rangements of the Co–N bonds that would be necessary for cis–trans isomerization to take place. It is also evident from the results in Table III that the formation of the diaqua complex from the μ-carbonato μ-hydroxo complexes is much more favorable than the formation of the diaqua complex from "triol".

It was also observed that while the *trans*-diaquabis(μ-hydroxo)bis(triamminecobalt(III)) complex ion could be constructed from a space-filling atomic model, the *trans*-diaqua(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) ion could not, which suggests that such a complex, if formed in aqueous solution, would be highly unstable.

It is also interesting to note that while the *trans*-diaquabis(μ-hydroxo)bis(triamminecobalt(III)) ion reacts with a number of ligands X (where X = NO_2^-, SO_3^{2-}, CH_3COO^-, and a wide variety of carboxylate ions) to form complexes of the type $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}X)Co(NH_3)_3]^{3+}$; NO_2^- is the only one of these ligands that reacts with the corresponding diaqua μ-carbonato complex to form a μ-carbonato μ-nitrito complex. The observed selectivity is believed to be the result of stereochemical constraints on the molecule due to the bridging carbonate ligand. The carbonate ligand bridges both Co(III) centers via an axial–axial connection, thus holding the aqua ligands in a rigid cis conformation. Therefore, only ligands of the correct size to span the cis position occupied by the aqua ligands will react with the diaqua complex.

These observations are true for all the bridged carbonato complexes whose equilibrium constants have been measured, and all the diaqua complexes prepared from them are hence characterized as *cis*-diaqua complexes. The equilibrium constants of the first three complexes in Table III, therefore, represent a combination of two equilibrium processes as shown for "triol" (see above). Since we have established that the isomerization of the *cis*-diaqua μ-carbonato complex does not take place, the equilibrium constant for the formation of the cis complex should therefore be compared with the value of K_a, 2.34 M^{-1}, for "triol". The large difference in the equilibrium constants for the two sets of complexes can probably be explained in terms of the difference in charge and the difference in their structure. The less positively charged unhydrolyzed μ-carbonato complexes will be more easily protonated, thereby indirectly increasing the basicity of the hydroxide group. The difference in the cofacial and edge-shared bis(octahedron) structures possessed by these complexes could also be partially responsible for the large difference in reactivity between the two sets of complexes.

Finally, it should be noted that the bridging NO_2^- group has quite a substantial influence on the basicity of the hydroxo group. As indicated in Table III, the value of the equilibrium constant of the μ-carbonato μ-hydroxo μ-nitrito complex has decreased from ~8000 to ~3000 M^{-1}. This is probably to be expected, as the NO_2^- group is known to be a powerful electron-withdrawing group and hence it will affect the basicity of the bridging hydroxide group.

Acknowledgment. This work was supported by grants provided by the Research and Publications Fund Committee and by the Board of Postgraduate Studies, University of the West Indies. G.S. wishes to thank the Aluminum Company of Canada (Jamaica) Ltd. for providing a postgraduate scholarship that helped to finance the study.

Registry No. triol, 22445-08-5; $[R(\mu\text{-}CO_3)(\mu\text{-}OH)_2R](ClO_4)_2$, 103621-42-7; $[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}OH)R(H_2O)](ClO_4)_3$, 103621-37-0; $[(H_2O)R'(\mu\text{-}OH)_2R'(NO_3)](ClO_4)_3$, 103621-39-2; $[R'(\mu\text{-}CO_3)(\mu\text{-}OH)_2R'](ClO_4)_2$, 103621-41-6; $[(H_2O)R'(\mu\text{-}CO_3)(\mu\text{-}OH)R'(H_2O)](ClO_4)_3$, 103621-44-9; $[R(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R](ClO_4)_2$, 103621-46-1; $[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}NO_2)R(H_2O)]Cl_3$, 103621-47-2; $[(H_2O)R(\mu\text{-}NH_2)(\mu\text{-}OH)R(H_2O)](NO_3)_4$, 49725-53-3; $[R(\mu\text{-}NH_2)(\mu\text{-}CO_3)(\mu\text{-}OH)R]I_2$, 103621-48-3; $[(H_2O)R(\mu\text{-}NH_2)(\mu\text{-}CO_3)R(H_2O)](ClO_4)_3$, 103621-50-7.

Contribution from the Department of Chemistry,
University of Nottingham, Nottingham NG7 2RD, England

Structure and Reactions of $Fe_2(CO)_8$: An IR Spectroscopic Study Using ^{13}CO, Photolysis with Plane-Polarized Light, and Matrix Isolation

Susan C. Fletcher,† Martyn Poliakoff,* and James J. Turner*

Received February 12, 1986

The UV/vis photolysis of $Fe_2(CO)_9$ isolated in Ar or Ar + 10% CO matrices at 15 K yields the CO-bridged isomer of $Fe_2(CO)_8$, B, as the primary photoproduct. Computer subtraction of the IR spectra in the ν(C–O) region is used to obtain the spectrum of "pure" B. The structure of B is determined by ^{13}CO enrichment. It is shown that the ν(C–O) IR bands of ^{13}CO-enriched $Fe_2(CO)_9$ can be analyzed *without* including coupling between the vibrations of bridging and terminal CO groups. Such a vibrational analysis is used to prove that isomer B of $Fe_2(CO)_8$ has two bridging CO groups with structure **2**, similar to that of $Co_2(CO)_8$ but with the $M(\mu\text{-}CO)_2M$ unit closer to planarity than in $Co_2(CO)_8$. The observed ν(C–O) IR spectra of the unbridged isomer, U, of $Fe_2(CO)_8$ are consistent with the D_{2h} structure **5**. Photolysis with plane-polarized light provides mechanistic evidence, both about the formation of B and also about the isomerization of B to U. Mechanisms are proposed for the isomerization and thermal reactions of B, involving the common singly bridged intermediate $(CO)_4Fe(\mu\text{-}CO)Fe(CO)_3$.

Introduction

There has long been interest in the photochemistry of transition-metal carbonyls.[1] Over the past few years, this interest has focussed increasingly on di- and polynuclear species,[2] from the viewpoint both of overall reactions and of detailed mechanisms. The understanding of these mechanisms frequently requires the identification of the appropriate intermediates, and it is in this area that matrix isolation techniques have played a key role.[3] Intermediates have been isolated at low temperature and their structures established by spectroscopic methods.

Some years ago, in the first application of matrix isolation to a dinuclear carbonyl,[4] we showed that UV/visible photolysis of $Fe_2(CO)_9$ produced both CO-bridged and unbridged isomers of $Fe_2(CO)_8$:

---

† Present address: BP Research Centre, Sunbury-on-Thames, Middlesex TW16 7LN, England.

(1) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

(2) Meyer, J. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

(3) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1. Hitam, R. B.; Mahmoud, K. A.; Rest, A. J. *Coord. Chem. Rev.* **1984**, *55*, 1. Poliakoff, M.; Turner, J. J. In *Inorganic Chemistry-Toward the 21st Century*; Chisholm, M. H., Ed., ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 35.

(4) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2403.

$$Fe_2(CO)_9 \xrightarrow{h\nu} \underset{\text{CO bridged}}{Fe_2(CO)_8} \xrightarrow[\text{anneal}]{h\nu\text{ or}} \underset{\text{unbridged}}{Fe_2(CO)_8}$$

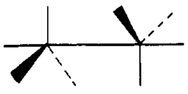
Matrix isolation is a particularly good method for studying $Fe_2(CO)_9$, which has a very low vapor pressure and is almost completely insoluble in all common solvents. Hence, $Fe_2(CO)_9$ does not lend itself to more conventional experiments in the gas phase or solution.

