Inorganica Chimica Acta, 29 (1978) L211–L212

Solution Structure and Dynamics of $H_2Ru_4(CO)_{13}$

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Received April 25, 1978

The study of the stereochemical non-rigidity of metal carbonyls is of considerable current interest in order to determine the mechanistic details of their dynamics [1] and to correlate their dynamic properties with their catalytic activity [2]. From the studies on the dynamics of tetranuclear species it appears that a variety of different mechanisms may occur and that the multistage nature of carbonyl scrambling is a common feature [1, 3].

In 1975 we reported about the stereochemical non-rigidity of the mixed metal hydride $H_2FeRu_3(CO)_{13}$ (I) (Fig. 1: Ru_1 = Fe) [4]. We observed that the intramolecular carbonyl exchange occurs in three distinguishable stages and we suggested that the first step is localised at iron, the second is localised at the three ruthenium atoms and the last is general over all metal centres. The interpretation of the second step of the mechanism has been recently questioned by a study of the dynamic properties of $H_2FeRuOs_2(CO)_{13}$ (II) [5], isostructural with I [6], which led to the reinvestigation of the dynamics of I [5]. We have examined the variable temperature ^{13}C-n.m.r. spectra of $H_2Ru_4(CO)_{13}$ (III) (Fig. 1), isostructural with I and II [7], in order to further assess the role of the nature of the metals in determining the dynamic behaviour of these systems.

Experimental

$Ru_3(CO)_{12}$ has been enriched by stirring it at 50 °C for five days in the presence of <1 atmosphere of 90% enriched ^{13}CO (Stohler Isotope Chemicals). $Ru_3(CO)_{12}$ has been hydrogenated to $H_4Ru_4(CO)_{12}$ by literature methods [8]. $H_4Ru_4(CO)_{12}$ has been reacted with 2-pentene according to the report that olefins readily dehydrogenate $H_4Ru_4(CO)_{12}$ to produce $H_2Ru_4(CO)_{13}$ [9]. The identity of the sample has been confirmed by mass and ^1H-n.m.r. spectra [10]. The solution of III in CD_2Cl_2 has been sealed under vacuum in a 10 mm tube with the addition of $Cr(acac)_3$ as an inert relaxation reagent and tetramethylsilane as an internal standard. The ^{13}C-n.m.r. spectra were recorded on a Jeol–PFT-100 operating at 25.1 MHz in the Fourier transform mode. The chemical shifts are reported downfield positive with respect to internal TMS.

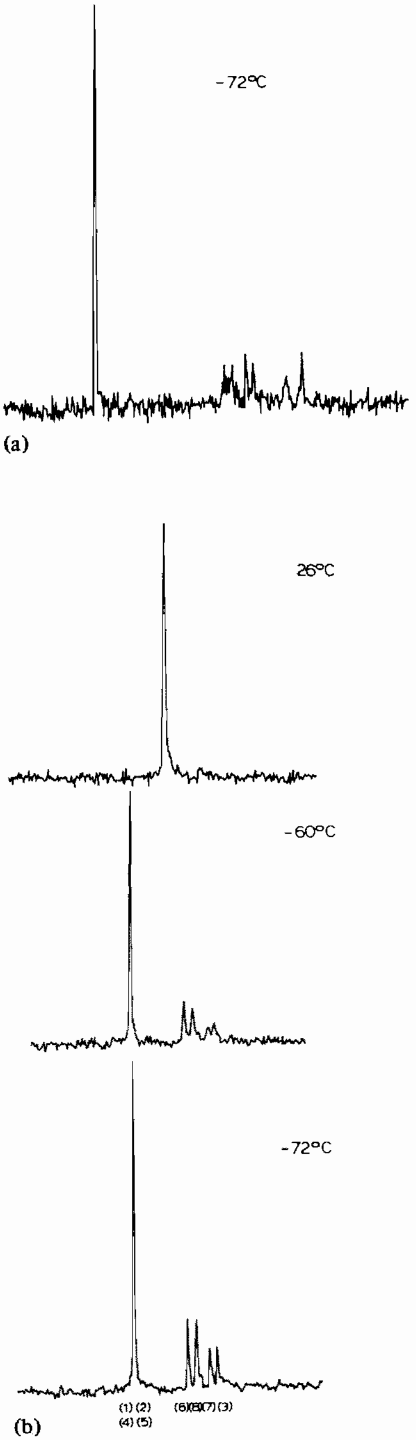

Figure 1. Variable temperature ^{13}C-n.m.r. spectra of $H_2Ru_4(CO)_{13}$. (a) ^1H-coupled spectrum (2.5 Kc sweep width); (b) ^1H-decoupled spectra (5 Kc sweep width).

