Nuclear Magnetic Resonance of Binuclear Complexes containing a Metallacyclopentadiene System

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A comparative study of the ^1H and ^{13}C n.m.r. spectra of complexes $[M_2(CO)_6\{(HC_2H)_2\}]$ (M = Fe, Ru, or Os) is reported. Carbon–carbon coupling constants have been observed for ^{13}C-enriched acetylene samples of iron and ruthenium. In the ruthenium complex the T_1 and nuclear Overhauser enhancement (n.O.e.) measurements of the ^{13}C nuclei of the organic moiety allowed the calculation of the correlation time for the molecular reorientation; furthermore the T_1 and n.O.e. data for the ^1H nuclei povided an opportunity to estimate the H_A–H_X distance ($CH_A=CH_X$) in the metallacycle. An improvement in the evaluation of this distance has been gained by measuring the ^1H spin-lattice relaxation time in a highly deuteriated sample.

Systems containing a metallacyclopentadiene ring are quite common in organometallic chemistry and often have been considered as stable intermediates in stoicheiometric and catalytic cyclotrimerization of alkynes.[1] Several spectroscopic and theoretical studies have been devoted to the elucidation of the electronic properties of this particularly stable structural arrangement.[2–4]

Although n.m.r. spectroscopy is now a routine technique to assign the solution structures of new synthetic compounds, its involvement in organometallic chemistry has not been as great as that in the study of complex organic and biological molecules.

It is easy to forecast that a more extensive use of all the n.m.r. armoury will provide new powerful tools to assess in more detail the electronic, structural, and dynamic properties of organometallic molecules.

The synthesis of $[Fe_2(CO)_6\{(HC_2H)_2\}]$ was reported by Hubel and Braye[5] and the X-ray structure determination of the analogous derivative $[Fe_2(CO)_6\{C_4Me_2(OH)_2\}]$ was resolved by Hock and Mills[6] in 1961. Since that time a number of structural determinations of variously substituted derivatives have been published;[7] among several important features, these structural analyses showed the presence of a 'semibridging' carbonyl whose ability to balance electronic charge between the two iron centres has been stressed.[8]

The preparation of the $[Os_2(CO)_6\{(HC_2H)_2\}]$ analogue was already reported[9] but the spectroscopic characterization was limited to the recording of its i.r. and mass spectra. No report on the synthesis of the ruthenium derivative has yet appeared in the literature.

We have chosen the molecules $[M_2(CO)_6\{(HC_2H)_2\}]$ (M = Fe, Ru, or Os) as models for an exploration of the n.m.r. spectra for several reasons: (i) the availability of the derivatives for the three metals of the triad would allow direct evaluation of the metal effect on the n.m.r. parameters; (ii) since different isotopomers of acetylene are accessible, a number of n.m.r. experiments are possible; (iii) although the molecular symmetry is low, the molecular motion can be considered as isotropic and the reorientation time of a C–H fragment can be used as the overall molecular correlation time.

Results and Discussion

^1H, ^{13}C Chemical Shifts, $J(HH)$ and $J(CH)$ Coupling Constants.—The assignment of H_A, H_X, C_A, and C_X resonances has been done on the basis of a complete analysis of the ^1H-coupled

Table 1. ^1H Chemical shifts and $J(HH)$ (Hz) of $[M_2(CO)_6\{(HC_2H)_2\}]$ (M = Fe, Ru, or Os)

M	$\delta(H_A)$	$\delta(H_X)$	$J(AA')$	$J(XX')$	$J(AX)$	$J(AX')$
Fe	6.81	6.24	0.3	3.6	5.3	2.1
Ru	7.01	6.37	0.3	3.5	6.2	2.0
Os	7.27	6.70	0.3	3.7	6.6	1.7
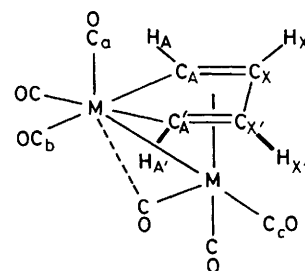
M = Fe, Ru, or Os

^{13}C spectrum followed by selective decoupling experiments which in turn allow the assignment of the ^1H spectrum.

The ^1H n.m.r. spectra of the three derivatives $[M_2(CO)_6\{(HC_2H)_2\}]$ (M = Fe, Ru, or Os) appear as $AA'XX'$ spin systems whose computer-simulated analyses afford the chemical shifts and spin–spin coupling constants reported in Table 1. The downfield shift observed for $\delta(H_A)$ and $\delta(H_X)$ on going from the Fe to the Os derivative seems to reflect mainly anisotropic effects of non-bonding electrons of the transition metal rather than changes in electron density in the metallacycle.

