Solution Dynamics of the Osmium Cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$† by ^{13}C and ^{17}O Nuclear Magnetic Resonance. Estimation of the ^{13}C Chemical Shift Anisotropy and ^{17}O Quadrupole Coupling Constant

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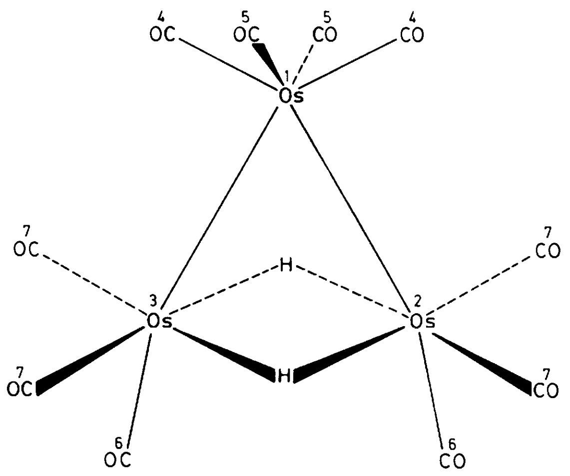
Application of the saturation-transfer technique to ^{13}C n.m.r. spectra of ^{13}C-enriched $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ shows that only localised ^{13}C exchange occurs, involving two of the four types of carbonyl ligand. Equations are derived to describe the recovery of the exchanging AX_2 spin system towards equilibrium, after an initial perturbation. When the initial perturbation is a selective inversion of A or X_2, values for the ^{13}C relaxation parameters and the $A \rightleftharpoons X_2$ exchange rate constant can be determined. The rate constant for this localised process is $0.36\ s^{-1}$ at 300 K in $CDCl_3$ solution. An estimate of the quadrupole coupling constant for ^{17}O in the complex (1.59 MHz), together with ^{17}O spin-lattice relaxation time measurements, yielded a value for the correlation time for molecular reorientation of 22 ± 4 ps. The ^{13}C spin-lattice relaxation rates are strongly field dependent and values for the ^{13}C shielding anisotropy in the region of 383 ± 50 p.p.m. were obtained.

The solid-state structure of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (1) has been extensively studied by both *X*-ray [1-3] and neutron diffraction [3,4] techniques, and shown to possess approximate C_{2v} symmetry which may be represented as shown (Figure 1) with a four-electron, four-centre bond at the $(\mu\text{-}H)_2Os(2)Os(3)$ fragment. The solution ^{13}C n.m.r.spectrum of (1) at ambient temperature shows [5,6] four resonances at δ 175.2, 176.3, 181.8, and 182.7 (relative intensities 2 : 1 : 1 : 1) corresponding to a C_{2v} structure. These resonances were assigned to carbonyls 7, 6, 5, and 4 respectively on the basis of ^{13}C–^{1}H and ^{13}C–^{13}C couplings, the latter obtained from the highly ^{13}C-enriched species. The ^{13}C spectra of (1) at elevated temperatures were qualitatively interpreted [6] as resulting from a localised CO(6)–CO(7) group exchange process. Our continued interest in this complex lies in the quantification of such exchange processes, particularly in the relatively slow exchange situation as exhibited by (1) at ambient temperature.

It was recently demonstrated by Heinekey and Graham [7] in a ^{13}C study of a (σ-cycloheptatrienyl)ruthenium derivative that a particularly useful method for the quantitative study of relatively slow exchange rates in fluxional organometallic complexes is the saturation-transfer technique as formulated by Forsén and Hoffman.[8] Mann *et al.*[9] also employed magnetisation transfer experiments in their qualitative ^{13}C study of carbonyl exchange in $[Ir_4(CO)_{11}(PEt_3)]$. The analysis employed by Heinekey and Graham [7] was simplified by the observation of ^{13}C at natural abundance and the consequent lack of ^{13}C–^{13}C nuclear Overhauser interactions. It was necessary in our study of (1) however, because of its low solubility and the anticipated long relaxation times, to take advantage of the sensitivity improvements afforded by a high degree (*ca.* 75%) of ^{13}C enrichment. Therefore a full analysis of the exchange problem, including ^{13}C–^{13}C cross relaxation, is required.



