reduction. Here, z is defined as the number of electrons added per ruthenium. In a 1-cm cell, ϵ_{eff} at a defined wavelength is given by eq A2, and in eq A3 in terms of the extinction coefficients and mole fractions (f) of the component absorbing species, Ru(II), Ru(III), and Ru(IV).

$$\epsilon_{eff} = \text{absorbance}/[\text{Ru}](\text{total}) \qquad (A2)$$

$$\epsilon_{eff} = f_{II}\epsilon_{II} + f_{III}\epsilon_{III} + f_{IV}\epsilon_{IV} \qquad (A3)$$

$$f_x = [\text{Ru}(x)]/[\text{Ru}(\text{total})]$$

At 477 nm

$$\epsilon_{II} = 9600\ M^{-1}\cdot\text{cm}^{-1};\ \epsilon_{III} = 620\ M^{-1}\cdot\text{cm}^{-1};\ \epsilon_{IV} = 600\ M^{-1}\cdot\text{cm}^{-1}$$

Equations A4 through A6 follow from definitions already given.

$$f_{II} + f_{III} + f_{IV} = 1 \qquad (A4)$$

$$200 = K = f_{III}^2/f_{II}f_{IV} \qquad (A5)$$

$$2f_{II} + f_{III} = z \qquad (A6)$$

Using eq A2 through A6 and the plot of Figure 5, the experimentally obtained absorbance vs. time curves can be converted into z vs. time curves, which give the normalized extent of reduction vs. time. In terms of z, the rate equation is given by eq A7.

$$dz/dt = 2k_{IV}f_{IV}[S] + 2k_{III}f_{III}[S] \qquad (A7)$$

The factors of 2 in eq A7 take into account the stoichiometries of the oxidations by Ru(III) and Ru(IV). dz/dt is readily obtainable at any time from the slope of the z vs. time plot. Slopes were determined either by computer calculation or by visual estimate by using a ruler without a noticeable difference in results. Rearrangement of eq A7 gives eq A8, which predicts that plots

$$(dz/dt)/(f_{IV}[S]) = 2k_{IV} + dk_{III}(f_{III}/f_{IV}) \qquad (A8)$$

of $(dz/dt)/f_{IV}[S]$ vs. f_{III}/f_{IV} should yield straight lines of slope $2k_{III}$ and intercept $2k_{IV}$. f_{III} and f_{III}/f_{IV} were calculated from the absorbance vs. time curve using eq A2 through A6. In Figure 6 is shown an actual plot of experimental data plotted as suggested by eq A8.

Straight lines were fitted to data points using a simple linear least-squares program and a Texas Instruments 59 programmable calculator. Each reported rate constant was determined from the average of at least 18 measurements. Experimental uncertainties were estimated from the manufacturer's reported error limits and the scatter observed in a series of measurements on a given system.

Registry No. $Ru(trpy)(bpy)O^{2+}$, 73836-44-9; $Ru(trpy)(bpy)OH^{2+}$, 81971-63-3; $Ru(bpy)_2(py)O^{2+}$, 76582-01-9; $Ru(bpy)_2(py)OH^{2+}$, 75495-07-7; $(CH_3)_2CHOH$, 67-63-0.

Weak Metal–Metal Bonds in an "Electron-Rich" Cluster. The Synthesis and X-ray Crystallographic Characterization of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ and $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$

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Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received December 7, 1981*

