

## References and Notes

- (1) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).
- (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  $^{13}\text{C}$  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<sup>1</sup> have made the statement "...the approximation  $k'_{\text{cis}}(\text{eq-eq}) = 1/2k_{\text{trans}}$  holds very well both for  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ , 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

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Sir:

It is indeed surprising that for  $\text{Cr}(\text{CO})_n(\text{C}^{12}\text{O})_n(\text{C}^{13}\text{O})_{6-n}$  the fit of experimentally observed infrared bands and the theoretical spectrum, estimated from a CO-factored force field, is so very good.<sup>1</sup> In fact, there are some features of the vibrational data for  $\text{Cr}(\text{CO})_6$  and its isotopes which are even more surprising than Jones implies.<sup>2</sup> On a CO-factored force field, since the  $\mathbf{G}$  matrix is diagonal in the reduced mass of CO, complete replacement of  $^{12}\text{C}^{16}\text{O}$  by either  $^{13}\text{C}^{16}\text{O}$  or  $^{12}\text{C}^{18}\text{O}$  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  $^{13}\text{C}^{16}\text{O}$  to  $^{12}\text{C}^{18}\text{O}$  is striking—this is also seen by refining the data. Using the energy-factored force field, Jones based his refinement on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{C}^{13}\text{O})_6$  (column A) and on  $\text{Cr}(\text{C}^{12}\text{O})_6$ ,  $\text{Cr}(\text{C}^{13}\text{O})_6$ , and  $\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$  (column B). The standard deviations between experimental and theoretical values for these calculations and also for refining on  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_6$  and  $\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$  and on  $\text{Cr}(\text{C}^{13}\text{C}^{16}\text{O})_6$  and  $\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$  are

	12,16-	12,16-	13,16-	12,16-
	13,16	12,18	12,18	13,16-
$\sigma, \text{cm}^{-1}$	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.<sup>3</sup> One possibly significant observation is that use of the infrared-active frequencies only of  $\text{Cr}(\text{CO})_n(\text{CO})_{6-n}$  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<sup>4</sup> confirms the structures determined experimentally, it is nonetheless intuitively surprising that  $\text{Co}(\text{CO})_4$  is  $\text{C}_{3v}$ ,<sup>5</sup>  $\text{Fe}(\text{CO})_4$  is  $\text{C}_{2v}$ ,<sup>6</sup>  $\text{Mo}(\text{CO})_4$  is  $\text{C}_{2v}$ ,<sup>7</sup> and  $\text{Cr}(\text{CO})_5$  is  $\text{C}_{4v}$  with a droop angle sensitive to the environment.<sup>8</sup> Confidence in

Table I

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

such structures is surely dependent on the match in both position and intensity of experimental and theoretical isotope patterns. The  $\text{Cr}(\text{CO})_6$   $^{13}\text{CO}$  data were reproduced<sup>1</sup> 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.<sup>3</sup> Suffice it to say that  $^{13}\text{CO}$  substitution *does* lead to reliable structural information where a full vibrational analysis is impossible.

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## References and Notes

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- (3) M. Bigorgne, *Spectrochim. Acta*, in press; J. K. Burdett, H. Dubost, M. Poliakoff, and J. J. Turner in "Advances in Ir and Raman Spectroscopy", Vol. 2, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1976; J. K. Burdett and M. Poliakoff, to be submitted for publication.
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- (6) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).
- (7) R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4800 (1975).
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## Carbon-13 Isotopic Exchange in Pentacarbonyliron

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Sir:

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

From studies of the NMR spectra of polynuclear carbonyls,<sup>7</sup> 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  $\text{Fe}(\text{CO})_5$  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".<sup>8</sup> Consequently the exchange experiment to determine whether the mechanism of nonrigidity in  $\text{Fe}(\text{CO})_5$  is intra- or intermolecular should be designed differently than heretofore. The exchange rate should be studied between equally activated carbon monoxide "molecules" in  $\text{Fe}(\text{CO})_5$  rather than between activated and unactivated CO groups as in ref 6.

In the course of our  $^{13}\text{C}$  NMR experiments published elsewhere<sup>5</sup> we observed what must be interpreted as a slow