(5)	2.29(3)	
Mo–CNT[a]	1.98(2)	2.036(8)
Bond angles (°)		
I(1)–Mo–I(2)	123.8(1)	132.2(1)
I(1)–Mo–P(1)	81.0(1)	77.5(1)
I(1)–Mo–P(2)	81.5(1)	
I(2)–Mo–P(1)	80.4(1)	80.0(1)
I(2)–Mo–P(2)	81.2(1)	
P(1)–Mo–P(2)/P(1′)	141.3(2)	122.6(1)
I(1)–Mo–CNT[a]	118.7(5)	113.7(2)
I(2)–Mo–CNT[a]	117.5(5)	114.1(2)
P(1)–Mo–CNT[a]	110.5(5)	118.7(1)
P(2)–Mo–CNT[a]	108.2(5)	

[a] CNT = Centroid of atoms C(1), C(2), C(3), C(4) or C(3′), C(5) or C(2′).

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for compound $[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]BF_4$

	x	*y*	*z*	U_{eq} [a]
Mo(1)	3267(1)	2500	1692(1)	30(1)
I(1)	2124(2)	2500	3036(2)	69(1)
I(2)	3144(1)	2500	−272(1)	64(1)
P(1)	2509(2)	489(2)	1428(2)	45(1)
C(1)	4781(8)	2500	1378(9)	41(2)
C(2)	4581(5)	1483(8)	1940(6)	42(1)
C(3)	4259(5)	1867(8)	2866(6)	38(1)
C(4)	5244(9)	2500	417(11)	68(2)
C(5)	4833(7)	237(11)	1676(8)	71(2)
C(6)	4071(7)	1114(11)	3714(7)	62(2)
C(7)	2891(9)	−543(10)	533(9)	77(2)
C(8)	1405(7)	745(10)	1063(8)	65(2)
C(9)	2400(8)	−482(9)	2483(8)	66(2)
B(1)	2(11)	−2500	1451(10)	40(2)
F(1)	706(14)	−2500	1774(18)	272(2)
F(2)	−527(15)	−2500	2240(14)	220(2)
F(3)	−129(9)	−1526(10)	1044(9)	180(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

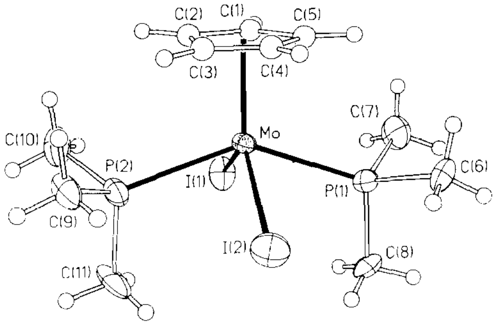


Fig. 1. Molecular view and labelling scheme for $[CpMoI_2(PMe_3)_2]^+$. Ellipsoids are at the 35% probability. Hydrogen atoms are drawn with arbitrary radii.

obviously because of adventitious oxidation of the starting material. Previous studies have shown that the neutral Mo(III) complex can be oxidized quite easily ($E_{1/2} = -0.61$ V versus Fc/Fc^+) [3]. We do not know the source of oxidation (possibly impurities in the BF_3 gas used may be involved), nor the fate of the oxidizing equivalents.

The structure of the cations in the two related complexes $[CpMoI_2(PMe_3)_2]^+I^-$ and $[Cp^*MoI_2(PMe_3)_2]^+BF_4^-$ are shown in Figs. 1 and 2, and selected bond distances and angles are compared in Table 3. For both structures, the anions do not show significant contacts with any of the molybdenum centers of the neighboring cations. The Cp* compound was found to exhibit positional disorder of atom I(1) with chlorine. The chlorine atom must be originating from the starting material, which had been obtained by halide exchange from $Cp^*MoCl_2(PMe_3)_2$ [3]. Although the product of such exchange was pure by elemental analysis, cyclic voltammetry and EPR [3], it is possible that undetected, minor impurities of the dichloride starting material or, more probably, the intermediate $Cp^*MoICl(PMe_3)_2$, provide the artificially high amount of chlorine found in the product through preferential crystallization. Since the I(2) ligand does not show any sign of positional disorder with chlorine atoms, it seems that the investigated crystal could best be described as a 50:50 mixture of $[Cp^*MoI_2(PMe_3)_2]^+$ and $[Cp^*MoICl(PMe_3)_2]^+$. Although both I(1) and I(2) reside on the crystallographic mirror plane, they have different environments in the crystal lattice. I(1) has nearest non-hydrogen neighbors at 3.6–3.7 Å from Cp* atoms, while I(2) makes contacts of greater than 3.9 Å with methyl groups of the phosphines. The arguments presented in this paper are not affected by this disorder. The sole effect of the I/Cl disorder is to render the observed Mo–I(1) distance artificially short (see Table 3), and therefore this structural parameter will not be considered any further, except to point out that its value is a rough average of normal Mo–I and Mo–Cl bond distances.