The values of vicinal $^3J(AX)$ coupling constants reflect the dependence of the cis olefin coupling on the ring size and the observed increase on descending the triad depends on the partial release of strain on internal angles as the atomic dimensions increase; this effect however is not observed for $J(XX')$. The larger value found for $^3J(AX)$ in respect to $^3J(XX')$ parallels the behaviour observed in $[M(CO)_3(diene)]$ complexes (M = Fe or Ru).[10]

In Table 2 the parameters obtained from the ^{13}C n.m.r. spectra of the three derivatives are reported. The chemical shift for carbons directly bonded to a metal is mainly determined by the nature of the metal: this effect may be related to large changes in the Q term of the Jameson–Gutowsky treatment[11] of the

Table 2. ^{13}C Chemical shifts (p.p.m.) and J(CH) (Hz) of $[M_2(CO)_6\{(HC_2H)_2\}]$ (M = Fe, Ru, or Os)

M	C_A	C_X	C_aO	C_bO	C_cO
Fe	154.6	110.5	210.8(1)	206.8(2)	211.1(3)
Ru	147.3	106.0	194.3(1)	195.7(2)	195.7(3)
Os	129.0	100.4	175.8(1)	181.2(2)	172.4(3)

M	$^1J(C_AH_A)$	$^1J(C_XH_X)$	$^2J(C_AH_X)$	$^2J(C_AH_{X'})$	$^2J(C_XH_{X'})$
Fe	158.1	167.7	12.7	7.2	9.5
Ru	153.4	166.9	12.7	7.1	8.7
Os	154.2	168.5	11.1	7.9	9.5

Table 3. J(CC) values (Hz) obtained from the spectrum reported in the Figure

M	$^1J(AX)$	$^1J(XX')$	$^2J(AX')$	$J(AA')$
Fe	31.0	36.0	10.3	−1.1
Ru	34.6	49.2	7.4	2.8
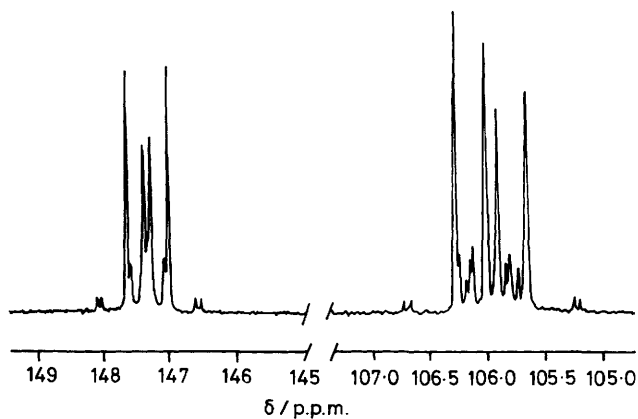
Figure. ^{13}C-$\{^1H\}$ N.m.r. spectrum of $[Ru_2(CO)_6\{(HC_2H)_2\}]$ obtained from $[Ru_3(CO)_{12}]$ and ^{13}C-labelled (90%) acetylene

paramagnetic contribution σ_p as a consequence of variations in the M–C bond order; conversely $\delta(C_x)$ span only a 10 p.p.m. range.

The resonances of the carbonyl groups appear as three absorptions in the relative intensity ratio of 1:2:3. In the case of the ruthenium derivative the resonances of intensity 2 and 3 overlap in $CDCl_3$ solution but can be split by changing the polarity of the solvent (for instance by using a 1:3 mixture of $CDCl_3$–CCl_4).*

The use of selective decoupling techniques has allowed the unambiguous determination of the coupling relationships between the ^1J(CH) and $^2J(C_XH_{X'})$ but the molecular symmetry did not allow the assignment of the remaining C–H coupling to ^2J or ^3J.

Upon complexation the central carbons exhibit an increase in the ^1J(CH) coupling with respect to the corresponding ones reported for butadiene: this behaviour, common to π-complexed unsaturated ligands, has been ascribed to an increase in the effective nuclear charge at the carbon atom as a consequence of the electron donation to the metal.[12–14] $^2J(C_XH_{X'})$ showed a marked increase with respect to the values reported for $[Fe(CO)_3(butadiene)]$ complexes,[10] but we are

* A detailed study of the carbonyl moiety of these complexes will be presented in a subsequent paper.

unable to establish if this is due to stereochemical changes or to a strengthening effect across the central carbons of the metallacycle.

