the latter figures but was small and will be smaller in the case of the organic complexes since the spin density on the metal ion is smaller. Thus, although this contribution could increase the ratio 2s:2p (f_{2s}/f_{2p}), we estimate that the maximum value for the ratio is 1/9. The above analysis assumes that the ^{17}O tensor is entirely accounted for by spin in the σ^* antibonding orbital. In principle the ground state will involve admixture of the $3d_{z^2}$ orbital and consequently out-of-plane π bonding can introduce spin into the out-of-plane 2p oxygen orbital. This would result in a deviation from axiality although distant dipolar interaction with the spin on the metal ion can also contribute. Both of these effects are certainly small in our case and we take the 2s:2p ratio to be directly indicative of the hybridization at the oxygen atom.

The strong deviation from sp^2 hybridization is in contrast to the generally accepted approximation. The σ^* orbital contains very little contribution from $2s_O$. If the ^{14}N tensor for copper(II) hydroxyquinolate[8] is analyzed in terms of its isotropic and anistropic parts, a value of 1/10 is found for the 2s:2p ratio, although the authors preferred to use the value of f_{2s} alone, and then assumed sp^2 hybridization to arrive at the values of α^2 and α'^2, the MO coefficients for the σ^* orbital. In $Cu^{II}(H_2O)_6$, the σ^* bond has a smaller relative contribution from $2p_O$.

In the σ^* orbital, the oxygen atoms are therefore represented almost entirely by the $2p_O$ orbital, with a very minor part played by the $2s_O$ orbital. The σ^* bond in the $Cu^{II}(H_2O)_6$ complex is probably less covalent than that in the organic complexes.

For manganese(III) acetylacetonate the measured ^{17}O NMR contact shifts were used[9] to give a maximum value of 0.0059 for f_s, considerably lower than f_s for Cu(acac). However the solution NMR results do not give the $2p_O$ contribution and so a comparison of covalency is not possible.

The observed ^{17}O tensor can be used to derive the coefficients α' and α in the MO containing the unpaired electron.[10] Using the values given by Smith[11] for $p\sigma$–$d_{x^2-y^2}$ metal–oxygen overlap integrals we find $\alpha'^2 = 0.43$ and $\alpha^2 = 0.76$. The value for α^2 is in excellent agreement with that derived from analysis of the g and ^{63}Cu hyperfine tensors.[10]

It is interesting to analyze the present results by the method of McMillan and Halpern.[12] Putting $A_{\parallel} = K + T_{\parallel}$ and $A_{\perp} = K + T_{\perp}$ for the metal ion hyperfine tensor, they wrote the contact term K as

$$K = \alpha^2 K_O + (1 - \alpha^2) K_L \qquad (1)$$

where $K_O = \langle \chi_O | \hat{K} | \chi_O \rangle$, $K_L = \langle \chi_L | \hat{K} | \chi_L \rangle$, $\hat{K}$ is the polarization operator, and the antibonding MO containing the unpaired electron is $|\chi\rangle = \alpha|\chi_O\rangle - \beta|\chi_L\rangle$. In our case χ_O is the $3d_{x^2-y^2}$ orbital of copper and χ_L an sp^n hybrid on oxygen, where $n \approx 9$. From an analysis of many ESR data on Cu^{2+} complexes, McMillan and Halpern arrived at the values $K_O = 204$ kG and $K_L = 63$ kG with a standard error of ~22 kG. Using these values and that obtained here for α we find $K = 133$ kG. We now use these figures to obtain estimates of $A_{\parallel}$ and $A_{\perp}$ from the equations

$$\begin{aligned} A_{\parallel} &= K + (\Delta g + (3/7)\Delta g - 4/7)\Omega\langle r^{-3}\rangle \\ A_{\perp} &= K + (\Delta g - (3/14)\Delta g + 2/7)\Omega\langle r^{-3}\rangle \end{aligned} \qquad (2)$$

where $\Omega\langle r^{-3}\rangle$ is estimated at 1194 MHz. Substituting the experimental g values, we find $A_{\parallel} = 1.87 \times 10^{-2}$ cm^{-1} and $A_{\perp} = -0.30 \times 10^{-2}$ cm^{-1}. These predictions can be compared with the experimental Cu hyperfine tensor, $A_{\parallel} = 1.60 \times 10^{-2}$ cm^{-1} and $A_{\perp} = 0.19 \times 10^{-2}$ cm^{-1}.

