Observation of Localised CO Exchange Mechanisms at the Iron and Ruthenium Centres of Di-μ-carbonyl (*Fe*: *Ru*^{2},*Ru*^{3})-di-μ-hydrido(*Ru*^{1}:*Ru*^{2},*Ru*^{3})-*tetrahedro*-tris(tricarbonylruthenium)dicarbonyliron(3*Fe–Ru*,3*Ru–Ru*) by ^{13}C N.m.r Spectroscopy

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Summary Variable temperature ^{13}C n.m.r. studies show that [$H_2FeRu_3(CO)_{13}$] is undergoing intramolecular carbonyl exchange in three distinguishable stages: the first localised at iron; the second localised at the three rutheniums; and the last general over all metal centres.

During the continuation of our studies[1] of the ^{13}C n.m.r. spectra of ruthenium hydride and other clusters, we observed that the room temperature ^{13}C spectrum of [$H_2FeRu_3(CO)_{13}$] (I),[2] showed only one broad signal, indicating that the molecule is stereochemically non-rigid, as might be expected from recent work.[3,4] Significantly, the slow exchange limit was successfully reached at −92 °C in $CHFCl_2$–CD_2Cl_2 solution and yielded a very rich and useful carbonyl spectrum displaying eight resonances (see Figure). The shifts from low to high field (relative to Me_4Si) are 231·9, 212·0, 204·4, 195·3, 191·1, 190·4, 188·2, and 187·7 p.p.m. They have integrated intensities of 2:1:1:2:2:2:1:2 respectively.

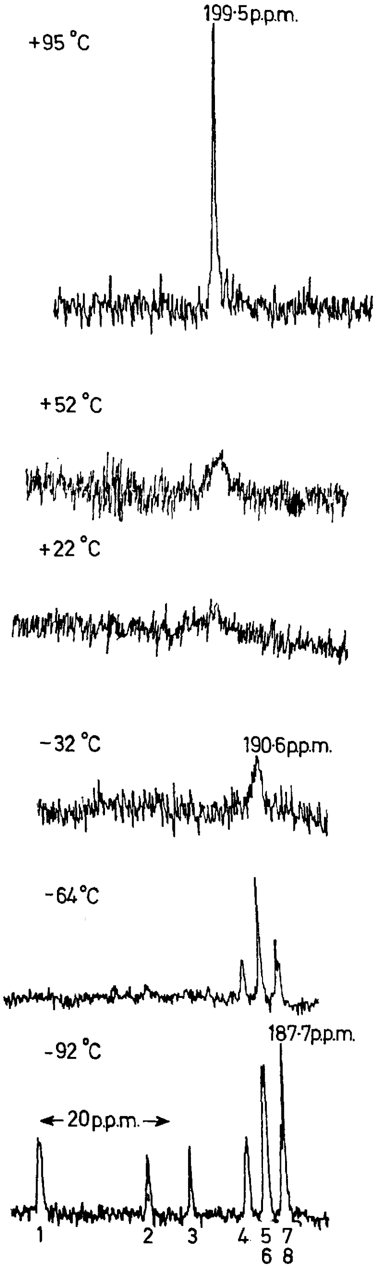
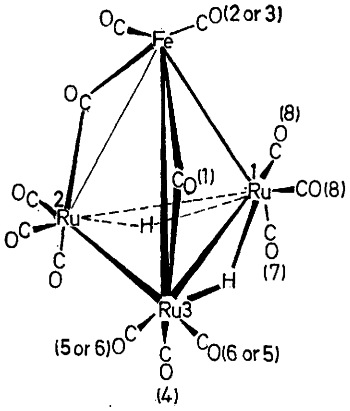


FIGURE Variable temperature ^{13}C-n.m.r. spectra of (I) from −90 °C to +95 °C in $CHFCl_2$–CD_2Cl_2 (50 mg in 3 cm^3) approximately 30% enriched ^{13}CO and 0·05 M in $Cr(acac)_3$. Spectra were run on a Jeol-PFT 100 at 25·1 MHz.

