Infrared Spectra and Structure of Bridging Carbonyls in $Fe_2Ru(CO)_{12}$ and $Fe_3(CO)_{12}$

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Abstract

IR spectra of crystal, solution and pseudo-gas phases (argon and nitrogen matrices) of $Fe_2Ru(CO)_{12}$ and of crystal and solution phases of $Fe_3(CO)_{12}$ were recorded. By quantitative data-handling procedures, structures and bond angles for bridging carbonyls were estimated. $Fe_2Ru(CO)_{12}$ in crystal has a bridging structure analogous to that of $Fe_3(CO)_{12}$, with two bridged carbonyls and C_{2v} or pseudo-C_{2v} symmetry. In solution, both samples contain the same carbonyl bridged structure of C_{2v} symmetry, just as in pseudo-gas phase; the latter, however, contains other bridged molecules of unknown structures, too.

Introduction

Study of the molecular natures of $Fe_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ in solutions has to be considered quite tricky because of the carbonyl bridging. As pointed out by Dorn and Hanson, the $Fe_3(CO)_{12}$ system has been the subject of experimental and speculative investigations to clarify its structure in different phases, while information available on the $Fe_2Ru(CO)_{12}$ is chiefly concerning its interest as precursor of a bimetallic catalyst [1]. However, on the basis of IR solution spectra and NMR measurements for this latter molecule, a behaviour like that of $Fe_3(CO)_{12}$ is suggested [2].

In the present work, IR spectra of $Fe_2Ru(CO)_{12}$ are reported in liquid and pseudo-gaseous phases. For a quantitative comparison between $Fe_2Ru(CO)_{12}$ and $Fe_3(CO)_{12}$, absorbance data in solutions of the latter molecule have also been measured.

Experimental

$Fe_3(CO)_{12}$ (STREM Chemicals) was used without purification. The method given in ref. 3 was applied to produce $Fe_2Ru(CO)_{12}$.

Infrared spectra of solutions and crystals (in Nujol) were recorded using a Digilab FTS 20C spectrometer equipped with a Data General Nova 3 computer. For all spectra recorded, a 50 scans data accumulation was carried out at resolution = 1 cm^{-1}.

Data Handling

All double beam spectra were baseline corrected. For analysing the spectra in the region of the bridging carbonyl stretching modes (1900–1780 cm^{-1}), the sum of Gaussians was fitted to the data points, as described recently [4]. Numerical integration over the entire terminal CO stretching region (2150–1900 cm^{-1}) and over that of the bridging one was also performed using the sum of the areas of theoretical trapezoids formed by successive pairs of data points above the zero baseline.

In the matrix isolation experiments, the apparatus consisted of a Perkin-Elmer 580 B spectrophotometer working in the 200–4000 cm^{-1} range and an Air Product and Chemicals closed-cycle refrigeration system (Displex CSA 202). The CsI sample window was mounted in a cold finger, free to rotate within the vacuum chamber, where the pressure was 10^{-6} torr. The temperature of the window was controlled by a Chromel-gold (0.07%Fe) thermocouple to precision of $\pm$=0.5 K. Best isolation conditions were achieved by evaporating the sample from a glass furnace at room temperature. More intense spectra were obtained by prolonging the deposition time. N_2 and Ar of high purity (Caracciolo Oss., 99.9%) were ulteriously purified through a liquid N_2 trap and the flow regulated by a needle valve.

The appearance of the band of free isolated CO at 2144 cm^{-1} in N_2 matrices is due to a very limited decomposition of the sample. This band seldom appears in Ar matrices. Auxiliary experiments were carried on samples of CO highly diluted in Ar and N_2 (1:10000) which proved that its intensity is strongly enhanced in N_2, keeping all other experimental conditions constant.

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Results and Discussion

The spectra of $Fe_2Ru(CO)_{12}$ in solution in the region 400–4000 cm^{-1} are reported in Fig. 1.