A particularly intriguing aspect of the matrix-isolated $Fe_2(CO)_9/Fe_2(CO)_8$ system was that the bridged isomer of $Fe_2(CO)_8$ could be generated in large amounts, although it appeared to be thermodynamically much less stable than the unbridged isomer. Even though warming the matrix from 20 to 35 K was enough to promote almost complete isomerization,[4] bridged $Fe_2(CO)_8$ was the major photoproduct in the initial stages of photolysis. In addition, on annealing, bridged $Fe_2(CO)_8$ was observed[4] to undergo addition reactions, when appropriate dopants were present in the matrix:

$$\underset{\text{CO bridged}}{Fe_2(CO)_8} + L \xrightarrow{\text{anneal}} Fe_2(CO)_8L \qquad L = CO \text{ or } N_2$$

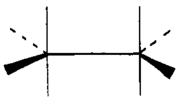
Unfortunately, matrix techniques were not sufficiently developed in 1971 for us to establish the detailed photochemical mechanisms or the precise structures of the two isomers of $Fe_2(CO)_8$. (We tentatively proposed structures **2** and **4** largely by analogy with the isomers of $Co_2(CO)_8$.) A number of recent developments have encouraged us to reexamine the photochemistry of $Fe_2(CO)_9$. There is new theoretical work on carbonyl structures, particularly Hoffmann's proposed structure, **5**, for unbridged $Fe_2(CO)_8$ and his isolobal analogy between $Fe(CO)_4$ and CH_2.[5] More importantly, there have been major technical developments in IR spectroscopy (including FT-IR[6]), in ^{13}CO isotopic methods,[7,8] and in the application of plane-polarized light to matrix experiments.[9-11]

1



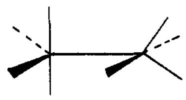
4

2

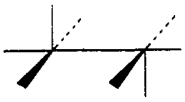


5

3



6



7

In this paper we have used these new techniques to establish the structure of the bridged isomer of $Fe_2(CO)_8$ and to clarify the mechanism of its reactions and isomerization. In describing our results we shall refer[12] to the CO-bridged isomer of $Fe_2(CO)_8$ as B and to the unbridged isomer as U.

Table I. Wavenumber (cm^{-1}) of ν(C–O) Bands of $Fe_2(CO)_9$ and Its Photoproducts in Ar + 10% CO Matrices at 15 K

molecule	ν, cm^{-1}	assignt[a]
$Fe_2(CO)_9$	2064	a_2''
	2037	e'
	1847.4[b]	e' bridging
$Fe_2(CO)_8$ (CO bridged, B)	2055	a'
	2032	a'
	2022	a''
	1857[c]	a' bridging
	1814	a''
$Fe_2(CO)_8$ (unbridged, U)	2038	
	2006	
	1978	
	1974	

[a] Based on structure **1** for $Fe_2(CO)_9$ and **2** for B; the assignment for U is discussed in the text. [b] There is also a shoulder at 1844 cm^{-1}, due to residual matrix splitting. [c] The very weak band at 1867 cm^{-1} reported in ref 4 does not appear to be due to B.

Experimental Section

General Details. The matrix isolation apparatus[6,13] and the photolysis equipment[10] at Nottingham have been described previously. UV/vis spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer with a Model 3600 data station. All IR spectra were obtained with a Nicolet MX-3600 FT-IR interferometer and Model 1280 data system (32K point data collection and 256K point Fourier Transfor, i.e. 0.7-cm^{-1} resolution). In our earlier experiments[4] a germanium filter was required to prevent photolysis by the UV/vis radiation from the sample beam of a dispersive spectrometer. In the interferometer, such a filter was not needed as the beam splitter cuts out the unwanted radiation. There is significant overlap of the ν(C–O) bands of $Fe_2(CO)_9$, B, and U, and computer subtraction is required to obtain the spectrum of "pure" B. Unfortunately, computer subtraction of IR spectra often exacerbates the problem of "matrix splitting" of IR bands, which undergo subtle changes in splitting during UV photolysis. Thus, as in our earlier experiments,[4] we have been forced to work in Ar matrices doped with 5% or 10% CO, where bands are broader but matrix splittings are largely absent.

Matrices were deposited by "slow spray-on" techniques.[4] Finely ground $Fe_2(CO)_9$ was coated onto a thermoelectrically cooled copper block, −20 °C, and was warmed to room temperature for evaporation into the matrix.[13] $Fe_2(CO)_9$ enriched with ^{13}CO was prepared by UV photolysis, in isopentane solution, of $Fe(CO)_5$ that had itself been enriched with ^{13}CO by IR laser pyrolysis.[14] Matrix gases Ar and N_2 (Messer-Griesheim), CO (BOC Grade X), and ^{13}CO (Amersham International) were used without further purification.

Photochemistry with Plane-Polarized Light. The principles of polarized photochemistry have been discussed elsewhere,[9,10] and here we give a very brief outline. Most molecules do not rotate thermally in matrices. Photolysis with plane-polarized light can therefore be used to destroy preferentially noncubic molecules with a particular orientation in the matrix. This is because, for any noncubic molecule, the transition moment associated with each vibrational or electronic transition lies in a particular direction (or, for a doubly degenerate transition, in a particular plane) relative to the axes of the molecules. In this type of experiment, irradiation with plane-polarized light can produce three different effects, all of which are reported in this paper.

(i) Dichroic Photodepletion. Molecules in a particular orientation are preferentially destroyed, and the absorptions of the unreacted material display linear dichroism. The sign of the dichroism often allows one to deduce the symmetries of the IR bands and of the photoactive UV/vis transition.

(ii) Dichroic Photoproduction. If the formation of the photoproducts does not involve random rotation of the molecules, their absorptions will also display linear dichroism and similar deductions can be made about the assignment of IR bands.

(iii) Photoreorientation. Sometimes irradiation does not destroy molecules but rather causes them to rotate or pseudorotate in the matrix until they reach an orientation where they no longer absorb the light.

---

(5) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(6) See for example: Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1983**, *22*, 3259.

(7) See for example: Burdett, J. K.; Dubost, H.; Poliakoff, M.; Turner, J. J. *Adv. Infrared Raman Spectrosc.* **1976**, *3*, 1.

(8) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022.

(9) Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

(10) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190.

(11) Dunkin, I. R.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248.

(12) These abbreviations are different from those of ref 4, where B was called *a* and U was *b*. Our present abbreviations are to be preferred as they have some mnemonic value.

(13) Fletcher, S. C. Ph.D. Thesis, University of Nottingham, 1985.

(14) Bristow, N. J.; Moore, B. D.; Poliakoff, M.; Ryott, G. J.; Turner, J. J. *J. Organomet. Chem.* **1984**, *260*, 181.

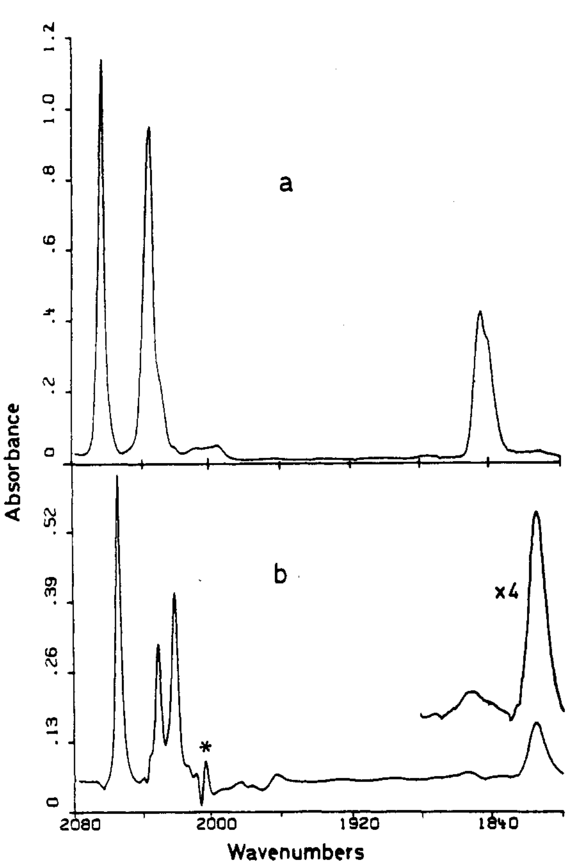


Figure 1. IR spectra in the ν(C–O) region, in an Ar + 10% CO matrix at 15 K: (a) $Fe_2(CO)_9$, before photolysis; (b) the CO-bridged isomer, B, of $Fe_2(CO)_8$. The spectrum of B was obtained by computer subtraction, and the asterisk indicates residual absorption due to U, which was incompletely removed by the subtraction. The insert shows the bridging ν(C–O) region on an expanded absorbance scale.

