

- (6) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
 (7) I. A. Cohen, *J. Am. Chem. Soc.*, **91**, 1980–1983 (1969); C. Maricondi, W. Swift, and D. K. Straub, *ibid.*, **91**, 5205–5210 (1969).
 (8) J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676–2681 (1975).
 (9) N. M. Karayannis, C. M. Mikulsi, L. L. Pytlewski, and M. M. Labes, *Inorg. Chem.*, **9**, 582–587 (1970).
 (10) C.-A. Yu, I. C. Gunsalus, M. Katagiri, K. Suhara, and S. Takemori, *J. Biol. Chem.*, **249**, 94–101 (1974).
 (11) P. M. Champion, E. Munck, P. G. Debrunner, P. F. Hollenberg, and L. P. Hager, *Biochemistry*, **12**, 426–435 (1973).
 (12) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 3994–4000 (1968).
 (13) W. McFarlane and R. F. M. White, *Chem. Commun.*, 744 (1969).
 (14) W. Strohmeier and F.-J. Müller, *Chem. Ber.* **100**, 2812–2821 (1967); C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953–2956 (1970).
 (15) C. A. Tolman, W. C. Seidel, and L. W. Goser, *J. Am. Chem. Soc.*, **96**, 53–60 (1974); W. C. Troglor and L. G. Marzilli, *Inorg. Chem.*, **14**, 2942–2948 (1975).
 (16) W. W. Adams and P. G. Linhart, *Acta Crystallogr., Sect. B.*, **29**, 2412–2425 (1973).
 (17) H. Eicher and A. Trautwein, *J. Chem. Phys.*, **50**, 2540–2551 (1969).

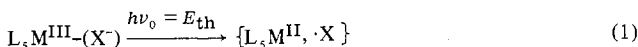
Correspondence

Homolytic Single-Bond Dissociation Energies and the Nature of the Coordinate-Covalent Bond¹

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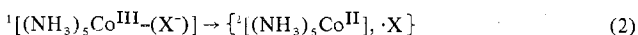
Sir:

Recent studies of photoredox reactions of transition metal complexes have resulted in reasonably good estimates of the minimum or threshold energy (E_{th}) required for the process described by eq 1.² Correlations of thermodynamic and



photochemical parameters indicate that most feasible processes occur with some sort of yield.² These values of E_{th} may be taken as measures of "single-bond dissociation energies" for homolytic bond cleavage in the respective transition metal complexes. It is the purpose of this correspondence to examine the bonding information contained in such threshold energies. Such an analysis should contribute to a better understanding of these complexes, especially of those in which the bonding has been claimed to be predominantly "ionic" (e.g., $FeBr^{2+}$)³ or unusually "covalent" (e.g., organo-cobalt bonds).⁴ Despite the contrasting descriptions of $FeBr^{2+}$ and the organo-cobalt complexes, homolytic processes occur in both kinds of systems following absorption of relatively low-energy radiation (e.g., $\lambda \geq 550$ nm).³⁻⁷

Components of Bond Dissociation Energies. At this time our most detailed information is for pentaammine complexes of cobalt(III). For these complexes E_{th} seems to be the energy difference between the singlet ground state and a radical pair containing the cobalt(II) fragment $Co(NH_3)_5^{2+}$ in its quartet ground state.^{2b,8} Comparisons of bond energy from compound to compound are simpler when not complicated by changes of spin multiplicity, and this requires consideration of a process yielding a thermally equilibrated doublet $Co(NH_3)_5^{2+}$ species. Since the difference in energy between high-spin (quartet) and low-spin (doublet) $Co(NH_3)_5^{2+}$ species has been estimated to be of the order of 48 kJ mol^{-1} ,^{2b,8} this quantity, ΔH_{spin} , may be added to the experimental threshold energies in order to estimate the homolytic bond dissociation energies, $\Delta H_B = E_{th} + \Delta H_{spin} - \Delta H_S$, for the spin-conservative process (2). The



solvation contribution to ΔH_B , ΔH_S , has been discussed elsewhere.^{2a,b}

The bond dissociation energies, ΔH_B , of $Co^{III}L_5(X^-)$ complexes are relatively large numbers, only approximately correlated to the crystal field strength, or the electronegativity, of the ligand oxidized (Figure 1): not unexpectedly the bond energy does not appear to approach zero as $Dq(X) \rightarrow 0$ or as $\chi_X \rightarrow \chi_{Co}$ (see Figure 1). The numerical values of ΔH_B are only about 10% smaller than the corresponding C-X bond energies. The large positive value of ΔH_B observed for $\chi_X \rightarrow$