Finally, small ^3J(CH) couplings have also been observed for the iron and ruthenium complexes, between CO_b and H_A and $H_{A'}$, affording values of 3.5 and 1.0 Hz respectively.

Carbon–Carbon Coupling Constants.—In order to gain further insight into the n.m.r. of these molecules, it was thought particularly interesting to determine the carbon–carbon spin–spin coupling constants J(CC). The good yields obtained in the synthesis of the iron and ruthenium derivatives allowed the preparation of samples containing ^{13}C-labelled acetylene (90% ^{13}C-enriched); unfortunately the low yield usually found in the synthesis of the osmium derivative discouraged any attempts to obtain the corresponding ^{13}C-labelled sample.

The ^{13}C-$\{^1H\}$ n.m.r. spectra of these samples (see Figure) for the Ru derivative showed the expected AA'XX' pattern for the isotopomer containing four ^{13}C nuclei (~90% abundant) overlapped with the AA'X and AXX' patterns resulting from the isotopomers (10% abundant) containing three ^{13}C nuclei. The spectra have been completely analysed and the final sets of J(CC), obtained by tentative simulation of our experimental spectra, reported in Table 3.

Few J(CC) values are known for organometallic molecules and in general they show a marked decrease in magnitude with respect to values reported for the corresponding unsaturated molecules.[15,16] In our case too, ^1J(CC) observed for directly bound sp^2 carbons are noticeably smaller than ^1J(CC) reported for ethylene (67.6 Hz) and other olefinic systems.

Since a linear dependence of ^1J(CC) upon carbon–carbon distance has been shown,[17] the main result from these data is the marked difference in the ^1J(XX') values in the two complexes which support the view that a noticeable shortening of the C_X–$C_{X'}$ distance has occurred in the case of the ruthenium derivative. On the other hand the similar values obtained for ^1J(AX) and ^1J(XX') for the iron derivative parallel the behaviour observed in the $[Fe(CO)_3(butadiene)]$ system.[10] Although a limited number of ^2J(CC) values have been reported, those observed for ^2J(AX') are noticeably large; conversely J(AA') are quite small but this is likely due to the presence of two alternative pathways for the transmission of the coupling information.

^1H *and* ^{13}C *Relaxation Studies on* $[Ru_2(CO)_6\{(HC_2H)_2\}]$.— Since the procedure to obtain atomic distances by T_1 measurement is now well established for organic and biological molecules, a relaxation study (^1H and ^{13}C) was undertaken on the ruthenium derivative. The spin–lattice relaxation times T_1 obtained for C_A and C_X are 3.51 ± 0.01 and 3.05 ± 0.01 s respectively; nuclear Overhauser enhancement (n.O.e.) measurement (1.94 and 1.98 respectively) indicates that the dominant relaxation mechanism is a dipole–dipole one *via* close interaction with the directly bonded protons. The knowledge of T_1 and n.O.e. allowed the evaluation of T_1^{DD} which in turn provides the opportunity to calculate the molecular correlation time τ_C; in fact by using a standard value for $r_{C-H} = 1.07$ Å, it is possible to apply equation (1, where γ is the gyromagnetic

$$\frac{1}{T_1^{DD}} = \frac{\gamma_H^2\gamma_C^2\hbar^2\tau_C}{r_{C-H}^6} \tag{1}$$

ratio). Evaluation of this equation affords $\tau_C = 11.6$ and 13.6 ps for C_A–H_A and C_X–H_X fragments respectively. It is likely that this difference in τ_C is related to the anisotropic components of the molecular motion but, for our purpose, an overall isotropic molecular motion can be assumed and an averaged $\tau_C = 12.7$ ps is used hereafter. A further development of this approach led us

to measure the T_1 relaxation time of the protons which provides the opportunity to estimate the H–H distances.[18,19] In order to minimize intermolecular relaxation effects, the measurement was performed on a dilute solution operating with selective irradiation of the coupled protons. The values obtained were 14.0 and 8.4 s for H_A and H_X respectively; the n.O.e. measurement (0.20 and 0.11 respectively) allowed the estimation of $1/T_1{}^{DD}$ values (0.028 and 0.026 s^{-1} for H_A and H_X respectively) and introduction of these data into equation (2) finally afforded a value of 2.6 Å for the H_A–H_X distance.

