

Synthesis and Characterization of New Chromium-Centered Radicals of the Type $\{\eta^3\text{-Tris(pyrazolyl)borato}\}\text{Cr}(\text{CO})_2\text{L}$ (L = CO, PMe_3): EPR Spectra of Organochromium and -molybdenum Compounds Undergoing Subtle Jahn-Teller Distortions

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Received February 12, 1992

Summary: The new 17-electron complexes $\text{TpCr}(\text{CO})_3$, $\text{Tp}^*\text{Cr}(\text{CO})_3$, $\text{Tp}'\text{Cr}(\text{CO})_3$, and $\text{TpCr}(\text{CO})_2(\text{PMe}_3)$ (Tp = hydridotris(pyrazolyl)borate, Tp^* = hydridotris(3,5-dimethylpyrazolyl)borate, Tp' = tetrakis(pyrazolyl)borate) have been prepared and characterized. EPR spectra of these compounds and of the known molybdenum analogues $\text{TpMo}(\text{CO})_3$ and $\text{Tp}^*\text{Mo}(\text{CO})_3$ are utilized to gain information concerning the electronic structures.

Interest in the synthesis and electronic structures of 17-electron, transition-metal-centered radicals has grown significantly in recent years, with EPR spectroscopy playing a major role both in the characterization of new compounds and in elucidation of the nature of their bonding.¹ The first such molecule examined by EPR spectroscopy was $\text{V}(\text{CO})_6$,^{1,2} for which a $^2T_{2g}$ ground state is anticipated in ideal O_h symmetry together with the Jahn-Teller distortions intrinsic to any orbitally degenerate species. Considerable effort has been spent interpreting the spectral parameters of $\text{V}(\text{CO})_6$ and derivatives in terms of static and dynamic Jahn-Teller distortions, but with mixed success. Paramagnetic molecules such as $\text{V}(\text{CO})_6$, with near-degenerate ground states, are generally difficult to detect by EPR spectroscopy because of the extreme line broadening resulting from the effects associated with Jahn-Teller distortions: (i) incomplete averaging of time-dependent g -factor or hyperfine interactions caused by internal motion or solvent interactions, and/or (ii) enhanced electron spin-lattice relaxation via spin-orbit coupling.³ Low temperatures are required in such cases to minimize line broadening and to make the resonances observable, but the pronounced sensitivity of the electronic properties of orbitally degenerate molecules to external perturbations unfortunately precludes an a priori assessment of EPR detectability.^{3e} Where electronic lability is suspected, therefore, great care is demanded during the search for and interpretation of an EPR spectrum.

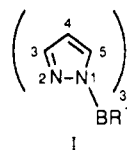
We have recently made use of such considerations to rectify mutually incompatible suggestions in the literature that the 17-electron species $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2^+$, which ex-

compd	$\nu(\text{CO})$ (THF), cm^{-1}	$\delta(^1\text{H})$ (CDCl_3)		
		H(Me)-3	H-4	H(Me)-5
$\text{TpCr}(\text{CO})_3$	2024, 1865	-8.0	3.03	-15.7
$\text{Tp}'\text{Cr}(\text{CO})_3$	2025, 1863	-9.5	3.70	-15.1 ^a
$\text{Tp}^*\text{Cr}(\text{CO})_3$	2015, 1844	15.8	1.10	26.7
$\text{TpMo}(\text{CO})_3$	2007, 1873	-8.0	3.57	-18.3
$\text{Tp}^*\text{Mo}(\text{CO})_3$	1997, 1863	18.5	1.45	35.6

^a Resonances of the uncoordinated pyrazolyl ring occur at δ 10.03, 8.77 and 7.35.

hibits a room-temperature EPR spectrum, is a trigonal-bipyramidal complex with a $^2E'$ ground state.⁴ In fact, the complex undergoes a very significant distortion to local C_{2v} symmetry at iron such that the complex essentially assumes a square-pyramidal structure with a 2A_1 ground state. In contrast, we have found that the complexes $(\eta^5\text{-C}_5\text{R}_5)\text{Cr}(\text{CO})_3$ (R = H, Me) resemble $\text{V}(\text{CO})_6$ in that they undergo dynamic Jahn-Teller distortions and exhibit EPR spectra only at very low temperatures.⁵ Slowing the rotation of the five-membered rings results in lowering of the effective symmetry from C_{3v} to C_3 , with concomitant removal of the otherwise implicit orbital degeneracies.⁵

