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$X\alpha$–SW Studies of Metal–Ligand Back-Bonding in Metal Carbonyls: 2π or Not 2π?

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There have been questions concerning the bonding in metal carbonyl compounds as predicted by the $X\alpha$ scattered-wave ($X\alpha$–SW) molecular orbital method. In a 1972 paper concerning the electronic structure of $Ni(CO)_4$, Johnson and Wahlgren (JW)[1] state, "There is no evidence for any significant metal-to-ligand 2π back-donation in $Ni(CO)_4$." A similar conclusion was reached for $Cr(CO)_6$ by Johnson and Klemperer (JK),[2] who state, "... (the Cr–C) bonding is predominantly σ in character with only a small π contribution." These authors cite the vibrational displacement interaction coordinates[3] of $Cr(CO)_6$ as support for their calculation. The conclusions of both of these calculations have been challenged. Larsson and Braga,[4] by use of a rather interesting albeit nonquantitative analysis of muffin-tin radial distribution functions, have concluded that there is significant 2π back-bonding in $Ni(CO)_4$. More recently, Sherwood and Hall[5] have disputed the JK analysis by demonstrating that the vibrational interaction data for $Cr(CO)_6$ are consistent with significant metal–ligand back-bonding.

In this note we will quantify the degree of back-bonding predicted by the $X\alpha$–SW calculations on $Cr(CO)_6$ and $Ni(CO)_4$ through the use of our projected $X\alpha$ ($PX\alpha$) method.[6] This formalism allows us to avoid the ambiguities inherent to the interpretation of $X\alpha$–SW charge distributions as well as facilitating the transformation of the molecular orbitals by the canonical orbitals of CO. It will be shown that the interpretations offered by JW and JK underestimate the degree of M→CO 2π back-bonding in both molecules.

Calculational Section

The $X\alpha$–SW calculations on $Cr(CO)_6$ and $Ni(CO)_4$ employed overlapping atomic spheres. For $Cr(CO)_6$, the atomic coordinates, sphere radii, and partial wave basis were identical with those used by JK.[2] For $Ni(CO)_4$, the following bond distances and sphere radii (both in au) were used: Ni–C = 3.460; C–O = 2.135; r(outer) = 7.217; r(Ni) = 2.174; r(C) = 1.605; r(O) = 1.622. Calculations on CO were performed by using the same C and O sphere radii as the corresponding metal carbonyl.

The Slater orbital basis used in the $PX\alpha$ calculations were optimized for maximum overlap with Herman–Skillman atomic calculations on neutral Cr, Ni, C, and O.[7] Contracted double-ζ metal 3d and ligand 2p STO's were used; all other basis orbitals were single ζ. The quadrature used for both molecules consisted of 25 radial points, 9 θ points, and 18 ϕ points. The MO's were transformed by the $PX\alpha$ MO's for free CO, for which the 6σ orbital was determined by Schmidt orthogonalization to the 3σ, 4σ, and 5σ orbitals.

Results and Discussion

The analyses of the $Cr(CO)_6$ and $Ni(CO)_4$ molecular orbitals by JK and JW were derived principally through the use of atomic sphere charges and orbital contour plots. The atomic spheres analysis suffers from several deficiencies: (1) The charge in the intersphere and outer-sphere regions cannot be unambiguously assigned to any given atom, precluding a detailed analysis of all the interactions in an orbital. (2) In $X\alpha$–SW calculations performed with overlapping atomic spheres, the charge in the overlap region is double counted.[8] (3) There is no way to quantitatively compare the orbitals of a complex to those of a free ligand, and hence it is impossible to quantify the effects of allowing a ligand to interact with a metal. The LCAO molecular orbitals yielded by the $PX\alpha$ method overcome all of these difficulties and should give a more accurate and useful description of the M–CO bonding.

Table I. Orbital Energies and Mulliken Percent Characters for the $5e_g$, $2t_{2g}$, $3t_{2g}$, and $6e_g$ Orbitals of $Cr(CO)_6$

orbital	ϵ, eV	Cr 3d	CO 5σ	CO 1π	CO 2π
$6e_g$[b]	−1.90	51	31		
$3t_{2g}$	−2.23	21		0	79
$2t_{2g}$[a]	−6.22	74		6	19
$5e_g$	−11.78	33	67		

[a] Highest occupied orbital. [b] Contains 18% CO 6σ character.