(1)

Figure 1. The structure of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ showing the carbonyl numbering

Theory

Campbell *et al.*[10] have detailed such an analysis for the equally populated two site case, based upon the Bloch equations modified [11,12] for chemical exchange. In application to (1) it is first necessary to consider the operational size of the spin system. Because the level of enrichment of (1) is less than 100% the ^{13}C spectra to be analysed are a superposition of spectra due to the various $^{12}C/^{13}C$ isotopomers. In general these isotopomers would have different values for the ^{13}C relaxation parameters (ρ and σ), and these differences would arise from the presence of ^{13}C–^{13}C dipole–dipole interactions contributing to ρ and σ. To a first approximation however such differences were ignored in order to simplify the analysis. Justification for neglect of these differences is subsequently obtained through the small values of the cross-relaxation parameter, σ. No measurable ^{13}C-{^{1}H} nuclear Overhauser enhancement (n.O.e.) was detected with ^{13}C observation at either 62.9 or 100.6 MHz, and accordingly the problem was formulated in terms of a three-spin system due to the ^{13}C nuclei of carbonyls 6 and 7. Secondly, we considered the

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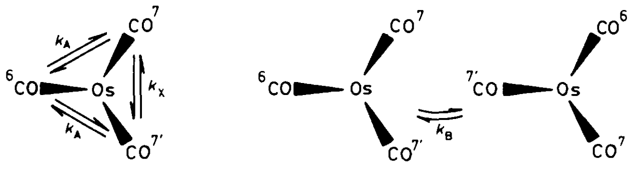
† Di-μ-hydrido-μ-tetracarbonylosmio-bis(tricarbonylosmium).

Table 1. Rate constant and relaxation data from the analysis [a] of ^{13}C selective inversion experiments

ν_0/MHz	CO Resonance inverted	ρ_A/s^{-1}	σ_{AX}/s^{-1}	$(\rho_X + \sigma_{XX})/s^{-1}$	k'/s^{-1}	
100.6	6(A)	0.213	−0.011	0.285	0.36	Selective inversion
100.6	7(X)	0.260	0.002	0.241	0.36	
62.9	7(X)	0.096	0.000	0.100	0.37	
62.9	6(A), 7(X)	0.102	−0.002	0.099	0.36 [b]	Non-selective inversion

[a] By equations (3) and (4). [b] Held constant in the iterative analysis.

modes of localised exchange between a CO(6) group and two CO(7) groups, and two mechanisms are possible: (*i*) a stepwise exchange and (*ii*) a concerted ' rotation ' as shown in the Scheme, with associated rate constants (k_A,k_X,k_B). With the observable (*z* axis) ^{13}C magnetisation of carbonyl site CO(6) labelled A_z and the total observable magnetisation at site CO(7) labelled X_z, the Bloch equations become equations (1) and (2), where $k' = k_A + k_B$, and σ_i and ρ_i are the relaxation rate constants. It should be noted that the rate constant for mutual exchange (k_x) between the CO(7) groups does not appear in these expressions. The integrated forms of these two equations are given by equations (3) and (4), where $\gamma_{\pm} = \frac{1}{2}\{-(3k' + \rho_A + \rho_X + \sigma_{XX}) \pm [\{(\rho_A + 2k') - (k' + \rho_X + \sigma_{XX})\}^2 - 4(k' - \sigma_{AX})(2\sigma_{AX} - 2k')]^{\frac{1}{2}}\}$, $l = (\rho_A + 2k' + \gamma_+)/(k' - \sigma_{AX})$, $m = (\rho_A + 2k' + \gamma_-)/(k' - \sigma_{AX})$, $\alpha = [m(A_0 - A_\infty) - (X_0 - X_\infty)]/(m - l)$, and $\beta = [(X_0 - X_\infty) - l(A_0 - A_\infty)]/(m - l)$.



