Notes

Carbon-13 and Oxygen-17 Nuclear Magnetic Resonance Relaxation Studies of $[M_3(CO)_{12}]$ Derivatives (M = Fe, Ru, or Os)

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The combined use of ^{13}C and ^{17}O spin–lattice relaxation times for co-ordinated carbonyl ligands in $[M_3(CO)_{12}]$ clusters (M = Fe, Ru, or Os) allows the determination of ^{17}O quadrupolar coupling constants and the correlation times for molecular tumbling at different temperatures.

N.m.r. spin–lattice relaxation experiments are currently under intense scrutiny in organometallic compounds,[1,2] since it is expected that they can provide insight into certain structural and dynamic features which are not obtainable from the observation of δ and J parameters alone. It was shown earlier by Spiess and co-workers[3,4] that T_1 values for co-ordinated CO groups in $[Fe(CO)_5]$ and $[Ni(CO)_4]$, at 1.4 T field strength, are rather long and both chemical shift anisotropy (c.s.a.) and spin rotation (s.r.) interactions contribute to the relaxation process at the applied magnetic field. Furthermore it was shown that the s.r. contribution overtakes the c.s.a. one only at higher temperatures, even in the abovementioned relatively small and highly symmetrical molecules. Then, at low temperature and at higher magnetic field (say 6.4 T, as used in this work), the T_1 values measured for large molecules such as $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os) derivatives can be assigned mainly to c.s.a. contributions.

Results and Discussion

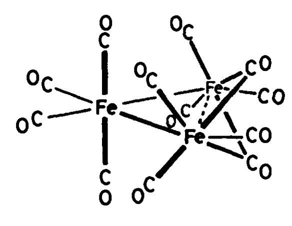
The ^{13}C relaxation times, T_1, obtained at different temperatures by applying the inversion-recovery method are reported in the Table. Although definitive proof can be achieved only by comparing T_1 measurements at different static magnetic field strengths, we assume that the observed relaxation rates for iron and ruthenium derivatives at −20 °C ought to be fully assigned to the c.s.a. mechanism. Support of this hypothesis arises from consideration of the related system $[Os_3H_2(CO)_{10}]$,[2] in which $T_1^{\text{c.s.a.}}$ contributes up to 98% of the observed T_1 at +35 °C and at 5.9 T. Similar situations have been found for $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ and $[Rh_6(CO)_{16}]$.[5]

The availability of $1/T_1^{\text{c.s.a.}}$ relaxation rates allow estimation of the molecular correlation time τ_c, equation (1), providing that the $\Delta\sigma$ term is known by independent experiment.[6] Values

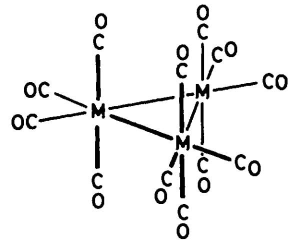
$$\frac{1}{T_1^{\text{c.s.a.}}} = \frac{2}{15}\gamma_C^{2}(\Delta\sigma)^2 B_0^{2}\tau_c \qquad (1)$$

of $\Delta\sigma$ for $[M_3(CO)_{12}]$ clusters (M = Fe, Ru, or Os) have recently been reported by Gleeson and Vaughan[7] *via* observation of the ^{13}C n.m.r. powder spectra.

We have obtained a very similar average value for $[Fe_3(CO)_{12}]$ by graphical analysis of the spinning side band (s.s.b.) intensities in the m.a.s. ^{13}C n.m.r. spectrum (m.a.s. = magic angle spinning) following the method developed by Herzfeld and Berger.[8] As reported in the Table, the evaluation of equation (1) gives the correlation times, τ_c, for molecular tumbling at −20 °C for $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$.



$[Fe_3(CO)_{12}]$



$[M_3(CO)_{12}]$ (M = Ru or Os)

Next, we have measured, at the same temperature, ^{17}O T_1 for the carbonyl groups, which is fully controlled by the quadrupolar relaxation mechanism,[6] equation (2), where $(e^2qQ/\hbar)^2$ is the quadrupolar coupling constant (q.c.c.)

$$\frac{1}{T_1^{q}} = \frac{3}{125}\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \qquad (2)$$

Since the value of τ_c involved in the modulation of the nuclear quadrupole coupling is the one already found in the evaluation of the ^{13}C c.s.a. relaxation process [equation (1)], straightforward computation of the ^{17}O q.c.c. for $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ can be carried out (see Table).