Abstract: The thermal decomposition of $HOs_3(CO)_{10}(\mu\text{-}SPh)$ in refluxing nonane leads to the elimination of benzene and formation of the known sulfidoosmium carbonyl clusters $H_2Os_3(CO)_9(\mu_3\text{-}S)$ (**1**) and $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**2**) in addition to the new higher nuclearity clusters $Os_4(CO)_{12}(\mu_3\text{-}S)$ (**3**), $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (**4**), and $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (**5**). The molecular structures of **4** and **5** were established by X-ray crystallographic methods; for **4**, space group $P\bar{1}$; $a = 8.491$ (2) Å; $b = 9.240$ (2) Å; $c = 14.389$ (5) Å; $\alpha = 80.54$ (2)°; $\beta = 85.94$ (2)°; $\gamma = 68.31$ (5)°; $Z = 2$, $\rho_{calcd} = 3.728$ g/cm³. The structure was solved by the heavy-atom method. Least-squares refinement on 2930 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals $R_1 = 0.032$ and $R_2 = 0.034$. **4** contains a butterfly cluster of four osmium atoms with sulfido ligands bridging the two open triangular faces and three carbonyl ligands on each metal atom. Electron counting shows that **4** is a 64-electron cluster and and thus should contain only four metal–metal bonds. However, the structural analysis shows the existence of five metal–metal bonds, although two are significantly elongated with internuclear separations of 3.091 (1) and 3.002 (1) Å. The relationship of the bonding in this cluster to current theories of cluster bonding is described and discussed. For **5**, space group $P2_1/c$; $a = 10.083$ (4) Å; $b = 12.633$ (4) Å; $c = 21.383$ (4) Å; $\beta = 91.73$ (2)°; $Z = 4$, $\rho_{calcd} = 4.03$ g/cm³. The structure was solved by a combination of direct methods (MULTAN) and difference-Fourier techniques. Least-squares refinement on 2629 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals $R_1 = 0.038$ and $R_2 = 0.039$. The structure of **5** contains a square-pyramidal cluster of five osmium atoms with a quadruply bridging sulfido ligand spanning the square base. The sixth metal atom bridges two metal atoms in the square base, and this group of three is capped by a triply bridging sulfido ligand. Sixteen linear carbonyl ligands cover the "surface" of the cluster.

The electronic structures and bonding in transition-metal cluster complexes are currently a topic of great interest and importance, but it is one that also lacks a fully uniform explanation.[1] The bonding in clusters containing up to four metal atoms can usually be explained through the traditional two-center–two-electron bonding model.[1-3] In higher nuclearity polyhedral clusters, molecular orbital treatments have successfully explained irregular electron counts.[1-6] As one might expect, there may be a family of important molecules that does not fall readily into either class. We have now synthesized the cluster compound $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ and feel that it may be a prototype for such anomalous clusters.

We have found that the thermal decomposition of (arenethiolato)osmium carbonyl hydride clusters provides a new route

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[1] Wade, K. in "Transition-Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980.

[2] Johnson, B. F. G.; Benfield, R. E. *Top. Stereochem.* **1981**, *12*, 253.

[3] Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99.

[4] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[5] Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1974**, 133.

[6] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

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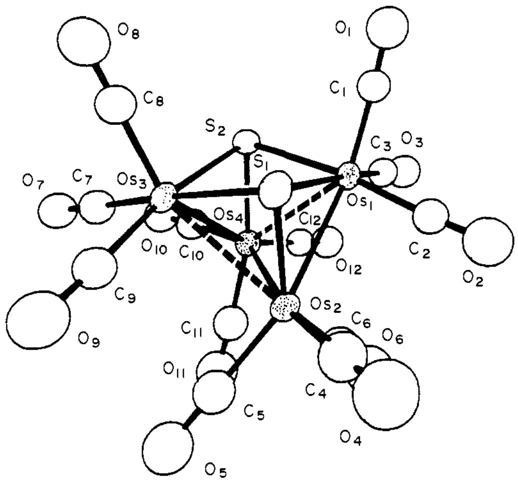

Figure 1. An ORTEP drawing of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (**4**) showing 50% electron-density probability ellipsoids.

