References and Notes

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(2) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).
(3) The following paper in this issue by Burdett et al. prompts me to make the following comment. The intent of this Note is not to criticize the use of ^{13}C isotopic frequency shifts to deduce structural information. Its purpose is to caution against attempts at explaining the "CO-factored" interaction constants in terms of bonding theory. Perutz and Turner[1] have made the statement "...the approximation $k'_{\text{cis}}(\text{eq–eq}) = {}^1/_2 k_{\text{trans}}$ holds very well both for $Cr(CO)_6$ and $Cr(CO)_5$, as predicted also by the valence-shell force field." To me the intent of such a statement appears to be to offer experimental evidence which supports a theoretical model. It is such attempts at fitting bonding models to admittedly meaningless force constants which I wish to discourage.

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Vibrational Frequency Shifts for Isotopes of Hexacarbonylchromium

AIC508466

Sir:

It is indeed surprising that for $Cr(^{12}C^{16}O)_n(^{13}C^{16}O)_{6-n}$ the fit of experimentally observed infrared bands and the theoretical spectrum, estimated from a CO-factored force field, is so very good.[1] In fact, there are some features of the vibrational data for $Cr(CO)_6$ and its isotopes which are even more surprising than Jones implies.[2] On a CO-factored force field, since the **G** matrix is diagonal in the reduced mass of CO, complete replacement of $^{12}C^{16}O$ by either $^{13}C^{16}O$ or $^{12}C^{18}O$ should shift all CO stretching bands by a factor of 0.9778 or 0.9759, respectively. In fact, from Jones' Table I, were obtained the values shown in our Table I. The difference between symmetry modes and from $^{13}C^{16}O$ to $^{12}C^{18}O$ is striking—this is also seen by refining the data. Using the energy-factored force field, Jones based his refinement on $Cr(^{12}CO)_6$ and $Cr(^{13}CO)_6$ (column A) and on $Cr(^{12}CO)_6$, $Cr(^{13}CO)_6$, and $Cr(^{12}C^{18}O)_6$ (column B). The standard deviations between experimental and theoretical values for these calculations and also for refining on $Cr(^{12}C^{16}O)_6$ and $Cr(^{12}C^{18}O)_6$ and on $Cr(^{13}C^{16}O)_6$ and $Cr(^{12}C^{18}O)_6$ are

	12,16-13,16	12,16-12,18	13,16-12,18	12,16-13,16-12,18
σ, cm^{-1}	0.60	1.71	2.26	1.93

The reasons for these surprising differences do indeed lie in fortuitous or less fortuitous cancelation of terms; the details of these subtleties are discussed elsewhere.[3] One possibly significant observation is that use of the infrared-active frequencies only of $Cr(CO)_n(CO')_{6-n}$ gives an excellent fit of the frequencies. Only when Raman-active modes are included, is the quality of the fit reduced when the frequency-factored force field is used.

However, we wish to point out that we are not primarily interested in the nuances of various force fields nor in the lack of chemical significance of the force constants obtained. Our major object is to use isotopic CO data to determine the structures of metal carbonyl and isolated fragments trapped in low-temperature matrices. Although recent theoretical work[4] confirms the structures determined experimentally, it is nonetheless intuitively surprising that $Co(CO)_4$ is C_{3v},[5] $Fe(CO)_4$ is C_{2v},[6] $Mo(CO)_4$ is C_{2v},[7] and $Cr(CO)_5$ is C_{4v} with a droop angle sensitive to the environment.[8] Confidence in such structures is surely dependent on the match in both position and intensity of experimental and theoretical isotope patterns. The $Cr(CO)_6$ ^{13}CO data were reproduced[1] to demonstrate how well the data can be fitted with a CO-factored force field for a molecule whose structure is not open to question. The bounds of reliability of such calculations are discussed at length elsewhere.[3] Suffice it to say that ^{13}CO substitution *does* lead to reliable structural information where a *full* vibrational analysis is impossible.

Table I

	T_{1u}	A_{1g}	E_g
$\nu[Cr(^{12}C^{16}O)_6]/\nu[Cr(^{13}C^{16}O)_6]$	0.9778	0.9769	0.9772
"Error", cm^{-1}	0.0	1.9	1.2
$\nu[Cr(^{12}C^{16}O)_6]/\nu[Cr(^{12}C^{18}O)_6]$	0.9764	0.9781	0.9774
"Error", cm^{-1}	−1	−4.6	−3.0

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Registry No. $Cr(CO)_6$, 13007-92-6.

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Carbon-13 Isotopic Exchange in Pentacarbonyliron

AIC50404U

Sir:

It has already been exhaustively proven that $Fe(Co)_5$ is a nonrigid molecule.[1–5]. This fact was initially recognized as a direct result of the unexpectedly simple appearance of the NMR spectrum of $Fe(CO)_5$.[1] Chemical exchange between free ^{13}CO and $C^{18}O$, observed with ir spectroscopy,[6] was unmeasurably small. This suggested that the nonrigidity of $Fe(CO)_5$ involved an intramolecular exchange mechanism.

From studies of the NMR spectra of polynuclear carbonyls,[7] the activation energy for the transition of a terminal carbon monoxide ligand to a bridging position has proved to be very small. This could imply intermolecular exchange between different $Fe(CO)_5$ molecules by a bridging path. In an earlier publication we showed that a CO group bound to a metal atom behaves like an activated CO "molecule".[8] Consequently the exchange experiment to determine whether the mechanism of nonrigidity in $Fe(CO)_5$ is intra- or intermolecular should be designed differently than heretofore. The exchange rate should be studied between equally activated carbon monoxide "molecules" in $Fe(CO)_5$ rather than between activated and unactivated CO groups as in ref 6.