Scheme.

$$dA_z/dt = -\rho_A(A_z - A_\infty) - \sigma_{AX}(X_z - X_\infty) + 2k'A_z - k'X_z \quad (1)$$

$$dX_z/dt = -(\rho_X + \sigma_{XX})(X_z - X_\infty) - 2\sigma_{AX}(A_z - A_\infty) + 2k'A_z - k'X_z \quad (2)$$

$$A_z = \alpha e^{\gamma_+ t} + \beta e^{\gamma_- t} + A_\infty \quad (3)$$

$$X_z = \alpha l e^{\gamma_+ t} + \beta m e^{\gamma_- t} + X_\infty \quad (4)$$

Equations (3) and (4) describe the recovery of the magnetisation from an initially perturbed situation (A_0, X_0) to equilibrium (A_∞, X_∞). Campbell *et al.*[10] described several modes of initial perturbation, which included selective inversion of one resonance (here A or X), selective saturation, and non-selective inversion of both A and X. This last may be compared with a non-selective inversion–recovery method of measuring spin-lattice relaxation rates. In this study both the selective and non-selective inversion methods were employed in preference to the selective saturation since the initial perturbation is greater for inversion (ideally $A_0 = -A_\infty$) than saturation ($A_0 = 0$).

Results

The Selective Inversion Technique.—This technique, described by Morris and Freeman [13] (see Experimental section) was used to invert the ^{13}C resonance of CO(7) at 100.6 MHz (WH-400), and the recovery of the spin system towards equilibrium was monitored as a function of time. The recovery of this inverted ' X ' resonance was almost exponential in time, but the intensity of the slowly exchanging CO(6) or A resonance initially decreased then increased towards the equilibrium value. The complementary experiment, *i.e.* selective inversion of the CO(6) or A resonance, was also performed. These resonance intensities were analysed as a function of time according to equations (3) and (4) using a non-linear least-squares optimisation program to derive best values for the various parameters, *i.e.* A_0, A_∞, X_0, X_∞, k', ρ_A, σ_{AX}, and $(\rho_X + \sigma_{XX})$. The results are shown in Table 1. Figure 2 shows a plot of the experimental intensities with the predicted behaviour of the intensities calculated from the best-fit values for the parameters listed above. The quantities A_0 and X_0 were treated as adjustable parameters since the selective inversion is always less than perfect and there may be problems associated with measurement of intensities *immediately after* the selective inverting pulse. A_∞ and X_∞ were likewise deemed adjustable parameters because of uncertainty in the measurement of these crucial ' infinity ' values at the necessarily long waiting times involved. As can be seen (Table 1) selective inversion of either the CO(6) or CO(7) resonance yielded the same value for k' (0.36 s^{-1}), a mean value for $\sigma_{AX} = 0.005 \pm 0.006$ s^{-1} (close to zero), a mean value for $\rho_A = 0.237 \pm 0.024$ s^{-1}, and a mean value for $(\rho_X + \sigma_{XX}) = 0.263 \pm 0.022$ s^{-1}. Selective inversion of either resonances A or X did not provide any evidence of exchange involving the CO(4) or CO(5) resonances, and in addition selective inversion of the CO(5) resonance did not produce intensity fluctuations at the CO(4) resonance. These observations show that there is no significant exchange process involving the carbonyls at Os(1) at this temperature.

The value of ρ_A is the inverse of the spin-lattice relaxation time (T_1) of A and gives $T_{1_A} = 4.2$ s. Since this relaxation time seemed shorter than is generally accepted for ^{13}C in metallocarbonyls, the selective inversion experiment was repeated for ^{13}C observation at 62.9 MHz (WM-250).

As shown in Table 1, the value obtained for k' (0.37 s^{-1}) was essentially the same as that derived from the 100.6-MHz data, but the relaxation time was $T_{1_A} = 10.4$ s. The implication from these experiments at 62.9 and 100.6 MHz is that the chemical shift anisotropy (c.s.a.) mechanism contributes significantly to the observed ^{13}C relaxation. Detailed measurements by Spiess and Mahnke [14] on the ^{13}C relaxation in [Fe(CO)$_5$] and [Ni(CO)$_4$] led to a similar conclusion and indeed estimates for the ^{13}C shielding anisotropies of 408 and 440 p.p.m. respectively were made.