to a variety of higher nuclearity sulfidoosmium carbonyl clusters (eq 1). From the thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$[7] (nonane

$$HOs_3(CO)_{10}(\mu\text{-}SPh) \xrightarrow{151\ °C} \underset{\mathbf{1}\ (\text{trace})}{H_2Os_3(CO)_9(\mu_3\text{-}S)} + \underset{\mathbf{2}\ (\sim 10\%)}{Os_3(CO)_9(\mu_3\text{-}S)_2} + \underset{\mathbf{3}\ (\sim 10\%)}{Os_4(CO)_{12}(\mu_3\text{-}S)} + \underset{\mathbf{4}\ (<2\%)}{Os_4(CO)_{12}(\mu_3\text{-}S)_2} + \underset{\mathbf{5}\ (\sim 15\%)}{(\mu_4\text{-}S)(\mu_3\text{-}S)Os_6(CO)_{16}} \quad (1)$$

reflux/10 h) we have isolated (in order of elution by TLC) the compounds shown in eq 1. Percentage yields are shown in parentheses. Copious amounts of benzene (>90% yield by GC analysis) are also formed, and except for trace amounts of **1**, none of the products contain hydride ligands.

1[8] and **2**[9] are known compounds, but **3**, **4**, and **5**[10] are new.[12] **3** contains a tetrahedral cluster of four metal atoms with three carbonyl ligands on each metal and an inorganic sulfide ligand bridging one of the threefold faces.[13] It is analogous to the compound $Os_4(\mu\text{-}NMe)(CO)_{12}$ recently reported by Kaesz.[15]

The structure of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (**4**) is shown in Figure 1.[16-18] The molecule consists of a butterfly cluster of four osmium atoms with sulfido ligands bridging the two "open" triangular faces and three carbonyl ligands on each metal atom. The internuclear separations in the core of the cluster suggest the existence of five metal–metal bonds. However, two of these, Os(1)–Os(4) = 3.091 (1) Å and Os(2)–Os(3) = 3.002 (1) Å, are long, while the other three, Os(1)–Os(2) = 2.914 (1) Å, Os(2)–Os(4) = 2.935 (1) Å, and Os(3)–Os(4) = 2.940 (1) Å, are significantly shorter and compare favorably with the Os–Os single-bond distance of 2.877 (3) Å found in $Os_3(CO)_{12}$.[19] Electron counting shows that the cluster core contains 64 electrons,[20] but an "electron-precise" tetranuclear cluster with five metal–metal bonds would have a closed-shell configuration of 62 electrons.[1-3] In this sense, **4** can be regarded as electron rich. However, electronic configurations of transition-metal clusters such as these can be rationalized within the framework of the skeletal electron-pair theory.[1,2] By viewing the Os_4S_2 core as a nido-cluster based on the pentagonal-bipyramidal polyhedron, one would predict, according to the skeletal electron-pair theory, the existence of a stable structure with five uniform, albeit weakened, metal–metal bonds. The presence of long and short metal–metal bonds shows that **4** does not fit readily into either category. Apparently, **4** would like to break one bond, but instead opts for two weak ones. We believe these distortions in the cluster core then lead to the arrangement of carbonyl ligands such that the molecular symmetry is reduced to approximately C_2.[21] Other examples of electron-rich (64 electron) tetranuclear clusters with anomalous metal–metal bonding that have appeared in the recent literature are $Ru_4(CO)_{13}(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}PPh_2)$,[22] $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$,[23] and $Ru_4(CO)_8$[glyoxal bis(isopropylimine)]$_2$.[24] All are butterfly clusters with heteronuclear bridging ligands. The first has two adjacent elongated metal–metal bonds, the second has three elongated metal–metal bonds, and the third has only one elongated bond.