Thus, there is a decrease in the number of molecules in an "absorbing" orientation and an increase in the number in "blind" orientations. Changing the plane of polarization of the irradiating light causes the molecules to reorient further.

In the experiments reported here, plane-polarized UV light was generated with a Polacoat 105 UV WMR polarizer on a quartz substrate. IR linear dichroism was measured with a Spec-Ac wire-grid polarizer on a KRS-5 substrate. Interestingly, the IR beam of the Nicolet MX interferometer has a significant (and unreported) horizontal polarization.[15] All interferograms were therefore collected with the polarizer set at angles of ±45° to the horizontal, which gave equal throughput at the two settings.[13] The polarizer was placed in the sample compartment of the MX bench, a position which was found to give optimal signal/noise in the transformed spectra.[13]

Results

IR Spectrum of CO-Bridged $Fe_2(CO)_8$ (B). B is the primary photoproduct of matrix-isolated $Fe_2(CO)_9$. In Figure 1, the ν(C–O) IR spectrum of B, isolated in a mixed Ar/CO matrix, is compared with the spectrum of $Fe_2(CO)_9$. This spectrum of B was obtained by computer subtraction to remove absorptions of $Fe_2(CO)_9$ and U. The wavenumbers of the bands are given in Table I. The spectrum of $Fe_2(CO)_9$ shows two strong bands in the *terminal* C–O stretching region, ~2000 cm^{-1}, as expected (a_2'' + e') for a D_{3h} structure, **1**. In the *bridging* C–O stretching region, ~1840 cm^{-1}, there is a single band, again as predicted, e'. By contrast, B has *three* strong terminal and *two* bridging ν(C–O) bands, although the higher frequency bridging band is rather weak. B must therefore have at least *two* bridging CO groups. It is perhaps surprising that the spectrum of B is so simple, particularly because B has one fewer CO group than $Fe_2(CO)_9$ and must necessarily have lower symmetry.

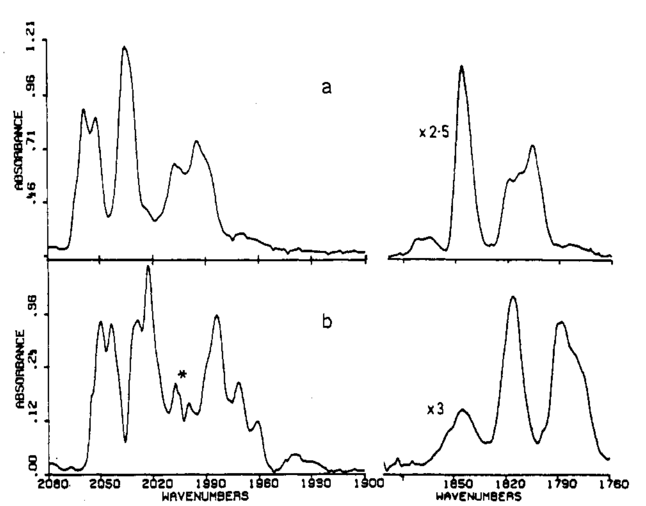


Figure 2. IR spectra of (a) $Fe_2(CO)_9$ and (b) $Fe_2(CO)_8$, both enriched with 35% ^{13}CO, obtained under conditions similar to those used in Figure 1. Again, computer subtraction was required to obtain the spectrum of B in the *terminal* ν(C–O) region. (The asterisk indicates residual absorption due to U.) In both spectra, the absorbance scale in the bridging ν(C–O) region has been expanded relative to the terminal ν(C–O) scale.

The most obvious structures for B are the C_{2v} structure **2**, formally derived by removing a bridging CO group from $Fe_2(CO)_9$, and the C_s structure **3**, obtained by removing a terminal CO group. However, additional IR data are required to distinguish between structures **2** and **3**. These data can be provided by ^{13}CO enrichment.

UV Photolysis of $Fe_2(CO)_9$ Enriched with ^{13}CO. A combination of ^{13}CO enrichment and IR spectroscopy has been used very successfully to characterize a large number of mononuclear metal carbonyl species, both in matrices[7] and in solution.[16] The method relies on a detailed quantitative analysis using a C–O factored force field to reproduce the observed spectra in both the frequency and the relative intensities of the bands. When applied to dinuclear or polynuclear metal carbonyls, these calculations become much more cumbersome because the number of force constants and particularly the number of isotopomers increases dramatically.[17] The technique has been successfully applied to $(\eta\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$, but this is rather a special case since it only contains bridging CO groups.[8]

Figure 2 shows the IR spectra of $Fe_2(CO)_9$ and B both enriched with 35% ^{13}CO. Clearly, both spectra contain more spectroscopic information than the corresponding spectra of the unenriched molecules (Figure 1). Equally clearly, the terminal and bridging ν(C–O) bands are still separated and the detailed band patterns for $Fe_2(CO)_9$ and B are different in the bridging ν(C–O) region. Is this difference significant and how can the spectra be analyzed?

The problem is analogous to that of matrix-isolated As_4O_{10}, which has both bridging and terminal oxygen atoms.[18] A detailed analysis of the spectra of $As_4(^{16}O)_{10-x}(^{18}O)_x$ isotopomers showed that band paterns could be successfully reproduced *without* considering vibrational coupling between bridging and terminal oxygen groups. In As_4O_{10}, however, the wavenumber separation between the bridging and terminal regions of the IR spectrum is much larger than the corresponding separation for bridging and terminal CO groups.

Before trying to analyze the two ν(C–O) regions in Figure 2 separately, we carried out calculations on the imaginary molecule[13]

---

(15) The beam is partially polarized so that the throughput is greater for a polarizer placed in the beam with the electric vector aligned horizontally, i.e. parallel to the base plate of the interferometer.

(16) See for example: Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27.

(17) Force field calculations have been successfully carried out for a number of polynuclear carbonyls of *known* structure. A recent example is: Bor, R.; Battiston, G. A.; Dietler, U. K.; Kettle, S. F. A.; Rossetti, R.; Sbrignadello, G.; Stanghellini, P. L. *Inorg. Chem.* **1980**, *19*, 1961.

(18) Brisdon, A. K.; Gomme, R. A.; Ogden, J. S. Presented at the Fifth International Conference on Spectroscopy of Matrix Isolated Molecules, Fontevraud, France, July 1985.

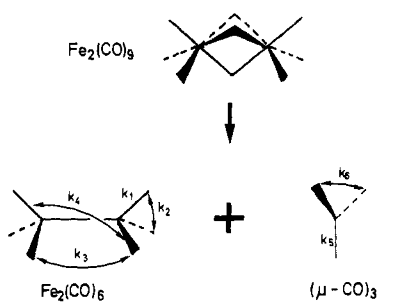


Figure 3. Schematic representation of the separation of bridging and terminal C–O stretching vibrations in $Fe_2(CO)_9$ and the definition of the C–O factored force constants. k_1 and k_5 are C–O stretching force constants. k_2, k_3, k_4, and k_6 are interaction constants. (A complete C–O factored force field would require two additional interaction constants, involving coupling between bridging and terminal CO groups.)