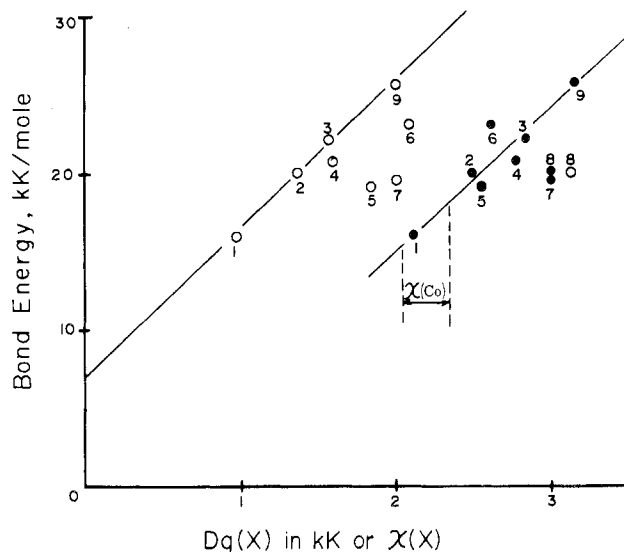
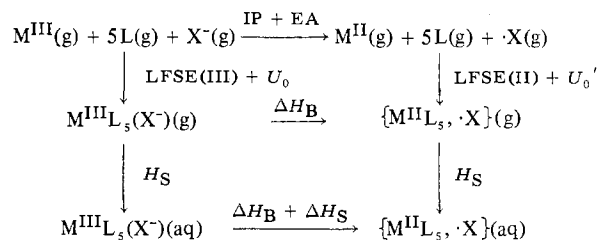


Figure 1. Correlation of homolytic bond dissociation energy (ΔH_B) with ligand field stabilization energy, $Dq(X)$, or electronegativity, χ , of the ligand oxidized. Open circles are for correlation to ligand field strength, closed circles for correlation to electronegativity. Complexes represented: 1, $Co(NH_3)_5I^{2+}$; 2, $Co(NH_3)_5Br^{2+}$; 3, $Co(NH_3)_5Cl^{2+}$; 4, $Co(NH_3)_5N_3^{2+}$; 5, $Co(NH_3)_5SCN^{2+}$; 6, $Co(NH_3)_5NCS^{2+}$; 7, $Co(C_2O_4)_3^{3-}$; 8, $Co(NH_3)_5NO_2^{2+}$; 9, $Co(EDTA)^-$.

Scheme I



χ_{Co} (Figure 1) might be interpreted in terms of a large covalent component except that one would expect a very weak $(NH_3)_5Co^{II}-Co^{II}(NH_3)_5$ bond.^{9,10} The homolysis component independent of the ligand X may be more reasonably attributed to the difference in ligand field stabilization energies ($\Delta LFSE$) of cobalt(III) and cobalt(II) pentaammines. The nonspherical components of $\Delta LFSE$ for process (2) may be readily estimated from parameters available in the literature (see Table II¹¹ and ref 12–14) and such estimates are included in Table I. Thus, we may write,¹⁵ per Scheme I, $\Delta H_B = (IP + EA + \Delta U_0) + \Delta LSFE$. The quantities in parentheses can be approximately related to the covalent or ionic character of the $M^{III}(X^-)$ bond, while the second term can be interpreted as a "distributed" contribution to bonding due to relative

Table I. Analysis of Chemical Bond Dissociation Energies^a in Some Cobalt(III) Complexes

Complex	E_{th}^b	ΔH_S^c	ΔH_B^- (obsd) ^d	-LFSE- (III) ^e	χ_X^f	Ionic 125(χ_X - 2.0) ^g	$4Dq(X)^e$	Δ - LFSE ^h	Covalent 7.2- (BE_{X_2}) ^{1/2} ⁱ	δ	ΔH_B^- (calcd) ^j
Co(NH ₃) ₅ Cl ²⁺	310	83	273	285	2.83	86	74	83	35	190	278
Co(NH ₃) ₅ Br ²⁺	260	73	236	273	2.74	68	66	80	31	156	245
Co(NH ₃) ₅ I ²⁺	198 ^k	55	~186	265	2.21	6	46	91	30	~95	173
Co(NH ₃) ₅ NO ₂ ²⁺	248	(60)	236	354	2.6	46	(149) ^l	77	18	159	(290)
Co(NH ₃) ₅ N ₃ ²⁺	259 ^m	(60)	247	281	2.77	74	75	79	<i>n</i>	168	≥228
Co(NH ₃) ₅ NCS ²⁺	285 ^m	(60)	273	313	2.61	47	99	86	<i>n</i>	187	≥232
Co(NH ₃) ₅ SCN ²⁺	236 ^o	(60)	225	294	2.53	35	88	90	<i>n</i>	135	≥213
Co(EDTA) ⁻	319	(60)	306	255	3.16	170	95	50	≤26 ^p	256	≤341
Co(C ₂ O ₄) ₃ ³⁻	244	(60)	233	187	3.0	125	95	8	≤24 ^p	225	≤253

