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Electronic Connections between Exceptional Low-Valent and High-Valent Organometallic Compounds: The Case of CpM(L)R_2 (M = W, Re; L = NO, O; R = Alkyl)

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Summary: The electronic structures of a d^2 high-valent and a 16-electron low-valent piano-stool compound are compared. The stability of each of these "electronically exceptional" complexes is attributed to the d orbital splitting pattern dictated by the ligands, in each case generating a nonbonding orbital.

High-valent organotransition-metal chemistry has been the subject of much recent chemical literature. Of the various types of high-valent organometallic systems known, those containing a metal–oxo bond have received considerable attention,[2] especially the rapidly growing family of piano-stool complexes containing at least one metal–oxo "leg". Over 20 such systems are already known involving formally d^0, d^1, or d^2 metal atoms.[3] We have been interested in extending our studies of low-valent piano-stool complexes into these seemingly very different high-valent systems and, in particular, to find whether an analogue to the 18-electron rule exists for the high-valent piano-stool complexes. Unlike the low-valent systems, there appears to be no preferred total valence electron count for the high-valent systems; molecules are known (in nearly equal numbers) with 14, 15, 16, and 18 electrons. The greatest number of high-valent piano-stool complexes are formally d^0, perhaps the closest we can get to an electronic structural pattern exhibited by them. We have previously demonstrated that molecular orbital theory can be used to explain deviations from the 18-electron rule for low-valent piano-stool complexes,[4] and it is in this spirit that we compare here the electronic structures of two structurally similar and electronically exceptional complexes, namely, the non-18-electron low-valent system CpW(NO)(CH$_2$CMe$_3$)$_2$[4] (**1**; Cp = η^5-C$_5$H$_5$) and the "non-d^0" high-valent system Cp*Re(O)(CH$_3$)$_2$[5] (**2**; Cp* = η^5-C$_5$Me$_5$). It will be shown that the electronic factors which are responsible for the stability of low-valent **1** operate in a directly converse manner in order to stabilize the high-valent **2** and that these concepts can be used to explain the wide variation in d count found for high-valent piano-stool complexes. complexes.

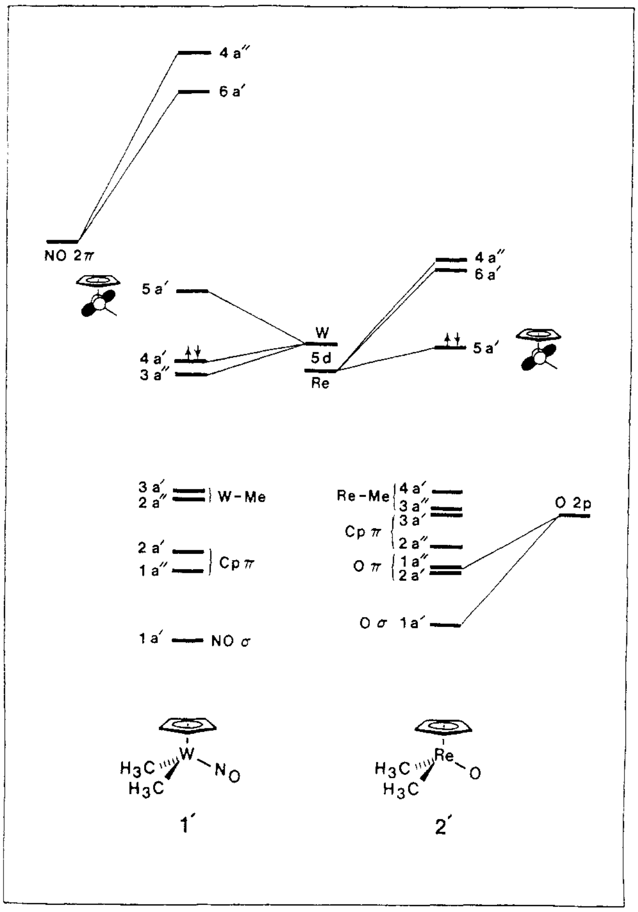

Figure 1. Molecular orbital diagrams displaying the frontier orbital regions of CpW(NO)Me$_2$ (**1′**) and CpRe(O)Me$_2$ (**2′**). The arrows indicate the highest occupied molecular orbital in each complex.