Acknowledgment. We thank the United States–Israel Binational Science Foundation for support.

Registry No. Cupric acetylacetonate, 13395-16-9; ^{17}O, 13968-48-4.

References and Notes

(1) A. R. Lorenz, J. Ammeter, and Hs. G. Gunthard, *Chem. Phys. Lett.*, **16**, 275 (1972).
(2) D. Getz and B. L. Silver, *J. Chem. Phys.*, **61**, 630 (1974).
(3) P. Freund, B. F. Hann, and J. Owen, *J. Phys. C*, **4**, L296 (1971); P. Freund, J. Owen, and B. F. Hann, *ibid.*, **6**, L139 (1973).
(4) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958).
(5) J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).
(6) Z. Luz and B. L. Silver, *J. Phys. Chem.*, **70**, 1328 (1966).
(7) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Natl. Phys. Lab.* (*U.K.*), *Circ.*, No. BPR 1.3.
(8) G. Rist, J. Ammeter, and Hs. H. Gunthard, *J. Chem. Phys.*, **49**, 2210 (1968).
(9) Z. Luz, B. L. Silver, and D. Fiat, *J. Chem. Phys.*, **46**, 469 (1967).
(10) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).
(11) D. W. Smith, *J. Chem. Soc., A*, 1498 (1970).
(12) J. A. McMillan and T. Halpern, *J. Chem. Phys.*, **55**, 33 (1971).

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Mechanism and Equilibrium Constants of the Reaction of Formation of (π-PhCH=CHCOR)$Fe(CO)_3SbPh_3$ from (π-PhCH=CHCOR)$Fe(CO)_3$ and $SbPh_3$

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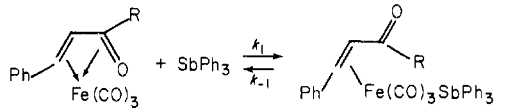
The formation of (π-R'CH=CHCOR)$Fe(CO)_3$L complexes from (π-R'CH=CHCOR)$Fe(CO)_3$ and the ligands L = MR_3 (M = P, As, Sb; R = H, Me, Ph) has been reported.[1,2]. Since the first step of the substitution reaction is much slower than the second one,[3,4] this type of reaction was not previously observed for other π-diene complexes. Only for polydentate ligands having well-separated nucleophilic atoms have partial substitution reactions been described.[5]

The present work describes the mechanism of the substitution of the heterodiene ligand in (π-PhCH=CHCOR)-$Fe(CO)_3$ by $SbPh_3$, as shown in reaction 1.



(1)

Experimental Section

The (π-PhCH=CHCOR)$Fe(CO)_3$ (R = H, Me, Ph) complexes were prepared as described in the literature.[6,7] Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer.

Preparation of Complexes. The reaction between (π-PhCH=CHCOR)$Fe(CO)_3$ and $SbPh_3$ leads to considerable accumulation of (π-PhCH=CHCOR)$Fe(CO)_3SbPh_3$ but does not go to completion. For L = $SbPh_3$ and temperatures lower than 20 °C, no further reactions were observed during handling. The preparation and purification of the products of reaction 1 were as follows. (π-PhCH=CHCOR)$Fe(CO)_3$ (0.5 g) and $SbPh_3$ (0.5 g) were dissolved in 10 ml of degassed acetone (RS grade, Carlo Erba). After 3 h of standing there was no further reaction. The solution was evaporated to dryness and the residue was chromatographed on neutral Al_2O_3 using 2:3 (v/v) dichloromethane–n-hexane as eluent. Two colored bands were observed, the faster corresponding to unreacted (π-PhCH=CHCOR)$Fe(CO)_3$ and the other to the product (π-PhCH=CHCOR)$Fe(CO)_3SbPh_3$. When the bands were well separated, the chromatography column was broken and the product recovered by extraction with acetone and evaporation to dryness. It was further purified by recrystallization from a dichloromethane–n-hexane mixture at −20 °C. During manipulations the solvents were maintained at <10 °C to avoid re-formation of initial reagent.