The Non-selective Inversion Technique.—This technique was

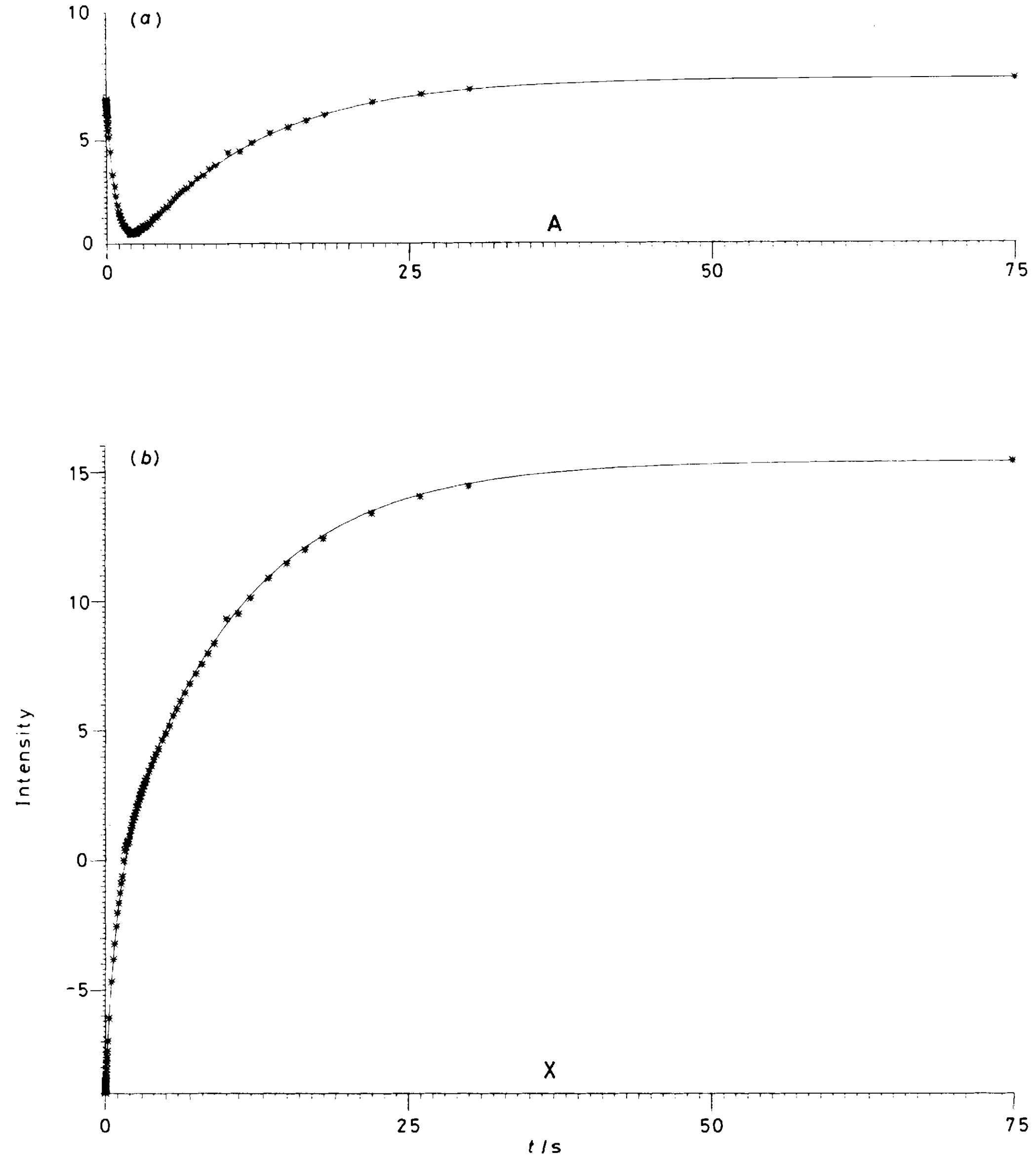


Figure 2. Calculated (——) and experimental (*) intensities of the (*a*) A and (*b*) X ^{13}C resonances as a function of time after selective inversion of the X resonance

applied to invert simultaneously both the CO(6) and CO(7) resonances (A and X) and the recovery of the intensities of these resonances towards equilibrium was analysed in a similar manner to that employed in the selective inversion experiments. However in these analyses it was apparent that the values of the relaxation parameters obtained were insensitive (as judged by the root mean square error between experimental and calculated intensities) to the value of the exchange rate constant (k') in the region 0.15—0.45 s^{-1}. Accordingly the best fit values of the relaxation parameters shown in Table 1 were obtained with k' held constant at 0.36 s^{-1}. The values for ρ_A and ($\rho_X + \sigma_{XX}$) are in excellent agreement with those obtained from the selective inversion experiments.