Figure 1 shows the comparative frontier orbital diagrams for the model compounds CpW(NO)(CH$_3$)$_2$ (**1′**) and CpRe(O)(CH$_3$)$_2$ (**2′**) as calculated by the Fenske–Hall molecular orbital method.[6] The electronic structure of the Mo analogue of **1′** has been discussed previously;[4] however, it will be useful to point out its relevant features here. The nitrosyl ligand acts as a very strong π-acceptor and interacts with the W 5d orbitals to stabilize two levels significantly. Because the methyl ligands function only as σ-donors,[8] the 5a′ orbital remains nonbonding. This

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(1) Camille and Henry Dreyfus Foundation Teacher–Scholar (1984–1989) and Fellow of the Alfred P. Sloan Foundation (1985–1987).

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(6) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775. The atomic parameters used for **1′** were taken from the crystal structure of CpW(NO)(CH$_2$SiMe$_3$)$_2$,[4] and the geometry was idealized to C_s symmetry. For **2′**, a normal three-legged piano-stool geometry was assumed along with the following bond distances: Re–O = 1.70 Å, Re–C(Me) = 2.11 Å, Re–C(Cp) = 2.342 Å, and C–C(Cp) = 1.413 Å. The atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[7] Contracted double-ζ representations were used for the W and Re 5d AO's and for the N, C, and O 2p AO's. For W and Re, the 6s exponents were fixed at 2.0 and the 6p exponents were fixed at 1.6 and 1.8, respectively.

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(8) The π-type orbitals of the methyl fragment are very low in energy and do not interact with the frontier metal-based orbitals to such an extent as to affect the argument. However, the π-interactions of alkyl groups have, in some cases, been shown to be important. See, for example: (a) Hoffman, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221–6223. (b) Hoffmann, R. *Pure Appl. Chem.* **1970**, *24* 567–584. (c) Lowe, J. P. *J. Am. Chem. Soc.* **1970**, *92*, 3799–3800. (d) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351–1358.

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results in a large splitting of the metal "t_{2g}" set (descending from O_h symmetry) such that this orbital is 2.23 eV above the other two. Compound 1′ is unusual in that it is a formally d^4, 16-electron complex and its stability is attributed to the strong splitting of the metal orbitals which concomitantly results in a substantial separation between the HOMO and LUMO. It is the strong π-acidity of the NO ligand in conjunction with a ligand set that by necessity generates a nonbonding d orbital which causes this splitting and allows such a complex to exist. Consistent with this, the carbonyl analogue (CO is generally considered to be a weaker π-acceptor ligand than NO^+[9-11]) $CpM(CO)R_2$ (M = Mn, Tc, or Re) is not known and would not be expected to be stable.

If we compare the molecular orbital picture of 2′ (right half of Figure 1) to that of 1′, the opposite picture emerges. The oxo ligand is a very good π-donor (as well as a good σ-donor) and interacts with the Re 5d orbitals to strongly destabilize two levels. This leads to a formal metal–oxo triple bond consisting of one σ- and two π-contributions.[12] As in 1′, the methyl ligands are σ-only donors, and, once again, the geometry dictates that one d orbital (5a′) remains nonbonding. Compound 2′ contains Re in the +5 oxidation state (d^2); therefore, the nonbonding 5a′ becomes the HOMO. As before, it is the large splitting of the pseudo-t_{2g} set which allows for a substantial separation (2.36 eV, comparable to that in 1′) to exist between filled and unfilled levels. However in 1′ the splitting was the result of strong π-accepting from nitrosyl to stabilize two orbitals below one, whereas in 2′ the converse effect is observed as strong π-donation from the oxo ligand destabilizes two orbitals above one.