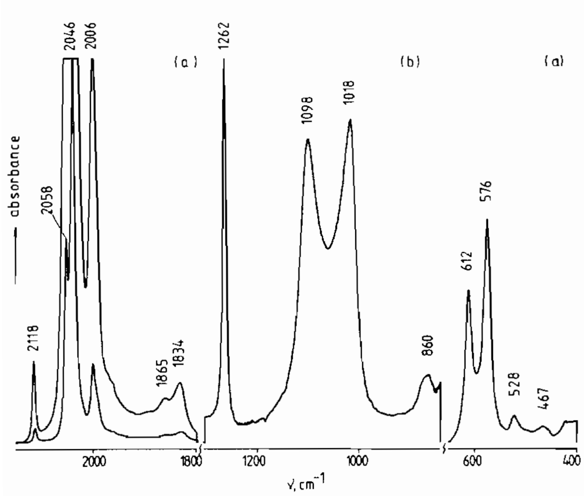

Fig. 1. Spectra of $Fe_2Ru(CO)_{12}$ in solution: (a) in C_6H_{12}; (b) in CCl_4.

Spectra recorded in the solvents CCl_4 and CH_2Cl_2 essentially resemble those in n-hexane, with the exception of the νCO stretching region. For the stretches of terminal carbonyls around 2000 cm^{-1}, a broadening of the bands is observed with the increase of the polarity of the solvent. The region of the bridging carbonyls around 1800 cm^{-1} in all solvents is reported in Fig. 2 in a very expanded scale for both $Fe_2Ru(CO)_{12}$ and $Fe_3(CO)_{12}$. A significant

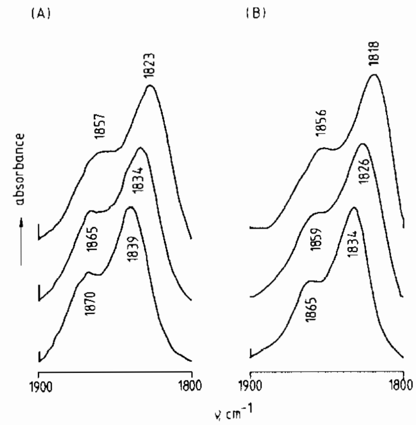

Fig. 2. The CO stretching region of bridging carbonyls in solutions; (a) $Fe_3(CO)_{12}$, (b) $Fe_2Ru(CO)_{12}$.

shift towards lower frequencies is shown with increasing polarity (for a detailed analysis of these band systems, see later).

The spectra of $Fe_2Ru(CO)_{12}$ isolated in argon and nitrogen are reported in Figs. 3 and 4, respectively, in the region 2150–1810 cm^{-1}. The most remarkable feature is that two bands are observed at 2055 and 2052 cm^{-1} in argon, while only a single band is seen in nitrogen. On grounds of the supposed C_{2v} symmetry, 11 IR active bands are expected in the terminal CO stretching region. G. A. Battiston *et al.* [5], in their very accurate calculations on similar bimetallic dodecacarbonyl clusters of $Os_2Ru(CO)_{12}$, demonstrate that the degeneration of the band around 2066 cm^{-1} (E′ in D_{3h}) is strictly kept, while the left

