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Hydrotris(pyrazolyl)borate molybdenum chemistry: spin triplet 16-electron carbonyl derivatives of molybdenum(II), and the X-ray structure of the Mo(V) oxo compound {HB(3,5-Me₂C₃N₂H)₃}MoOI₂

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Abstract - The hydrotris(3,5-dimethylpyrazolyl)borate complexes Tp*Mo(CO)₂X (X = Cl, I) are rare examples of 16-electron carbonyl derivatives with a spin triplet ground state, which exhibit relatively sharp contact-shifted ¹H NMR spectra. Oxidation of Tp*MoI(CO)₂ led to the isolation and crystallographic characterization of Tp*MoOI₂.

Keywords: molybdenum; hydrotrispyrazolylborate; paramagnetic organometallic compounds.

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The hydrotris(pyrazolyl)borate (Tp) ligand provides a structurally rigid and chemically inert capping ligand, which in many respects resembles (but in many other aspects it differs from) the ubiquitous cyclopentadienyl ring. We were interested in extending some of the chemistry we have recently explored for intermediate oxidation state cyclopentadienyl molybdenum compounds to the Tp ligand system. Although Tp systems of Mo have been studied extensively in low-oxidation states [1-10], much less work has been carried out in high oxidation states [11-13] and the only reported compound of Mo^{III} appears to be a salt of [Tp*MoCl₃]⁻ [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate] [14].

We have focused our attention on the sterically more demanding Tp*. In an attempt to access higher-valent Tp*Mo halide derivatives by oxidative decarbonylation of lower-valent derivatives, a technique which successfully provides an entry into higher-valent CpMo halides (Cp = η^5 -C₅H₅) [15], we have investigated the reaction of excess halogen with [Tp*Mo(CO)₃]⁻. During the course of this study we have been able to isolate and fully characterize the product of partial oxidation, [Tp*MoX(CO)₂] (X = Cl, I). Such a compound (for X = I) was first mentioned by Templeton, but neither it nor the corresponding tricarbonyl derivative were isolated nor spectroscopically characterized other than by *in situ* IR spectroscopy [4]. More recently, the compound Tp*MoI(CO)₂ has been isolated from the reaction between [MoI₂(CO)₃(MeCN)₂] and KTp*, and has been described as a diamagnetic compound, showing well-defined ¹H NMR spectroscopic properties [16]. The latter publication prompted us to submit the results of our own investigations, since they substantially differ from those therein reported. We also describe here the X-ray structure of Tp*MoI₂O, a product of further aerobic oxidation of Tp*MoI(CO)₂.

EXPERIMENTAL

General data

All operations were carried out under dinitrogen with standard Schlenk-line techniques. Solvents were distilled directly from the drying agent (toluene and heptane from Na, THF from Na/K/benzophenone, CH₂Cl₂ from P₄O₁₀) under argon prior to use. FT-IR spectra were recorded with

KBr cells on a Perkin Elmer 1800 spectrophotometer. ^1H NMR spectra were recorded on Bruker WP200 and AF200 spectrometers: the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks. The magnetic susceptibility measurements were carried out with a Johnson Matthey magnetic balance, which operates by a modified Gouy method whereupon the effect of the immersion of a sample in the magnetic field gradient is measured by a change of the magnet weight rather than by a change of the sample weight. The magnetic moments were calculated by the formula $\mu_B = 2.828 \cdot (\chi_M T)^{-1/2}$, the molar susceptibility χ_M being corrected by the diamagnetism of the ligands by using Pascal's constants. The elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. Compounds KTp* [17] and PhICl_2 [18,19] were prepared as previously described. Mo(CO)_6 (Aldrich) was used without any further purification.

