The remaining goal of separating geometrical isomers has been successfully achieved (Figure 2). The sym-cis and uns-cis isomers of $[Co(EDDA)(en)]^+$ were rapidly eluted completely resolved from one another and in the same order as on TLC.

The loss of retention and resolution which was seen in the diastereomer separations upon increased loading occurs when the sample's adsorption isotherm is nonlinear.[10] The isotherm describes sample partitioning between the mobile and stationary phases as a function of the amount of sample applied. It is always advisable to operate in the linear portion of the isotherm so that retention (and hence resolution) are invariant with sample loading. Isotherm nonlinearity is an inherent property of each sample, solvent system, and stationary phase combination. Therefore a change in the solvent system is usually necessary to modify the isotherm so that larger samples can be accomodated. Lowering the polarity of the IS–TEA solvent system does not improve resolution and in many cases causes the sample to precipitate out of solution on contact with the mobile phase. We have yet to find another solvent system with comparable resolving power. Unless one can be found, 5–10-μ silica packing materials will be required to improve resolution greatly, increasing operating expenses and difficulties.

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Registry No. $[Co(en)_2(Tyr)](HCO_3)_2 \cdot NEt_3$, 76705-33-4; Λ-$[Co(en)_2(Tyr)]^{2+}$, 76740-68-6; Δ-$[Co(en)_2(Tyr)]^{2+}$, 76740-69-7; *sym-cis*-$[Co(EDDA)(en)]^+$, 20084-73-5; *uns-cis*-$[Co(EDDA)(en)]^+$, 28459-65-6; $[Co(en)_2(Asp)]^{2+}$, 76705-34-5.

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[10] Lloyd R. Snyder, "Principles of Adsorption Chromatography", Marcel Dekker, New York, 1968, pp 22–52.

Correspondence

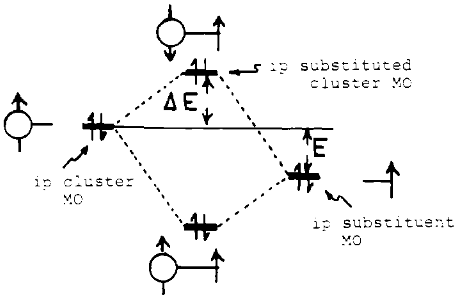
Nature of the Highest Occupied Molecular Orbital in $R_2C_2Co_2(CO)_6$

Sir:

Efforts have been made to rationalize the behavior of compounds containing metal–metal (M–M) bonds in terms of properties associated with the M–M interaction.[1] As numerous examples of bridged dinuclear complexes exist, these compounds have played a prominent role in the investigations of systems containing a M–M bond. Experimental[2,3] studies as well as theoretical work[4-7] indicate that the LUMO in these systems is a M–M antibonding orbital of b_2 symmetry. On the other hand, we have pointed out that for $S_2Fe_2(CO)_6$, at least, there is no ionization associated with a M–M bonding orbital that is strongly favored in an energetic sense over electron removal from the other metal orbitals.[8] Recent SCF-Xα-SW calculations[9] support this conclusion and the previous suggestion that the HOMO is an orbital having M–M bonding character and little contribution from the bridging ligand. At face value, this would agree with the model for the redox behavior of compounds containing a M–M bond in which the primary effect of oxidation is a reduction in the M–M bond strength.[1] However, the latest calculations[9] also demonstrated an intimate role for the bridging ligand in the net M–M interaction, thereby suggesting that orbital ordering might well be significantly different with ligands of lower electronegativity. In the following, we demonstrate experimentally that the HOMO in $R_2C_2Co_2(CO)_6$ is a bridging ligand–metal orbital rather than a "simple" M–M bonding orbital. This shows that the nature of the highest filled metal orbitals in bridged dinuclear metal complexes is a sensitive function of the bridging atoms and oxidative behavior in these compounds cannot be simply described in terms of a perturbation of the M–M interaction.

