The observed weakness of the Co–CH_3 bond has further implications which are best illustrated with reference to $Co([14]aneN_4)(OH_2)CH_3^{2+}$. If the bonding and antibonding molecular orbitals describing the formation of $Co(N_4)(OH_2)CH_3^{2+}$ from $Co(N_4)OH_2^{2+}$ and $\cdot CH_3$ are designated as Φ(Co–Me) and Φ^*(Co–Me), respectively, then in the approximately C_{4v} symmetry of the complex the $\Phi(\text{Co–Me}) \rightarrow \Phi^*(\text{Co–Me})$ 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 $\Delta H_B < 220$ 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 $\Delta H_B \approx 200$ kJ mol^{-1} suggests that Φ(Co–Me) is relatively high in energy and that the lowest energy transitions observed for $Co([14]aneN_4)(OH_2)CH_3^{2+}$ can be assigned as $\Phi(\text{Co–Me}) \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$, 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–CH_3 homolysis are manifested in methylcobalamin[5,6,29] and related complexes,[7,29–31] and the inferences drawn for $Co([14]aneN_4)(OH_2)CH_3^{2+}$ must be reasonably similar for these systems as well.

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Registry No. $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^+$, 15376-36-0; $Co(NH_3)_5I^{2+}$, 15392-08-2; $Co(NH_3)_5NO_2^{2+}$, 14482-68-9; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(EDTA)^-$, 15136-66-0; $Co(C_2O_4)_3^{3-}$, 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

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(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 ($\chi_{CH_3} \approx 2.3$[27]) component of ΔH_B is very small and that "ΔLFSE" < 70 kJ mol^{-1}.
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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 thiocarbonyls[1] 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 crystallography[2] 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 ^{13}C 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]

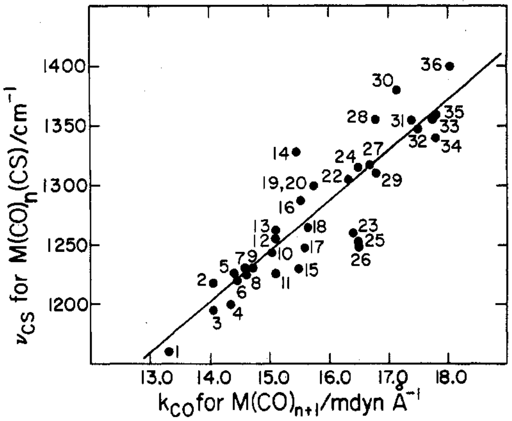

Figure 1. Plot of ν_{CS} for $M(CO)_n(CS)$ vs. CO stretching force constant for $M(CO)_{n+1}$.

than for coordinated CO. Recent evidence suggests that CS may also function as a π donor.[5] It will be shown that a unified description of the bonding can be derived by examining a greater cross section of the known thiocarbonyls. Specifically, a crossover in the relative electronic properties of CS and CO exists which can be correlated semiquantitatively with the carbonyl stretching force constant of the parent carbonyl complex. This reversal is a result of the basic similarity of CS and CO as ligands coupled with a greater adaptability of CS to its total coordination environment.

The only comprehensive data currently available for use in the analysis of metal thiocarbonyls are the CS (and, if also present, CO) stretching frequencies. Table I lists the reported spectra for a series of carbonyl complexes, $M(CO)_{n+1}$, and their thiocarbonyl analogues, $M(CO)_n(CS)$. When applicable, literature or calculated Cotton–Kraihanzel[12] CO stretching force constants have also been included.[13]

We turn first to an examination of the CS stretching frequency. Figure 1 shows that ν_{CS} in $M(CO)_n(CS)$ increases as k_{CO} for the CO it replaces in $M(CO)_{n+1}$ increases. A linear least-squares analysis[15] indicates that they are correlated at greater than 99.9% significance (correlation coefficient R = 0.90 for 35 points) by the relationship