The products had the following physical properties. For R = H, a yellow solid formed, mp 104–105 °C. Anal. Calcd: C, 57.64; H, 3.70. Found: C, 57.31; H, 3.58. Ir spectrum (CH_2Cl_2): two CO stretching bands at 2040 and 1970 cm^{-1}. For R = Me, the compound was also a yellow solid, mp 108–111 °C. Anal. Calcd: C, 58.16; H, 4.09. Found: C, 58.41; H, 3.99. Ir spectrum (CH_2Cl_2): two CO stretching bands at 2042 and 1975 cm^{-1}. The compound with R = Ph was not obtained in the pure state because of the high rate of back-reaction, which did not allow separation of bands in the chromatography column.

The mode of reaction is similar for $AsPh_3$, but the successive reactions of formation of (π-PhCH=CHCOR)$Fe(CO)_2AsPh_3$ and $Fe(CO)_3(AsPh_3)_2$ did not allow separation of (π-PhCH=CHCOR)$Fe(CO)_3AsPh_3$ complexes.[1] However, the presence of the latter was observed spectroscopically.

Kinetic Measurements. Kinetic measurements were carried out in acetone in a closed vessel immersed in a thermostated bath (±0.1 °C). Variations in concentration were measured by following the intensity of the highest CO stretching band of the reagent complex on the spectrophotometer, for aliquots taken at intervals with a syringe. The k_1 values were obtained from plots of $\ln [(D_0 - D_e)/(D_t - D_e)]$ vs. t, where D_0, D_e, and D_t correspond to reagent complex absorbance at zero time, at equilibrium, and at time t, respectively. These plots are linear for a large excess of $SbPh_3$. Under these conditions reaction 1 may be considered a pseudo-first-order equilibrium reaction with $k = k_1[SbPh_3]$ and the experimental value, k_{obsd}, is equal to kC_0/C_e, where C_0 is the initial concentration of reactant and C_e is the equlibrium concentration of product.[8]

Since in the absence of $SbPh_3$ the back-reaction is shifted completely toward the reagent complex, k_{-1} values were measured by following the disappearance of the lowest frequency CO stretching band of the purified (π-PhCH=CHCOR)$Fe(CO)_3SbPh_3$ and plotting $\ln [(C_0 - C_\infty)/(C_t - C_\infty)]$ vs. t for this complex. These plots were linear up to 90% completion. The k_{-1} values thus obtained corresponded, within experimental error, to those obtained by following the increase in concentration of (π-PhCH=CHCOR)$Fe(CO)_3$.

The concentration of the complexes was ca. (3–7) × 10^{-3} M; that of $SbPh_3$, ca. 0.1–0.3 M. The temperature range was 10–40 °C. The rate constants obtained were reproducible to about ±5%.

Equilibrium Measurements. The equilibrium constant for reaction 1

$$K = \frac{[(\pi\text{-PhCH=CHCOR})\text{Fe(CO)}_3\text{SbPh}_3]}{[(\pi\text{-PhCH=CHCOR})\text{Fe(CO)}_3][\text{SbPh}_3]}$$

was measured in acetone solution between −20 and +20 °C. The temperature was constant to ±0.2 °C for temperatures below 10 °C. Equilibrium concentrations were measured from the absorbances of the CO stretching bands of reactant and product, for which Beer's law was first verified. Since the concentration of ligand was 50–100 times that of the reactant, it was treated as a constant. For (π-PhCH=CHCOPh)$Fe(CO)_3SbPh_3$, which was not obtained in a pure state, the equilibrium concentrations were determined from the decrease in reactant. This method is valid since no decomposition of the product was observed even after considerable lengths of time. The measurements were repeated at least three times at two different concentrations of $SbPh_3$. The reproducibility of the results was better than ±5%. Several of the measurements carried out at 30 °C were less precise because of subsequent reaction and the results are not reported here. The experimental equilibrium constants are slightly higher than the k_1/k_{-1} ratios, presumably because of experimental uncertainties.

Results and Discussion

The rate constants (k_1) and activation parameters ($\Delta H^{\ddagger}_1$, $\Delta S^{\ddagger}_1$) for the forward reaction and those for the back-reaction (k_{-1}, $\Delta H^{\ddagger}_{-1}$, $\Delta S^{\ddagger}_{-1}$) are listed in Table I. The forward reaction is first order in complex and in ligand $SbPh_3$. The back-reaction is first order in complex.