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Results and Discussion

In the proton decoupled spectrum of $H_2Ru_4(CO)_{13}$ at –72 °C (Fig. 1) [11] five resonances have been observed at 201.2, 191.1, 189.5, 187.0 and 185.7 ppm with integrated intensities 7:2:2:1:1. The number and the intensity of the resonances are not in accord with the solid state structure [7], suggesting that at this temperature some carbonyls are still exchanging. The absence of any peak in the region of bridging carbonyls indicates that the two bridging carbonyls and five terminal carbonyls are involved in the scrambling. The proton coupled spectrum shows that sizable coupling of the carbonyls with the hydrides is observed only for the two peaks of intensity 2($^2J_{H-C}$ = 13.7 Hz in both cases). Accordingly the resonances at 191.1 and 189.5 are assigned to carbonyls (6) and (8) respectively [12]. The peak of intensity 1 at 187.0 ppm is assigned to the unique carbonyl (7) bonded to Ru_4 on the basis of the broadening observed in the ^1H coupled spectrum. All the above features clearly show that the carbonyl scrambling occurs around the Ru_1–Ru_2–Ru_3 face and allow to assign the last resonance at 185.7 ppm, which is a sharp singlet also in the ^1H coupled spectrum, to carbonyl (3). Thus the suggestion of the occurrence in the second step of the exchange process in I and in II of the in-plane scrambling of the eight carbonyls in the face which contains the two bridging carbonyls [5], receives further support from the similar behaviour of III. On the other hand, the substitution of iron with ruthenium increases the energy of activation for the local scrambling at Ru_1, such that carbonyl (3) is not participating at this stage to the exchange process. Secondly, the lower energy of activation for the in-plane scrambling in III than in I may be explained by the higher stability of the bridging carbonyls in the metal carbonyls of the transition metals of the first row. The cyclic motion of the CO's has been shown to occur also in the trimetallic clusters $Os_3(CO)_{10}C_7H_8$ [15], $M_3(CO)_{10}C_4H_4N_2$ (M = Ru [16], Os [17]).

Upon raising the temperature all the resonances broaden, collapse and merge into a new peak whose chemical shift (195.5 ppm) is in excellent agreement with the weighted average chemical shift (195.6 ppm) of all carbonyls; this resonance does not show any hydrogen–carbon coupling.

It has been suggested that in I and in II the final stage of the carbonyl exchange occurs by a shift in the metal framework in which the iron atom (Fig. 1: Ru_1 = Fe) moves closer to the ruthenium atom without bridging carbonyls [5]. Since in III the bond distance between Ru_1 and Ru_4 (2.78 Å) [7] is almost identical to that between Ru_1 and Ru_2 or Ru_3 (2.77 Å) [7], in this case the motion of Ru_1 is not necessary. The simplest mechanism accounting for the total scrambling of the CO's is a sequence of in-plane scrambling around the faces Ru_1–Ru_2–Ru_3 (the first stage of the exchange), Ru_1–Ru_2–Ru_4 and Ru_1–Ru_3–Ru_4, requiring in the second stage the reorganization of the Ru_2–Ru_3–Ru_4 triangle. For instance the in-plane scrambling around the Ru_1–Ru_2–Ru_4 face requires that two carbonyls bridge the edges Ru_1–Ru_2 and Ru_1–Ru_4 [18], whilst the hydrides bridge the edges Ru_2–Ru_3 and Ru_3–Ru_4.

Other mechanisms would require carbonyl bridge formation in the plane Ru_2–Ru_3–Ru_4, but each edge of this face has a longer distance (average 2.89 Å) [7].

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11 Runs at lower temperature were prevented by the poor solubility of the sample.

12 This assignment is based on the larger value of $^2J_{H-C}$ found in hydridocarbonyl metal clusters for carbonyls *trans* to a hydride [13]. Resonance (8) is assigned to the carbonyls bonded at Ru_4 by analogy with the shift in $H_4Ru_4(CO)_{12}$ [14].

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18 The almost identical values of the bond distances Ru_1–Ru_4 and Ru_1–Ru_2 (Ru_1–Ru_3) suggest that the formation of bridging carbonyls between Ru_1 and Ru_4 is a facile process.