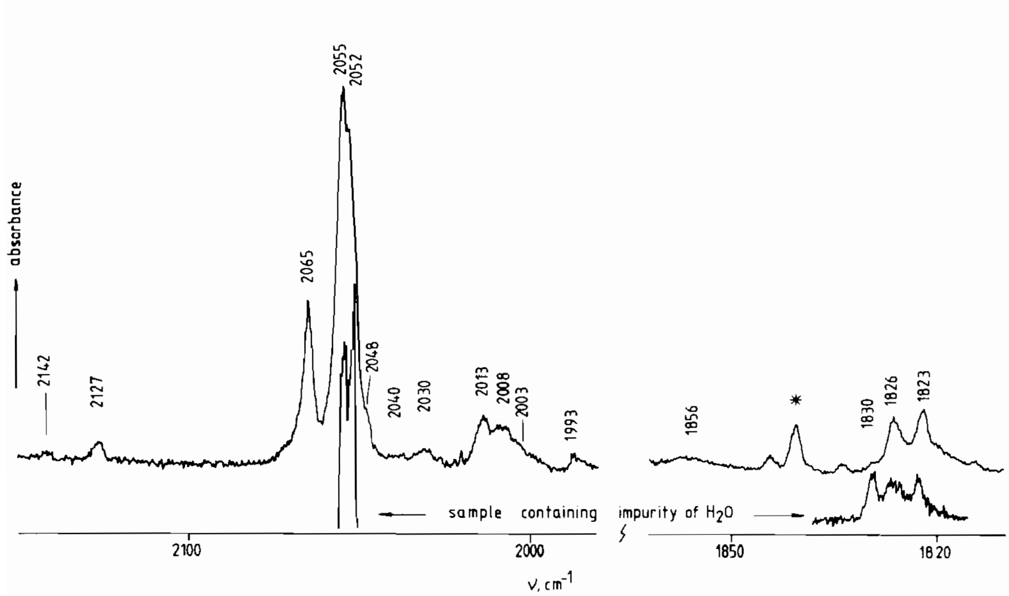

Fig. 3. Spectra of $Fe_2Ru(CO)_{12}$ isolated in argon matrix.

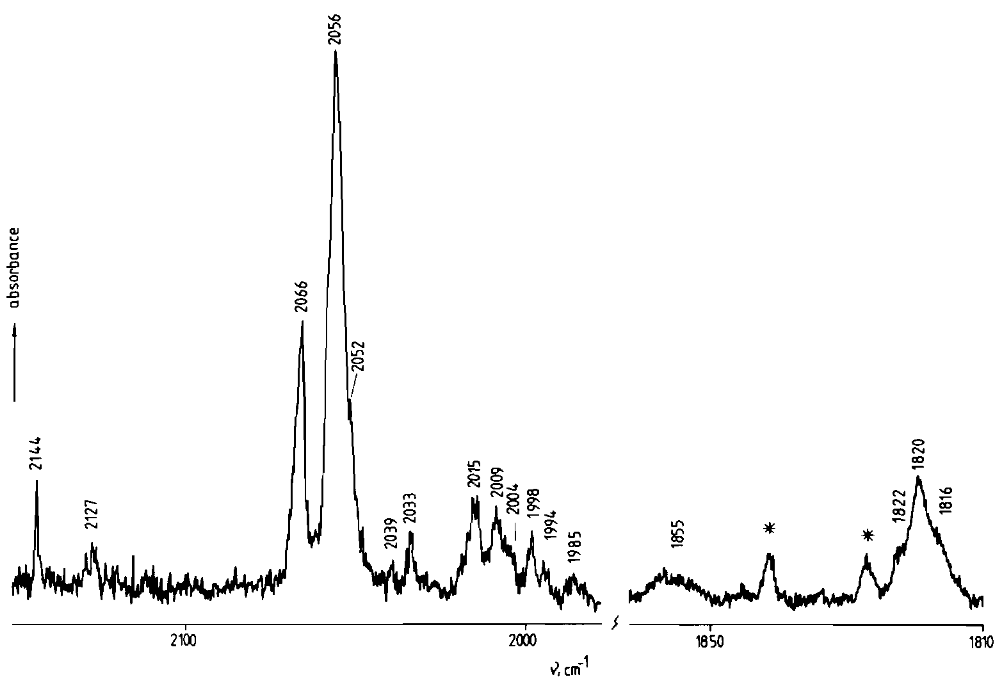

Fig. 4. Spectra of $Fe_2Ru(CO)_{12}$ isolated in nitrogen matrix.

two bands of lower frequencies split; so 10 bands are expected, as we have observed. A_1 bands in the C_{2v} point group originated from IR-inactive A_1 bands in the pseudo-symmetry. D_{3h} are expected to be very weak, as observed for the band at 2127 cm^{-1} in both Ar and N_2. In accordance with this expectation, the other A_1 band of the same origin is probably overlapped by the very strong B_2 band which is supposed to be quite close in frequency [5]. It is worth mentioning that in Ar, in the presence of water impurity, this very strong band splits into two components whose relative intensity depends on the amount of water. Poor isolation degree cannot explain this behaviour because no changes are observed in annealing cycles, excluding also the possibility of second site effects. Also, the increase in intensity of the A_1 mode lying in this region seems unlikely [5]. The most reasonable explanation seems to be the coexistence of two different, rather static structures. This hypothesis is supported by some similar features in the region of the CO bridging stretches (see later). All frequencies in different phases are collected in Table I. A tentative assignment is also reported for the complete spectrum.