Preparation of $\text{Tp}^\text{MoI(CO)}_2$*

A solution of $[\text{Tp}^*\text{Mo(CO)}_3]$ was prepared *in situ* by refluxing Mo(CO)_6 (2.63 g, 10.0 mmol) and KTp* (3.36 g, 10.0 mmol) in THF (85 cm^3). To this solution I_2 (2.54 g, 10.0 mmol) was added. Immediately after the I_2 addition, the IR spectrum of the reaction mixture exhibited CO stretching vibrations at 2025 (s), 1998 (m), 1937 (s) and 1922 (s) cm^{-1} . After stirring overnight at room temperature, the absorptions at 2025 and 1937 cm^{-1} had disappeared, while those at 1937 and 1923 cm^{-1} had grown in intensity. The mixture was concentrated to *ca* 20 cm^3 and *n*-heptane (50 cm^3) was added. The red brown precipitate was filtered off, washed with heptane and dried *in vacuo*. Yield: 4.26 g (74%). Found: C, 35.2; H, 4.01; N, 14.5. Calc. for $\text{C}_{17}\text{H}_{22}\text{BI MoN}_6\text{O}_2$: C, 35.4; H, 3.3; N, 14.6%. IR (THF, cm^{-1}): 1999 s. 1920 s. ^1H NMR (CDCl_3 , δ , 298 K): 87.8 (s, CH_3 , 3H), 70.5 (s, CH_3 , 3H), 47.2 (s, CH_3 , 6H), 34.8 (s, CH_3 , 6H), 8.6 (s, CH, 2H), -2.3 (br, BH, 1H), -7.2 (s, CH, 1H). $\mu_{\text{eff}} = 3.00 \mu_B$.

Preparation of $\text{Tp}^\text{MoCl(CO)}_2$*

By a procedure analogous to that reported above, a solution of $\text{KTp}^*\text{Mo(CO)}_3$ (2.83 mmol) was prepared from Mo(CO)_6 and KTp* in THF (50 cm^3). To this solution PhICl_2 (0.779 g, 2.83 mmol) was added. Immediately after the addition PhICl_2 , the IR spectrum of the reaction mixture exhibited CO stretching vibrations at 2007 (s) and 1923 (s) cm^{-1} . After stirring overnight at room temperature,

the IR spectrum had not changed. The mixture was concentrated to *ca* 10 cm³ and *n*-heptane (30 cm³) was added. The orange precipitate was filtered off, washed with heptane and dried *in vacuo*. Yield: 0.869 g (63%). IR (THF, cm⁻¹): 2007 s, 1923 s. ¹H NMR (CDCl₃, δ 298 K): 96.9 (s, CH₃, 3H), 71.5 (s, CH₃, 3H), 41.9 (s, CH₃, 6H), 31.7 (s, CH₃, 6H). $\mu_{\text{eff}} = 2.81 \mu_{\text{B}}$.

*Reaction of Tp*MoCl(CO)₂ with I₂*

Formation of Tp*MoI₂O. Tp*MoI(CO)₂ (0.542 g, 0.941 mmol) and I₂ (0.239 g, 9.42 mmol) were dissolved in toluene (30 cm³). The mixture was stirred at room temperature overnight. Monitoring by IR spectroscopy revealed the complete loss of the CO stretching absorptions. The mixture was evaporated to dryness and the residue was used for several recrystallization attempts. A small amount (< 20 mg) of single crystals which were suitable for an X-ray structural determination was obtained from a toluene/*n*-heptane layer. Found: C, 31.5; H, 3.6; N, 11.6. Calc. for C_{18.5}H₂₆BI₂MoN₆O (Tp*MoOI₂·1/2C₇H₈): C, 31.3; H, 3.7; N, 11.8 %.

*X-ray crystallography for Tp*MoI₂O·C₇H₈*

A dark purple, nearly black colored crystal with dimensions 0.400 x 0.125 x 0.00 mm was placed on the Enraf Nonius CAD-4 diffractometer. The cell parameters and crystal orientation matrix were determined from 25 reflections in the range $35.2 < 2\theta < 40.64$ and confirmed with axial photographs. Data were collected [Mo-K α] with $\omega/2\theta$ scans over the range $2.23 < \theta < 24.98$ with a scan width of $(0.64 + 0.56 \tan \theta)$ and a variable scan speed of 2.3–2.7 min⁻¹ with each scan recorded in 96 steps with the outermost 16 steps on each end of the scan being used for background measurement. The diffractometer was controlled with a Digital Equipment Corporation Micro VAX II (MVII) computer and the automated Enraf-Nonius control program Express (version 5.1). Three nearly orthogonal standard reflections were monitored at 1 h intervals of X-ray exposure with minimal variations in intensity being observed. Data were collected with the indices $-hkl$; resulting in the measurement of 2461 unique reflections. Data were corrected for Lorentz and polarization factors, and for absorption based on nine ψ -scan reflections in the range $5.1 < \theta < 15.3$, with transmission factors ranging from 0.3809–0.5015. Systematic absences indicated the centrosymmetric space group *Pnma* (no. 62) or the noncentrosymmetric space group *Pna2₁* (no. 33); intensity statistics clearly