^a All tabulated energy quantities are in kJ. ^b Data from ref 2b except as indicated. ^c Estimated from the bandwidth of Ru(NH₃)₅X²⁺ for X = Cl, Br, I; the Franck-Condon terms appear to be largely due to solvation effects in the ruthenium complexes.^{2a,b} The other values used are based on these numbers and " $\lambda_0/4$ " values discussed elsewhere.^{2a,b} In principle only the nonequilibrium part of the polarization should contribute to ΔH_S ; since the experimental bandwidths of Ru(NH₃)₅X²⁺ complexes are comparable to the nonequilibrium polarizations estimated^{2b} by the approach of R. A. Marcus (*J. Phys. Chem.*, **67**, 853 (1963); **72**, 891 (1968); *Annu. Rev. Phys. Chem.*, **15**, 155 (1964)), we have used the experimental bandwidths. ^d $\Delta H_B = (E_{th} + \Delta H_{spin}) - \Delta H_S$ where $\Delta H_{spin} \approx 47$ kJ (see ref 2, 12, 14). ^e For Co^{III}L₅X, LFSE(III) = -24 Dq(L) + 5B + 8C + 14Dt. Values of Dq, B, C, and Dt used are mostly from Wentworth and Piper¹⁹ and are tabulated in Table II.^{11,15} ^f Allred-Rochow (A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1959)) values for Cl, Br, and I; optical electronegativities² have been used for all others. Note that the scale of optical electronegativities used is in reasonably good agreement with the Allred-Rochow values where these are available. ^g χ_{Co} has been chosen as 2.0. The optical electronegativity of Co(III), based on charge-transfer absorption maxima, is 2.3;^{2,12} charge-transfer absorption maxima and thresholds differ by about 120 kJ or the equivalent of 0.3 electronegativity unit. Electronegativity values 2.0 < χ_{Co} < 2.3 are adequate (but not equivalent) in the present application. ^h $\Delta LFSE = LFSE(Co^{III}L_5) - LFSE(Co^{II}L_5)$. $LFSE(Co^{III}L_5) = LFSE(III) + 4Dq(X)$; $LFSE(Co^{II}L_5) \approx -15Dq'(L) + 4B' + 4C'$, where $(4B' + 4C') \approx 95$ kJ and $Dq(L) \approx 2Dq'(L)$. ⁱ Bond energies of X₂ are from F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972. $(BE_{Co_2})^{1/2}$ was adjusted to best fit data for Co(NH₃)₅X (X = Cl, Br, I). ^j $\Delta H_B(\text{calcd}) = 10.5(\chi_X - 2.1)^2 + 4Dq(X) + \Delta LFSE(CoL_5) + 0.9(BE_{X_2})^{1/2}$. ^k Based on the charge-transfer absorption threshold. ^l $Dq(NO_2)$ probably contains appreciable " π " components. ^m Reference 2c. ⁿ Data not available. ^o N. Sutin, private communication. ^p $(RCO_2)_2$ BE taken as less than or equal to the bond energy of HO-OH.

stabilization of nonbonding electrons in the nonspherical ligand field of the complex. That is, the average "localized" bonding component is approximately given by $\delta = \Delta H_B - \Delta LFSE$.¹⁶ This part of the total energy of homolysis includes a substantial component [equal to $4Dq(X)$] of the LFSE of M^{III}L₅(X⁻). Using literature parameters,^{17a,17-19} the available data for process (2) are reasonably fitted to (3) with $(BE_{Co_2})^{1/2} \approx 7.2$

$$\Delta H_B = \{125(\chi_X - \chi_{Co})^2 + [(BE_{Co_2})(BE_{X_2})]^{1/2}\} + 4Dq(X) + \Delta LFSE \quad (3)$$

