J. Am. Chem. Soc. **1994,** *116,* 6021–6022

Ligand Control of Electronic Stability: 17- vs 18-Valence-Electron Configurations of $CpCr(NO)(ligand)_2$ Complexes[1]

Peter Legzdins* and W. Stephen McNeil

Department of Chemistry,
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Z1

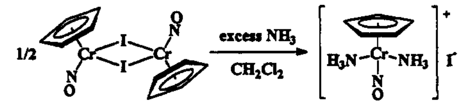
Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received February 23, 1994

A fundamental and long-standing principle of transition-metal organometallic chemistry is the 18-valence-electron rule, which states that stable organometallic complexes will contain a total of 18 valence electrons.[2] In general, such complexes may be rendered kinetically labile by conferring a 17- or 19-valence-electron configuration upon them by removing or adding an electron, respectively.[3] A particularly good example of this phenomenon is the electron-transfer catalysis of CO-substitution reactions undergone by metal carbonyls.[3] Much less common (and unknown until recently) is the situation in which a stable 17-valence-electron complex is rendered kinetically more labile by imposing upon it a 16- or 18-valence-electron configuration. An illustration of such an effect is provided by the oxidation of $CpMoI_2(PMe_3)_2$ recently reported by Poli and co-workers.[4] We now report our unprecedented observations that members of one family of compounds, namely, piano-stool $CpCr(NO)(L)_2$ species, can exhibit both types of behavior. We have found that the stability of a particular valence-electron configuration of one of these complexes is determined by the nature of the ligands L.

An unreactive 17-electron member of this family of complexes, namely, the $[CpCr(NO)(NH_3)_2]^+$ cation ($\mathbf{1}^+$), is isolable as the I^- salt in virtually quantitative yield from the reaction of excess ammonia with $[CpCr(NO)I]_2$ in CH_2Cl_2 (eq 1). The product



(1)

salt precipitates immediately from solution as an analytically pure green solid, and the counterion may be easily metathesized for other anions (e.g., $[PF_6]^-$, $[BPh_4]^-$) by use of the appropriate silver salt in THF. The solid-state molecular structure of the organometallic cation, $\mathbf{1}^+$, as it occurs in $[\mathbf{1}]^+[BPh_4]^-\cdot NCMe$ has been established by a single-crystal X-ray crystallographic analysis at 200 K,[5] and its ORTEP diagram is presented in Figure 1. The structure has a typical three-legged piano-stool arrangement, and there are no significant intermolecular contacts between non-hydrogen atoms. The metrical parameters of the cation (presented in the caption to Figure 1) are normal and resemble those established for the related 17- and 18-valence-electron complexes, $CpCr(NO)(PPh_3)(CH_2SiMe_3)$[6] and $CpCr(NO)(CO)_2$,[7] respectively.