In view of these findings, we were intrigued by a report that the related metal-centered radical $\text{TpMo}(\text{CO})_3$ (Tp = hydridotris(pyrazolyl)borate, i.e. I with R = H) assumes



a structure at 104 K which possesses a C_3 crystallographic axis and hence local C_{3v} symmetry about the molybdenum atom.^{6a,b} Apparently abnormal were observations of a 2E ground state, reasonably narrow resonances in the ^1H NMR spectra at ambient temperature, and a well-resolved, nearly isotropic EPR spectrum in THF at 90 K for the

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same radical species.⁷ Although the inconsistencies between these observations were noted, no rationalization was offered. Similar NMR results have, moreover, been observed with the analogous $\text{Tp}^*\text{Mo}(\text{CO})_3$ ($\text{Tp}^* = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$).^{6c}

In an effort to gain further information on this system, we have synthesized and characterized four new chromium analogues, $\text{TpCr}(\text{CO})_3$, $\text{Tp}^*\text{Cr}(\text{CO})_3$, $\text{Tp}'\text{Cr}(\text{CO})_3$ ($\text{Tp}' = \text{tetrakis}(\text{pyrazolyl})\text{borate}$, i.e. I with $\text{R} = \text{pyrazolyl}$), and $\text{TpCr}(\text{CO})_2(\text{PMe}_3)$.⁸ The new chromium compounds are yellow, crystalline solids and are stable under nitrogen at ambient temperature for days, at least, but are unstable in solution and readily oxidized both in solution and in the solid state. IR and ^1H NMR data are listed in Table I, where they may be compared with data for the molybdenum analogues. The frequencies of the carbonyl stretching bands of the compounds are comparable both to each other and to those reported for the compounds $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).¹ Assignments of the chemical shifts are based on literature precedents,⁶ and we note that the patterns of isotropic shifts of the compounds $\text{TpCr}(\text{CO})_3$ and $\text{Tp}^*\text{Cr}(\text{CO})_3$ are also internally consistent. Interestingly, and in contrast to $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3$,⁹ we find that $\text{TpCr}(\text{CO})_3$ undergoes slow substitution with the small phosphine PMe_3 but not with larger phosphines. In addition, preliminary experiments suggest that $\text{TpMo}(\text{CO})_3$ reacts only with phosphines smaller than PPh_3 and that the two much more sterically crowded compounds $\text{Tp}^*\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}$) are inert to thermal substitution by tertiary phosphines.

In a preliminary attempt to better understand the EPR properties of $\text{TpMo}(\text{CO})_3$ and $\text{Tp}^*\text{Mo}(\text{CO})_3$, we doped $\text{TpMo}(\text{CO})_3$ as a substitutional impurity into single crystals of its 18-electron, isostructural manganese analogue.¹⁰

(7) The long electronic relaxation times necessary for a well-resolved EPR spectrum to be observed normally results in such short nuclear relaxation times that ^1H NMR resonances are too broad to be observed. See: La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds.; *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(8) (a) The published synthesis of $\text{TpMo}(\text{CO})_3$ ^{6b} was modified since, in our hands, the room-temperature oxidation of $[\text{NET}_4][\text{TpMo}(\text{CO})_3]$ with ferrocenium or silver hexafluorophosphate in THF generated substantial quantities of $\text{TpMo}(\text{CO})_3\text{H}$; formation of the latter was eliminated by cooling the solution to -40°C . The compounds $\text{TpCr}(\text{CO})_3$, $\text{Tp}^*\text{Cr}(\text{CO})_3$, and $\text{Tp}'\text{Cr}(\text{CO})_3$ were likewise prepared by oxidation of the corresponding tetraethylammonium salt^{6b} with ferrocenium hexafluorophosphate in THF at -40°C for 30 min. The reaction mixtures were then filtered through Celite, the solvents were removed under reduced pressure, and the residues were extracted with acetonitrile. The compounds $\text{TpCr}(\text{CO})_3$ and $\text{Tp}'\text{Cr}(\text{CO})_3$ crystallized on concentration, but only the latter was sufficiently stable that satisfactory elemental analyses could be obtained. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{BCrN}_6\text{O}_3$: C, 43.40; H, 2.91. Found: C, 43.48; H, 2.93. The compound $\text{Tp}^*\text{Cr}(\text{CO})_3$ is insoluble in acetonitrile, and thus extraction of the reaction mixture with this solvent resulted in the formation of analytically pure, crystalline product. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{BCrN}_6\text{O}_3$: C, 49.90; H, 5.12. Found: C, 49.78; H, 5.10. The compound $\text{TpCr}(\text{CO})_2(\text{PMe}_3)$ was prepared by adding a 5-fold excess of PMe_3 to the THF solution of $\text{TpCr}(\text{CO})_3$ after the oxidation and filtration steps had been carried out. The reaction mixture was stirred for 10 h, followed by removal of volatile materials under reduced pressure and chromatography on an alumina column with hexanes and then 1:3 hexanes-methylene chloride to give, after removal of solvent, the pure product. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{BCrN}_6\text{O}_2\text{P}$: C, 42.35; H, 4.82. Found: C, 42.03; H, 4.99. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.