The nature of the HOMO in $(R_2C_2)Co_2(CO)_6$ is revealed by shifts in ionizations associated with electron removal from bridging ligand–metal orbitals caused by changing R. The two bands in the gas-phase UV photoelectron spectrum of pertinent interest here are shown in Figure 1.[10] These bands correspond to the ionization of MO's with large Co 3d character and in the compound with R = H band 1 contains one metal–metal bonding (a_1), two bridging ligand–metal bonding (a_2, b_1), and six metal "nonbonding" ($2a_1$, $2b_2$, a_2, b_1) ionizations while band 2 contains two bridging ligand–metal bonding (a_1, b_2) ionizations.[11] This assignment is based on the relative intensity of all observed bands, relative intensity measurements as a function of photon energy, and the spectra of model compounds, e.g., $Co_2(CO)_8$, as well as simple orbital arguments. General band character as well as ordering has been verified with the use of nonparameterized calculations.[12] The a_1 metal–metal bonding and a_2, b_1, a_1, b_2 bridging ligand–metal orbitals constitute five of the six orbitals providing the primary bonding of the C_2Co_2 core, the last four correlating with the π^* and π orbitals of free acetylene.[7] The ionizations corresponding to these last four orbitals are expected to be sensitive to π substituents, i.e., substituents with filled orbitals having π symmetry with respect to the C–R axis.

Substituent effects in photoelectron spectra are described in a particularly simple fashion by using a filled orbital model (LCBO–MO),[13] essential features of which appear in I. (The



I

$$-\beta = \left[\Delta E^2 + E\Delta E\right]^{1/2}$$

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[1] See for example: Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1. Vahenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.

[2] Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

[3] Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1980**, *102*, 156.

[4] Mason, R.; Mingos, D. M. P. *J. Organomet. Chem.* **1973**, *50*, 53.

[5] Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103.

[6] Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 423.

[7] (a) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126. (b) Anderson, A. B. *Ibid.* **1976**, *15*, 2598.

[8] Andersen, E. L.; Fehlner, T. P. *Inorg. Chem.* **1979**, *18*, 2325.

[9] Andersen, E. L.; Fehlner, T. P.; Foti, A. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1980**, *102*, 7422.

[10] These spectra were obtained with He(I) radiation at a sample temperature of 25 °C.

[11] This nomenclaure is drawn from Thorn and Hoffmann (ref 7) and constitutes oversimplification of the situation; e.g., in $S_2Fe_2(CO)_6$ there is a distinguishable a_1 M–M bonding orbital whereas in the isoelectronic $B_2H_6Fe_2(CO)_6$ there is not. However, for the purposes of this discussion it is retained.

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symbol combining a circle and an arrow represents a cluster MO and the upward arrow alone represents a substituent MO both of which have π symmetry with respect to the substituent–cluster bond.) The net substituent shift, ΔE, consists of two parts: an inductive effect (not shown), usually small, affecting all bands uniformly and a conjugative shift (represented by I) which can be large and of the same or opposite sign of the inductive shift, affecting only those bands directly coupled to the substituent. The latter shift depends on E, net overlap of the adjacent atoms, and the intrinsic strength of the interaction and is expressed with an interaction parameter β. These properties of the conjugative shift allow substituent effects to be used to identify specific ionizations in the parent compounds, i.e., to assign components of a complex band.

The changes in the photoelectron spectra for R = CH_3 are shown in Figure 1, and a line representation of the interactions is shown in Figure 2. With the use of the "nonbonding" Co 3d band as a measure of the inductive effect, introduction of CH_3 causes a shift of band 2 to lower ionization potential and a small, but real, shift of a component of band 1 in the same direction. The former demonstrates a measurable, conjugative, substituent effect on the a_1,b_2 pair in the expected direction. Thus, a similar, but smaller, substituent shift on the a_2,b_1 pair should be observed and the change in band 1 on substitution is attributed to just such an effect. As there is no reason to believe methyl substitution will cause an increase in ionization potential for any of the d ionizations, the shoulder on band 1 of the parent compound that becomes a separate band on methyl substitution is associated with ionization of a bridging ligand–metal orbital (either the a_2 or b_1). Finally, as energies of cation states tend to predict too high energies for metal MO's with respect to ligand MO's (Koopmans' defects),[14] these results show that the HOMO of $H_2C_2Co_2(CO)_6$ is associated primarily with metal–bridging ligand bonding.[15]

The results of nonparameterized calculations fully support this conclusion. On methyl substitution the a_2, b_1, a_1, b_2 bridging ligand–metal orbitals pick up 0.65%, 2.40%, 6.77% and 3.90% methyl character, respectively. Treating the calculated eigenvalues for substituted and unsubstituted molecules in the same manner as the PES bands (Figure 2) yields substituent interaction parameters −0.94 and −1.63 eV which may be compared to the experimental values (see Figure 2) of −0.8 and −1.5 eV.[16] The calculations demonstrate that the major substituent effect is with the b_1 and a_1 orbitals and, thus, that the HOMO is the b_1 bridging ligand–metal orbital.[17]