In order further to substantiate the dominance of the c.s.a. mechanism for ^{13}C relaxation, a non-selective inversion experiment was performed at 25.1 MHz. The results collected in Table 2 are the relaxation rates ρ_{si} derived from a straightforward semi-logarithmic analysis of peak intensities as a function of time after the inversion. This is a valid analysis for resonances 4 and 5 which are not involved in the exchange process, but strictly speaking is not valid for resonances 6 and 7. However comparison of the non-selective inversion data at 62.9 MHz in Tables 1 and 2 substantiates the point concerning the insensitivity of the non-selective inversion method to the exchange rate.

Discussion

Mechanisms of Relaxation.—The experimentally determined value for σ_{AX} (Table 1) is very small. The two possible relaxation mechanisms contributing to σ_{AX} are the ^{13}C–^{13}C dipole–dipole mechanism, and relaxation through modulation of the ^{13}C–^{13}C scalar coupling by chemical exchange. We may estimate the relaxation rates associated with each of them theoretically.

The ^{13}C–^{13}C dipole–dipole contribution to σ_{AX} is given [15] by equation (5). The AX internuclear distance, r, may be

Table 2. Relaxation rates, (ρ_{s1}/s^{-1}) derived from a semi-logarithmic plot analysis of the ^{13}C non-selective inversion experiments

	Resonance			
ν_0/MHz	4	5	6 (A)	7 (X)
100.6	0.22	0.19	0.22	0.22
62.9	0.092	0.089	0.100	0.099
25.1	0.039	0.039	0.042	0.042

$$\sigma_{AX} = \frac{\gamma_C^4 \hbar^2 \tau_c}{2 r_{AX}^6} \qquad (5)$$

estimated [1] as 2.816 Å, and an approximate value for the correlation time (τ_c) is 22 ± 4 ps. This method for determining this value for τ_c is described later (section on ^{17}O spectra). Equation (5) then yields a value for σ_{AX} of $(1.1 \pm 0.1) \times 10^{-4}$ s^{-1}.

The ^{13}C–^{13}C scalar contribution to σ_{AX} is given [15] by equation (6). The ^{13}C–^{13}C coupling (J) can be assigned [6] a maximum value of 3.5 Hz, the exchange correlation time

$$\sigma_{AX} = \frac{-2\pi^2 J^2 \tau_{ex}}{1 + (\Delta w \tau_{ex})^2} \qquad (6)$$

($\tau_{ex} = 1/k'$) given by the above analysis is *ca.* 2.8 s, and the A–X chemical shift separation (Δw) is 111 Hz (^{13}C at 100.6 MHz). Substitution of these values in equation (6) yields a value for σ_{AX} of -2×10^{-4} s^{-1}.

Thus σ_{AX} is expected from theory to be negligible, as is observed. Similarly the ^{13}C–^{13}C dipole–dipole contribution to σ_{XX} is negligible and the values for ($\rho_X + \sigma_{XX}$) in Table 1 may be approximated to ρ_X.

The values for ρ_A and ρ_X are strongly field dependent, however, as mentioned above, a fact which points to the importance of the c.s.a. mechanism for ^{13}C relaxation. This mechanism may be quantified according to equation (7), where B_0

$$\rho = \frac{2}{15} \gamma^2 B_0^2 (\Delta\sigma)^2 \tau_c \qquad (7)$$

is the external field and $\Delta\sigma$ the shielding anisotropy for an axially symmetric group. This equation predicts a linear dependence of ρ upon B_0^2 and Figure 3 depicts such a plot for the relaxation rates of carbonyl 5 (using the data from Table 2). The slopes of such plots, combined with the above value for τ_c, yielded values for the chemical shift anisotropies of carbons 4—7 of 376, 371, 430, and 354 p.p.m. respectively.