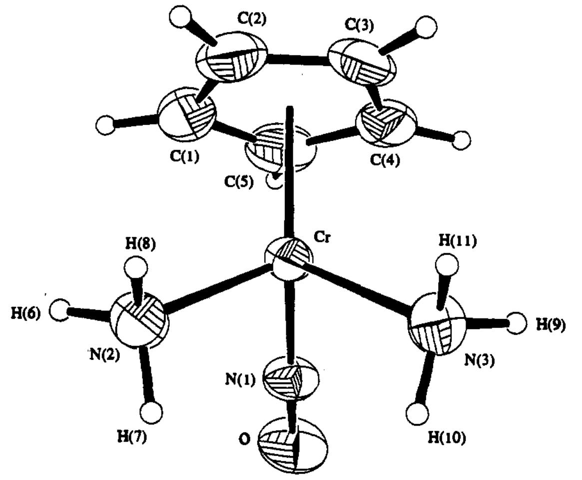


Figure 1. Solid-state molecular structure of the organometallic cation $\mathbf{1}^+$ as it occurs in $[\mathbf{1}]^+[BPh_4]^-\cdot NCMe$ at 200 K; 50% probability thermal ellipsoids are shown for all non-hydrogen atoms, and hydrogen atoms are depicted as spheres of arbitrary radius. Selected interatomic distances (Å) and angles (deg): Cr–N(1) = 1.665(3), Cr–N(2) = 2.082(3), Cr–N(3) = 2.077(3), O–N(1) = 1.203(4), Cr–CP = 1.881, N(2)–Cr–N(1) = 98.5(1), N(3)–Cr–N(1) = 97.0(1), N(3)–Cr–N(2) = 89.6(1), O–N(1)–Cr = 170.3(3), N(1)–Cr–CP = 122.7, N(2)–Cr–CP = 120.5, N(3)–Cr–CP = 121.2. CP denotes the center of mass of the carbon atoms of the cyclopentadienyl ring.

The coordination sphere of the metal in $\mathbf{1}^+$ remains intact when $[\mathbf{1}]^+[PF_6]^-$ is dissolved in either THF or MeCN, even though both the $[CpCr(NO)(THF)_2]^+$ and $[CpCr(NO)(NCMe)_2]^+$ cations are well-known, thermally stable species.[8] Furthermore, $[\mathbf{1}]^+[PF_6]^-$ in THF also does not react with either an excess of H_2O or an atmosphere of CO when stirred for 1 day at ambient temperatures. This inertness of $\mathbf{1}^+$ toward ligand substitution is somewhat surprising, given its paramagnetic nature ($\mu_{eff} = 1.49$ μ_B in benzene),[9] the lack of steric crowding at the metal center, and the documented substitutional lability of other related, 17-valence-electron chromium(I) species.[10] As well, $[\mathbf{1}]^+[PF_6]^-$ does not react with 1 equiv of $HSn(n\text{-}Bu)_3$, in contrast to many 17-electron transition-metal radicals which function as potent H-atom abstraction reagents.[11] The cyclic voltammogram of $[\mathbf{1}]^+[PF_6]^-$ in THF (Figure 2a) reveals an irreversible reduction feature at $E_{p,c} = -1.3$ V vs SCE, thereby indicating that the 18-electron neutral **1** is not a stable species. Again, this is an unexpected observation, since it suggests that the coordination sphere of $\mathbf{1}^+$ does not remain intact upon reduction to a closed-shell, 18-valence-electron configuration which might be expected to be the more stable form. Nevertheless, this irreversible reduction of $\mathbf{1}^+$ may be exploited synthetically. For instance, reduction of $\mathbf{1}^+$ in THF by an excess of zinc power in the presence of an atmosphere of

---

(1) Presented in part at the 76th Canadian Chemical Conference and Exhibition, Sherbrooke, PQ, June 1993, Abstract 432, and at the 207th National Meeting of the American Chemical Society, San Diego, CA, March 1994; Abstract INOR 30.

(2) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH Publishers: New York, 1992; pp 186, 412.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(4) Poli, R.; Owens, B. E.; Linck, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1302.

(5) Crystal data for $[\mathbf{1}]^+[BPh_4]^-\cdot NCMe$ at 200 K: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.478(3)$ Å, $b = 19.288(7)$ Å, $c = 15.427(6)$ Å, $\beta = 91.99(3)°$, $V = 2818.5$ Å^3, $R = 0.038$, $R_w = 0.036$ for 2185 reflections with $I_o \geq 2.5\sigma(I_o)$ and 310 variables.

(6) Herring, F. G.; Legzdins, P.; McNeil, W. S.; Shaw, M. J.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1991**, *113*, 7049.

(7) Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P. E.; Alt, H. G. *J. Organomet. Chem.* **1979**, *165*, 65.

(8) (a) The $[CpCr(NO)(THF)_2]^+$ cation is easily prepared by the treatment of a THF solution of $[CpCr(NO)I]_2$ with silver salts: Legzdins, P.; McNeil, W. S. Manuscript in preparation. (b) Chin, T. T.; Legzdins, P.; Trotter, J. Yee, V. C. *Organometallics* **1992**, *11*, 913.