A complete description of the spectra and calculations will be forthcoming in due course.[18]

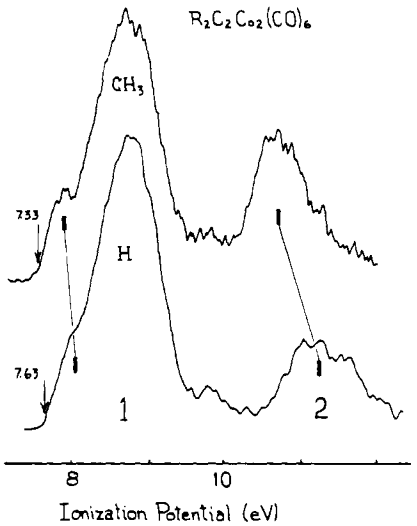

Figure 1. Co 3d region of the photoelectron spectra of $C_2H_2Co_2(CO)_6$ and $(CH_3)_2C_2Co_2(CO)_6$. The spectrum of the latter has been shifted 0.21 eV to higher ionization potential to remove the inductive shift caused by methyl substitution.

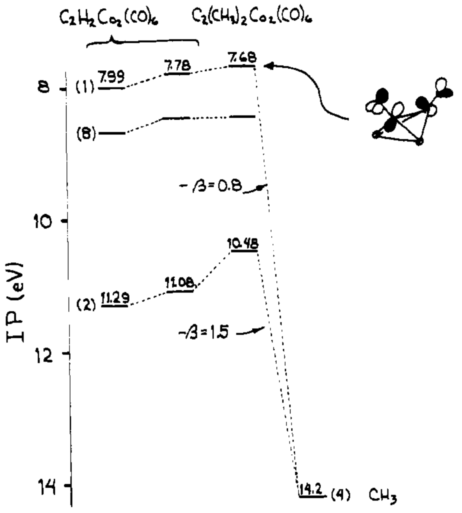

Figure 2. Line representation of the PES of $C_2(CH_3)_2Co_2(CO)_6$ resulting from the interaction of the filled methyl substituent orbitals with the filled bridging ligand–metal orbitals of $C_2H_2Co_2(CO)_6$. The second set of levels from the left represents the spectrum of $C_2H_2Co_2(CO)_6$ shifted by 0.21 eV to lower ionization potential representing the inductive shift $\Delta\alpha$. The parameter β is the conjugative interaction parameter and is defined in ref 13. The numbers in parentheses indicate the number of ionizations in each band represented by a line in this diagram.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE 79-15220) and the University of Notre Dame Computer Center and the support of T.L. as an NSF undergraduate research participant are gratefully acknowledged. Thanks are due Professor M. B. Hall for his aid with the Fenske–Hall calculations.

Registry No. $C_2H_2Co_2(CO)_6$, 12264-05-0; $(CH_3)_2C_2Co_2(CO)_6$, 37726-81-1.

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(12) These calculations are of the Fenske–Hall type: Hall, M. B.; Fenske, R. F. *Inorg. Chem* **1972**, *11*, 768. Hall, M. B. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1971. Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61.

(13) (a) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734. (b) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* **1974**, *96*, 2757.

(14) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45.

(15) The same conclusion results from an analysis of the spectra of $(C_6H_5)_2C_2Co_2(CO)_6$ and $[(C_6H_5)CCH]Co_2(CO)_6$.

(16) The calculations, however, place the a_1 M–M bonding orbital above the a_2 and b_1 bridging ligand–metal orbitals by 0.57 and 1.37 eV, respectively. This illustrates the danger of using the results of a calculation in an absolute sense.

(17) The calculations indicate that there are two b_1 symmetry orbitals that are significantly affected by methyl substitution; however, the second one is buried in the Co 3d band and the substituent shift cannot be observed.

(18) Another study of the $R_2C_2Co_2(CO)_6$ system has appeared: Van Dam, H.; Stufkens, D. J.; Oskam, A.; Doran, M.; Hillier, I. H. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 47. On the basis of ΔSCF calculations they conclude that the HOMO in $H_2C_2Co_2(CO)_6$ is a_1; however, the b_2 orbital (b_1 in our notation) is calculated to be only 0.2 eV more stable. Although substituent effects were not interpreted, the assignment otherwise agrees with that reported herein.