favored the centric case. The structure was determined by direct methods, with the successful location of the three heavy atoms and several carbon and nitrogen atoms. The remaining nonhydrogen atoms were found from two subsequent difference-Fourier maps. The toluene molecule was found to be disordered with two of the atoms nearly overlapping with their symmetry equivalents that represented other positions of the ring, namely, the C12, C16 pair and the C11 and C17 pair. AFIX commands were used to impose the molecular geometry as a six-membered ring with C17 as the methyl group. Hydrogen atoms were placed in calculated positions, these being dependent on both the type of bonding at the carbon atom, with the aromatic hydrogen atoms calculated with $d(\text{C-H}) = 0.950 \text{ \AA}$ and U_{H} set equal to $1.2U_{\text{parent}}$, whereas the methyl hydrogen atoms were initially determined with a rotational difference-Fourier map about the central carbon atom that was further optimized for tetrahedral geometry with $d(\text{C-H}) = 0.980 \text{ \AA}$ and U_{H} set equal to $1.5U_{\text{parent}}$. The hydrogen atom attached to the boron atom was placed in an idealized tertiary position with $d(\text{B-H}) = 1.00 \text{ \AA}$ and U_{H} set equal to $1.2U_{\text{parent}}$. All nonhydrogen atoms were refined anisotropically during the final series of cycles and to convergence [$\delta/\sigma \leq 0.001$] with $R(F) = 4.47\%$, $wR(F^2) = 7.23\%$ and GOF = 1.075 for all 2460 unique reflections [$R(F) = 3.10\%$, $wR(F^2) = 6.67\%$ for those 2000 data with $F_0 > 4\sigma(F_0)$]. A final difference-Fourier map was essentially featureless with the largest peaks being within 1 Å from a heavy atom and $|\Delta\rho| \leq 0.65 \text{ e \AA}^{-3}$. The function minimized during the full-matrix least-squares refinement was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.0320 * P)^2 + 4.4833 * P]$ and $P = (\max(F_o^2, 0) + 2 * F_o^2)/3$. An empirical correction for extinction was also attempted but Found to produce a negative value and was not applied.

Crystal data and refinement parameters are listed in Table 1. and selected bond distances and angles are collected in Table 2 (the atomic positions have been deposited with the Cambridge Crystallographic Data Centre).

Table 1. Crystal and refinement parameters for compound $\text{Tp}^*\text{MoOI}_2 \cdot \text{C}_7\text{H}_8$

Empirical Formula	$\text{C}_{22}\text{H}_{30}\text{BI}_2\text{MoN}_6\text{O}$
Formula weight	755.07
Temperature (K)	153(2)

Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	$a = 18.1680(11) \text{ Å}, \alpha = 90$
	$b = 18.2579(11) \text{ Å}, \beta = 90$
	$c = 8.1580(3) \text{ Å}, \gamma = 90$
Volume (Å ³), <i>Z</i>	2706.1(3), 4
Density (calculated) (Mg m ⁻³)	1.853
Absorption coefficient (mm ⁻¹)	2.792
F(000)	1460
Data/restraints/parameters	2460 4 181
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0310, wR_2 = 0.0667$ [2000 data]
<i>R</i> indices (all data)	$R_1 = 0.0447, wR_2 = 0.0723$
Largest difference peak and hole (e Å ⁻³)	0.655 and -0.413