$\text{kJ}^{1/2}$. The quantity $\{\delta - 4Dq(X)\}$ is related to classical bonding descriptions of saturated molecules of the main-group elements. The quantity $\Delta LFSE$ is due to electronic interactions distributed over the remainder of the molecule (somewhat analogous to the resonance energy associated with the C-C homolysis of benzene); this "distributed" component varies from 3% to 50% of the total homolysis energy in the cobalt(III) complexes considered in Table I. Since one would expect the Co^{II}-Co^{II} bond in (L₅Co)₂ to be weak, the small (~10%) "covalent" contributions to the total homolysis energy are reasonable.

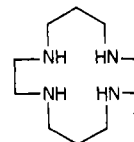
Applications. This approach provides a convenient means for analysis of the homolytic dissociation energies of several other systems. The small energy for homolysis of FeBr²⁺ ($\Delta H_B < 130$ kJ mol⁻¹)³ compared to that for Co(NH₃)₅Br²⁺ is readily seen to originate in $\Delta LFSE \approx 0$ for FeBr²⁺, rather than in an exceptionally ionic Fe^{III}-Br⁻ bond (note that $\chi_{Fe} \approx \chi_{Co}$).

The onset of homolysis for Rh(NH₃)₅I²⁺ is in the middle of the lowest energy $I(\pi) \rightarrow Rh^{III}$ charge-transfer band and corresponds to $\Delta H_B \approx 303$ kJ mol⁻¹.²⁰ Since $\Delta LFSE$ should be about 50% greater for rhodium than cobalt and since $\chi_{Rh} \approx \chi_{Co}$,^{2a,12} this implies that the Rh-I bond has a far larger covalent component than the Co-I bond, consistent with the established formation of Rh^{II}-Rh^{II} bonds under relatively mild conditions.²¹

The onset for homolysis of Cr(NH₃)₅Br²⁺ is in the middle of the highest energy ligand field quartet band²² and corresponds to a value of $\Delta H_B = 261$ kJ mol⁻¹. By using the Jorgensen relationship¹² and by comparison to Co^{III}(NH₃)₅X

(see ref 2a), the lowest energy X⁻ → Cr^{III} charge-transfer transitions of chromium complexes can be fitted with an optical electronegativity of about 1.85; this suggests $\chi_{Cr} \approx 1.55$ (see footnote g of Table I). Using this and the pertinent literature parameters¹⁹ one may estimate $125(\chi_{Br} - \chi_{Cr})^2 \approx 177$ kJ mol⁻¹, $\Delta LFSE(CrL_5) \approx 69$ kJ mol⁻¹, and $2Dq(Br) \approx 27$ kJ mol⁻¹, so that $\Delta H_B(\text{calcd}) \approx 273$ kJ mol⁻¹ provided the "covalent" component is negligible (i.e., very weak Cr^{II}-Cr^{II} bond).

A particularly interesting but less straightforward application of the proposed partitioning is to organo-cobalt complexes. Recent studies of cobalt-methyl complexes containing synthetic macrocyclic ligands have shown that Co-CH₃ homolysis occurs with $E_{th} < 217$ kJ mol⁻¹ for Co([14]tetraeneN₄)(OH₂)CH₃²⁺ and Co([14]aneN₄)(OH₂)CH₃²⁺.^{7,23} The latter observation is most striking since the electronic absorption spectrum of Co([14]aneN₄)(OH₂)CH₃²⁺

[14]aneN₄

is particularly "simple", exhibiting two weakly allowed transitions with λ_{max} 478 and 367 nm (ϵ 81 and 104, respectively)²⁴ and a charge-transfer transition with λ_{max} 205 nm ($\epsilon \sim 10^4$). The transition at 478 nm would be consistent with a value of $\Delta LFSE \approx 210$ kJ mol⁻¹ for Co-CH₃ homolysis, assuming a traditional analysis of "ligand field" transitions. Together with a covalent component estimated to be ~ 135 kJ mol⁻¹, this would result in an estimated value of $\Delta H_B(\text{calcd}) \approx 340$ kJ mol⁻¹. In fact the quantum yield for Co-CH₃ cleavage has been found to be nearly independent of excitation energy for 254 nm $\leq \lambda \leq 540$ nm⁷ so that $\Delta H_B(\text{obsd}) < 220$ kJ mol⁻¹ (assuming $\Delta H_S \approx 0$ and that low-spin Co^{II}(N₄) products are formed). These observations demonstrate that the Co-CH₃ bond is very weak and imply that $\Delta LFSE$ is very small for these complexes.