$$\nu_{CS} = 42.62k_{CO}[M(CO)_{n+1}] + 604.0$$

A similar correlation of low CS stretching frequencies with long CS bond distances has been reported recently.[2] Both of these trends are consistent with a σ-donor–π-acceptor model for thiocarbonyls similar to that for carbonyls.[16] The relatively large standard deviation of ν_{CS} (25 cm^{-1}) is probably due to several factors. One is possible variations in the magnitude of the coupling between ν_{CS} and other vibrational modes, especially ν_{M-CS}.[1,6c] More important is the existence of an additional bonding mode for CS, π donation by the filled 2π orbitals.[5] This smaller secondary effect should be most pronounced for complexes with low π-electron density on the metal and would lead to anomalously low ν_{CS} values. Indeed, most of the compounds where ν_{CS} falls below the mean (**4**, **11**, **15**, **17**, **23**, **25**, **26**, and **34**) contain good π-acceptor ligands. Conversely, compounds where ν_{CS} falls above the mean (**14**, **19**, **20**, **28**, **30**, and **36**) contain π-donor ligands. The majority of other compounds contain intermediate combinations. Thus ν_{CS} for new thiocarbonyl complexes can be estimated from the CO stretching force constant of the generally available parent carbonyl complex.

For thiocarbonyls which also contain one or more carbonyls, an additional correlation can be derived. Carbonyl stretching force constants can be used to study the electronic properties of other ligands.[17] Variations in the relative bonding characteristics of two ligands, L_1 and L_2, can be examined by plotting k_{CO} in $M(CO)_n(L_2)$ vs. k_{CO} in $M(CO)_n(L_1)$.[18] If L_1 and L_2 have the same electronic and symmetry properties under all circumstances, then the pairs of CO force constants must always be equal, and the points will fall on the line $y = x$ (line A of Figure 2). This is nearly the case for L_2 = CS and L_1 = CO (line B of Figure 2). If, however, L_2 creates a higher electron density on the adjacent carbonyl(s) (e.g., by greater σ donation, lower π acceptance, greater direct donation,[16,19] or orbital symmetry–ligand competition effects[20]) than does L_1, then the points will fall below the line $y = x$. This follows from the relationship that exists between k_{CO} and the orbital occupancies of the carbonyl carbon lone pair (5σ) and π^* (2π) molecular orbitals.[16] This is illustrated by a few representative points for $L_2 = P(C_6H_5)_3$ and L_1 = CO (line C of Figure 2).

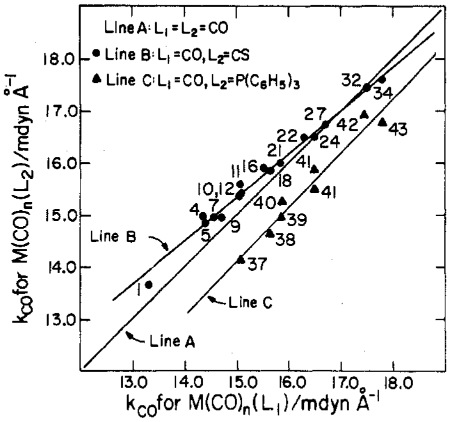

Figure 2. Plot of CO stretching force constant for $M(CO)_n(L_2)$ vs. CO stretching force constant for $M(CO)_n(L_1)$.

Although it is evident that CS and CO are basically similar ligands, a more careful analysis of Figure 2 reveals a subtle difference. A linear least-squares fit of the L_2 = CS and L_1 = CO case gives

$$k_{CO}[M(CO)_n(CS)] = 0.843k_{CO}[M(CO)_{n+1}] + 2.68$$

where the standard deviations of the slope, intercept, and calculated $k_{CO}[M(CO)_n(CS)]$ are 0.02, 0.38, and 0.12, respectively. This line is significantly different from $y = x$. The relationship is more apparent in Figure 3 where the results are replotted with the y axis representing the vertical difference between lines A and B of Figure 2. Figure 3 therefore represents the variations in the relative electronic properties of CS and CO as a function of k_{CO} for the parent carbonyl. Although the small differences between individual pairs of CO force constants are of doubtful significance,[13] trends of these differences can be meaningful. Thus, the least-squares correlation

$$k_{CO}[M(CO)_{n+1}] - k_{CO}[M(CO)_n(CS)] = 0.157k_{CO}[M(CO)_{n+1}] - 2.68$$

is significant at the 99% level (R = 0.85 for 16 points; standard deviation of slope 0.02 and of intercept 0.38). It can be seen from Figure 2 that the charge on the adjacent carbonyls (proportional to k_{CO}) varies less in $M(CO)_n(CS)$ than in $M(CO)_{n+1}$. This "charge buffering effect" requires that the charge on L_2 = CS must vary more than on L_1 = CO. This is a logical consequence of the ability of the soft CS group to undergo larger charge fluctuations than the harder CO group. (This also follows from the fact that the CS frontier orbitals are closer in energy to the metal d orbitals than are the CO frontier orbitals.) Coupled with the basic similarity of CS and CO, this phenomenon leads to a crossover in the relative electronic properties of CS and CO near $k_{CO}[M(CO)_{n+1}]$ = 17.1 mdyn/Å.