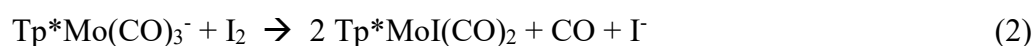
Table 2. Selected bond distances (Å) and angles (°) for compound Tp*MoOI₂·C₇H₈

Mo(1)-I(1)	2.7363(5)
Mo(1)-N(1)	2.150(3)
Mo(1)-N(3)	2.358(5)
Mo(1)-O(1)	1.695(5)
I(1)-Mo(1)-I(1)#	94.56(2)
I(1)-Mo(1)-O(1)	96.21(11)
I(1)-Mo(1)-N(1)	90.55(9)
I(1)-Mo(1)-N(1)#	167.63(9)
I(1)-Mo(1)-N(3)	86.51(8)
N(1)-Mo(1)-O(1)	94.4(2)
N(1)-Mo(1)-N(1)#	82.3(2)
N(1)-Mo(1)-N(3)	82.55(13)

O(1)-Mo(1)-N(3)	176.0(2)
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RESULTS

The reaction between $\text{Tp}^*\text{Mo}(\text{CO})_3$ and the halogenating agents PhICl_2 and I_2 provide a simple and high yield synthesis of the Mo^{II} 16-electron derivatives $\text{Tp}^*\text{MoX}(\text{CO})_2$ ($\text{X} = \text{Cl}, \text{I}$), see Eqs (1) and (2). Both derivatives have been isolated as crystalline solids and characterized by elemental analysis (C, H, N, for $\text{X} = \text{I}$ only), ^1H NMR, IR and magnetic susceptibility.



The iodo derivative has already been reported twice in the literature, but in one case it was not isolated [4], whereas in the other case it has been mischaracterized [16]. Templeton *et al.* carried out the same reaction reported here and reported the initial formation of the tricarbonyl derivative, $\text{Tp}^*\text{MoI}(\text{CO})_3$, which is characterized by IR absorptions at 2025 and 1937 cm^{-1} in THF [4]. Upon further stirring for 20 h in THF, a gradual conversion to the dicarbonyl compound, which is characterized by absorptions at lower energy (*i.e.* 1998 and 1921 cm^{-1}) [4], was reported by these authors. It was also reported that the CO loss process is inhibited by a CO atmosphere. No further characterization data were provided in that work. Our IR observations fully match those reported in the above-mentioned contribution. The IR absorptions of the isolated solid, which was crystallized from the THF solution by addition of *n*-heptane, are 1999 and 1920 cm^{-1} in THF. We have also established that the exposure of $\text{Tp}^*\text{MoI}(\text{CO})_2$ to an atmosphere of CO does not produce any observable amounts of the tricarbonyl derivative.

Cano and coworkers on the other hand, have prepared the compound by an alternative route, namely the reaction of KTp^* with $\text{MoI}_2(\text{CO})_3(\text{MeCN})_2$. They have obtained a crystalline solid, for which they report satisfactory C, H, N analyses for the formulation $\text{Tp}^*\text{MoI}(\text{CO})_2 \cdot 2\text{MeCN}$, directly from the reaction medium (MeCN) after only 30 min stirring at room temperature [16]. The

formulation of this product was based on the observation of only two IR stretching vibrations (at 2000 and 1850 cm^{-1} in KBr pellet), whereas a tricarbonyl derivatives with a four-legged piano stool structure and C_s symmetry should exhibit three absorptions ($2A' + A$), as is indeed observed for the related $\text{TpMoI}(\text{CO})_3$ complex [2]. This assignment is, however, dubious because broad and sometimes shifted bands are usually observed in polycrystalline samples; the lower frequency absorption does not match either of those observed by Templeton *et al.* for the tricarbonyl and dicarbonyl complexes. Although mention is made of the solubility of the isolated product in common organic solvents, no IR data in solution were reported.