Some assignments of these resonances can be made relative to the solid-state structure obtained by *X*-ray methods.[5] The three low-field resonances can be ascribed to the carbonyl groups attached to iron, on the basis of the intensities and of the expected low field effects due to bridging, together with the observed shift to higher field for terminal carbonyl groups attached to ruthenium,[3,4] but we cannot discriminate between (2) and (3). The resonance of the axial carbonyl group on Ru(1) is readily assigned, since it is the only carbonyl group bound to ruthenium which should give a signal of relative intensity one. The equatorial carbonyl groups (8) on Ru(1) are assigned to the highest field resonance, on the basis of a shift similar to (7) and by analogy with the shift in $[H_4Ru_4(CO)_{12}]$[4,6] Resonances (5) and (6) can be assigned (but not discriminated) because of the expected similarity of the two equatorial environments for carbonyl groups on Ru(2) and Ru(3). The remaining resonance (δ 195·3) is assigned to the axial carbonyl groups (4) on Ru(2) and Ru(3). This resonance and resonance (1), each intensity 2, are broader than the other resonances which possibly reflects some localised distortions in the structure. Distortions in the crystal have been observed.[4]



(I)

Figures in brackets are tentative assignments only.

^1H-coupled ^{13}C spectra at a sample temperature as low as −100 °C show only minor broadening of the ruthenium-bound carbonyl groups. $^2J(^1H-^{13}C)$, therefore, is probably smaller in (I) than in other ruthenium hydrides,[6] although residual exchange of the hydride could still be rapid enough to collapse this coupling.

At −72 °C, the ^{13}C n.m.r. spectrum shows broadening of the iron carbonyl resonances, (1), (2), and (3), whereas the resonances of the remaining ruthenium carbonyl groups remain sharp. At slightly higher temperatures the differential affect is accentuated (see Figure). The simplest explanation is that the bridges open on the ruthenium side and that complete localised scrambling then occurs at iron.

At −45 °C the ruthenium-bound carbonyl resonances have collapsed to a single resonance at δ 190·6. The average shift expected for a localised scrambling at ruthenium is 190·8. Two general mechanisms are possible; one involving bridged carbonyl intermediates, and a second which does not.[3,6] Either could apply to the mixed iron–ruthenium trinuclear species $[Fe_2Ru(CO)_{12}]$, but the latter is indicated for $[Ru_3(CO)_{10}(NO)_2]$.[3]

Above −30 °C the resonance at 190·6 p.p.m. broadens further as the temperature is increased and is lost in noise until at +35 °C a broad resonance emerges and gradually sharpens to a single resonance at +95 °C. The shift of this resonance, 199·5 p.p.m., is in excellent agreement with the value for the weighted average chemical shift of all carbonyl groups (199·8 p.p.m.). This last stage of the exchange leads to a scrambling of all carbonyl resonances and must involve exchange of carbonyl groups between iron and ruthenium. The rate-determining step for exchange of carbonyl groups between iron and ruthenium requires opening of the unsymmetrical bridge at the Fe–CO(1) bonds (bond length 1·63—1·84 Å)[4] and would be expected to have a higher activation energy than the bridge opening at Ru–CO(1) (bond length 2·25—2·32 Å)[4] which is probably the rate determining step for the first stage of the exchange. At higher temperatures all three stages of exchange are occurring simultaneously. Since the entire process is reversible and is independent of solvent and sample concentration,† the possibility of intermolecular exchange can be ruled out.

These mechanisms clearly show the multi-stage nature of the overall exchange process in (I).

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† Samples at various concentrations were run in pure CD_2Cl_2 and $CDCl_3$ over the entire temperature range of these solvents and the spectra obtained were not significantly different from those reported here. Repeated runs at room temperature or above sometimes resulted in formation of an impurity peak at 199·0 p.p.m., probably $[Ru_3(CO)_{12}]$, which remained sharp in the temperature range studied and had no effect on the observed exchange process.

[1] M. Evans, M. B. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545.

[2] D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 502.

[3] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042, and references therein.

[4] (a) L. J. Todd and J. R. Wilkinson, *J. Organometallic Chem.*, 1974, **77**, 1; (b) two resonances have been reported for $[Ru_3(CO)_{12}]$ by the authors of ref. 4(a), whereas the authors of ref. 3 report only one down to −50 °C (δ_{CO} 199·7 p.p.m.) We have found that $[Ru_3(CO)_{12}]$ shows only one resonance down to −100 °C (δ_{CO} 198·9 p.p.m.). We have recorded the spectrum of $[H_4Ru_4(CO)_{12}]$ (see below) and its shift is identical with one of those reported for $[Ru_3(CO)_{12}]$ by Todd and Wilkinson.

[5] C. J. Gilmore and P. Woodward, *J. Chem. Soc. (A)*, 1971, 3453.

[6] E. Rosenberg, L. Milone, and S. Aime, to be published.