As was mentioned earlier, most low-valent organometallic complexes adhere to the 18-electron rule, a rule that is especially relevant when all three of the pseudo-t_{2g} orbitals are stabilized as in $CpM(CO)_3$ (M = Mn, Re).[13] The fact that the 16-electron 1 is an exception to this rule was explained by the electronic properties of its nitrosyl ligand and by the geometric generation of a nonbonding d orbital. The 18-electron analogue of 1 would be expected to be stable since the additional two electrons would reside in the nonbonding 5a′ orbital and a substantial HOMO–LUMO gap would still be present. Consistent with this analysis, $CpRu(NO)(CH_2SiMe_3)_2$ has been prepared.[14] In the case of high-valent organometallic complexes the 18-electron rule is no longer valid as the d levels are generally destabilized by π-donors and would rather remain unoccupied. Indeed, all known piano-stool systems containing at least two oxo ligands (thereby guaranteeing that all three pseudo-t_{2g} orbitals are destabilized) are d^0 as is the case for $CpW(O)_2R$,[3b] $CpMo(O)_2X$,[3c] or Cp^*ReO_3.[3d] The nonbonding orbital generated in 2′ allows for the violation of this "d^0 rule".[15] Further, just as the 18-electron analogue of 1′ can be generated by occupying its nonbonding orbital, it is to be expected that the d^0 analogue of 2′ (which results from the *removal* of electrons from its nonbonding orbital) should exist. Such a compound, namely, $CpV(O)Ph_2$,[3a] is known. In fact, for the series $CpM(O)Cl_2$ (which is homologous to the oxo–alkyl complexes discussed above), d^0 (M = V,[3e] d^1 (M = Mo),[3c] and d^2 (M = Re)[3f] examples are known, underscoring the facility with which the nonbonding orbital can be occupied and deoccupied.

We believe that molecular orbital theory can prove to be very useful in understanding the connections between the relatively mature area of low-valent organometallic chemistry and the relatively unexplored area of high-valent organo transition-metal chemistry. To this end, subsequent contributions will address such connections in both mono- and dinuclear piano-stool systems.

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[15] The "d^0 rule" will be presented in greater detail in a subsequent contribution addressing the electronic structures of the series $CpML_n$ where L = O, CO, or CH_3 and $n = 3$: McKee, S. D.; Cayton, R. H.; Bursten, B. E. Presented at the 19th Central Regional Meeting of the American Chemical Society, Columbus, OH, June 1987; paper 258.

Reaction of (μ-C_7H_7)Ru(CO)$_3$Rh(CO)$_2$ with Bis(diphenylphosphino)methane: Conclusive Demonstration of the Importance of Cycloheptatrienyl Ring Slippage in CO Substitution Reactions

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Summary: The reaction of (μ-C_7H_7)Ru(CO)$_3$Rh(CO)$_2$ with bis(diphenylphosphino)methane (DPPM) gives (μ-C_7H_7)(μ-DPPM)Ru(CO)$_2$Rh(CO). The progress of the reaction was followed by low-temperature ^{31}P NMR spectroscopy. This allowed the identification of two well-defined intermediates prior to final product formation and conclusively established that CO substitution proceeds via hapticity changes of the bridging cycloheptatrienyl moiety.

According to currently held wisdom, ring slippage accompanied by η^5 to η^3 bonding mode changes is responsible for both the associative nature of the substitution process in cyclopentadienyl[1] and indenyl[2] metal carbonyls and for the greatly enhanced reactivity of the latter type compounds over their cyclopentadienyl analogues (the "indenyl effect"[3]). Recently ligand-induced η^5 to η^3 conversion was conclusively demonstrated by the isolation and structural characterization of (η^3-indenyl)IrL$_3$ (L = P(CH$_3$)$_3$, P(CH$_3$)$_2$(C$_6$H$_5$)) from (η^5-indenyl)Ir(η^2-cyclooctene)$_2$.[4]

During our studies on the ^{13}CO/CO exchange and phosphine substitutional processes in (μ-C_7H_7)Fe(CO)$_3$Rh(CO)$_2$ we were led to postulate similar hapticity changes of the bridging C_7H_7 ring in order to account for the facility of these reactions.[5] Here we wish to report direct and unambiguous NMR evidence that substantiates this proposal.

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