The most critical discrepancy between the previously reported [16] characterization of $\text{Tp}^*\text{MoI}(\text{CO})_2$ and ours is related to the ^1H NMR properties. The previously reported spectrum [16] was characterized by the expected pattern for a Tp^* ligand sitting on a mirror plane, the resonances being in a region of the spectrum which is typical for *diamagnetic* compounds. However, the compound isolated by us is paramagnetic, the solid-state magnetic moment being $3.00 \mu_B$ in agreement with a spin triplet state and shows relatively sharp but highly contact-shifted resonances in the ^1H NMR spectrum, see Fig. 1. The simplest explanation that we can advance is that the relatively rapid precipitation and isolation of the product from MeCN by the previous workers [16] did not allow a complete conversion of the tricarbonyl derivative to the dicarbonyl derivative. Although the composition of the reported product may indeed be close to that of the dicarbonyl, the observed resonances in the diamagnetic region are probably due to residual amounts of the diamagnetic tricarbonyl derivative.

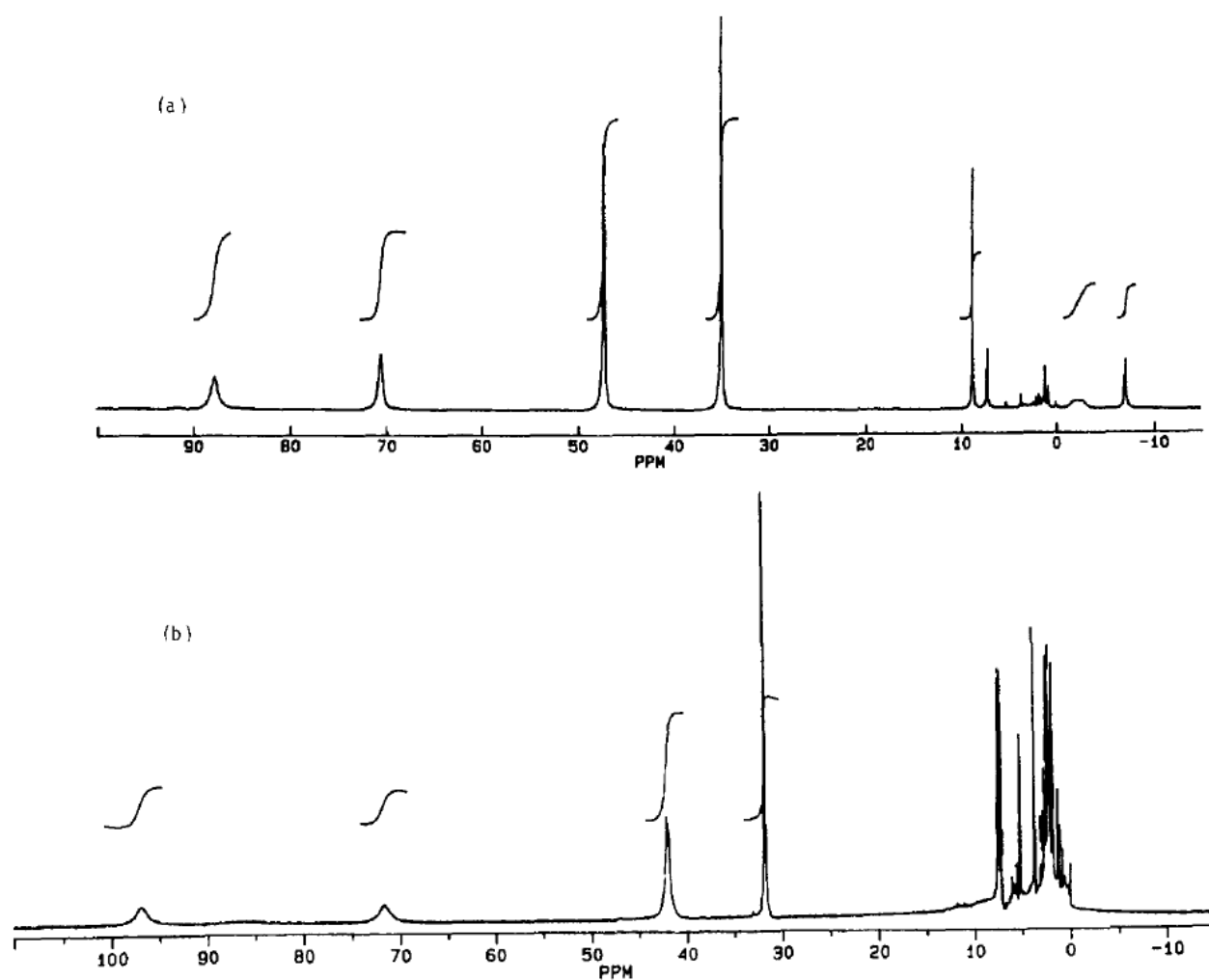


Fig. 1. Room-temperature ^1H NMR spectra of compounds $\text{Tp}^*\text{MoX}(\text{CO})_2$ [(a) $\text{X} = \text{I}$; (b) $\text{X} = \text{Cl}$]. Solvent = CDCl_3 .

The ^1H NMR spectrum of $\text{Tp}^*\text{MoI}(\text{CO})_2$ clearly shows two sets of resonances in a 2:1 ratio for each type of Tp^* proton, consistent with the structural rigidity of the C_s pseudo-octahedral structure. There is greater spin density transmitted to the unique pyrazole ring with respect to the other two, the resonance for each type of proton of this ring being shifted to a much greater