Five structures are possible in principle for both $Fe_3(CO)_{12}$ [2, 6] and $Fe_2Ru(CO)_{12}$ in solution, as shown in Fig. 5. Molecules may possibly pass more or less through these structures via scrambling of the carbonyl groups around the metal atoms.

In principle, two mechanisms for the scrambling have been proposed:

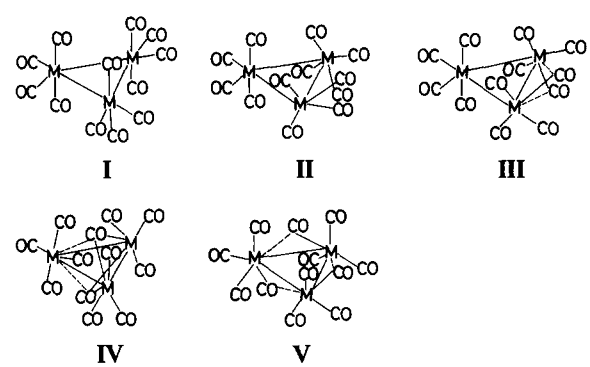

Fig. 5. Hypothetic structures for $Fe_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ molecules. In the case of the $Fe_3(CO)_{12}$ molecule, the respective symmetries are: D_{3h}(I), D_3(II), C_{2v}(III), C_2(IV) and C_{3v}(V), and those of $Fe_2Ru(CO)_{12}$: C_{2v}(I), C_2(II), C_{2v}(III), C_{2v}(IV) and C_s(V).

(i) a repeated interconversion of the carbonyl groups is maintained while a continuous reorientation octahedral arrangement over the structures:

$$\mathrm{V} \rightleftarrows \mathrm{I} \rightleftarrows \mathrm{III}$$

(ii) the icosohedral arrangement of the twelve CO groups is maintained while a continuous reorientation (rotation or oscillation) of the Fe_3 triangle within the icosohedron takes place:

$$\mathrm{III} \rightleftarrows \mathrm{II} \rightleftarrows \mathrm{IV}$$

Analogous structures and mechanisms of scrambling can also be supposed for $Fe_2Ru(CO)_{12}$.

TABLE I. IR Frequencies (cm^{-1}) of $Fe_2Ru(CO)_{12}$ Observed in Solutions and Noble Gas Matrices

C_6H_{12}	CCl_4	CH_2Cl_2	N_2-matrix	Ar-matrix	Assignment[a]
			2144m	2142vvw	Molecular CO
2127w	2128w	2128w	2127w	2127w	term. CO st. (a_1)
2057ms	2057ms	2057ms	2066ms	2066ms	term. CO st. ($a_1 + b_1$)
			2056s	2055s	term. CO st. (b_2)
2044s	2044s	2044s		2052s	
			2052sh	2048sh	
			2039vw	2040vw	
			2033w	2029vw	
2030w	2029w	2028w			
			2015w	2013w	term. CO st. ($a_1 + b_1$)
2006m	2004m	2001m	2009w	2007w	term. CO st. ($a_1 + b_1$)
			2004vvw	2003vvw	term. CO st.
			1998w		
			1994vw	1993vw	term. CO st. (b_1)
1975vw			1985vw		($a_2^b + b_1$)
1963vw			1939vw		
			1920vw		
			1916vvw		
1865w	1859w	1850w	1855w, br	1855w, br	bridged CO sym. st.
			1822w	1830w	bridged CO asym. st.
1834mw	1826mw	1818mw	1820m	1826w	bridged CO asym. st.
			1816w	1823w	bridged CO asym. st.
1262w	1262w				
1250m					
1100w	1100w	1095w			
	1018w	1017w			
	862vw	860vw			
	661vw		650w		
612vw	610vw	610vw	622vw	623vw	
			618m	615w	
576m	574m	573m			
523w	523w	521w			
476w, br	465w, br				

[a] Symmetries in C_{2v} point group. [b] Inactive in C_{2v}.