Our discussion of $Cr(CO)_6$ will focus on the occupied $5e_g$ and $2t_{2g}$ orbitals and the virtual $3t_{2g}$ and $6e_g$ orbitals. These are the only MO's containing >2% Cr 3d character. The orbital energies and Mulliken percent characters for the $5e_g$, $2t_{2g}$, $3t_{2g}$, and $6e_g$ orbitals are presented in Table I. It is clear that there is significant CO σ donation and π acceptance in the molecule. The $5e_g$ orbital contains 33% Cr 3d character, indicative of strong CO 5σ → Cr 3d donation. More importantly, the highest occupied $2t_{2g}$ orbital contains 19% CO 2π character due to back-bonding from the Cr 3d to the empty CO 2π orbitals. The $6e_g$ and $3t_{2g}$ MO's are the antibonding counterparts of the $5e_g$ and $2t_{2g}$ orbitals, respectively. They both show extensive metal–ligand interaction, supporting the conclusion that the Cr–CO bonds are highly synergic. The total Mulliken orbital populations indicate that 1.42 e is donated to and 1.25 e is back-donated from the Cr 3d orbitals. Similarly, for $Ni(CO)_4$ our results show a total of 1.11 e back-donated from the Ni 3d orbitals to the CO 2π orbitals; this is offset by forward donation from the carbonyls into the empty Ni 4s and 4p orbitals. The back-donation of 0.2–0.3 e/CO in these compounds represents strong π back-bonding, contravening the JK and JW conclusions.

We believe that the major fault in the JK and JW analyses lies in the overreliance on the $X\alpha$–SW atomic sphere charges and orbital contour plots. Contour diagrams, although aesthetically pleasing, can be misleading and seemingly inconsistent with the atomic spheres charge distribution. As an example, we shall consider the 4π orbital of the linear triatomic molecule FeCO.[9] This orbital, shown in Figure 1, represents the major component of Fe 3d → CO 2π back-bonding. The $X\alpha$–SW orbital has been projected onto an AO basis, allowing consideration of the individual atomic contributions to the orbital. Thus, the top diagram represents the contribution to the orbital from the Fe atom only, the middle diagram shows only the CO contribution, and the bottom contour is the total orbital. Two observations are notable. First, it is apparent from the middle diagram that the CO contribution to the orbital is essentially pure 2π. This is not clear in the bottom diagram, however, for the mixing of the metal and carbon contours obscures the comparison of relative carbon and oxygen contributions to the MO. Second, because the carbon atomic orbitals are more diffuse than those of oxygen, a greater fraction of the carbon charge density will "spill out" into the intersphere region. Thus the oxygen atom will have a greater atomic sphere population than that of the carbon, despite the

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(9) The calculation on FeCO was performed by using nonoverlapping spheres. The assumed bond distances (in au) were Fe–C = 3.420 and C–O = 2.135.

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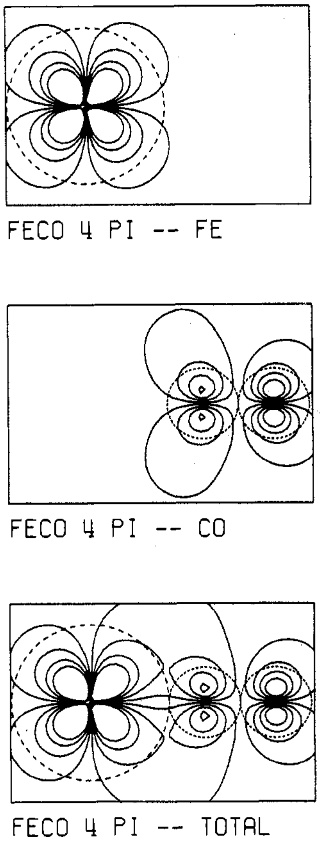

Figure 1. Contour diagrams of the 4π orbital of FeCO. The dashed circles represent the atomic sphere boundaries. Relative contour values, from outermost to innermost, are ±1, ±2, ±4, and ±8, where the contours change sign at the nodes: top diagram, the Fe contribution to the orbital only; middle diagram, the CO contribution to the orbital only; bottom diagram, the total orbital.

fact that there is more carbon than oxygen character in the orbital. This effect is noted in the $3t_{2g}$ orbital of $Cr(CO)_6$. The contour diagram of this orbital (Figure 4 of ref 2) clearly shows that the orbital is primarily CO 2π in character, yet the atomic spheres charge analysis attributes a greater fraction of the charge to the oxygen atoms. By using the PXα method we have circumvented these interpretative difficulties and have arrived at the chemically more reasonable conclusion that metal–ligand back-bonding is an important factor in metal–carbonyl bonding.