Two possible mechanisms may be put forward to explain these results. An associative mechanism as in (1) is possible, as also is a mechanism which involves reversible dissociation of the carbonyl group, followed by L attack on the four-coordinate intermediate, as observed previously in chelate ring-opening reactions for a phosphorus–nitrogen donor chelate ligand.[5] The back-reaction may also follow either of these mechanisms. The data are not sufficient, by themselves, to allow a decision as to which mechanism operates, even if the negative entropy $\Delta S^{\ddagger}_{-1}$ suggests the associative one.

Table I. Kinetic and Equilibrium Results[a] for Reaction 1

R	T, °C	$10^5 k_1$, $M^{-1}\ s^{-1}$	$10^5 k_{-1}$, s^{-1}	K, M^{-1}
Ph[b]	30	151 ± 3	136 ± 1	
	20	58.7 ± 0.8	45.7 ± 0.2	1.57 ± 0.05
	10	19.0 ± 0.5	10.1 ± 0.3	2.50 ± 0.05
	0			4.10 ± 0.19
	−10			6.20 ± 0.20
Me[c]	30	353 ± 11	93.0 ± 2.1	
	20	130 ± 4	23.6 ± 0.4	6.15 ± 0.25
	10	48.9 ± 0.9	5.3 ± 0.1	11.6 ± 0.5
	0			19.5 ± 0.1
	−10			33.4 ± 0.3
H[d]	40		102 ± 5	
	30	200 ± 7	26.4 ± 0.4	
	20	72.3 ± 0.9	7.68 ± 0.01	10.3 ± 0.3
	10	25.7 ± 0.2	1.65 ± 0.03	19.1 ± 0.2
	0			33.2 ± 0.2
	−10			61.5 ± 0.3

[a] Error limits are average deviations. [b] $\Delta H^{\ddagger}_1 = 16.9 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger}_1 = -16 \pm 3$ eu; $\Delta H^{\ddagger}_{-1} = 21.6 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger}_{-1} = -2 + 5$ eu; $\Delta H = -7.7 \pm 0.3$ kcal/mol, $\Delta S = -25 \pm 1$ eu. [c] $\Delta H^{\ddagger}_1 = 16.3 \pm 1$ kcal/mol, $\Delta S^{\ddagger}_1 = -16 \pm 3$ eu; $\Delta H^{\ddagger}_{-1} = 23.8 \pm 1$ kcal/mol, $\Delta S^{\ddagger}_{-1} = +6 \pm 3$ eu; $\Delta H = -9.0 \pm 1$ kcal/mol, $\Delta S = -26 \pm 3$ eu. [d] $\Delta H^{\ddagger}_1 = 16.9 \pm 1$ kcal/mol, $\Delta S^{\ddagger}_1 = -15 \pm 3$ eu; $\Delta H^{\ddagger}_{-1} = 22.9 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger}_{-1} = +1 \pm 5$ eu; $\Delta H = -9.4 \pm 0.7$ kcal/mol, $\Delta S = -27 \pm 2$ eu.

The k_1 values increase in the order Ph < H < Me, which follows the electron-donating ability of the ligands. This donation destabilizes the metal–diene bond and facilitates substitution.

The k_{-1} values increase in the order Ph > Me > H, which corresponds to that of increasing steric hindrance. This suggests that breaking of the Fe–$SbPh_3$ bond is an important factor in the back chelation reaction.

The equilibrium constants (K) and thermodynamic parameters (ΔH, ΔS), shown in Table I, indicate that the final complexes are more stable than the reactant complexes and that the reaction is exothermic. The difference in enthalpy between reactants and products indicates that the energy of an iron–heterodiene bond is lower than the sum of the energies of Fe–olefin and Fe–$SbPh_3$ bonds by 8–9 kcal. These values are not easy to interpret because of changes in the symmetry of the molecule from square-based pyramidal to trigonal bipyramidal during the reaction.[9] The ΔS values are negative and in agreement with the decrease in the number of molecules during the reaction.