As the q.c.c. values are expected to remain unchanged in the small temperature range considered in this study,* knowledge of them allows an estimation of the τ_c value at any temperature at which the ^{17}O T_1 is measured. Furthermore use of the τ_c values obtained through this procedure permits estimation of the $1/T_1^{\text{c.s.a.}}$ contribution to the overall ^{13}C relaxation at temperatures higher than −20 °C. This shows that, even at room temperature, the observed relaxation rate (at 6.4 T) for ^{13}C nuclei in $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ can be almost completely ascribed to the c.s.a. term.

On the basis of these results, we consider the $[Os_3(CO)_{12}]$ case, whose limited solubility prevents any measurements at temperatures lower than 20 °C. Assuming that ^{13}C T_1 is fully c.s.a. dependent, τ_c and ^{17}O q.c.c. values are easily obtained. Using the same $\Delta\sigma$ value for axial and equatorial carbonyls, the molecular motion appears highly isotropic. The ^{17}O q.c.c. values found by this procedure are in the range reported for other metal carbonyl derivatives[10,11] and confirm the marked decrease in this parameter on going from free to co-ordinated CO. This feature is generally interpreted as a consequence of

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* Small changes (10—20%) are reported on going from solid to gaseous state.[9]

Table. Chemical shifts and relaxation rates of $[M_3(CO)_{12}]$ clusters (M = Fe, Ru, or Os)

Compound	$\Delta\sigma$/p.p.m.	T/K	$\delta(^{13}C)^a$/p.p.m.	$\delta(^{17}O)^b$/p.p.m.	$T_1(^{13}C)$/s	$T_1(^{17}O)$/ms	τ_c/ps	Q.c.c.(^{17}O)/MHz
$[Fe_3(CO)_{12}]$		253			11.6	12.5	33.2	
	327	273			13.5	14.5	28.7	1.592
		293	212.9	395.5	17.1	21.5	19.8	
$[Ru_3(CO)_{12}]$		253			8.3	10.2	31.5	
	397	273			9.1	11.1	28.9	1.814
		293	199.7	378.7	10.7	13.1	24.4	
eq.			170.4	370.4	11.0	17.0	31.2	1.406
$[Os_3(CO)_{12}]$	347	293						
ax.			182.3	346.5	10.9	14.6	31.4	1.524

[a] Relative to $SiMe_4$. [b] Relative to H_2O.

the metal to CO ($d\pi$–$p\pi^*$) back bonding, which increases the electron density at oxygen. In this context the effect of different metals within the $[M_3(CO)_{12}]$ series is not clear cut. However, in the case of the $[Os_3(CO)_{12}]$ cluster, the larger q.c.c. value for the axial carbonyls with respect to the equatorial ones is in agreement with the competition for $d\pi$ electron density between the mutually *trans* axial carbonyls, as indicated in an accurate structure redetermination of $[Os_3(CO)_{12}]$.[12]

Experimental

The $[M_3(CO)_{12}]$ (M = Fe,[13] Ru,[14] or Os[15]) clusters were prepared according to the published procedures. Carbon-13 labelled CO was purchased from Isotec Inc., U.S.A., and the isotopic exchange was performed in sealed ampoules under ^{13}CO (*ca.* 1 atm, 101 325 Pa) for a few days at 40 (Fe), 60 (Ru), and 100 °C (Os). The spectra were recorded on a JEOL GX 270/89 spectrometer operating at 67.9 (^{13}C) and 36.6 (^{17}O) MHz. The samples were prepared with rigorously oxygen-free $CDCl_3$ using Schlenk techniques. The non-selective inversion-recovery pulse sequence was used to obtain T_1 values, which were calculated from a three-parameter exponential fit of the peak integrals. Errors are estimated to be ±5%.

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