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Reactions of Coordinated Molecules. 24. Reaction of the Triacetyltricarbonylrhenate Dianion with the Boron Trihalides

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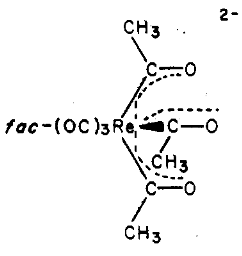
In an earlier communication we reported the preparation of the triacetyltricarbonylrhenate dianion, $[fac\text{-}(OC)_3Re(CH_3CO)_3]^{2-}$ (**1**), and its coordination to Al(III) and Hf(IV) metal ions.[2] This dianion coordinates to metal ions presumably as a symmetrical, tridentate chelating ligand as shown in **2**. Subsequently, we reported a general preparative route for the synthesis of these metalla ligands and their coordination complexes and confirmed their solution structure by demonstrating the existence of geometrical isomerism when one of the alkyl substituents of each ligand is not a methyl group.[3]



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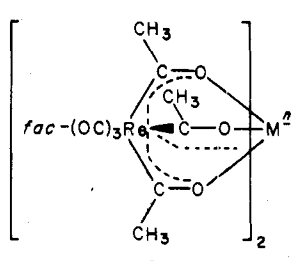

2

We wish to report that the dianion, **1**, reacts with the boron trihalides at −50 °C, affording the neutral (*fac*-triacetyltricarbonylrhenato)B(X) compounds, **3–6**, where X is F, Cl, Br, or I, in low to moderate yields, and that the boron bromide complex reacts with excess silver tetrafluoroborate in primary alcohol solutions, affording the neutral (*fac*-triacetyltricarbonylrhenato)B(OR) compounds, **9–11**, where R is methyl, ethyl, or *n*-propyl. These boron complexes are related to the (rhena-β-diketonato)BX_2 complexes,[4] and they represent an interesting class of neutral, four-coordinate boron compounds. To our knowledge these are the only known boron complexes having trioxygen, vicinal, bifurcated chelating ligands.[5,6] The tripodal ligand **1** formally contains two anionic oxygen donor atoms and one neutral oxygen donor atom; however, electronic delocalization within the boron complexes of **1** should alter the electronic environment of the boron atom quite considerably from that observed in the classical neutral boron adduct complexes.

Experimental Section

All reactions and other manipulations were performed under prepurified nitrogen at 25 °C unless otherwise stated. Tetrahydrofuran and hexane were dried over Na/K alloy, methylene chloride was dried over phosphorus pentoxide under a nitrogen atmosphere, and all solvents were distilled before use. Methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol were stored over 4A molecular sieves and were purged with nitrogen before use. Boron trifluoride and boron trichloride were purchased from K and K Laboratories (Plainview, NY) and Matheson Gas Products, respectively, while boron tribromide and boron triiodide were purchased from Alfa-Ventron. Silver tetrafluoroborate was purchased from Ozark-Mahoning Co. (Tulsa, OK). Acetylpentacarbonylrhenium was prepared according to an established procedure.[7]

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a JEOL MH-100 NMR spectrometer with Me_4Si as an internal reference. Mass spectra were obtained on a LKB 9000 spectrometer in the direct ionization mode. Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

General Preparation of the Complexes $[fac\text{-}(OC)_3Re(CH_3CO)_3]B(X)$ Complexes, 3–6. A solution of 0.20–0.41 g of acetylpentacarbonylrhenium in 30 mL of methylene chloride was cooled to 0 °C. To this solution was added 2.3 molar equiv of low halide methyllithium (as an ether solution), and the reaction mixture was stirred at 0 °C for 30 min. The solvent was removed at 0 °C under reduced pressure, and the reaction residue was dried at 0 °C under high vacuum for

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