The equilibrium constants vary in the order H > Me > Ph and this variation is greater than that in the rate constants. Since ΔS remains almost constant for the different complexes, the difference in stability is mainly due to differences in enthalpy and hence in bond energy. Given the order of the rate constants, this energy is mainly a function of steric hindrance.

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Registry No. (π-PhCH=CHCHO)$Fe(CO)_3$, 38720-33-1; (π-PhCH=CHC(O)Me)$Fe(CO)_3$, 38720-22-8; (π-PhCH=CHC(O)Ph)$Fe(CO)_3$, 38720-23-9; $SbPh_3$, 603-36-1; (π-PhCH=CHCHO)$Fe(CO)_3SbPh_3$, 56556-31-1; (π-PhCH=CHC(O)Me)$Fe(CO)_3SbPh_3$, 56556-34-4; (π-PhCH=CHC(O)Ph)$Fe(CO)_3SbPh_3$, 56556-37-7.

References and Notes

(1) G. Cardaci and C. Concetti, *J. Organomet. Chem.*, **90**, 49 (1975).
(2) A. Vessieres and P. Dixneuf, *Tetrahedron Lett.*, 1499 (1974).
(3) H. W. Quinn and J. H. Tsai, *Adv. Inorg. Chem. Radiochem.*, **13**, 249 (1969).
(4) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).
(5) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627, 632 (1974).
(6) A. M. Brodie, B. F. G. Johnson, P. L. Josty, and J. Lewis *J. Chem. Soc., Dalton Trans.*, 2031 (1972).
(7) K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch., B*, **19**, 284 (1963).
(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley New York, N.Y. 1965, p 186.
(9) A. De Cian and E. Weiss, *Acta Crystallogr., Sect. B*, **28**, 3264, 3273 (1972); M. I. Davis and C. S. Speed, *J. Organomet. Chem.*, **21**, 401 (1970).

Correspondence

Vibrational Frequency Shifts for Isotopes of Hexacarbonylchromium

AIC50651Y

Sir:

Recently Perutz and Turner[1] reported an interesting study of the infrared spectra of various isotopic species of Cr(^{12}CO)$_n$(^{13}CO)$_{6-n}$ isolated in a low-temperature matrix of CH_4. It is quite remarkable that they were able to fit 19 observed infrared-active CO stretching peaks with a mean error of 0.3 cm^{-1} and maximum error of 0.9 cm^{-1} using a "CO-factored force field". It is difficult to present an analytical explanation for the applicability of this approximate force field; however, it is apparent that the approximations are compensated for similarly for the various Cr(^{12}C^{16}O)$_n$(^{13}C^{16}O)$_{6-n}$ isotopic species. The anharmonicities are also apparently distributed satisfactorily for this agreement.

In their text, Perutz and Turner stated that this agreement demonstrates "the model used in the calculations is valid...". They also stated "The force constants show that the Cotton–Kraihanzel (C–K) approximation $2k_{\mathrm{cis}} = k_{\mathrm{trans}}$ holds well for all the hexacarbonyls." I believe these statements are misleading as they should include the qualification "for making frequency assignments for the ^{13}C-substituted species." As the statements stand, they imply that the force field is chemically meaningful—it is much later in the paper that the authors mention the "lack of direct chemical meaning in the absolute values of the force constants (particularly the interaction constants)...."

The frequencies of ^{18}O isotopic species show that there are serious limitations to the CO-factored force field. If the species Cr(^{12}C^{16}O)$_n$(^{12}C^{18}O)$_{6-n}$ are included in such a calculation, the agreement is quite unsatisfactory, as can be seen from Table I. In the first column are given the observed frequencies[2] for Cr(CO)$_6$ in CCl_4 solution. Column A gives the frequencies calculated using a CO-factored force field, refining the potential constants F_{CO}, $F_{\mathrm{CO,C'O'}}$(c), and $F_{\mathrm{CO,C'O'}}$(t) and using only the six CO stretching frequencies of Cr(^{12}C^{16}O)$_6$ and Cr(^{13}C^{16}O)$_6$. One notes that the calculated values for the E_g mode and particularly the A_{1g} mode of Cr(^{12}C^{18}O)$_6$ are far from the observed values. In column B are given calculated values from an attempt to fit all nine of the observed frequencies using a CO-factored force field. The A_{1g} and E_g modes of both the ^{13}C and ^{18}O species are in significant error. Column C gives the values calculated when the force constants are fixed at realistic values as estimated in ref 2 rather than being fixed at zero as for the CO-factored force field. Solution C, of course, shows much better agreement. The calculated values are listed for the pentasubstituted mixed isotopic species also. Though we do not have observed values for comparison, it is apparent that the different solutions give rather different values. One would expect column C to be more nearly correct than A or B.