Table I. Carbonyl Stretching Frequencies, Carbonyl Stretching Force Constants, and Thiocarbonyl Stretching Frequencies for M(CO)$_n$(L) Complexes

No.	Compd	ν_{CO}, cm^{-1}	k_{CO},[a] mdyn Å^{-1}	ν_{CS}, cm^{-1}
	L$_1$ = CO and L$_2$ = CS			
1a	*cis*-W(CO)$_2$(diphos)$_2$[e]	1846, 1781	13.29	
1b	*cis*-W(CO)(CS)(diphos)$_2$[e]	1838	13.64	1161
2a	CpMn(CO)[P(OMe)$_3$]$_2$[f]	1865	14.05	
2b	CpMn(CS)[P(OMe)$_3$]$_2$[f]			1218
3a	[W(CO)$_5$I]$^-$[g]		14.05[b]	
3b	[*trans*-W(CO)$_4$(CS)I]$^-$[e]			1195
4a	(PhCOOMe)Cr(CO)$_2$P(OEt)$_3$[h]	1908, 1860	14.34	
4b	(PhCOOMe)Cr(CO)(CS)P(OEt)$_3$[i]	1926	14.98	1201
5a	CpMn(CO)$_2$PCy$_3$[j,gg]	1928, 1848	14.40	
5b	CpMn(CO)(CS)PCy$_3$[f]	1914 1923	14.86[c]	1226[c]
6a	CpMn(CO)[P(OPh)$_3$]$_2$[f]	1892	14.46	
6b	CpMn(CS)[P(OPh)$_3$]$_2$[f]			1219
7a	CpMn(CO)$_2$PPhMe$_2$[k]	1932, 1867	14.57	
7b	CpMn(CO)(CS)PPhMe$_2$[f]	1920 1928	14.95[c]	1231[c]
8a	W(CO)$_5$py[l]		14.59[b]	
8b	*trans*-W(CO)$_4$(CS)py[m]			1224
9a	CpMn(CO)$_2$PPh$_3$[n,o]	1934, 1874 1944, 1883	14.72[c]	
9b	CpMn(CO)(CS)PPh$_3$[f]	1925	14.96	1231
10a	CpMn(CO)$_2$(C$_8$H$_{14}$)[n]	1956, 1893	14.96	
10b	CpMn(CO)(CS)(C$_8$H$_{14}$)[p]	1951	15.37	1242
11a	(PhCOOMe)Cr(CO)$_3$[h]	1985, 1905	15.07	
11b	(PhCOOMe)Cr(CO)$_2$(CS)[i]	1992, 1939	15.60	1225
12a	CpMn(CO)$_2$P(OPh)$_3$[n]	1963, 1900	15.07	
12b	CpMn(CO)(CS)P(OPh)$_3$[f]	1951	15.37	1254
13a	[Ir(CO)(diphos)$_2$]$^+$[a]	1933	15.09	
13b	[Ir(CS)(diphos)$_2$]$^+$[r]			1263
14a	Ir(CO)Cl(PPh$_3$)$_2$[s]	1956	15.45	
14b	Ir(CS)Cl(PPh$_3$)$_2$[s]			1328
15a	Cr(CO)$_5$PPh$_3$[a]		15.50[b]	
15b	*trans*-Cr(CO)$_4$(CS)PPh$_3$[m]			1230
16a	Ir(CO)$_2$(PPh$_3$)$_2$(COOMe)[r]	1980, 1940	15.52	
16b	Ir(CO)(CS)(PPh$_3$)$_2$(COOMe)[r]	1985	15.91	1287
17a	W(CO)$_5$PPh$_3$[a]		15.58[b]	
17b	*trans*-W(CO)$_4$(CS)PPh$_3$[m]			1247
18a	CpMn(CO)$_3$[n]	2024, 1939	15.64	
18b	CpMn(CO)$_2$(CS)[p]	2006, 1954	15.83	1266
19a	Rh(CO)Cl(PPh$_3$)$_2$[t]	1975	15.75	
19b	Rh(CS)Cl(PPh$_3$)$_2$[t]			1299
20a	Rh(CO)Br(PPh$_3$)$_2$[t]	1975	15.75	
20b	Rh(CS)Br(PPh$_3$)$_2$[t]			1298
21a	CpMn(CO)$_2$(CS)[p]	2006, 1954	15.83	