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Selected crystals were mounted in quartz EPR tubes and examined first at liquid-nitrogen and subsequently at liquid-helium temperatures. To our surprise, no EPR spectrum could be observed at either temperature, although NMR spectra of the samples run both prior to and immediately following the EPR measurements provided unambiguous evidence that the doping experiments had been successful. A frozen solution of pure $\text{TpMo}(\text{CO})_3$ in CH_2Cl_2 was therefore examined at 5 K and found to display a broad, anisotropic ($g_1 = 1.94$, $g_2 = 2.08$, $g_3 = 2.40$) resonance which broadened beyond detection at higher temperatures. This observation is reasonable for the type of metal-centered radical involved^{6d} but is different from that reported previously for THF solutions.^{6b} However, we find on examining the EPR spectra of frozen THF solutions of $\text{TpMo}(\text{CO})_3$ at 77 K that the signal initially observed is unstable and decays to other unidentified radicals over a period of hours.

The compounds $\text{TpMo}(\text{CO})_3$, $\text{Tp}^*\text{Mo}(\text{CO})_3$, $\text{TpCr}(\text{CO})_3$, and $\text{Tp}^*\text{Cr}(\text{CO})_3$ were found to display very similar EPR spectra at 5 K ($g_1 \approx 1.94\text{--}1.98$, $g_2 \approx 2.03\text{--}2.08$, $g_3 \approx 2.15\text{--}2.40$). In addition, all of the resonances broaden beyond recognition at higher temperatures, and thus, given the similarities in IR and NMR spectroscopic properties, it is clear that the compounds form a homologous series with very similar electronic structures. Since the low-temperature X-ray crystal structure of $\text{TpMo}(\text{CO})_3$ gives no indication for a static Jahn-Teller distortion,^{6b} a reasonable interpretation of our single-crystal EPR experiment on this compound, at least, is that the system undergoes a sufficiently subtle dynamic Jahn-Teller distortion such that the SOMO retains its degeneracy in the crystal lattice. In contrast, the overall lowering of site symmetries achieved in the glassy-solvent matrices for all four tricarbonyl compounds is sufficient to distort the structures and thus to break the degeneracies so that EPR signals may be observed.

In more direct attempts to lower the symmetry of the metal centers, the tetrakis(pyrazolyl) compound $\text{Tp}'\text{Cr}(\text{CO})_3$ and the phosphine-substituted derivative $\text{TpCr}(\text{CO})_2\text{PMe}_3$ ($\nu(\text{CO}) = 1912, 1758\text{ cm}^{-1}$) have also been prepared. As anticipated, we find that an EPR spectrum of the latter compound in CH_2Cl_2 solution may be observed at temperatures close to ambient ($g_{\text{iso}} = 2.0235$, $a(^{31}\text{P}) = 33.5\text{ G}$ at 225 K) and that resonances in the ^1H NMR spectrum are broadened considerably. In the case of $\text{Tp}'\text{Cr}(\text{CO})_3$, an EPR resonance ($g_1 = 1.988$, $g_2 = 2.036$, $g_3 = 2.114$) is observable in frozen solution at 120 K, but the signal is broadened beyond recognition at 176 K.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for an operating grant to M.C.B. and a graduate fellowship to J.H.M.

OM920075E

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