The spectra of $Fe_2Ru(CO)_{12}$ recorded in solutions, like those of $Fe_3(CO)_{12}$, are rather in agreement with the expectation for the structures **I** and **II**. That means that most of the molecules, in the IR time scale, are unbridged, as also supported by their very strong relative intensity in the CO terminal region, in comparison with very low absorptions in the CO bridging region.

As seen in Fig. 2, the latter region contains very broad bands. In order to get more information on the molecules containing bridged carbonyls, we analyzed the spectra obtained in this region for the $Fe_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ in hexane, tetrachloromethane and chloromethane together with the spectra recorded on crystals, by fitting the sums of Gaussians to experimental data. In Table II we collected the wave numbers and integrated intensities of the Gaussian components. In all cases, the band system of the bridging carbonyls produced only two components.

The broadness of the Gaussians may suggest an assignment to a degenerated mode of a three-bridged structure (that is, to structure **V**). This expectation, however, should be ruled out for $Fe_2Ru(CO)_{12}$ because its highest symmetry is C_{2v}. In addition, any attempt to split one of the Gaussians of $Fe_2Ru(CO)_{12}$ into two components failed.

The intensity data derived by the fitting procedure makes it possible to calculate the angles between the C–O bond directions of the two bridging carbonyls (Fig. 6). For the crystal of $Fe_3(CO)_{12}$, this angle can be easily calculated from X-ray data. Using the data of Wei and Dahl [7] this angle is calculated to be of

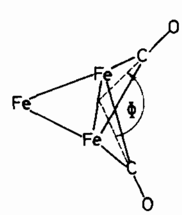

Fig. 6. Definition of angle ϕ between the two C–O bonds of bridging carbonyls.

TABLE II. Frequencies of the ν_s and ν_{as} Stretching Modes of the Bridging Carbonyls; Intensity Ratios $I_{\nu_{as}}/I_{\nu_s}$ and Bond Angles ϕ of the Bridging C–O Bonds as Defined in Fig. 6

Phase	$Fe_3(CO)_{12}$				$Fe_2Ru(CO)_{12}$			
	ν_s (cm^{-1})	ν_{as} (cm^{-1})	$I_{\nu_{as}}/I_{\nu_s}$	Bond angle ϕ(°)	ν_s (cm^{-1})	ν_{as} (cm^{-1})	$I_{\nu_{as}}/I_{\nu_s}$	Bond angle ϕ(°)
C_6H_{12} solution	1870	1839	1.97	126.2	1865	1834	2.41	134.8
CCl_4 solution	1865	1834	1.70	119.2	1859	1826	1.76	121.0
CH_2Cl_2 solution	1857	1823	0.47	50.1	1850	1818	0.85	80.8
Crystal	1857	1815	2.90	142.0 140.73[c]	1856	1819	3.80	150.5
N_2 matrix	1867[a] 1862[a]	1829[a] 1827[a]	~3.2[b]	~145[b]	1855	1822 1820 1816	~3.6	~149
Ar matrix	1871[a] 1867[a]	1833[a]	~3.4[b]	~147[b]	1856	1830 1826 1823	~3.6	~149

[a]Ref. 9. [b]Values estimated using the spectra in Fig. 5 of ref. 9. [c]Value calculated from the X-ray data of ref. 8.