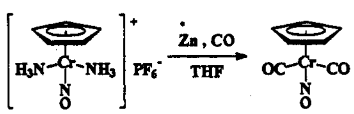
(9) Determined by the Evans method: (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

(10) (a) Trogler, W. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 9. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

(11) (a) Coville, N. J. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 4. (b) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 3. (c) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125.

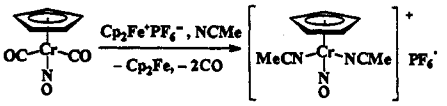
0002-7863/94/1516-6021$04.50/0

CO produces the well-known,[12] 18-electron complex CpCr(NO)-$(CO)_2$ (**2**) as an orange solid (eq 2). In other words, whereas the 17-electron cation in THF does not react with carbon monoxide, upon reduction to the 18-electron, neutral species, the ammonia ligands are readily replaced by CO.



(2)

The reduction behavior described in the preceding paragraph prompted us to investigate the possibility of the reverse process, namely, the oxidation of **2** to obtain a 17-electron species. Geiger has previously established electrochemically that solutions of **2** exhibit an irreversible oxidation feature at approximately +1.2 V vs SCE,[13] thereby indicating that the 17-electron cation $\mathbf{2}^+$ is not a stable species. Attempts to effect this oxidation preparatively in the presence of ammonia are hampered by the consumption of ammonia rather than the organometallic reactant. Nevertheless, reaction of **2** with 1 equiv of $[Cp_2Fe]^+[PF_6]^-$ in acetonitrile affords the known salt[8b] $[CpCr(NO)(NCMe)_2]^+[PF_6]^-$ (eq 3), which contains 17-valence-electron cation similar to $\mathbf{1}^+$.



(3)

From transformations 2 and 3 it appears that the preferred electronic configuration of $CpCr(NO)(L)_2$ molecules, i.e., the stability of the 17-valence-electron paramagnetic form versus that of the 18-valence-electron diamagnetic form, is determined by the nature of the ancillary ligands L. Thus, σ-donor ligands such as NH_3 stabilize the 17-electron cationic compounds which decompose upon reduction to their 18-electron analogues. On the other hand, π-acceptor ligands such as CO evidently stabilize the 18-electron configuration in the neutral complexes which decompose upon oxidation to their 17-electron analogues. The chemical literature provides further supporting evidence for this generalization. Thus, a wide range of $CpCr(NO)L_2$ compounds are now known, and apparently without exception, those bearing σ-donor ligands are 17-electron species[8b,14] (e.g., $[CpCr(NO)(phen)]^+$) and those containing π-acid ligands are 18-electron complexes[15] (e.g., $CpCr(NO)(CO)(C_2H_4)$).

Given the above conclusion concerning ligand control of the stability of valence-electron configurations, it then stands to reason that a ligand possessing both σ-donor and π-acceptor properties should allow for the formation of a $CpCr(NO)(L)_2$ compound between the two extremes, i.e., one stable in either the 17- or 18-valence-electron form. $P(OMe)_3$ is just such a ligand, and we have found that the two species $CpCr(NO)(P\{OMe\}_3)_2$ (**3**) and $[CpCr(NO)(P\{OMe\}_3)_2]^+[PF_6]^-$ ($[\mathbf{3}]^+[PF_6]^-$) may indeed by synthesized independently. The 18-electron neutral species is obtainable as a bright orange solid by the zinc reduction of $[CpCr(NO)I]_2$ in the presence of $P(OMe)_3$. Halide abstraction from $CpCr(NO)(P\{OMe\}_3)(I)$ by $AgPF_6$ in THF followed by addition of 1 equiv of the phosphite affords the yellow-green 17-electron cation as its $[PF_6]^-$ salt. The species **3** and $\mathbf{3}^+$ constitute the only two such related compounds yet known for this system. As expected, these complexes exhibit identical cyclic voltammetry, displaying a reversible redox couple at $E^{\circ\prime} = -0.03$ V in THF as shown in Figure 2b.