extent (δ 87.3 and 70.5 for the two Me groups and -7.2 for the ring H, with respect to 47.2, 34.8, and 8.6 for the corresponding protons of the two equivalent rings). A much broader resonance at δ -2.3 is assigned to the B-H proton. Resonances in the diamagnetic region are quite small, attesting to the purity of the compound, and resonances that may be assigned to the tricarbonyl derivative, equivalent to those reported by Cano and coworkers are not visible [16].

The spectroscopic properties of the chloro compound, which has not been described before, parallel those of the iodo analog. The magnetic moment of this derivative is $2.81 \mu_B$. The ^1H NMR resonances are broader relative to those of the iodo analogue, a phenomenon which is commonly observed in the ^1H NMR spectra of paramagnetic halide derivatives [20]. The pyrazole ring CH and the BH protons are not visible in this case (see Fig. 1).

Further diiodine oxidation of compound $\text{Tp}^*\text{MoI}(\text{CO})_2$ in THF afforded, after workup and crystallization from toluene/heptane, single crystals of compound Tp^*MoOI_2 , the oxygen atom being possibly provided by adventitious moisture or air. This reaction was monitored by ^1H NMR spectroscopy, showing a complex behavior with the formation of several reaction intermediates, none of which has been isolated to date. A similar process has been described in the literature for the oxidation of $\text{Tp}^*\text{Mo}(\text{CO})_3^-$ with thionyl chloride, followed by exposure to air, to afford $\text{Tp}^*\text{MoOCl}_2$ [13,14].

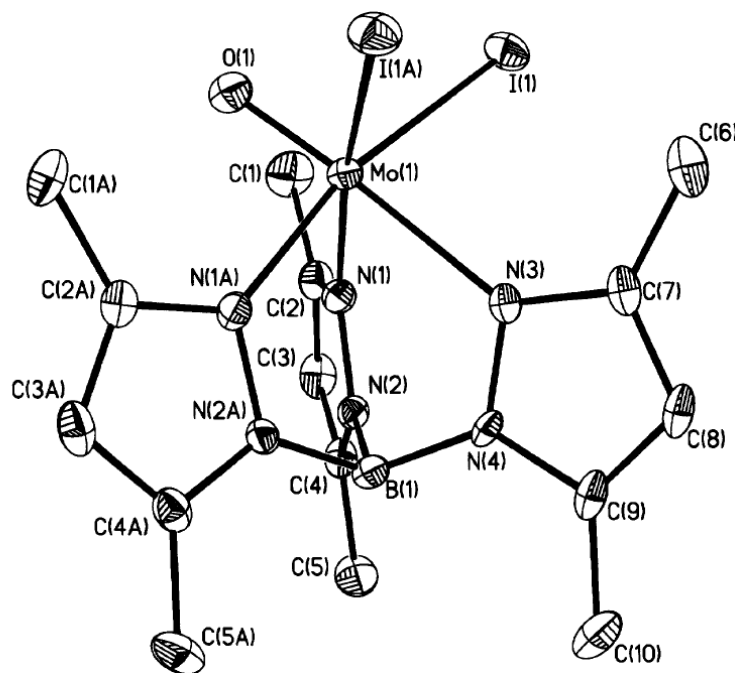


Fig. 2. An ORTEP view of the Tp^*MoOI_2 molecule with the numbering scheme used. Ellipsoids are shown at the 40% probability level.