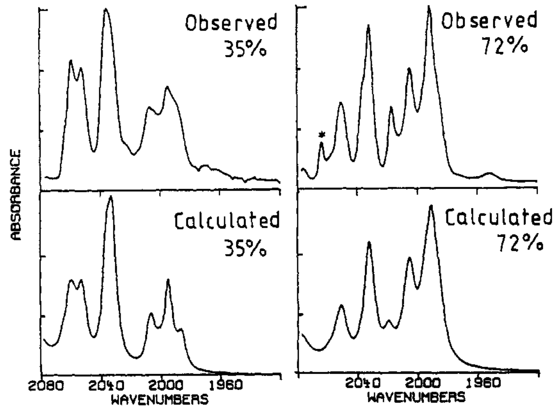


Figure 4. Observed and calculated IR spectra in the terminal ν(C–O) region for $Fe_2(CO)_9$ with two different degrees of ^{13}CO enrichment. See Table II and ref 13 for more details of the calculated spectra, which were computed with the assumption of a Lorentzian line shape and 7 cm^{-1} fwhm. The band marked with an asterisk in the observed spectrum (72%) is due to a small trace of unenriched $Fe_2(^{12}CO)_9$ that contaminated the sample.

$M(CO)_2(\mu\text{-}CO)_2M(CO)_2$. We calculated the IR spectrum of a mixture of isotopomers corresponding to 50% enrichment with ^{13}CO, while varying the degree of vibrational coupling between bridging and terminal CO groups. Surprisingly, the size of this coupling had relatively little effect on the overall IR band pattern, although, of course, there was some effect on the exact wavenumbers of the bands. Thus, our conclusion was that the vibrations of bridging and terminal CO groups could be analyzed without including coupling between them. This analysis would establish the correct number of bridging or terminal CO groups, but the precise values of the force constants would have little significance.

It seemed sensible to begin by testing these conclusions on $Fe_2(CO)_9$, which has the known structure **1**. For the analysis, $Fe_2(CO)_9$ is divided into two vibrational fragments, $[M(CO)_3]_2$ and $(\mu\text{-}CO)_3$, both with D_{3h} symmetry (see Figure 3). With use of these two fragments, it proved possible[19] to reproduce the observed spectra in both the frequencies (Table II) and intensities of the bands (Figures 4 and 5). The agreement between the observed and calculated spectra is striking, particularly since only six force constants were used in the calculations.

The bridging and terminal CO regions of the spectrum can therefore be treated separately. Of particular relevance is the fact that the bridging CO spectra in Figure 5 could be fitted on the basis of *three* bridging CO groups but not with *two*. Thus, we have a means of establishing the number of bridging CO groups in a dinuclear carbonyl.

Structure of $Fe_2(CO)_8$: Number of Bridging CO Groups. We have already seen (Figure 1) that without ^{13}CO enrichment B has two bridging ν(C–O) bands. If these two bands are assumed to be due to *two* bridging CO groups, we can use their relative intensities to calculate the angle θ between the two groups (eq 1, where *high* and *low* refer to the wavenumbers of the two

$$\tan^2(\theta/2) = I_{\text{low}}/I_{\text{high}} \quad (1)$$

Table II. Observed and Calculated Wavenumbers (cm^{-1}) of ^{13}CO-Enriched $Fe_2(CO)_9$ with the Force Field Illustrated in Figure 3

Terminal ν(C–O) Region (Cf. Figure 4)

fragment[a]	obsd	calcd[c]
$Fe_2(^{12}CO)_6$ (D_{3h})	*d*	2108.02
	2063.9	2065.30
	2037.0	2036.57
	d	2027.80
$[Fe_2(^{12}CO)_2(^{13}CO)]_2$[b] ($C_2$)	2061.0	2058.56
	1995.0	1994.63
$[Fe(^{12}CO)_2(^{13}CO)Fe(^{12}CO)(^{13}CO)_2]$[b] ($C_s$)	2052.5	2052.34
	2007.5	2007.68
$Fe_2(^{12}CO)(^{13}CO)_5$[b] (C_s)	2076.1	2075.96
	2031.4	2032.17
	2004.4	2005.61

Bridging ν(C–O) Region (Cf. Figure 5)

fragment	obsd	calcd[e]
$(\mu\text{-}^{12}CO)_3$ (D_{3h})	*d*	1879.8
	1847.1	1847.1
$(\mu\text{-}^{12}CO)_2(\mu\text{-}^{13}CO)$ (C_{2v})	1872.7	1873.0
	1847.1	1847.1
	1813.6	1812.5
$(\mu\text{-}^{12}CO)(\mu\text{-}^{13}CO)_2$ (C_{2v})	1865.2	1864.3
	1819.2	1821
	1806.1	1806
$(\mu\text{-}^{13}CO)_3$ (D_{3h})	*d*	1837.0
	1806.1	1806

[a] There are 13 isotopomers of $Fe(^{12}CO)_{6-x}(^{13}CO)_x$, but the relatively small number of resolved bands in the observed spectrum (see Figure 4) can be assigned to four principal isotopomers for the purposes of the "least-squares" refinement of the force constants. Of course, the simulation of the observed spectra (Figure 4) requires the inclusion of bands for *all* 13 isotopomers with the appropriate statistical weighting. [b] Only the observed IR bands have been tabulated for these isotopomers. [c] Calculated with use of the force constants (N m^{-1}) k_1 = 1698.6, k_2 = 30.3, k_3 = 16.8, and k_4 = 9.6. For full details of the calculation, see ref 13. [d] IR-inactive vibrations. [e] Calculated with use of the force constants (N m^{-1}) k_5 = 1394.7 and k_6 = 16.4.

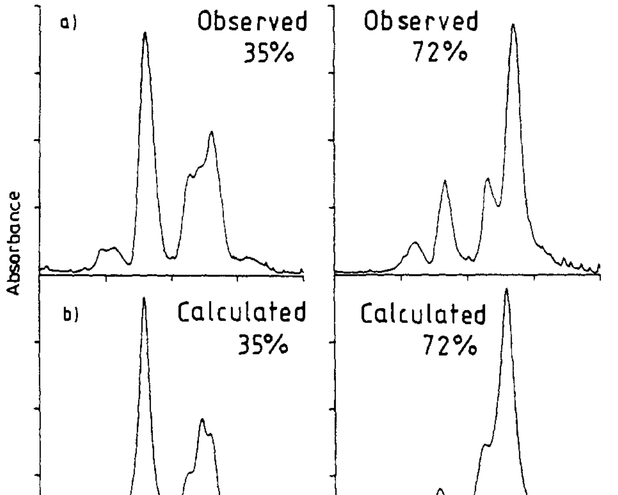


Figure 5. Observed and calculated IR spectra in the *bridging* ν(C–O) region of ^{13}CO-enriched $Fe_2(CO)_9$ (cf. Figure 4 and Table II). The spectra are calculated on the basis of an isolated $(\mu\text{-}CO)_3$ moiety (see Figure 3), consistent with the established structure of $Fe_2(CO)_9$.

---

(19) For full details of the initial assignment procedure for the terminal ν(C–O) bands see ref 13.