In the course of our ^{13}C NMR experiments published elsewhere[5] we observed what must be interpreted as a slow

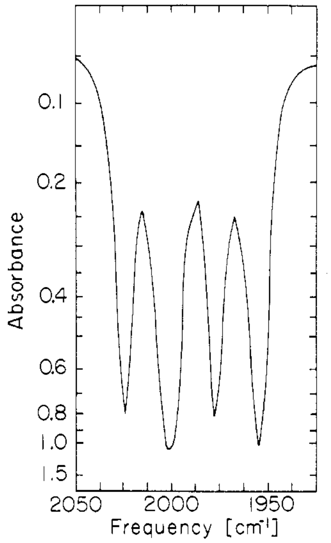

Figure 1. Infrared spectrum in the CO stretching region for a 1:1 mixture of $Fe(CO)_5$ (99% ^{12}C) with $Fe(CO)_5$ (92.5% ^{13}C) in *n*-hexane.

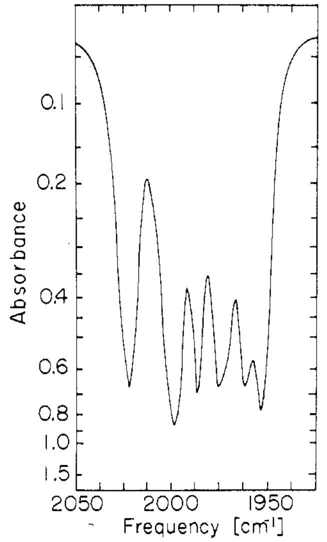

Figure 2. Infrared spectrum in the CO stretching region for a 1:1 mixture of $Fe(^{12}CO)_5$ with $Fe(^{13}CO)_5$ in *n*-hexane after the addition of a catalytic amount of Pd/C.

intermolecular migration of CO ligand groups. We used $Fe(CO)_5$ with natural ^{13}C abundance (1.1%) as a solvent for $Fe(^{13}CO)_3(PF_3)_2$ which was enriched to 92.5% in ^{13}C. We observed that the relative intensities of the peaks due to the species with natural ^{13}C abundance and the highly enriched species changed over several weeks. This indicated that an intermolecular migration of CO groups must have occurred, though at a slow rate. Based upon this experimental observation, we designed a new exchange experiment in order to get an unequivocal answer to the question of intra- vs. intermolecular exchange in $Fe(CO)_5$.

For the experiment we used 92% enriched $Fe(^{13}CO)_5$ and $Fe(^{12}CO)_5$ with only natural abundance of ^{13}C, therefore containing 99% ^{12}C. Each of these two compounds belongs to the D_{3h} symmetry group and consequently exhibits two bands in the CO stretching region of the ir spectrum, corresponding to the A_1 and E representations of the group. When equal amounts of the two compounds are mixed, the preliminary result is a superposition of thier respective spectra (Figure 1). Four distinct bands are observed in the CO stretching region, since the bands for ^{13}C species are shifted to lower frequencies relative to bands for the ^{12}C species according to the expected mass dependence of the frequencies

$$\nu_{^{13}C} = 0.96\nu_{^{12}C} \tag{1}$$

If complete intermolecular exchange takes place, the major products would be $Fe(^{13}CO)_2(^{12}CO)_3$ and $Fe(^{13}CO)_3(^{12}CO)_2$. Each of these compounds can occur as three stereoisomers belonging to the symmetry groups D_{3h}, C_{2v}, and C_s. Consequently, a large number of ir bands would be expected if intermolecular exchange occurs. However, only very minor changes were observed in the mixture of $Fe(^{13}CO)_5$ with $Fe(^{12}CO)_5$ over several days in the absence of light. This experiment sets a limit for the half-time for intermolecular exchange greater than 5 days. It should be noted that autocatalysis of small amounts of impurities and possible wall catalysis have not been excluded as partial or complete alternative explanations of the experimental effect interpreted as intermolecular exchange. In order to observe the ir spectrum when intermolecular exchange had occurred to equilibrium, catalytic amounts of Pd/C were added and the mixture was stirred well for about 5 min. The CO stretching region of the resulting ir spectrum is shown in Figure 2.

From the comparison of Figures 1 and 2 we conclude that the spectrum obtained from the mixture of both isotopic species without Pd/C was very far from equilibrium. Therefore, the intermolecular exchange is very slow, although it appears to happen at a more rapid rate than the exchange of free ^{13}CO with $Fe(^{12}CO)_5$. The slowness of $Fe(^{13}CO)_5$–$Fe(^{12}CO)_5$ exchange without catalyst definitely proves that the CO ligand exchange between axial and equatorial positions follows an intra- rather than an intermolecular path.

An intramolecular exchange path is also indicated by the high contribution of spin–rotation interaction to the relaxation mechanism in $Fe(CO)_5$.[4] Relaxation due to spin–rotation interaction must decrease with rising temperature and this is observed as shown in ref 4. Thus, although $Fe(CO)_5$ is a rather large molecule, its relaxation is largely due to spin–rotation interaction. This indicates that the molecules are unperturbed, that the intermolecular interaction is small, and therefore that an intermolecular exchange will be far slower than the intramolecular exchange as shown by this experiment.

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Registry No. $Fe(^{13}CO)_5$, 16997-09-4; $Fe(^{12}CO)_5$, 13463-40-6.

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