A ^{13}C Nmr Investigation of Stereochemical Non Rigidity in Hydrido Olefinic Carbonyl Clusters of Ruthenium

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^{13}C n.m.r. spectra of hydrido olefinic carbonyl clusters of ruthenium show that localized scrambling of the carbonyls occurs with different energy barriers which depend on the nature of the bonding between the ligand and the metal cluster and on the nature of the substituents in the olefinic chain. Resonances of carbons "sigma" bonded to one ruthenium and "pi" bonded to a second one are in the lowfield region (198-162 ppm).

Introduction

In the reactions of metal carbonyls with olefinic ligands quite often rearrangement of the ligand occurs in order to satisfy the electronic requirement of the metal clusters [1].

$Ru_3(CO)_{12}$ reacts with olefins to give two isomeric hydrido trinuclear species $HRu_3(CO)_9L$ (L = olefin) (I, II) [2–4]; I is converted to II on heating if either R_2 or R_3 is an hydrogen atom.

I

II

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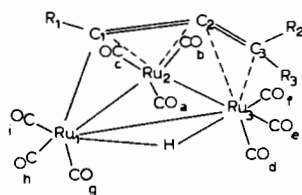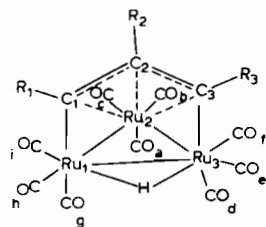
X-ray analysis of I and II has indicated that the olefin gives five electrons to the cluster as a whole, *via* one 'sigma' bond and two 'pi' bonds in I [5] and *via* two 'sigma' bonds and three 'pi' electrons from an allyl group in II [2].

An earlier ^{13}C n.m.r. study of II (R_1 = C_2H_5; R_2 = H; R_3 = CH_3) showed the basic feature of this cluster, but the resonances of the quaternary carbons were not located and no attempt was made to study the dynamic properties of the complex [2]. Recently we have shown that the electronic environments of carbon atoms 'sigma' bonded to one metal and 'pi' bonded to a second, [$C(\sigma, \pi)$], lead to a remarkable downfield shift [6]. Studies of the dynamic properties of substituted hydridometal carbonyl clusters have shown the importance of at least three factors in determining different mechanisms for the scrambling of the CO [7–9] and their relative activation energies: the bonding scheme between the ligand and the metal atoms; the presence of the hydrido hydrogen; and the nature of the metal. We have undertaken a ^{13}C n.m.r. investigation of several complexes of I and II type in order to get further details on the bonding of the olefin with the cluster and to examine their stereochemical non rigidity.

Results and Discussion

The ^{13}C n.m.r. data are reported in the Table. The [$C(\sigma, \pi)$] resonances fall in the range 160–200 ppm, the exact value depending on the nature of the substituent. Some of them are therefore in the same region as the carbonyl groups. However their assignment is possible based mainly on the pattern of the resonances at different temperature and on the observed dependence of the chemical shift of [$C(\sigma, \pi)$] on temperature (an upfield shift of about 1 ppm is observed as the temperature is lowered by about 100 °C).

In the room temperature spectrum of the symmetric complex IIa (R_1 = R_3 = CH_3; R_2 = H) five resonances are observed in the carbonyl region at

TABLE. ^{13}C N.m.r. Data for HRu$_3$(CO)$_9$L (L = olefin)[a].