21b	CpMn(CO)(CS)$_2$[p]	1991	16.01	
	L$_1$ = CO and L$_2$ = CS			
22a	[Ir(CO)$_3$(PCy$_3$)$_2$]$^+$[u]	2056, 1987[c]	16.32	
22b	[Ir(CO)$_2$(CS)(PCy$_3$)$_2$]$^+$[r]	2043, 2001	16.51	1304
23a	W(CO)$_6$[a]		16.41	
23b	W(CO)$_5$(CS)[m]			1258
24a	CpFe(CO)$_2$(COOMe)[v]	2046, 1995	16.49	
24b	CpFe(CO)(CS)(COOMe)[w]	2020	16.48	1316
25a	Cr(CO)$_6$[a]		16.49	
25b	Cr(CO)$_5$(CS)[m]			1253
26a	Mo(CO)$_6$[a]		16.52	
26b	Mo(CO)$_5$(CS)[m]			1247
27a	[Ir(CO)$_3$(PPh$_3$)$_2$]$^+$[u]	2074, 2014[c]	16.71	
27b	[Ir(CO)$_2$(CS)(PPh$_3$)$_2$]$^+$[r]	2057, 2016	16.75	1317
28a	[Ir(CO)(NO)Cl(PCy$_3$)$_2$]$^+$[r]	2039	16.79	
28b	[Ir(CS)(NO)Cl(PCy$_3$)$_2$]$^+$[r]			1355
29a	[CpMn(CO)(NO)PPh$_3$]$^+$[x]	2039	16.79	
29b	[CpMn(CS)(NO)PPh$_3$]$^+$[y]			1310
30a	[Ir(CO)(NO)Cl(PPh$_3$)$_2$]$^+$[r]	2060	17.14	
30b	[Ir(CS)(NO)Cl(PPh$_3$)$_2$]$^+$[r]			1381
31a	Rh(CO)Cl(PPh$_3$)$_2$(TCNE)[z]	2075	17.39	
31b	Rh(CS)Cl(PPh$_3$)$_2$(TCNE)[z]			1355
32a	[CpFe(CO)$_3$]$^+$[aa,bb]	2114, 2060 2130, 2078	17.59[c]	
32b	[CpFe(CO)$_2$(CS)]$^+$[cc]	2093, 2064	17.45	1348
33a	Rh(CO)Br$_3$(PPh$_3$)$_2$[t]	2096	17.74	
33b	Rh(CS)Br$_3$(PPh$_3$)$_2$[t]			1355
34a	[CpMn(CO)$_2$(NO)]$^+$[x]	2118, 2074	17.74	
34b	[CpMn(CO)(CS)(NO)]$^+$[y]	2089	17.62	1339
35a	Rh(CO)Cl$_3$(PPh$_3$)$_2$[t]	2100	17.81	
35b	Rh(CS)Cl$_3$(PPh$_3$)$_2$[t]			1362
36a	[Pt(CO)Cl(PPh$_3$)$_2$]$^+$[dd]	2115	18.06	
36b	[Pt(CS)Cl(PPh$_3$)$_2$]$^+$[dd]			1400
	L$_1$ = CO and L$_2$ = PPh$_3$			
37a	(PhCOOMe)Cr(CO)$_3$[h]	1985, 1905	15.07	
37b	(PhCOOMe)Cr(CO)$_2$PPh$_3$[h]	1896, 1844	14.12	
38a	CpMn(CO)$_3$[n]	2024, 1939	15.64	
38b	CpMn(CO)$_2$PPh$_3$[n]	1934, 1874	14.64	
39a	CpMn(CO)$_2$(CS)[p]	2006, 1954	15.83	
39b	CpMn(CO)(CS)PPh$_3$[p]	1925	14.96	
40a	Cr(CO)$_5$PPh$_3$[a]		15.88[d]	
40b	*trans*-Cr(CO)$_4$(PPh$_3$)$_2$[a]		15.28	
41a	Cr(CO)$_6$[a]		16.49	
41b	Cr(CO)$_5$PPh$_3$[a]		15.50[b,ee] 15.88[d,ee]	
42a	[CpFe(CO)$_3$]$^+$[aa]	2114, 2060	17.44	
42b	[CpFe(CO)$_2$PPh$_3$]$^+$[ff]	2070, 2030	16.97	
43a	[CpMn(CO)$_2$(NO)]$^+$[x]	2118, 2074	17.74	
43b	[CpMn(CO)(NO)PPh$_3$]$^+$[x]	2039	16.79	