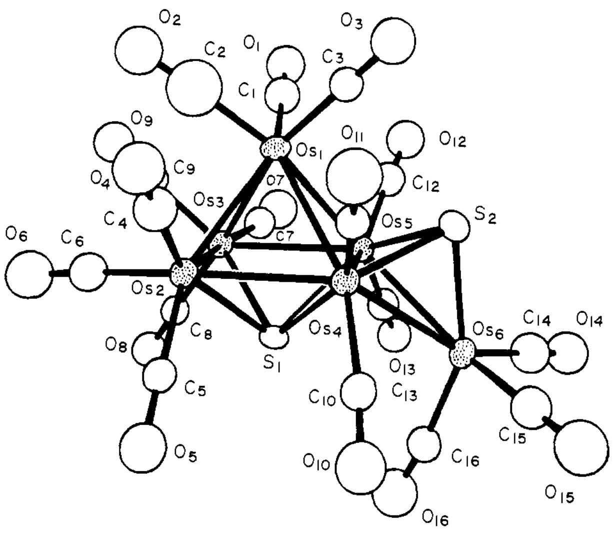

Figure 2. An ORTEP drawing of $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (**5**) showing 50% electron-density probability ellipsoids.

The importance of this electron-rich, "incipient" cleavage upon the reactivity of the cluster has yet to be realized, but its implications are obvious. Binuclear oxidative addition[25] should be facilitated, and the cleavage of metal–metal bonds should play a key role in this process. In this regard, the structure of the molecule $H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2$ should be mentined for comparison.[9] Its structure is analogous to that of $H_2Os_4(CO)_{12}(\mu_3\text{-}Se)_2$ (**6**), which contains an Os_4 cluster with only three metal–metal bonds.[9] It is thus an electron-precise, 66-electron cluster (i.e., all bonds

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(7) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797.

(8) Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* **1972**, *42*, C60.

(9) Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1979**, 719.

(10) Small amounts of this compound have also been obtained by the reaction of $Os_3(CO)_{12}$ with elemental sulfur.[9,11]

(11) Johnson, B. F. G., private communication.

(12) ^1H NMR spectroscopy of **3**, **4**, and **5** showed no resonances, even at low temperatures, that could be attributed to hydride ligands. The molecular formulas of **3** and **4** have been confirmed by mass spectrometry.

(13) The structure of **3** was established by an X-ray crystallographic analysis:[14] IR ν_{CO} in hexane solvent 2060 s, 2055 vs, 2007 m, 2000 m sh, 1973 w cm^{-1}.

(14) Adams, R. D.; Yang, L. W., to be published.

(15) Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, C41.

(16) Space group: $P\bar{1}$, No. 2; $a = 8.491\ (2)$ Å; $b = 9.240\ (2)$ Å; $c = 14.389\ (5)$ Å; $\alpha = 80.54\ (2)°$; $\beta = 85.94\ (2)°$; $\gamma = 68.31\ (5)°$; $M_r = 1161.05$; $Z = 2$; $\rho_{calcd} = 3.728$ g/cm^3. The structure was solved by the heavy-atom method. For 2930 reflections $F^2 \geq 3.0\sigma(F_o^2)$, least-squares refinement produced the final residuals $R_1 = 0.032$ and $R_2 = 0.034$. IR ν_{CO} in hexane, 2069 vs, 2062 vs, 2055 vs, 2015 m, 2010 m, 1992 s cm^{-1}.

(17) All crystallographic programs were those of the Enraf-Nonius SDP Program Library, Version 16. All calculations were done on a Digital Equipment Corp. PDP 11/45 computer.

(18) Selected internuclear distances (Å) and angles (deg) for **4** are as follows: Os(1)–Os(2) = 2.914 (1), Os(1)–Os(4) = 3.091 (1), Os(2)–Os(4) = 2.935 (1), Os(2)–Os(3) = 3.002 (1), Os(3–Os(4) = 2.940 (1), S(1)···S(2) = 3.191 (2), Os(1)···Os(3) = 3.551 (1); Os(1)–Os(2)–Os(3) = 73.75 (1), Os(1)–Os(4)–Os(3) = 72.09 (1), Os(2)–Os(1)–Os(4) = 58.43 (1), Os(2)–Os(3)–Os(4) = 59.19 (1).

(19) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(20) Assuming the sulfide ligands both serve as four-electron donors.