Compound Tp^*MoOI_2 exhibits a broad EPR resonance ($w_{1/2} = 57$ G at the X-band; $g = 2.045$), in agreement with its d^1 configuration. The formulation of this oxo product is confirmed by X-ray crystallography (see Fig. 2). The geometry parallels that established for the related TpMoOCl_2 . There

is no sign of positional disorder between the smaller oxygen and the bigger iodine atoms, whereas a O/Cl positional disorder was observed for TpMoOCl_2 [12]. The oxygen atom exerts a greater *trans* influence than the iodine atoms, lengthening the Mo-N(3) distance by *ca* 0.2 Å with respect to the Mo—N(1) distance. The other distances in the molecule are quite typical, including the short Mo-O distance, which is close to that reported for the terminal Mo-O bonds in $[\text{TpMoOCl}]_2\text{O}$ [1.67(4) Å] [12]. The I-Mo-I and I-Mo-O angles are slightly greater and all N-Mo-N angles are smaller than the ideal octahedral angle.

DISCUSSION

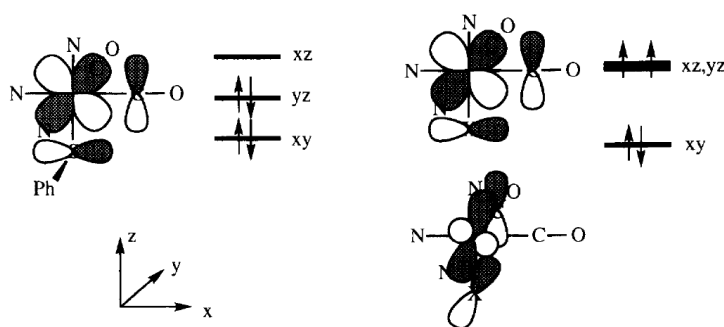
The spontaneous CO loss from hydrotris(pyrazolyl)boratotricarbonylhalomolybdenum(II) is a phenomenon first observed by Templeton for $\text{Tp}^*\text{MoI}(\text{CO})_3$. No analogous process has been reported for the corresponding $\text{TpMoX}(\text{CO})_3$ at room temperature. While mild thermolysis of $\text{TpMoI}(\text{CO})_3$ in MeCN has been shown to lead to disproportionation products [2]. These observations suggest that the greater steric encumbrance of the Tp^* ligand contributes significantly to the thermodynamics of the CO dissociation process. The $\text{Tp}^*\text{WI}(\text{CO})_3$ compound, on the other hand, yielded the decarbonylated $\text{Tp}^*\text{WI}(\text{CO})_2$ product only upon reflux for several hours in THF [21,22], attesting to the stronger W-CO bond relative to the Mo-CO bond. Another related literature report concerns compound $[\{\text{HB}(3,5\text{-Me}_2\text{C}_2\text{N}_3)_3\}\text{MoI}(\text{CO})_3]$, *i.e.* a system completely analogous to $\text{Tp}^*\text{MoI}(\text{CO})_3$, except for the formal substitution of the pyrazole rings CH groups with N atoms to yield 1,2,4-triazole rings. This compound was isolated from the I_2 oxidation of $[\{\text{HB}(3,5\text{-Me}_2\text{C}_2\text{N}_3)_3\}\text{Mo}(\text{CO})_3]^-$ in MeCN and gas evolution was observed upon dissolution in other organic solvents [9]. The decarbonylated product, however, was not isolated or characterized.