[a] Reference 12. [b] Trans CO. [c] Average value. [d] Cis CO. [e] B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, 97, 1261 (1975); *Inorg. Chem.*, 15, 1089 (1976). [f] N. J. Coville and I. S. Butler, *J. Organomet. Chem.*, 64, 101 (1974). [g] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, 63, 45 (1967). [h] G. Jaouen and R. Dabard, *J. Organomet. Chem.*, 61, C36 (1973). [i] G. Jaouen, *Tetrahedron Lett.*, 5159 (1973). [j] W. P. Anderson, T. B. Brill, A. R. Schoenberg, and C. W. Stangler, Jr., *J. Organomet. Chem.*, 44, 161 (1972). [k] R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, 26, 1977 (1964). [l] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 2, 533 (1963). [m] B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, 95, 7516 (1973); *Inorg. Chem.*, 15, 1089 (1976). [n] Reference 7. [o] J. Müller and K. Fenderl, *J. Organomet. Chem.*, 19, 123 (1969). [p] A. E. Fenster and I. S. Butler, *Inorg. Chem.*, 13, 915 (1974). [q] L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, 88, 5324 (1966). [r] M. J. Mays and F. P. Stefanini, *J. Chem. Soc. A*, 2747 (1971). [s] M. P. Yagupsky and G. Wilkinson, *ibid.*, 2813 (1968). [t] M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1966). [u] M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc. A*, 2909 (1970). [v] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organomet. Chem.*, 5, 341 (1966). [w] L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, 10, 78 (1971). [x] H. Brunner and H.-D. Schindler, *J. Organomet. Chem.*, 19, 135 (1969). [y] Reference 9. [z] M. C. Baird, G. Hartwell, Jr., and G. Wilkinson, *J. Chem. Soc. A*, 2037 (1967). [aa] R. J. Haines and A. L. duPreez, *ibid.*, 2341 (1970). [bb] R. H. Reimann and E. Singleton, *J. Organomet. Chem.*, 32, C44 (1971). [cc] L. Busetto and R. J. Angelici, *J. Am. Chem. Soc.*, 90, 3283 (1968). [dd] J. M. Lisy, E. D. Dobrzynski, R. J. Angelici, and J. Clardy, *ibid.*, 97, 656 (1975). [ee] Reference 20. [ff] A. Davidson, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961). [gg] Cy = cyclohexyl.

The simplest bonding model consistent with this observation is that the π-acceptor to σ-donor ratio varies more for CS than for CO. This conclusion is also supported by the greater variation in C–S bond lengths found in thiocarbonyls than in the C–O bond lengths in carbonyls.[2] π donation by CS could also be a factor in the crossover. This additional bonding interaction, which is insignificant for CO, would increase the flexibility of the electronic response of CS to its total environment. The lower ionization energies of thiocarbonyls[3,5] and near orbital degeneracies observed in their photoelectron

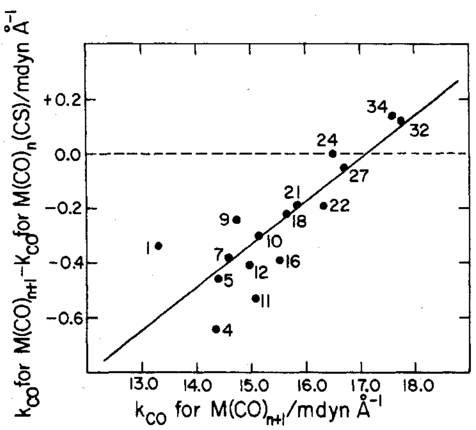

Figure 3. Plot of the difference in CO stretching force constants for $M(CO)_{n+1}$ and $M(CO)_n(CS)$ vs. CO stretching force constant for $M(CO)_{n+1}$.

spectra[5] are undoubtedly due in part to the operation of this effect in the π-electron-deficient, 17-electron complexes produced on ionization.