$$\frac{1}{T_1{}^{DD}} = \tfrac{3}{2}(\gamma_H{}^4\hbar^2\tau_C/r_{H_A\text{-}H_X}{}^6) \qquad (2)$$

However, owing to the chemical equivalence of each proton pair, the T_1 of each of these nuclei also contains the contribution to its relaxation from the other equivalent proton. A way to overcome this limitation has been found by using a sample highly enriched in ^2H; for this purpose a suitable sample has been prepared by reacting $[Ru_3(CO)_{12}]$ with acetylene $\sim 90\%$ enriched in deuterium. Operating in this way, the complexity of the ^1H n.m.r. spectrum was considerably reduced since $J(^1H^2H)$ couplings are 6.52 times smaller than those of $J(HH)$. In the case of the H_A resonance it was possible to detect a pattern corresponding to the overlap of a singlet (isotopomer $[Ru_2(CO)_6\{(^1H)C=C(^2H)\text{--}C(^2H)=C(^2H)\}]$) and a doublet (isotopomer $[Ru_2(CO)_6\{(^1H)C=C(^1H)\text{--}C(^2H)=C(^2H)\}]$). The T_1 of H_A protons of these two isotopomers were measured (being 19.0 and 14.5 s for the singlet and the doublet respectively) and the difference in their relaxation rates was determined as 0.017 s^{-1} [equation (3)]. The 0.94 factor is

$$R_i = \left[\frac{1}{T_1{}^{doublet}} - \frac{1}{T_1{}^{singlet}}\right] \cdot \frac{1}{0.94} \qquad (3)$$

introduced to account for the dipolar relaxation contribution of ^2H nuclei.[20] Evaluation of equation (2) then provided a more accurate value of 2.8 Å for the H_A–H_X distance.

In doing this work, we have assumed the negligibility of the cross-correlation terms; this assumption is based on the fact that for coupled systems the relaxation time can be described by a single exponential function if the δ/J ratio is larger than 10;[19] in the case herein considered this ratio is ~ 30.

Experimental

The synthesis of the three $[M_2(CO)_6\{(HC_2H)_2\}]$ complexes (M = Fe, Ru, or Os) was performed in sealed vials (160-cm^3 volume) by reacting the appropriate $[M_3(CO)_{12}]$ complex (1 mmol) with acetylene (20 mmol). The reaction times, temperature, solvents, and yields are as follows. M = Fe: 72 h, +70 °C, cyclohexane, 20%; M = Ru: 2 h, +70 °C, cyclohexane, 50%; M = Os: 48 h, +100 °C, n-heptane, 5%. T.l.c. work-up [eluant Et$_2$O– light petroleum (b.p. 40—70 °C) (1:9)] affords $[M_2(CO)_6\{(HC_2H)_2\}]$ as yellow-brown oils. I.r. spectra (n-hexane): [Fe$_2$-(CO)$_6\{(HC_2H)_2\}$], 2 078m, 2 041vs, 2 006s, 1 998s, and 1 960w; [Ru$_2$(CO)$_6\{(HC_2H)_2\}$], 2 086s, 2 056vs, 2 016vs, 2 006s, and 1 999s; [Os$_2$(CO)$_6\{(HC_2H)_2\}$], 2 088s, 2 055vs, 2 018vs, 2 008vs, 1 998s, and 1 978vs cm^{-1}. All three products gave satisfactory mass spectra.

The parent carbonyls $[M_3(CO)_{12}]$ were prepared according to published procedures.[21] ^{13}C-Labelled acetylene was purchased from Merck-Sharp and Dome Inc.

N.m.r. spectra were recorded on a JEOL GX 270/89 spectrometer. The samples were prepared with rigorously oxygen-free CDCl$_3$ using Schlenk-tube techniques. The purity of the compounds was assessed by the combined use of mass, i.r., and n.m.r. spectroscopies.

The T_1 measurements were performed on specially designed microcells. The sample height was limited to 1 cm, to ensure the best homogeneity of the radio frequency. Temperatures were controlled using a thermocouple immersed in a dummy sample. In all the experiments the temperature was maintained at 297 ± 2 K. The non-selective inversion–recovery pulse sequence was used to obtain T_1 values. The integrals of the relevant peaks were obtained and subjected to three kinds of analysis: spectrometer-based non-linear fit, linear least-squares fit, and full three-parameter exponential fit. These last values were used for further calculations.

Proton and carbon spectra were simulated by an iterative procedure using the LACX program obtained from the Daresbury n.m.r. program library.

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