	R$_1$	R$_2$	R$_3$	CO$_a$	CO$_b$	CO$_c$	CO$_d$	CO$_e$	CO$_f$	CO$_g$	CO$_h$	CO$_i$	C$_1$	C$_2$	C$_3$	Others	
I	C$_2$H$_5$	CH$_3$	H	196.2 203.9[b]	196.2 192.8[b,c]	196.2 192.3[b,c]	197.2	188.1	190.8 13[d]	195.7	191.4	192.1 8[d]	176.7	149.3	43.0 166[e]	CH$_2$ CH$_2$CH$_3$ CH$_3$	40.8 15.8 24.5
IIa	CH$_3$	H	CH$_3$	197.7 206.0[f]	197.7 193.2[f]	197.7 193.2[f]	195.9	192.3	190.4 12[d]	195.9	192.3	190.4 12[d]	190.0	120.3 157[e]	190.0	CH$_3$	39.6
IIb	H	CH$_3$	CH$_3$	197.9	197.9	197.9	196.1	192.7	190.2 11[d]	195.8	191.6	188.9 12[d]	161.6 150[e]	130.4	186.8	C$_2$CH$_3$ C$_3$CH$_3$	27.0 37.6
IIc	C$_2$H$_5$	H	CH$_3$	197.7 205.7[f]	197.7 193.0[f]	197.7 193.0[f]	196.1	192.3	190.5	196.1	192.0	190.5	198.2	119.8 162[e]	191.0	CH$_2$ CH$_2$CH$_3$ CH$_3$	47.2 20.0 39.8

[a]At room temperature if not otherwise stated. [b]At −76 °C. [c]The assignment can be reversed. [d]$^2J_{C-H}$. [e]$^1J_{C-H}$. [f]At −85 °C.

197.7, 195.9, 192.3, 190.4 and 190.0 ppm with integrated intensities 3:2:2:2:2 with the three inner ones being slightly broad. Upon lowering the temperature the three inner lines sharpen and the line of intensity 3 begins to broaden. At −86 °C the latter splits in two broad peaks with relative intensities 1:2 (T$_c$ −60 °C). At high temperature, +55 °C, the three inner lines are almost lost in the noise, whereas the other resonances remain sharp. Extensive decomposition at higher temperature prevented the observation of the average peak. These results are consistent with localised scrambling of CO at Ru$_2$, followed by stepwise scrambling at Ru$_1$ and Ru$_3$. In the second stage two mechanisms are possible: one involving a bridged intermediate and a second which does not. The averaging of the three inner resonances leads to the straightforward assignment of the signal at 190.0 ppm to the two carbons of type [C(σ, π)]. ^{1}H coupled spectra, in the range of temperature studied, show only a small broadening of the resonances, indicating that the couplings are small and unresolved, except that for a sharp doublet for the signal at 190.4 ($^2J_{C-H}$ = 12 Hz). It has been observed for several hydrido carbonyl metal clusters that one carbonyl of a M(CO)$_3$ is more strongly coupled than the others with the hydrido [7, 8, 10, 11], and that where unequivocal assignment was possible, the larger coupling constant is between the hydrido and the carbonyl *trans* to it [10, 11]. Further, axial carbonyl resonances are generally observed to be lowfield to the equatorial ones. The signals at 195.9, 192.3 and 190.4 ppm are therefore assigned to CO$_{d, g}$, CO$_{e, h}$, CO$_{f, i}$ respectively. We note that an alternative assignment would have no effect on the conclusions concerning the stereochemical non rigidity of this complex and the others. The results support the idea of a bridging position between Ru$_1$ and Ru$_3$ for the hydride.

In IIb (R$_1$ = H; R$_2$ = R$_3$ = CH$_3$) the asymmetry due to the different substituents on C$_1$ and C$_3$ is reflected in the observation at low temperature of *six* resonances for the six non equivalent carbonyls bonded to Ru$_1$ and Ru$_3$. At −56 °C eight resonances are observed in the carbonyl region with integrated intensities 3:1:1:1:1:1:1:1. (Fig. 1).