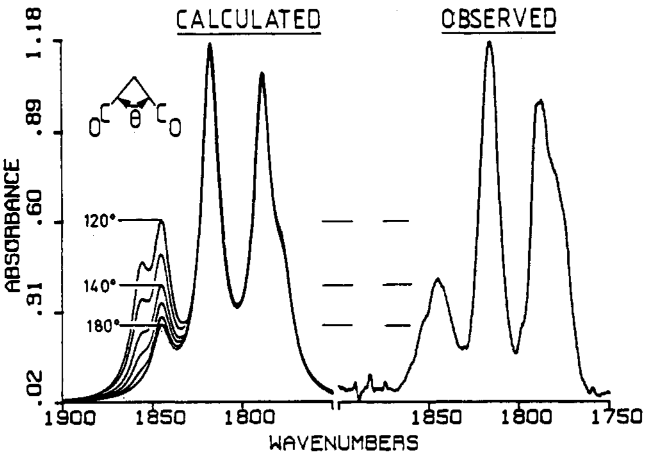


Figure 6. Observed and calculated IR spectra in the bridging ν(C–O) region of isomer B of $Fe_2(CO)_8$. These spectra constitute the principal evidence for assigning structure 2 to isomer B. The observed spectrum was recorded for B, enriched with 35% ^{13}CO (cf. Figure 2). The spectra have been calculated for a series of $(\mu\text{-}CO)_2$ groups with angles between the CO groups from 120 to 180°, all with 35% ^{13}CO enrichment. The calculated spectra only differ significantly in the region of 1850 cm^{-1}. The best agreement between observed and calculated spectra occurs at 140°.

Table III. Observed and Calculated Wavenumbers (cm^{-1}) of Bridging ν(C–O) Bands of ^{13}CO-Enriched B in Ar + 10% ^{12}CO Matrices (Cf. Figure 6)

molecule	obsd	calcd[a]
$(\mu\text{-}^{12}CO)_2$	1857.0	1856.84
	1815.8	1817.40
$(\mu\text{-}^{12}CO)(\mu\text{-}^{13}CO)$	1845.1	1844.92
	1787.3	1788.37
$(\mu\text{-}^{13}CO)_2$	*b*	1815.45
	1779.4	1775.89

[a] Calculated on the basis of structure 2 with use of the force constants (N m^{-1}) k_{CO} = 1363.6 and $k_{CO,CO}$ = 27.3. [b] Predicted to be obscured by stronger absorptions.

bands).[7] The observed intensities (peak heights) are in the ratio 7.6 ± 2, which gives an angle θ = 140 ± 5°.

Figure 6 shows the bridging ν(C–O) region of the observed spectrum of B with 35% ^{13}CO enrichment and the spectra calculated for two bridging CO groups as θ is varied from 120 to 180°. The most obvious effects of changing θ occur in the region of 1850 cm^{-1} of the calculated spectra. Comparison of the observed and calculated spectra in this region shows good agreement for θ = 140°—precisely the angle calculated from the unenriched spectrum via eq 1.

The observed spectrum in Figure 6 cannot easily be fitted to a model with *three* bridging CO groups. Thus, given the excellent agreement between observed and calculated spectra (Figure 6 and Table III), there is little doubt that isomer B of $Fe_2(CO)_8$ has only *two* bridging CO groups, as in structure 3.

As explained above, there is little meaning in the precise numerical value of the C–O factored force constants calculated for isolated bridging CO groups. Is the calculated bond angle any more meaningful? In mononuclear metal carbonyls, bond angles calculated from the intensities of ν(C–O) bands are usually considered to be reliable, unless the compound also contains non-carbonyl ligands (e.g. CS, PPh_3, etc).[7] For polynuclear carbonyls with CO bridges there is so little data that generalization is more difficult. However, from our own spectra, we have calculated the angles between bridging CO groups for $Co_2(CO)_8$ (119° in liquid xenon solution, 127° X-ray[20]) and $Fe_3(CO)_{12}$ (120° in a CO-doped Ar matrix,[21] ~140° X-ray[22]). Thus our calculated angle of 140° for $Fe_2(CO)_8$ probably indicates an $M(\mu\text{-}CO)_2M$ unit closer to planarity than in $Co_2(CO)_8$ but the true bond angle is uncertain.

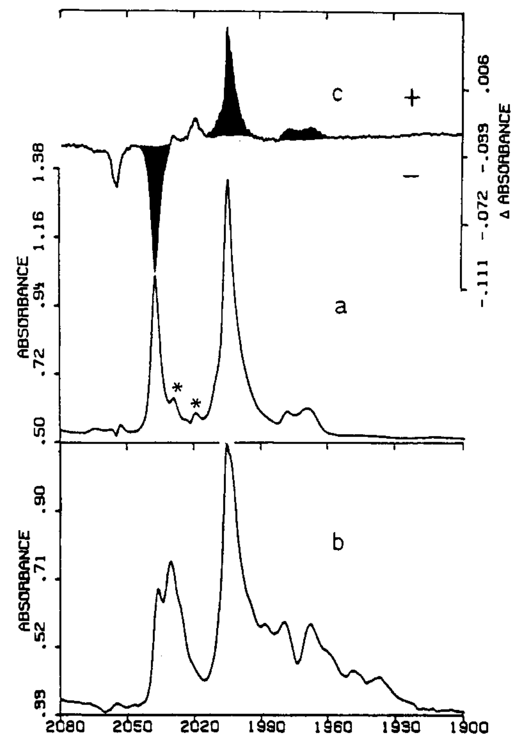


Figure 7. IR spectra of the unbridged isomer, U, of $Fe_2(CO)_8$ in Ar + 10% CO matrices at 15 K: (a) U, natural-abundance ^{13}CO (bands of B removed by computer subtraction, residual absorptions marked with asterisks); (b) U, with 35% ^{13}CO enrichment; (c) linear dichroism spectrum obtained by *prolonged* photolysis with plane-polarized light (λ > 375 nm). Bands due to U are colored black. Negative dichroism (marked −) indicates an IR transition moment *parallel* to the direction of the electric vector of the photolyzing visible radiation.

Bridged $Fe_2(CO)_8$: Terminal CO Groups. Although we analyzed the terminal ν(C–O) bands of $Fe_2(CO)_9$ most successfully (Figure 4), the calculations were relatively simple with 4 force constants and 13 isotopomers. Unfortunately, the symmetry of structure 2 requires no less than *8* force constants and *24* isotopomers. Even with judicious approximations to reduce the number of force constants, the observed spectrum of B (Figure 2b) does not have enough bands to allow a detailed analysis. However, we have already shown that the terminal and bridging CO regions can be treated separately. So we can deduce that the geometries of the terminal CO groups in $Fe_2(CO)_9$ and B are probably similar, because both compounds contain six terminal CO groups and their terminal ν(C–O) spectra are very similar (cf. Figure 2).

We now consider briefly the structure of unbridged $Fe_2(CO)_8$, U, before looking at the reactions of B.

Unbridged Isomer of $Fe_2(CO)_8$, U. There are a number of possible structures for U, 4–7. Of these, the D_{2h} structure, 5, has been predicted[5] to be the most stable and the observed spectra are consistent with this structure. The IR spectrum of U (natural-abundance ^{13}CO) has two strong ν(C–O) bands and two rather weak bands (Figure 7a). At first sight these weak bands might be assigned to ^{13}CO satellites. However, this assignment appears to be incompatible[23] with the observed spectrum of ^{13}CO-enriched U (Figure 7b). Thus all *four* bands of U must

---

(20) Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

(21) Crayston, J. A. Ph.D. Thesis, University of Nottingham, 1984.

(22) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

(23) For a metal carbonyl totally enriched with ^{13}CO, the fundamental vibrational frequencies will be reduced[7] by a factor of 0.9778. Thus, if the band at 2006 cm^{-1} were the lowest fundamental of U, no band should be observed for the ^{13}CO-enriched species at a wavenumber lower than 2006 × 0.9778 cm^{-1} = 1961 cm^{-1}. It is clear from Figure 7b that there are significant absorptions below 1960 cm^{-1} so that the band at 2006 cm^{-1} cannot be the lowest frequency fundamental of U.