$\phi = 157.68°$, while using the most recent data published by Cotton and Troup [8] for ϕ we calculated 140.73°. (The angle ϕ shows a value very close to that of the dihedral angle of the planes Fe(3)–Fe(2)–C(1) and Fe(3)–C(2)–Fe(2)!) The rather large difference between the angles ϕ calculated from data reported in the two different papers indicates the difficulties caused by the disorder effect. Between the angle ϕ and the intensity ratio of the symmetric (I_s) and asymmetric (I_{as}) combinations of the two CO stretches, the equation

$$I_{as}/I_s = \frac{\sin \phi/2}{\cos \phi/2}$$

holds. If we suppose that the band at higher wave number belongs to the ν_s mode and the band at lower frequency to the ν_{as} modes, the intensity ratio is found to be $I_{as}/I_s = 2.9$, and the angle ϕ calculated from this intensity ration is $\phi = 142°$, which is very close to the value of $\phi = 140.73°$ calculated from the X-ray data published by Cotton and Troup [8]. This excellent agreement indicates that the above assignment of the ν_s and ν_{as} modes is correct. The opposite assignment would give a value of $\phi = 38°$. Using this assignment we have calculated the values of angle ϕ for $Fe_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$, in hexane, tetrachloromethane and dichloromethane solutions, together with the values in crystal, as shown in Table II. In the case of the molecule of $Fe_3(CO)_{12}$ in crystal, a pseudosymmetry of C_{2v} has been found [7–8], which is in principle identical to the structure **III** in Fig. 5. The IR spectrum of the crystal in the region of bridging carbonyl stretches essentially resembles those of the solutions; therefore, we can suppose that the structure **III** holds for the bridged molecules in solution. Further, for the same reasons, the structure of the bridging $Fe_2Ru(CO)_{12}$ molecules in both crystal and solutions should be analogous with that of $Fe_3(CO)_{12}$, that is, with the structure **III** of C_{2v} symmetry. The analogy between both clusters is rather wide: in hexane the angle between the bridging C–O bonds is somewhat closer than in the crystal, and it rapidly decreases with the polarity of the solvent. The frequencies of both ν_s and ν_{as} decrease, which infers that the C–O bond length increases with the polarity. The frequencies measured in crystals lie between those found in CCl_4 and CH_2Cl_2.

Poliakoff and Turner [9], in their matrix isolation study of $Fe_3(CO)_{12}$, found two bands in carbonyl bridging region, both split into two components. They attributed the splitting to a distorting effect of the matrix on the two bridges (C_{2v} structure). For $Fe_2Ru(CO)_{12}$ we found four bands at 1855, 1822, 1820 and 1816 cm^{-1} in N_2 and at 1856, 1830, 1826 and 1823 cm^{-1} in Ar. Their relative intensities are different when passing from N_2 to Ar; as no changes were observed in repeated annealing cycles, we are of the opinion that matrix effects may be excluded. Therefore, more than one (possibly two) bridged structure has to be taken into account. In Table II we also show the averaged values of the angles ϕ. They are very close to the values calculated for the crystals.

Finally, ratios between integrated intensities of stretching modes of terminal and bridged carbonyls are shown in Table III. Cotton and Hunter in their qualitative IR study of $Fe_3(CO)_{12}$ observed that with increasing solvent polarity, the absorption in the bridging region increased [10]. The quantitative values that we obtained for $Fe_3(CO)_{12}$ support this prediction, and, for $Fe_2Ru(CO)_{12}$ in the same solvents, they are of the same order of magnitude and show the same trend with the polarity of the solvent

TABLE III. Ratios of the Integrated Intensities of the Band System of the Terminal Carbonyls (2150–1900 cm^{-1}) and that of the Bridging Ones (1900–1780 cm^{-1}), R = $I_{CO(terminal)}/I_{CO(bridged)}$, in Different Phases

	R = $I_{CO(terminal)}/I_{CO(bridged)}$	
	$Fe_3(CO)_{12}$	$Fe_2Ru(CO)_{12}$
C_6H_{12} solution	48.3	25.92
CCl_4 solution	36.6	21.58
CH_2Cl_2 solution	28.3	17.58
Crystal	7.71	10.97
N_2-matrix	–	~3.2
Ar matrix	–	~4.7

itself. It seems that the fraction of $Fe_3(CO)_{12}$ molecules containing bridges is somehow lower than that of $Fe_2Ru(CO)_{12}$ ones.