One of the resonances of intensity 1 is to be associated with C$_3$. Low solubility prevented observations at temperature below −94 °C at which the downfield signal collapsed. At room temperature three resonances of intensity 1 have disappeared; we tentatively associate these with the carbonyls bonded to Ru$_1$ which are undergoing localised exchange with a lower energy barrier than for those bonded to Ru$_3$. At higher temperature a broadening and a collapse of the resonances associated with CO$_{d, e, f}$ is observed suggesting that also in IIa the scrambling is localised at Ru$_1$ and Ru$_3$, rather than delocalised between the two metal atoms.
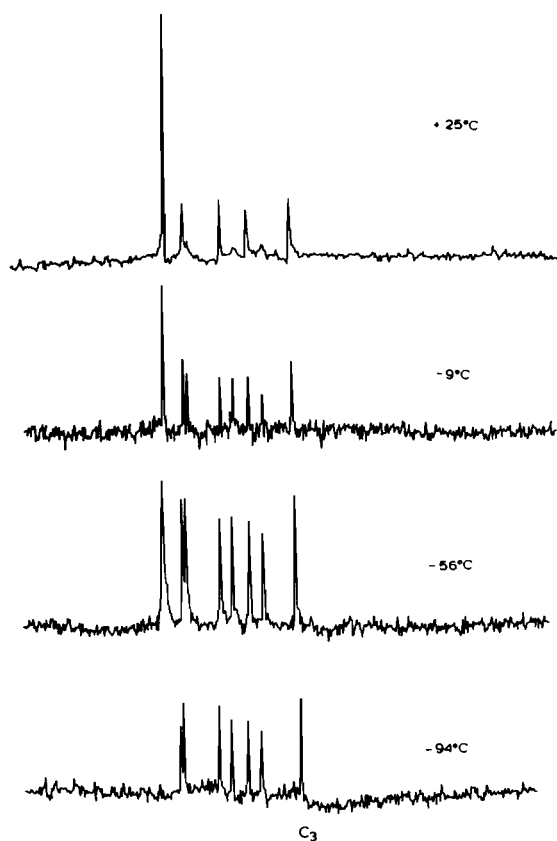
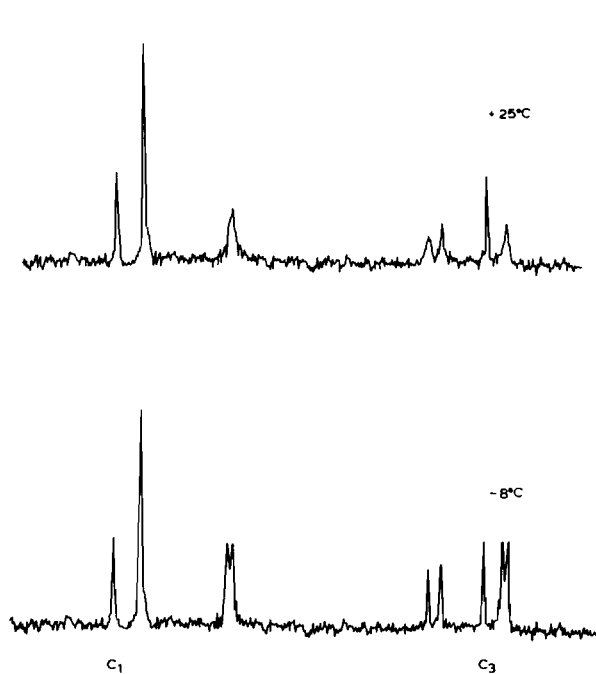Fig. 1. Variable temperature ^{13}C n.m.r. spectra of IIb in the carbonyl region.

The room temperature spectrum of IIc (R_1 = C_2H_5; R_2 = H; R_3 = CH_3) has already been reported, but the quaternary carbons were not located [2]. Since it is evident from the above observation that they fall in the carbonyl region the former CO assignment has been reinvestigated.

The room temperature spectrum of IIc in the CO region (Fig. 2) exhibits the basic features common to IIb except for a different shift due to C_1. The chemical shift difference within the pairs $CO_{d, g}$ and $CO_{f, i}$ is very small, being only 0.7 Hz and 1.3 Hz respectively, but is 7.5 Hz within the pair $CO_{e, h}$. In this case the narrow spacing of the resonances does not allow the evaluation of the $^4J_{C-H}$ in the ^1H coupled spectra.

At -84 °C the resonance of intensity 3 is split in two resonances (1:2): these are still broad so that the expected small difference in the chemical shift of CO_b and CO_c is not observed. The localised scrambling at Ru_2 has an activation energy comparable with that in IIa. Upon raising the temperature differential broadening of the CO bonded to Ru_1 and Ru_3 can be detected since within the pair $CO_{e, h}$ one resonance is broadening faster than the other (Fig. 2). The localised scramblings at Ru_1 and Ru_3 have therefore slightly different activation energies with the higher energy barrier probably ascribable to the interchange at Ru_1.