Table IV. Summary of the IR-Active ν(C–O) Modes and Their Associated Transition Moments for Four Possible Structures of the Unbridged Isomer, U, of $Fe_2(CO)_8$

structure	point group	IR-active ν(C–O)	transition moment direction
4	D_{3d}	2 a_{2u} e_u	T_z (T_x, T_y)
5	D_{2h}	2 b_{1u} b_{2u} b_{3u}	T_z T_y T_x
6	D_{2d}	2 b_2 2 e	T_z (T_x, T_y)
7	C_{2h}	a_u 3 b_u	T_x[a] (T_y, T_z)

[a] The C_2 axis is taken to be the *x* axis so that the *z* axis should represent the direction of the Fe–Fe bond in all four structures.

be assigned to fundamental ν(C–O) vibrations. This allows us to eliminate structure **4**, which should have only *three* IR-active ν(C–O) modes (see Table IV).

Further structural information[24] comes from the IR dichroism observed when U is generated with plane-polarized light (Figure 7c). (See the Experimental Section for details of polarized photochemistry and IR dichroism.) The spectrum shows that of the four bands of U (colored black in Figure 7c): three bands are polarized in one direction and one band is polarized in the other direction. It can be seen from Table IV that such polarization is consistent with structures **5** and **7** but it is incompatible with structures **4** and **6**.

Molecular orbital considerations[25,26] suggest that structure **7** would be much less stable than structure **5** for *singlet* $Fe_2(CO)_8$. Thus, it is probable that U does have structure **5**, but clearly our results for U are less conclusive than for B. Nevertheless, we can still obtain useful insights into the reactions of B without definitive proof of the structure of U.

Photolysis with Polarized Light (See Experimental Section). Figure 8 shows the spectrum of the IR dichroism produced by photolysis of $Fe_2(CO)_9$ with plane-polarized light. This single spectrum provides a surprisingly large amount of information about $Fe_2(CO)_9$ and $Fe_2(CO)_8$.

(a) Bands of $Fe_2(CO)_9$ (Marked with Arrows in Figure 8). $Fe_2(CO)_9$ has one IR-active bridging ν(C–O) vibration, of e′ symmetry, and two terminal ν(C–O) vibrations, a_2'' and e′. It is clear from Figure 8 that the higher frequency band must have a_2'' symmetry as it exhibits dichroism opposite to that of the bridging e′ band. This assignment is consistent with earlier vibrational studies.[13,27] The overall sign of the IR dichroism shows that the photoactive *UV*/vis transition of $Fe_2(CO)_9$ has a_2'' symmetry. An a_2'' transition moment correlates well with the predicted[28] HOMO → LUMO transition, $(e'')^4 \rightarrow (e'')^3(e')^1$, for $Fe_2(CO)_9$. Calculations by Burdett[25] show that this transition is essentially (Fe–Fe)$\pi^* \rightarrow \pi$ in character, resulting in a large change in overlap population for Fe–$CO_{(\mathrm{terminal})}$ groups. This suggests that the primary photochemical step on photolysis of $Fe_2(CO)_9$ may be loss of a *terminal* CO group, followed by isomerization to B, which is formally derived by loss of a *bridging* CO group.

(b) Bands of Bridged $Fe_2(CO)_8$ (B). The bridging ν(C–O) bands of B will necessarily have transition moments perpendicular to the direction of the Fe–Fe axis in structure **2**. In Figure 8 the bridging ν(C–O) band of B shows dichroism *opposite* to that of the bridging band of unphotolyzed $Fe_2(CO)_9$. This means that B must be formed from $Fe_2(CO)_9$ without significant reorientation of the Fe–Fe axis in the matrix. This contrasts sharply with the case for many mononuclear carbonyls (e.g. $Cr(CO)_5(N_2)$), where photochemical reactions involve rotation or pseudorotation of the photoproducts.[9]

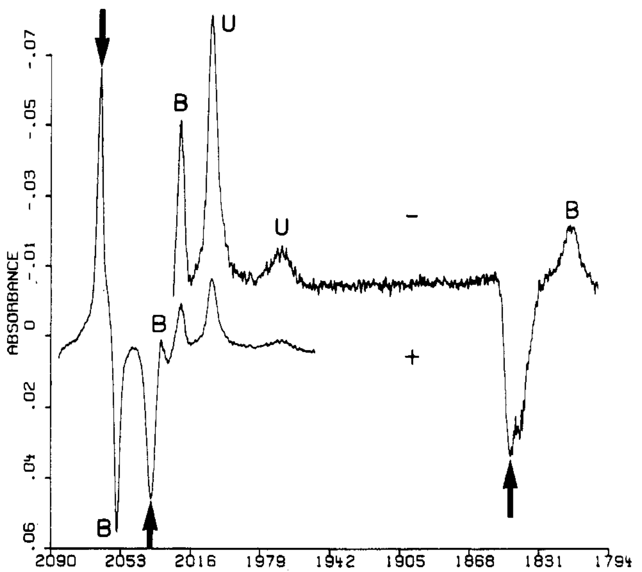


Figure 8. IR dichroism spectrum obtained by *brief* photolysis of Fe_2(CO)$_9$ with plane-polarized light (λ > 375 nm): (↑) $Fe_2(CO)_9$; (B) isomer B of $Fe_2(CO)_8$; (U) isomer U of $Fe_2(CO)_8$. The lower wavenumber region of the spectrum is plotted with a ×4 absorbance expansion. The sign of the IR dichroism has the same meaning as in Figure 7. See text for a detailed discussion of the spectrum.

After prolonged UV/vis photolysis when B is largely converted to U, the sign of the IR dichroism is reversed (not illustrated), indicating a photoactive transition parallel to the Fe–Fe axis (b_1 or b_2 symmetry). Again this can be correlated with a HOMO → LUMO transition. However, since the isomerization B → U can also be promoted by warming the matrix, the overall effect of UV/vis irradiation is probably thermal rather than photochemical.

(c) Bands of Unbridged $Fe_2(CO)_8$ (U). The dichroism of U has already been discussed in connection with its structure (see above). Only two additional points need to be made here. (i) *U* can be photoreoriented. That is, rotation of the plane of polarization of the irradiating UV/vis light causes a rotation or apparent rotation of the molecules in the matrix. Photoreorientation has been observed for smaller molecules, e.g. $Cr(CO)_5$,[9] CrO_2Cl_2,[29] C_5H_4CO,[10] etc., but not previously for a molecule of this size. (ii) The sign of the IR dichroism of the bands of U relative to those of B and $Fe_2(CO)_9$ in Figure 8 is only consistent with structure **5** if formation of U involves a substantial reorientation of the Fe–Fe bond.[30]

There is no evidence that the Fe–Fe bonds of either B or U are broken under the conditions of our experiment. Although $Fe(CO)_5$ can be generated from U in *pure* CO matrices by irradiation with an unfiltered Hg arc for many hours, no traces of $Fe(CO)_4$, $Fe(CO)_5$, or $Fe(CO)_4(N_2)$ were observed in the experiments described here.[31] Any apparent reorientation of U must therefore involve a rotation or pseudorotation of the *intact* $Fe_2(CO)_8$ unit.

---

(24) All our attempts to obtain Raman spectra of these matrix-isolated species failed because of the photosensitivity of the compounds. We are grateful to Professor M. Moskovits and his co-workers for their help with these experiments.

(25) Burdett, J. K., unpublished results.

(26) Ceulemans, A., unpublished results.