In the pseudo-gas phase, however, a significantly larger part, if not all, of the molecules must be bridged.

Conclusions

$Fe_3(CO)_{12}$ undergoes rapid CO scrambling in solution [1, 2, 6] and the activation energy for this process is $\leqq 5$ kcal mol^{-1} [7]. Thus carbon-13 NMR spectroscopy has too slow a time scale (10^{-1}–10^{-9} s) to resolve the different solution structures [1]. Even in crystal, a very rapid rotation of the iron triangle takes place, which, on the time scale of NMR, is not resolvable either. On the X-ray crystallography time scale (10^{-18} s), the sample is in the slow exchange limit and two enantiomers are observable [1]; however, X-ray crystallography is not applicable for studies in solutions.

Infrared spectroscopy (time scale: 10^{-13}–10^{-14} s) is expected to supply useful structural information on different isomers in both crystal and solution. By quantitative treatment of the IR spectra recorded on crystals, solutions and pseudo-gas phases, we have come to the following conclusions:

(a) $Fe_2Ru(CO)_{12}$ in crystal has a bridging carbonyl structure of C_{2v} symmetry or pseudo-symmetry analogous to $Fe_3(CO)_{12}$, with two carbonyls per molecule, and the angle between the C–O bonds of the bridging carbonyls ($\phi = 150.5°$) is very close to that of $Fe_3(CO)_{12}$ ($\phi = 140.73°$ calculated from X-ray data of ref. 8, and $\phi = 142.4°$ from our IR intensity data).

(b) In solutions, most of the molecules of both clusters are unbridged with a D_3 or D_{3h} ($Fe_3(CO)_{12}$) or pseudo D_3 or D_{3h} ($Fe_2Ru(CO)_{12}$ structure. The ratios of the integrated intensities of the terminal and bridging carbonyl stretching bands suggest that the bridged part is higher in solutions of $Fe_2Ru(CO)_{12}$ than in those of $Fe_3(CO)_{12}$.

(c) With the increasing polarity of the solvents, the bridged part of the molecules of both clusters increases; however, the increase is more rapid for $Fe_3(CO)_{12}$ than for $Fe_2Ru(CO)_{12}$.

(d) In solutions the angle between the C–O bonds of the bridging carbonyls closes slightly in the non- or less-polar C_6H_{12} or CCl_4 and drastically in the highly polar CH_2Cl_2. Also in this respect, $Fe_3(CO)_{12}$ is more sensitive than $Fe_2Ru(CO)_{12}$.

(e) Points b–d indicate that in $Fe_2Ru(CO)_{12}$ ruthenium stabilizes the bridge structure somewhat.

(f) The existence of three-carbonyl-bridged isomer in solution has been excluded.

(g) In the pseudo-gas phase, most of the molecules of $Fe_2Ru(CO)_{12}$ are found in bridged states with C_{2v} symmetry.

(h) A minimum of two isomers with bridged structures in pseudo-gas phases can be distinguished. The most pronounced isomer, on the basis of its IR frequencies, relative intensities and, consequently, angle ϕ, must have a structure very similar to that found in the crystal.

References

1 H. Dorn and B. E. Hanson, *Inorg. Chim. Acta, 54,* L71 (1981).
2 A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson and W. G. Jackson, *J. Chem. Soc. Chem. Commun.,* 1042 (1974).
3 D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A:,* 502 (1969).
4 S. Dobos, I. Böszörményi, V. Silberer, L. Guczi and J. Mink, *Inorg. Chim. Acta, 96,* L13 (1985).
5 G. A. Battison, G. Bor, U. K. Dietler, S. F. A. Kettle, R. Rossetti, G. Sbrignadello and P. L. Stanghellini, *Inorg. Chem., 19,* 1961 (1980).
6 B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.,* 703 (1976).
7 C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc., 91,* 1351 (1969).
8 F. A. Cotton and I. M. Troup, *J. Am. Chem. Soc., 96,* 4155 (1974).
9 M. Poliakoff and J. J. Turner, *J. Chem. Soc. A:,* 654 (1971).
10 F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta, 11,* L9 (1974).