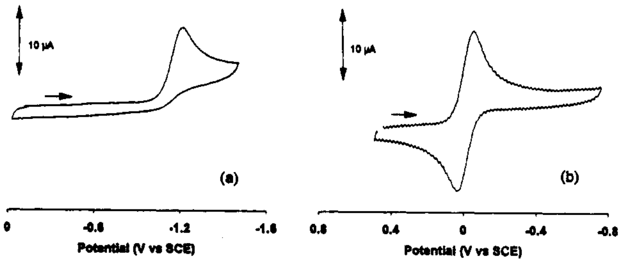


Figure 2. Ambient-temperature cyclic voltammograms of 5×10^{-4} M solutions of (a) $[\mathbf{1}]^+[PF_6]^-$ and (b) **3** in THF containing 0.1 M $[n\text{-}Bu_4N]^+[PF_6]^-$ measured at platinum-bead electrodes at scan rates of 0.4 V s^{-1}.

In summary, we have found that, for $CpCr(NO)(L)_2$ species, those having σ-donor ligands L are stable as 17-valence-electron cations, whereas those with π-acid ligands L are stable as 18-valence-electron neutral compounds. It thus appears that the greater reactivity of odd-electron species is not a universal trend, but rather that the nature of the ligands in odd-electron species plays a role in determining their stability. The caveat that must therefore now be applied to generalizations of electronic stability of organometallic compounds is that they are probably ligand-dependent. Thus, among these chromium complexes we have discovered an example of an unreactive odd-electron complex in which reactivity may be induced by reduction to an even-electron species. This process results in facile substitution of ligands in the metal's coordination sphere, the opposite of the normally observed trend. We have also found a similar increase in substitutional lability for the stable 18-electron complexes upon oxidation. Previous studies have established the effect of the ligand on the redox stability of other related systems such as $[M(CO)_xL_{6-x}]^{n+}$ (M = Cr, Mo, W)[16] and $[CpMoL_3Cl]^{n+}$.[17] However, to the best of our knowledge, the extent of ligand stabilization extant in the CpCr(NO) systems is unprecedented.

In closing, it is interesting to note that the $CpCr(NO)L_2$ complexes examined during this study range from traditional organometallic species (e.g., L = CO) to compounds that are more "coordination-like" in character (e.g., L = NH_3). In a future paper we expect to be able to rationalize the observed stability and reactivity trends in terms of a molecular-orbital description of the metal–ligand interactions in these complexes. The observations summarized in this paper also give rise to the possibility of new synthetic routes (e.g., those involving electron-transfer catalysis) to compounds containing the CpCr(NO) fragment. Investigations designed to examine this possibility are currently in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and a postgraduate scholarship to W.S.M.

Supplementary Material Available: Experimental procedures and characterization data for all new complexes and full details of crystal structure analysis including associated tables for $[\mathbf{1}]^+[BPh_4]^-\cdot NCMe$ (23 pages); tables of measured and calculated structure factor amplitudes for $[\mathbf{1}]^+[BPh_4]^-\cdot NCMe$ (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[12] Chin, T. T.; Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1990**, *28*, 196.

[13] Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

[14] Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803.

[15] (a) Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001. (b) Hermann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978. (c) Herberhold, M.; Alt, H. *Liebigs Ann. Chem.* **1976**, 292, 300. (d) Brunner, H. *J. Organomet. Chem.* **1969**, *16*, 119.

[16] (a) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (b) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879. (c) Bond, A. M.; Colton, R.; Jackowski, J. *Inorg. Chem.* **1975**, *14*, 274.

[17] Lau, Y. Y.; Huckabee, W. W.; Gipson, S. L. *Inorg. Chim. Acta* **1990**, *172*, 41.