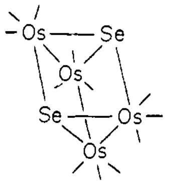
(21) It appears that the converse (i.e., preferred ligand arrangement induces cluster distortion) is not true since inspection of models indicates that a structure with C_{2v} symmetry would not produce any significant nonbonded repulsions among the CO ligands.

(22) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(23) Churchill, M. R.; Bueno, C.; Young, D. A. *J. Organomet. Chem.* **1981**, *213*, 139.

(24) Staal, L. H.; Polm, L. H.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3590.

(25) (a) Collman, J. P.; Hegedus, L. "Principles and Applications of Organotransition-Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 4. (b) Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.



6

are of the two-center, two-electron type). It could, in principle, be formed through the addition of 1 mol of H_2 to **4** accompanied by the complete cleavage of the two weak metal-metal bonds. In **6** these Os⋯Os distances have increased to approximately 4 Å.

The molecular structure of **5** is shown in Figure 2.[17,26,27] This hexanuclear cluster consists of a square-pyramidal group of five metal atoms with a rare quadruply bridging sulfido ligand, S(1), spanning the square base.[28] An $Os(CO)_3$ group bridges a pair of metal atoms in the square base, and that group of three is bridged by the second sulfido ligand. If both sulfido ligands serve as 4-electron donors, the molecule is electron precise and each metal atom achieves an 18-electron configuration.[29] Thus, all the metal-metal bonds are single, although the Os(4)-Os(5) separation at 2.686 (1) Å is short for an Os-Os single bond.[19] This shortening is probably due to the fact that the Os(4)-Os(5) bond contains four single-atom bridges, S(1), S(2), Os(1), and Os(6). A similar shortening was observed for an analogous metal-metal bond in the structurally related molecule $Os_6(CO)_{16}(\mu_4\text{-CMe})(\mu_3\text{-CMe})$. As one might expect, the Os-S distances to the quadruply bridging sulfide ligand, $\text{Os-}\mu_4\text{-S}_{av}$ = 2.44 (1) Å, are significantly longer than those to the triply bridging ligand, $\text{Os-}\mu_3\text{-S}_{av}$ = 2.34 (2) Å. The Os(1)⋯S(1) distance at 3.472 (4) Å is probably completely nonbonding. Sixteen linear carbonyl ligands cover the surface of the cluster.

In summary, we have now found that the elimination of benzene from (arenethiolato)osmium carbonyl hydride clusters provides a new and convenient route for the synthesis of higher nuclearity carbonyl clusters containing sulfido bridges.[31] Most importantly, as exemplified by **4**, there appears to be a class of polynuclear metal complexes containing heteronuclear bridges that has anomalous structural and bonding properties. This could have profound implications on reactivity and perhaps ultimately on the use of cluster compounds as catalysts.[32]

Acknowledgment. This research was supported by the National Science Foundation and by the A. P. Sloan Foundation through a fellowship to R.D.A.

Supplementary Material Available: Complete tables of fractional atomic coordinates, bond distances, and bond angles are available for structures **4** and **5** (9 pages). Ordering information is given on any current masthead.

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(26) Space group: $P2_1/c$, No. 14; a = 10.083 (4) Å; b = 12.633 (4) Å; c = 21.383 (4) Å; β = 91.73 (2)°; M_r = 1653.50, Z = 4; ρ_{calcd} = 4.03 g/cm³. The structure was solved by a combination of direct methods and difference-Fourier techniques. Least-squares refinement on 2629 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.038 and R_2 = 0.039. IR ν_{CO} (hexane) 2090 s, 2070 s, 2055 s, 2042 s, 2030 m cm^{-1}.