(27) Adams, D. M.; Taylor, I. D. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1551. Butler, I. S.; Kischner, S.; Plowman, K. R. *J. Mol. Struct.* **1978**, *43*, 9. Griffith, W. P.; Wickham, A. J. *J. Chem. Soc. A* **1969**, 834. Kristoff, J. S.; Shriver, D. F. *Can. J. Spectrosc.* **1974**, *19*, 156.

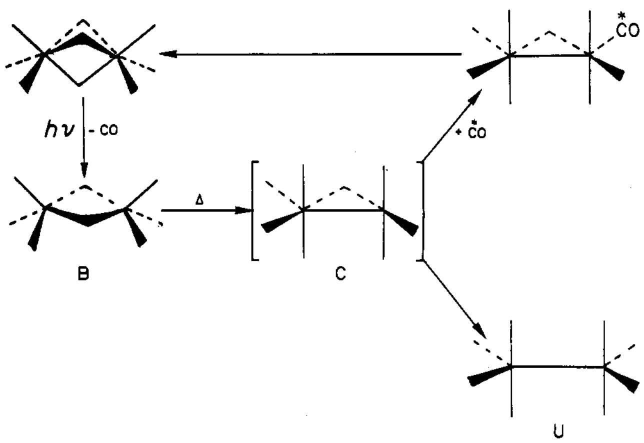
(28) Hoffmann, R.; Lauher, J. W.; Elian, M.; Summerville, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

(29) Grzybowski, J. M., unpublished results.

(30) Our assignment of the ν(C–O) bands requires the molecules of U to be oriented with respect to an axis (either *x* or *y* axis) *perpendicular* to the Fe–Fe bond. To explain the relative signs of the dichroism of B and U, the *x* or *y* axis of U must be oriented at less than 45° to this Fe–Fe bond axis in B. Thus, the isomerization of B → U requires apparent rotation of the Fe–Fe bond axis by an angle *greater* than 45°.

(31) For IR bands of these species, see: Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.

Scheme I



It is not clear however whether these rotations involve the large-scale motion of CO groups or rather a movement of the Fe_2 unit akin to Johnson's proposed mechanism[32] for the isomerization of $Fe_3(CO)_{12}$.

Thermal Reactions of Bridged $Fe_2(CO)_8$ (B). When the matrix is warmed, called "annealing", B undergoes three simultaneous processes: (i) recombination with CO to regenerate $Fe_2(CO)_9$, (ii) reaction with other dopants in the matrix, i.e. N_2, and (iii) isomerization to the unbridged isomer, U. The three processes are clearly in competition. Doping the matrix with CO increases the regeneration of $Fe_2(CO)_9$ and reduces isomerization to U. Interestingly, when the matrix is doped with ^{13}CO, annealing gives rise to an IR band at 2059 cm^{-1}, due to $Fe_2(CO)_8(^{13}CO)$ with the ^{13}CO in a *terminal* position. Thus, the ^{13}CO does not insert into the "vacant" bridging position:

$$\underset{\textbf{B}}{(CO)_3Fe(\mu\text{-}CO)_2Fe(CO)_3} + {}^*CO \xrightarrow{\Delta} (CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_2({}^*CO)$$

Similar effects are observed with N_2. When B is annealed in a pure N_2 matrix, recombination with CO is almost totally suppressed. Instead, $Fe_2(CO)_8(N_2)$ is formed with a terminally bonded N_2 group ($\nu(N{\equiv}N)$ = 2266 cm^{-1}). Again the N_2 does not enter the vacant bridging site but the molecule rearranges to give substitution in the terminal position:

$$\underset{\textbf{B}}{(CO)_3Fe(\mu\text{-}CO)_2Fe(CO)_3} + N_2 \xrightarrow{\Delta} (CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_2(N_2)$$

The fact that the isomerization B → U and substitution reactions appear to be in competition suggests that a common intermediate could be involved in both processes. The observations can be most easily rationalized by a *singly bridged* isomer of B, $(CO)_4Fe(\mu\text{-}CO)Fe(CO)_3$ (see Scheme I). This isomer, C, could either isomerize further to U or add CO to N_2 to its vacant coordination site. In some of our experiments in Ar matrices doped with 5% CO, we observed transient formation of ν(C–O) bands at 2049, 2016, and 1790 cm^{-1}. This could possibly have been due to the singly bridged isomer of $Fe_2(CO)_9$ (cf. $\nu(C\text{–}O)_{bridging}$[33] of $Os_2(CO)_9$, 1778 cm^{-1}), which then reverts to the more stable triply bridged isomer of $Fe_2(CO)_9$. Interestingly, similar transient ν(C–O) bands (~2060 and ~2020 cm^{-1}) have been observed in hydrocarbon solution *at room temperature* both during the thermal decomposition[34] of $Fe_2(CO)_9$ and after the flash photolysis[35] of $Fe(CO)_5$.

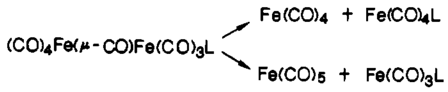
Discussion

Both B and U are unreactive by comparison with coordinatively unsaturated mononuclear metal carbonyl fragments. Thus, B and U are indefinitely stable in pure N_2 matrices at 15 K while $Cr(CO)_5$ reacts instantly[9] under these conditions, to form $Cr(CO)_5(N_2)$. Unsaturated dinuclear metal carbonyls, on the other hand, are often quite unreactive. For example, the 32-electron compound $(\eta\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)_3$ has recently been isolated as a stable solid at room temperature.[36]

However, the most striking feature of the *bridged* isomer of $Fe_2(CO)_8$ is the low activation energy for its thermal reactions and isomerization. Thus, in an Ar/CO matrix, the half-life of isomerization is ~100 s at 35 K, which for a unimolecular process would correspond[37] to an activation energy of ~10 kJ mol^{-1}. Even with an activation energy as small as this, one would predict a substantial temperature dependence in the rate (e.g. at 30 K, $t_{1/2} \approx$ 10 h, which is slow on the time scale of our experiment). Although B does not isomerize rapidly to U at 30 K in an Ar matrix, it does isomerize in less than 10 min at this temperature in an N_2 matrix. Thus, it is probable that the activation barriers are largely due to the softening of the particular matrix material and *not* to an inherent property of B.

Our experiments with polarized light (q.v.) suggest that the isomerization of B to U involves substantial reorientation of the molecules, and it is likely that at 15 K the matrix will hinder such processes. Such "clamping" effects are unusual in matrix isolation but not unprecedented. For example, the primary photoproduct of α-pyrone was observed to undergo thermal rotamerization on annealing the matrix.[38] We are therefore fortunate that B is sufficiently stabilized by the matrix to be observed.

Many dynamic NMR experiments have been rationalized on the basis of the interconversion of two isomers, one unbridged and one with two CO bridges. Most mechanisms invoked in such processes favor the concerted breaking of both CO bridges, because sequential bridge breaking would cause one metal center to exceed an 18-electron configuration, albeit transiently. The isomerization of B to U does not suffer from this constraint as, formally, the two metal centers both have a 16-electron configuration. As explained above, our observations are most easily explained by the transient formation of a singly CO-bridged isomer, C, of $Fe_2(CO)_8$ (see Scheme I). It is worth noting that this scheme can be easily developed to explain how, in solution, the thermal reaction of $Fe_2(CO)_9$ with L (L = ^{13}CO, PPh_3, etc.) leads to the simultaneous formation[39] of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ via the decay of $Fe_2(CO)_8L$:



$$(CO)_4Fe(\mu\text{-}CO)Fe(CO)_3L \begin{cases} \nearrow Fe(CO)_4 + Fe(CO)_4L \\ \searrow Fe(CO)_5 + Fe(CO)_3L \end{cases}$$

Conclusions

The spectroscopic techniques, originally developed for determining the structures of mononuclear metal carbonyls, can be applied to dinuclear compounds. We have established that the bridged isomer of $Fe_2(CO)_8$ has structure **2**. It is more difficult to reach definite conclusions for compounds *without* bridging CO groups. Nevertheless, the unbridged isomer has IR spectra consistent with Hoffmann's predicted structure, **5**.