Stable low-oxidation state organometallic compounds with an open-shell configuration are rare, especially for metals of the 4*d* and 5*d* series. Compounds with a 16-electron configuration are often stabilized by ligands that are capable of providing two additional electrons from a lone pair *via* a π -donation mechanism [23]. In order for this interaction to be most effective, the lone pair must interact with an empty metal orbital, thus leading to a spin-paired (diamagnetic) configuration. Half-sandwiched Mo(II) compounds such as $\text{CpMo}(\text{CO})_2(\text{AsBu}'_2)$ [24], $\text{CpW}(\text{CO})_2[\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})]$

[25] and $\text{Cp}^*\text{Mo}(\text{PPh}_2)(\text{PMe}_3)_2$ [26] ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), can be rationalized in this light. We have recently provided the first example of a spin triplet analogue of the above compounds, namely $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_2$ [27]. The chloride ligand is apparently a less efficient π -donor than phosphido or arsenido groups. Analogous complexes with carbonyl ligands, however, have always been found to be diamagnetic, even with weak π -donors such as halides. Examples are $\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2$ [28], $\text{Mo}(\text{O}^i\text{Bu})_2(\text{CO})_2(\text{py})_2$ [29] and $\text{Mo}(\text{S}_2\text{CNPr}^i_2)_2(\text{CO})_2$ [30]. Octahedral complexes of d^4 centers can in principle adopt two spin configurations: a high-spin (quintet) $t_{2g}^3e_g^1$, or a low-spin (triplet) t_{2g}^4 . Both are observed for complexes of Cr(II) and the spin triplet configuration is adopted by carbonyl-free Mo^{II} complexes. *e.g.* $\text{MoCl}_2(\text{PMe}_3)_4$ [31]. In carbonyl complexes, however, the Jahn-Teller unstable (for d^4) octahedral geometry undergoes remarkable distortions to maximize the π -interactions and lead to diamagnetic ground states [32]. The $\text{Tp}^*\text{MoX}(\text{CO})_2$ ($\text{X} = \text{Cl, I}$) compounds described here are the first reported examples of octahedral carbonyl derivatives of Mo^{II} with a spin triplet ground state. They are also rare examples of spin triplet carbonyl complexes for any element, especially heavier metals of the $4d$ and $5d$ series. The only other magnetically characterized example known to us is $\text{ReI}_3(\text{CO})_3$ [33]. The compound $\text{Tp}^*\text{WI}(\text{CO})_2$, *i.e.* a W^{II} analog of the Mo compounds discussed here, has also been described as paramagnetic [22], but no magnetic susceptibility nor NMR data for this compound have been reported. Given that severe distortions of the octahedral coordination geometry for Mo^{II} complexes are related to the electrons being paired in a singlet state, we postulate that the geometry of the $\text{Tp}^*\text{MoX}(\text{CO})_2$ should describe a relatively undistorted octahedron (*e.g.* bond angles close to 90°). We were unfortunately unable to grow suitable single crystals of this compound.

It is interesting to compare the paramagnetism of $\text{Tp}^*\text{MoX}(\text{CO})_2$ ($\text{X} = \text{Cl, I}$) with the diamagnetism of the related $\text{Tp}^*\text{M}(\text{SPh})(\text{CO})_2$ ($\text{M} = \text{Mo, W}$) [1, 22] and other W^{II} derivatives, *e.g.* $\text{Tp}^*\text{W}(\text{NR}_2)(\text{CO})_2$ [34]. The halide on one side, and the thiolato and amide ligands on the other side, differ in the strength and symmetry of the π -interactions. While SPh (if bent) and NR_2 are single-sided π -donors, a halide ligand has two equivalent and orthogonal lone pairs. Thus, in an undistorted octahedral structure, the SPh and NR_2 ligands will be able to remove the degeneracy of the metal d_{xz} and d_{yz} orbitals (see Scheme 1, left) and lead to a spin paired ground state, while the halide ligands, even if they engage in a significant π interaction, will not (Scheme 1, right). The imido ligand in complex $[\text{Tp}^*\text{W}(\text{NPh})(\text{CO})_2]^-$ also has the ability of participating in M-N π -bonding with both lone

pairs. The structure shows a linear W-N-Ph moiety and a relatively undistorted octahedral geometry, but the reported NMR properties of the compound indicate diamagnetism [34].



Scheme 1

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