(27) Selected internuclear distances (Å) and angles (deg) for **5** are as follows: Os(1)-Os(2) = 2.849 (1), Os(1)-Os(3) = 2.833 (1), Os(1)-Os(4) = 2.888 (1), Os(1)-Os(5) = 2.843 (1), Os(2)-Os(3) = 2.884 (1), Os(1)-Os(4) = 2.781 (1), Os(3)-Os(5) = 2.863 (1), Os(4)-Os(5) = 2.686 (1), Os(5)-Os(6) = 2.828 (1), Os(1)⋯S(1) = 3.472 (4), Os(2)-S(1) = 2.432 (4), Os(3)-S(1) = 2.414 (4), Os(4)-S(1) = 2.440 (4), Os(5)-S(1) = 2.476 (4), Os(4)-S(2) = 2.352 (4), Os(5)-S(2) = 2.372 (4), Os(6)-S(2) = 2.285 (4); Os(2)-Os(3)-Os(5) = 87.42 (3), Os(3)-Os(2)-Os(4) = 88.54 (3), Os(2)-Os(4)-Os(5) = 93.15 (3), Os(3)-Os(5)-Os(4) = 90.86 (3), Os(1)-Os(5)-Os(6) = 122.68 (3), Os(1)-Os(4)-Os(6) = 120.49 (3).

(28) Wei, C. H.; Dahl, L. F. *Cryst. Struct. Commun.* **1975**, *4*, 583.

(29) **5** is structurally and electronically similar to the compound $Os_6(CO)_{16}(\mu_4\text{-C})(\mu_3\text{-MeC}{\equiv}\text{CMe})$, and both can also be rationalized within the framework of the skeletal electron-pair theory.[30]

(30) Eady, C. R.; Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 421.

(31) (a) Marko, L. *Gazz. Chim. Ital.* **1979**, *109*, 247. (b) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(32) (a) Sivak, A. J.; Muetterties, E. J. *J. Am. Chem. Soc.* **1979**, *101*, 4878. (b) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *Ibid.* **1977**, *99*, 743. (c) Muetterties, E. L.; Band, E.; Kokorin, A.; Pretzer, W. R.; Thomas, M. G. *Inorg. Chem.* **1980**, *19*, 1552. (d) Whyman, R. In "Transition-Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 8.

Substituent Effect of Chelated Cobalt. 5. Acidities of (Carboxymethyl)- and (1-Carboxyethyl)cobaloximes. A Quantitative Analysis of the β Effect[1,2]

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Abstract: pK_a's of the weakly acidic (carboxymethyl)(ligand)cobaloximes and (1-carboxyethyl)(ligand)cobaloximes with 16 different axial ligands have been determined and correlated with those of 11 substituted acetic acids or 9 1-substituted propionic acids, respectively. Comparison of apparent σ_I values thus calculated with those previously determined by correlation of (carboxyethyl)(ligand)cobaloxime pK_a's with the pK_a's of 2-substituted propionic acid indicates that the (1-carboxyalkyl)cobalt complexes show a substantial β effect as an apparent extreme donation of electron density to the carboxyl carbon. the β effect in these complexes has been quantitated by use of a dual substituent parameter equation, the results of which show that the effect is only some 8-10% enhanced in (1-carboxyethyl)cobaloximes relative to (carboxymethyl)cobaloximes. This result is consistent with the β effect being mediated by σ-π hyperconjugation rather than neighboring group participation. Structural effects on the extent of σ-π conjugation and the effects of σ-π conjugation on reactivity of the cobalt atom in these complexes are discussed.

(Carboxymethyl)cobalt complexes, including both cobalamins[3,4] and cobaloximes,[5-7] as well as several other carboxymethyl transition-metal complexes[6] are well-known to be extremely weak carboxylic acids with acidities ranging from 2 to 3 orders of magnitude lower than that of acetic acid. This phenomenon is

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[*] To whom correspondence should be addressed at The University of Texas at Arlington. All experimental work was performed at UTA.

(1) Part 4. Brown, K. L.; Lu, L.-Y. *Inorg. Chem.* **1981**, *20*, 4178-4183.

0002-7863/82/1504-4117$01.25/0 © 1982 American Chemical Society