We have not addressed the question of the electronic ground states of the isomers of $Fe_2(CO)_8$. Isomer B is extremely photosensitive, but isomer U would be an excellent candidate for matrix isolation/MCD studies,[40] particularly since we have ob-

---

(32) See for example: *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 473.

(33) Moss, J. R.; Graham, W. A. *J. Chem. Soc., Chem. Commun.* **1970**, 835; *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(34) Manning, A. R., unpublished observations, 1971.

(35) Church, S. P., private communication.

(36) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. W.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561.

(37) Calculated by using preexponential factor of 10^{13} s^{-1}. The calculation is not sensitive to the precise value of this factor (i.e. $A = 10^{14}$ s^{-1} gives $E_a \approx 11$ kJ mol^{-1}).

(38) McIntosh, C. L.; Chapman, O. L. *J. Am. Chem. Soc.* **1973**, *95*, 244.

(39) See for example: Braterman, P. S.; Wallace, W. J. *J. Organomet. Chem.* **1971**, *30*, C17. Noack, K.; Ruch, M. *Ibid.* **1969**, *17*, 309.

(40) See for example: Barton, T. J.; Grinter, R.; Thomson, A. J.; Davies, B.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1977**, 841.

served two weak visible absorption bands (515 and 620 nm). Even if one isomer of $Fe_2(CO)_8$ had a triplet ground state, spin changes would be unlikely to account for the observed activation barriers for thermal reactions, because previous experiments with $Fe(CO)_4$ have shown that spin-forbidden reactions can proceed thermally in matrices without difficulty.[31]

The characterization of photofragments is clearly more complicated for dinuclear species than for mononuclear. $Fe_2(CO)_9$ is a special case because its physical properties make it difficult to study outside matrices. In general, however, we believe that the problem is best tackled by combining the results of matrix isolation with those of other techniques such as photochemistry in liquefied noble gases[17] or time-resolved IR spectroscopy.[41] Such a combination[42,43] has recently been most successful in the study of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and promises to broaden greatly our understanding of dinuclear compounds.

Acknowledgment. We thank the SERC, Nicolet Instruments Ltd., and NATO (Grant No. 591/83) for generous support. We are grateful to Dr. J. M. Grzybowski for carrying out some of the preliminary experiments and to Professor J. K. Burdett, Dr. A. Ceulemans, Dr. I. R. Dunkin, Dr. D. Fairclough, Dr. G. V. Fraser, Professor S. F. A. Kettle, Dr. J. S. Ogden, Professor M. Moskovits, Dr. C. J. Shields, and Professor E. Weitz for helpful discussions. We thank Dr. N. J. Bristow, Dr. M. A. Healy, and J. G. Gamble for their help.

Registry No. B, 103671-06-3; U, 100459-39-0; $Fe_2(CO)_9$, 15321-51-4; Fe, 7439-89-6; ^{13}C, 14762-74-4.

---

(41) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277.

(42) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

(43) Firth, S.; Poliakoff, M.; Turner, J. J. Presented at the Fifth International Conference on Spectroscopy of Matrix Isolated Molecules, Fontevraud, France, July 1985.

Contribution from the Department of Chemistry,
University of Nottingham, Nottingham NG7 2RD, England

IR Detection and Characterization of $Co(CO)_2NO(\eta^2\text{-1-btn})$ and $Fe(CO)_{2-x}(NO)_2(\eta^2\text{-1-btn})_x$ (x = 1 or 2; 1-btn = 1-Butene) in Liquid Xenon Solution

Gerard E. Gadd, Martyn Poliakoff,* and James J. Turner*

Received February 21, 1986

UV photolysis of $Co(CO)_3NO$ or $Fe(CO)_2(NO)_2$ dissolved in liquid xenon, doped with 1-butene, at −104 °C, yields the previously unknown species $Co(CO)_2(NO)(\eta^2\text{-1-butene})$ and $Fe(CO)_{2-x}(NO)_2(\eta^2\text{-1-butene})_x$, x = 1 or 2, in solution. The disubstituted species $Fe(NO)_2(\eta^2\text{-1-butene})_2$ is thermally unstable at −55 °C and rapidly reacts with CO to form $Fe(CO)(NO)_2(\eta^2\text{-1-butene})$, which is stable at −30 °C. The absence of IR absorptions due to the solvent allows a complete IR characterization of these compounds. With use of FT-IR techniques, it is even possible to observe IR bands due to the coordinated olefins as well as the intense bands due to CO and NO groups.

Introduction

Olefinic and hydrogen complexes of transition metals are often crucial intermediates in homogeneous catalysis.[1] It is clearly important to obtain the maximum possible information on the structure and stability of such complexes, particularly for those unstable, highly reactive species for which X-ray crystallography is generally inapplicable.

We have recently demonstrated that a combination of liquid noble gases as solvents, photochemical techniques, and sophisticated FT-IR spectroscopy can provide very detailed information on unstable organometallic species. For instance, we have generated[2] $Ni(CO)_3N_2$ by photolysis of $Ni(CO)_4$ in N_2-doped liquid Kr (LKr) at −150 °C, and by monitoring the thermal back-reaction $Ni(CO)_3N_2 \rightarrow Ni(CO)_4$, we have obtained detailed kinetic and energetic information about $Ni(CO)_3N_2$. Further examples include the photogeneration of $Cr(CO)_{6-x}(N_2)_x$[3] in liquid Xe (LXe) and that of $Fe(CO)_{2-x}(NO)_2(N_2)_x$ in LKr.[4] Each of these species possesses excellent, intense IR chromophores, ν(C–O), ν(N–N), and ν(N–O), and thus characterization of photoproduct was generally straightforward.

More recent, and more relevant to catalytic systems, was the production[5] of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ by photolysis of $Cr(CO)_6$ in LXe under a pressure of H_2 of several atmospheres. The H_2 in $Cr(CO)_5(H_2)$ is *sideways* bonded, as in the analogous stable compound[6] $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$. The bonding of H_2 in $Cr(CO)_5(H_2)$ was proved by observation[5] of the very weak ν(H–H), ν(D–D), and ν(H–D) stretching vibrations. Similar procedures[7] were used to generate $Co(CO)_2(NO)(H_2)$ and $Fe(CO)(NO)_2(H_2)$ in LXe.

Before examining catalytic systems generally, it is necessary to demonstrate whether the IR spectra of *organic* ligands can be probed in the same way.[8] Such IR spectra have been used extensively to characterize organometallic intermediates in noble-gas matrices,[9] but the interpretation of photochemical experiments in solution has relied almost entirely on ν(C–O) bands since the absorptions of conventional solvents obliterate any weak features due to the coordinated organic ligand.

---

(1) E.g.: Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman & Hall: London, 1981.

(2) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 3898.

(3) Maier, W. B.; Poliakoff, M.; Simpson, M. B.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1980**, 587. Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B., II; Graham, M. A. *Inorg. Chem.* **1983**, *22*, 911.

(4) Gadd, G. E.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 630.

(5) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, *27*. Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645.

(6) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(7) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

(8) It could be argued that NMR is an extremely powerful diagnostic tool for such species, and currently we are exploring NMR in liquid xenon (Gregory, M. F. Ph.D. Thesis, Nottingham University, 1985). However, the sensitivity of IR spectroscopy is likely to be greater.

(9) For recent examples see: Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1982**, *21*, 3647. Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1372.

0020-1669/86/1325-3604$01.50/0 © 1986 American Chemical Society