The observed weakness of the Co-CH₃ bond has further implications which are best illustrated with reference to Co([14]aneN₄)(OH₂)CH₃²⁺. If the bonding and antibonding molecular orbitals describing the formation of Co(N₄)-(OH₂)CH₃²⁺ from Co(N₄)OH₂²⁺ and ·CH₃ are designated as Φ(Co-Me) and Φ*(Co-Me), respectively, then in the approximately C_{4v} symmetry of the complex the Φ(Co-Me) → Φ*(Co-Me) transition should be strongly allowed. The only strongly allowed transitions for this complex occur in the ultraviolet region and must correspond to equilibrated orbital energies equivalent to or greater than 429 kJ mol⁻¹. In order to be consistent with ΔH_B < 220 kJ mol⁻¹, this requires a relatively more significant contribution of the exchange integral to the Φ(Co-X) orbital energy for the organo-cobalt complexes than for the halo-cobalt complexes;^{7,25,26} i.e., the organo-cobalt bonds are appreciably more covalent than the halo-cobalt bonds.

The spectroscopy of the synthetic methyl-cobalt complexes will be discussed in detail elsewhere.^{7b} For present purposes it will suffice to note that a value of ΔH_B ≈ 200 kJ mol⁻¹ suggests that Φ(Co-Me) is relatively high in energy and that the lowest energy transitions observed for Co([14]aneN₄)-(OH₂)CH₃²⁺ can be assigned as Φ(Co-Me) → d_{x²-y²} and d_{xy} → d_{x²-y²}, both of which are symmetry forbidden. The inference that Φ(Co-Me) is relatively high in energy is consistent with a very small distributed component in the wave function. Thus the spectroscopic and photochemical observations argue that the ligand field model is not useful for cobalt-methyl complexes; this is undoubtedly a consequence of the negligible electron affinity of the methyl radical.²⁸ While the spectroscopic analysis is not as simple for complexes containing unsaturated equatorial ligand systems, similar patterns of low-energy Co-CH₃ homolysis are manifested in methyl-cobalamin^{5,6,29} and related complexes,^{7,29-31} and the inferences drawn for Co([14]aneN₄)(OH₂)CH₃²⁺ must be reasonably similar for these systems as well.

Acknowledgment. The author is grateful for some helpful discussions with Dr. G. J. Ferraudi and Professor R. L. Lintvedt and for some provocative and critical comments from Professor T. L. Brown.

Registry No. Co(NH₃)₅Cl²⁺, 14970-14-0; Co(NH₃)₅Br⁺, 15376-36-0; Co(NH₃)₅I²⁺, 15392-08-2; Co(NH₃)₅NO₂²⁺, 14482-68-9; Co(NH₃)₅N₃²⁺, 14403-83-9; Co(NH₃)₅NCS²⁺, 14970-18-4; Co(NH₃)₅SCN²⁺, 15005-69-3; Co(EDTA)⁻, 15136-66-0; Co(C₂O₄)₃³⁻, 15053-34-6.

Supplementary Material Available: Table II, listing the crystal field parameters used in calculating quantities for Table I (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Partial support of this research by the National Science Foundation (Grants GP 36888X and CHE 76-00429) and by the Public Health Service (Grant AM 14341) is gratefully acknowledged.
- (2) (a) J. F. Endicott, *Concepts Inorg. Photochem.*, Chapter 3 (1975); (b) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975); (c) G. J. Ferraudi, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **97**, 6406 (1975); (d) P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, **77**, 2049 (1973).
- (3) S.-N. Chen, N. N. Lichtin, and G. Stein, *Science*, **190**, 879 (1975).
- (4) J. M. Pratt, "The Inorganic Chemistry of Vitamin B₁₂", Academic Press, New York, N.Y., 1972.
- (5) J. M. Pratt and B. R. D. Whitear, *J. Chem. Soc. A*, 252 (1971).
- (6) R. T. Taylor, L. Smucker, M. L. Hanna, and J. Gill, *Arch. Biochem. Biophys.*, **156**, 521 (1973).
- (7) (a) C. Y. Mok and J. F. Endicott, submitted for publication; (b) in preparation.
- (8) J. F. Endicott and G. J. Ferraudi, *Inorg. Chem.*, **14**, 3133 (1975).
- (9) Although dimeric (CN)₁₀Co₂⁹⁺ species have been identified,⁷ the solution species are generally believed to be monomeric and no evidence has yet been found for Co-Co bonding in low-spin cationic cobalt(II) complexes.
- (10) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed., Interscience, New York, N.Y., 1972, p 879; (b) L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **94**, 7664 (1972); (c) G. L. Simon, A. W. Adamson, and L. F. Dahl, *ibid.*, **94**, 7654 (1972); (d) A. W. Adamson *ibid.*, **73**, 5710 (1951).