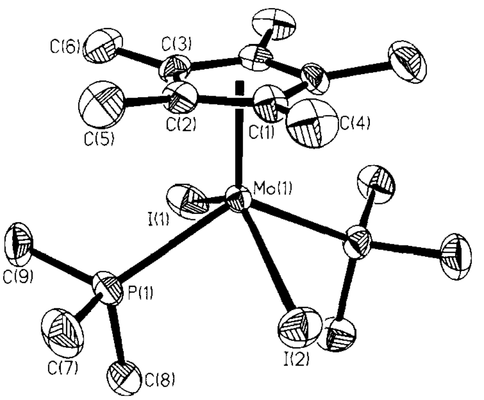
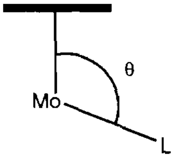


Fig. 2. Molecular view and labeling scheme for $[Cp^*MoCl_{0.5}I_{1.5}(PMe_3)_2]^+$. Ellipsoids are at the 35% probability. Hydrogen atoms are not drawn.

Two separate comparisons can be made using the data from the present study, one involving the Cp and Cp* structures described here, and the other one relating the Cp cationic structure and that of its neutral precursor reported earlier [1]. The structural changes in the $[CpMoI_2(PMe_3)_2]^{n+}$ ($n = 0$, 1) series are analogous to those observed for the corresponding dichloride system [1]. In particular, the bond angles remain unchanged within 2° on going from neutral to cationic complex. The average Mo–I distance in the cation is 0.100 Å shorter than in the neutral system (cf. 0.094 Å for the average Mo–Cl distance in the dichloride system), while the average Mo–P distance is 0.044 Å longer in the oxidized complex (cf. 0.048 Å in the dichloride system). However, contrary to the dichloride case [1], the Mo–Cp separation in the diiodide system does not significantly increase on going from the neutral complex to the cation (average Mo–C = 2.28(3) Å in the cation, 2.29(4) Å in the neutral complex). All these effects have been rationalized earlier [1] as due to a decrease of Mo–PMe$_3$ π backbonding and Mo–Cp δ backbonding, and an increase of Mo–X π bonding on going from Mo(III) to Mo(IV).

Concerning the Cp/Cp* comparison for the Mo(IV) structures, the Mo–I distances (except for I(1)) remain unchanged, whereas a significant elongation is observed in the Mo–P distances and especially in the Mo–C(ring) distances, which might be attributed to steric effects. The conformation of the Cp ring is a substantially regular η^5 in both Cp and Cp* cationic complexes, whereas it was found to be significantly distorted toward a η^3,η^2 conformation in the corresponding neutral Cp complex [1]. The most interesting changes on going from Cp to Cp* structure concern the θ angles (e.g. angles between the metal-to-ring center vector and the metal-to-ligand bond, see **I**) [6]. Whereas the θ angles of the PMe$_3$ ligands are greater in the Cp* system, as might be expected on the basis of a greater steric interaction, the corresponding angles of the I ligands show the opposite trend.



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A possible rationalization is based entirely on steric arguments. Since the Cp* ligand is sterically more encumbering, it induces a greater bending of the PMe$_3$ ligands away from it. Consistent with this view are also the lengthenings observed for the Mo–P and Mo–C(ring) distances (see above). The distortion of the PMe$_3$ ligands causes, in turn, a secondary distortion of the smaller iodide ligands. In other words, the iodide ligands would interact sterically with the PMe$_3$ ligands (I–Mo–PMe$_3$ angles = *c.* 80°; cone angle of PMe$_3$ = 118°) to a greater extent than with the Cp* ligand (θ angle = 114°; cone angle of Cp* = 168.2(min.), 188.4°(max.), depending on the conformation of the five CH$_3$ groups; the cone angle for the Cp* ligand was calculated from the observed Mo–CNT, average C–C(ring), and average C(ring)–C(Me) distances in the Cp* complex, and a C–H distance of 1.08 Å, a C–C–H angle of 109.5°, and a van der Waals radius of 1.2 Å for H). Steric repulsions between *cis* ligands have been invoked to explain small θ angles in CpTa(SPh)$_4$ and other compounds [7]. It is also observed that the $|\Delta\theta|$ (difference between Cp and Cp* structures) for the I ligands is approximately half the size of the $|\Delta\theta|$ for PMe$_3$ ligands. This may be attributed to a greater strength of the Mo–I interaction and consequently to an increased resistance of the I ligands to deviate from their ideal position.

It is also possible that an electronic effect based on a decrease in Mo–I π interactions on going from the Cp to the more electron-rich Cp* system is responsible for the observed changes in θ angle for the iodide ligands or that this electronic effect adds to the secondary steric effect described above. The greater electron density on the Cp* complex is shown by the Mo(III)/Mo(IV) redox potential, which is 0.19 more negative than the corresponding potential for the Cp system [1, 3]. However, since both Cp and Cp* Mo(IV) complexes have a high spin 16-electron configuration (e.g. $(d_{xy})^1(d_{z^2})^1$) as shown by ^{1}H NMR investigations [2], and since the predicted angular distortions for the interaction of the two metal orbitals are opposite in sign [4], it is not possible to use the data to establish the presence of electronic effects beyond any possible doubt.

Supplementary material

Full tables of bond distances and angles, anisotropic displacement parameters, hydrogen atom positions, and F_o/F_c data for compounds [CpMoI$_2$(PMe$_3$)$_2$]I and [Cp*MoCl$_{0.5}$I$_{1.5}$(PMe$_3$)$_2$]BF$_4$ are available from R.P. upon request.

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