Nine resonances, with equal integrated intensities, appear in the carbonyl region in the limiting spectrum of I at -76 °C (Fig. 3). Three of them coalesce at

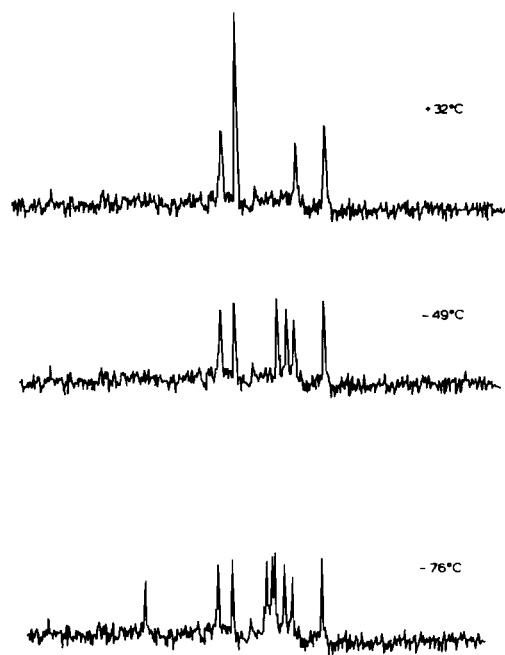Fig. 2. Variable temperature ^{13}C n.m.r. spectra of IIc in the carbonyl region.

Fig. 3. Variable temperature ^{13}C n.m.r. spectra of I in the carbonyl region.

—49 °C while the others remain sharp. At +32 °C a sharp peak of intensity 3 is observed due to the first exchange process, three other signals coalesce and almost disappear, while the remaining three peaks are broadened slightly. Higher temperature runs were prevented by isomerization of I to IIc.

The overall results show that localised scrambling of the carbonyls occurs at each metal centre and that exchange is more facile at the metals with no hydrido bridge.

Upon complexation with a transition metal the resonances of the terminal carbons of an allyl group are shifted upfield very much, whereas the resonance of the central carbon is only slightly shifted in the same direction [12]. On the other hand, the resonances of sp^2 carbons 'sigma' bonded to a transition metal are shifted downfield [12]. We have observed in binuclear and trinuclear iron olefin complexes a downfield shift for $[C(\sigma, \pi)]$ [6]. The observation in the downfield region of the resonances of $C_{1,3}$ in II is in accord with there being, in addition to the π bond with the metal cluster, a 'sigma' bond with ruthenium for the outer carbons of the ligand. ^{13}C n.m.r. observations parallel ^1H n.m.r. observations of a downfield shift for hydrogen atoms bonded to $[C(\sigma, \pi)]$ in these [3] and other complexes [13].

Experimental

Compounds I and II were prepared by the reaction of $Ru_3(CO)_{12}$ and the appropriate olefin as described in detail elsewhere [3, 4]. Deuterated solvents were purchased from NMR Ltd. and were used directly after being dried over molecular sieves.

CD_2Cl_2/CF_2Cl_2, CD_2Cl_2, $CDCl_3$ and $C_6D_5CD_3$ were the solvents used in the temperature study. Solutions were sealed under vacuum in 10 mm tubes and were treated with 0.05 M $Cr(acac)_3$ as an inert relaxation reagent and tetramethylsilane as an internal standard. ^{13}C n.m.r. spectra were recorded on a Jeol-PFT-100 operating at 25.15 MHz in the Fourier transform mode. Chemical shifts are reported downfield positive with respect to TMS. Accumulations of 1,000–30,000 transients were performed at a spectral width of 500–5000 Hz. The temperature was monitored by a Jeol JNM-DBT-P-5-H100E temperature control unit with a thermocouple approximately 1 cm above the sample (outside of the RF and decoupling coils).

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