- (11) Supplementary material.
- (12) (a) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Elmsford, N.Y., 1962; (b) "Oxidation Numbers and Oxidation States", Springer-Verlag, New York, N.Y., 1969; (c) "Modern Aspects of Ligand Field Theory", North-Holland Publishing Co., Amsterdam, 1971.
- (13) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968.
- (14) M. Gerloch and R. C. Slade, "Ligand-Field Parameters", Cambridge University Press, London, 1973.
- (15) IP = third ionization potential of Co; EA = electron affinity of ·X. U₀ and U₀' contain the spherical components of the ligand field potentials and bond energy terms referenced to the free metal ion for M^{III}L₅X and M^{II}L₅, respectively.
- (16) ΔLFSE(ML₅) = LFSE(Co^{II}L₅) - LFSE(Co^{III}L₅).
- (17) J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, N.Y., 1972.
- (18) L. Pauling, "The Nature of the Chemical Bond", 3d ed., Cornell University Press, Ithaca, N.Y., 1960.
- (19) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).
- (20) T. L. Kelley and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972).
- (21) (a) F. Maspero and H. Taube, *J. Am. Chem. Soc.*, **90**, 7361 (1968); (b) C. R. Wilson and H. Taube, *Inorg. Chem.*, **14**, 405 (1975).
- (22) R. Sriram and J. F. Endicott, submitted for publication.
- (23) [14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane; [14]tetraeneN₄ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
- (24) T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1575 (1974).
- (25) We are grateful to Professor H. B. Gray for a useful discussion of some of these points.
- (26) In view of the present state of our knowledge, many of the numerical details of the above argument must be regarded as illustrative. Thus it is not altogether obvious that the Co-C bond is a "pure σ bond" with a covalent component of about 135 kJ mol⁻¹. Nevertheless it is evident that the ionic (χ_{CH₃} ≈ 2.3²⁷) component of ΔH_B is very small and that "ΔLFSE" < 70 kJ mol⁻¹.
- (27) Reference 17, p 167.
- (28) For example see J. E. Williams, Jr., and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).
- (29) J. F. Endicott and G. J. Ferraudi, submitted for publication.
- (30) (a) C. Giannotti and J. R. Bolton, *J. Organomet. Chem.*, **80**, 379 (1974); (b) C. Giannotti and G. Merle, VIIth International Conference on Photochemistry, Edmonton, Canada, August 7-13, 1975, Paper X2; (c) C. Giannotti, private communication.
- (31) For some conditions of photolysis it appears that the predominant products resulting from low-energy irradiations of alkylbis(dimethylglyoximate)cobalt complexes are not cobalt(II) and an alkyl radical.³⁰ This raises the possibility of competing photochemical processes but does not demonstrate a high-energy threshold for homolysis. There is no reason to expect that the Co-CH₃ bond strength should be profoundly altered by the nature of the equatorial ligand.

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Correlations of the Vibrational Stretching Frequencies of Transition Metal Thiocarbonyls with Those of Their Carbonyl Analogues. Comparison of the Bonding Characteristics of Carbon Monosulfide and Carbon Monoxide Ligands

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Sir:

Transition metal thiocarbonyls¹ have been examined by a variety of techniques with the goal of comparing the ligating properties of CS with those of its better known homologue CO. The M-CS bond has been shown to be stronger than the corresponding M-CO bond by x-ray crystallography² and mass spectrometry.^{1,3} The source of this greater metal-thiocarbonyl bond strength has been probed by molecular orbital calculations,^{4,5} photoelectron spectroscopy,⁵ infrared spectroscopy,^{3,6-9} mass spectrometry,³ Mössbauer spectroscopy,¹⁰ and ¹³C NMR spectroscopy.^{7,11} Depending on the specific technique and compound used, the π-acceptor to σ-donor ratio for coordinated CS appears to be either greater^{6b,7,9,11} or smaller^{3,7,9}