The conflicting descriptions of thiocarbonyl bonding reported by previous workers is a direct consequence of the crossover in CS and CO electronic properties. When $k_{CO}[M(CO)_{n+1}]$ < 17.1 mdyn/Å, the π-acceptor to ($\sigma + \pi$)-donor ratio is greater for CS than for CO. This is in agreement with the infrared spectra of $CpMn(CO)_2(CS)$[6,7] and $[CpMn(CS)(NO)L]^+$ [9] and ^{13}C NMR spectra of $CpMn(CO)_2(CS)$[7] and $[CpFe(CS)(CO)L]^+$.[11] On the other hand, when $k_{CO}[M(CO)_{n+1}]$ > 17.1 mdyn/Å, the π-acceptor to ($\sigma + \pi$)-donor ratio is lower for CS than for CO. This is in agreement with the infrared spectrum of $[CpMn(CS)(CO)(NO)]^+$ [9] and the ^{13}C NMR data for $[CpFe(CO)_2(CS)]^+$.[7] It presumably also applies to $[CpMn(CO)_2(CS)]^+$, the species actually involved in the mass spectral dissociation energy studies of $CpMn(CO)_2(CS)$.[3] Finally, the integrated infrared intensities for $CpMn(CO)_2(CS)$[8] and Mössbauer spectra of $[CpFe(CO)_2(CS)]^+$ [10] have been used to show that on an absolute basis CS is a better π acceptor than CO. Combined with the lower π-acceptor to ($\sigma + \pi$)-donor ratio found for CS in $[CpFe(CO)_2(CS)]^+$, this implies that for this compound CS is also a better donor than CO on an absolute scale. Thus, a unified understanding of the relative ligating properties of CS and CO is possible but only when all of the experimental evidence is combined to provide a broader perspective on thiocarbonyl bonding interactions.

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(13) Several points should be noted here. (1) Most of the CO force constants in Table I can be derived with only the minimal assumptions of neglect of anharmonicity and energy factoring of the CO stretching modes. (Force constants for compounds **3b**, **8b**, **15b**, **17b**, **23b**, **25b**, and **26b** were not calculated because additional assumptions regarding spectral assignments and interaction force constants would be required.) (2) The assumption of CO energy factoring could break down if the CO and CS stretches were significantly coupled. Normal-coordinate calculations, however, indicate that the coupling is small,[6c] and its inclusion in a force constant refinement had little effect on k_{CO}.[14] (3) The reported spectra were obtained in a variety of solvents. Examination of compounds for which more than one spectra have been reported (indicated by average k_{CO} values in Table I) suggest that the errors in k_{CO} are probably about 0.1–0.2 mdyn/Å.
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One-Electron Mechanism for the Electrochemical Reduction of Molecular Oxygen

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Sir:

There is major interest in the electrochemical reduction of molecular oxygen in aqueous solutions. In part this is due to its relevance to the development of hydrogen–oxygen fuel cells and metal–air batteries. Oxygen is a readily available and convenient oxidizing agent which theoretically is capable of undergoing a four-electron reduction to water at a standard potential of +0.98 V vs. the saturated calomel electrode. Several comprehensive reviews on the reduction of oxygen in aqueous solutions have appeared during the last decade.[1-4]

Evidence for the one-electron reduction of oxygen in aprotic solvents was first presented in 1965–1967[5-8] and has resulted in numerous additional investigations.[9] These have led to the confirmation that superoxide ion is the reduction product in aprotic media and is generated in aqueous media[10-12]

On the basis of previous studies of the electrochemical reduction of oxygen in both aqueous[13-15] and aprotic[6,16,17] media, together with the consideration of the entire body of experimental data for oxygen reduction,[1-4] two mechanistic schemes are proposed for the reduction process. One is based on an initial one-electron reduction of oxygen to superoxide ion, followed by chemical reactions which involve superoxide ion and are governed by solution conditions. It is common to both aqueous and aprotic media. The other applies to noninert electrodes in aqueous media and involves a preceding chemical reaction with the electrode instead of direct electron transfer to molecular oxygen. Direct electrochemical reduction of oxygen to water or hydroxide by a four-electron process does not occur.[18]

Reliable numerical values for the standard potential of the O_2/O_2^- couple[19,20] and for the rate constants for reactions of reactive oxygen species in solution[21] recently have become available. As a result, the oxygen-reduction schemes can be