Table I. CO Stretching Frequencies[a] and Calculated Force Constants[a] for Some Isotopic Species of Cr(CO)$_6$ in CCl_4 Solution

	Obsd[b]	A	B	C
	Frequencies			
	Cr(^{12}C^{16}O)$_6$			
A_{1g}	2112.4	2111.5[c]	2113.4[c]	2113.0[c]
E_g	2018.4	2017.8[c]	2019.1[c]	2018.7[c]
F_{1u}	1984.4	1984.5[c]	1984.8[c]	1984.6[c]
	Cr(^{13}C^{16}O)$_6$			
A_{1g}	2063.6	2064.5[c]	2066.3[c]	2063.0[c]
E_g	1972.3	1972.9[c]	1974.1[c]	1972.0[c]
F_{1u}	1940.3	1940.2[c]	1940.6[c]	1940.1[c]
	Cr(^{12}C^{18}O)$_6$			
A_{1g}	2066.2	2060.5	2062.4[c]	2066.2
E_g	1972.8	1969.1	1970.3[c]	1972.5
F_{1u}	1937.6	1936.5	1936.9[c]	1937.3
	Cr(^{12}C^{16}O)(^{13}C^{16}O)$_5$			
A_1		2075.8	2077.6	2075.2
A_1		1994.2	1995.3	1994.0
A_1		1952.5	1953.0	1952.1
B_2		1972.9	1974.1	1972.0
E		1940.2	1940.6	1940.1
	Cr(^{12}C^{16}O)(^{12}C^{18}O)$_5$			
A_1		2073.3	2075.1	2077.6
A_1		1992.4	1993.5	1994.6
A_1		1949.2	1949.7	1950.7
B_2		1969.1	1970.3	1972.5
E		1936.5	1936.9	1937.3
	Force Constants			
F_{CO}		16.44	16.45	16.54
$F_{\mathrm{CO,C'O'}}$(t)[d]		0.53	0.54	0.26
$F_{\mathrm{CO,C'O'}}$(c)		0.26	0.26	0.16
F_{MC}		[0][e]	[0][e]	[2.1][e]
$F_{\mathrm{MC,MC'}}$(t)		[0]	[0]	[0.4]
$F_{\mathrm{MC,CO}}$		[0]	[0]	[0.69]
$F_{\mathrm{MC,C'O'}}$(c)		[0]	[0]	[−0.09]
$F_{\mathrm{MC,C'O'}}$(t)		[0]	[0]	[−0.10]
F_α		[0]	[0]	[0.79]
F_β		[0]	[0]	[0.56]
Other F_{ij}		[0]	[0]	[0]

[a] Units are cm^{-1} for frequencies and are as given in ref 2 for force constants. [b] From ref 2. [c] These frequencies were used in refinement. [d] (t) is for trans; (c) is for cis. [e] Values in brackets were constrained for the calculations.

It must be pointed out that anharmonicity has been neglected so that the values of the CO,C'O' interaction constants, even in column C of Table I, are not meaningful. The correct results[2] are $F_{\mathrm{CO,C'O'}}$(t) = 0.08 and $F_{\mathrm{CO,C'O'}}$(c) = 0.17 mdyn/Å, bearing little resemblance to the results of Table I. It is clear that the CO-factored force field is indeed useful for assigning isotopic frequency shifts for the ^{13}C isotope alone but not both the ^{13}C and ^{18}O isotopic species together.[3]

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Registry No. Cr(^{12}C^{16}O)$_6$, 13007-92-6; Cr(^{13}C^{16}O)$_6$, 25941-09-7; Cr(^{12}C^{18}O)$_6$, 25875-16-5; Cr(^{12}C^{16}O)(^{13}C^{16}O)$_5$, 53109-12-9; Cr(^{12}C^{16}O)(^{12}C^{18}O)$_5$, 58167-58-1.