Oxygen-17 *Spectra*.—The value for the correlation time (τ_c) was obtained using the dual spin-probe technique.[16] Oxygen-17 relaxation in metallocarbonyl complexes is dominated [17,18] by the quadrupolar mechanism [equation (8)],

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3(2I+3)}{40I^2(2I-1)}\left(1 + \frac{\eta^2}{3}\right)\left(\frac{e^2 Q q_z}{\hbar}\right)^2 \tau_c \qquad (8)$$

where I is the nuclear spin value ($=\frac{5}{2}$ for ^{17}O), η is the electric-field gradient asymmetry parameter (which should be very small for ^{17}O in terminal carbonyl groups), and $e^2Qq_z/\hbar$ is the quadrupolar coupling constant. Assuming isotropic reorientation, then the correlation time τ_c is equal to that for ^{13}C–^{1}H dipole–dipole relaxation [equation (9)], where $1/T_1^{DD}$ is the relaxation rate for each C–H interaction and γ is the nuclear gyromagnetic ratio.

$$\frac{1}{T_1^{DD}} = \frac{\hbar^2 \gamma_C^2 \gamma_H^2 \tau_c}{r_{CH}^6} \qquad (9)$$

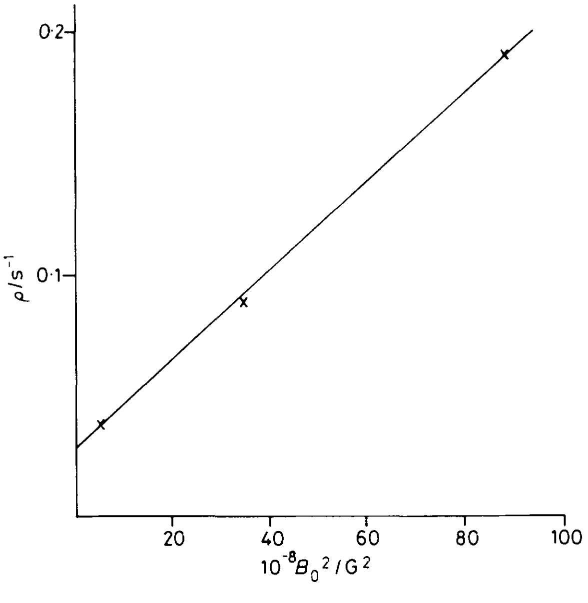


Figure 3. ^{13}C Spin-lattice relaxation rate of carbonyl 5 as a function of the square of the spectrometer magnetic field (B_0) (G = 10^{-4} T)

The ^{17}O spectrum of (1) in CDCl$_3$ solution displayed all four resolved resonances [Figure 4(*a*)], in which the most intense resonance is assigned to carbonyls 7. To assign the resonance due to carbonyl 6 use was made of the exchange situation. The spectrum in [^{2}H$_8$]toluene solution at 343 K [Figure 4(*b*)] did not show any significant broadening of the resonances, but when the resonance due to carbonyls 7 was selectively presaturated [13] the lowest frequency resonance also decreased in intensity [Figure 4(*c*)] due to transfer of saturation by the exchange. Therefore the assignment of the ^{17}O resonances from (1) in CDCl$_3$ solution is CO(6) 333.6, CO(7) 346.5, and CO(4, 5) 358.4, 357.5 p.p.m.

The ^{17}O spectrum of the complex [Os$_3$H(CO)$_{10}$(CH=CH$_2$)] (2) at 310 K in CDCl$_3$ solution shows [17] six resolved ^{17}O resonances for which T_1's were measured by the inversion recovery technique to be in the region 14.9—23.4 ms. Carbon-13 relaxation times, similarly measured, and ^{13}C-{^{1}H} nuclear Overhauser enhancement measurements for the CH and CH$_2$ carbons yielded values for T_1^{DD} for these carbons which in equation (9) gave an average value for the correlation time τ_c of 22.6 ps. This value, together with the ^{17}O T_1's and an asymmetry parameter of zero substituted in equation (8), gave values of the quadrupole coupling constants for the six ^{17}O resonances in the region 1.41—1.77 MHz. A mean value for the ^{17}O quadrupole coupling in (1), which is structurally similar to (2), of 1.59 MHz was therefore assumed. This, combined with ^{17}O T_1 measurements on (1) in CDCl$_3$ solution, gave by use of equation (8) the value for the correlation time τ_c for (1) of 18—26 ps.

Conclusions

With the particular combination of exchange and relaxation parameters determined for ^{13}C in (1), the non-selective inversion method is insensitive to the value of the exchange parameter k', whereas the selective inversion method is sensitive to k' and yields a value of $k' = 0.36$ s^{-1}. The field-dependent relaxation rates obtained yielded a value for the ^{13}C chemical shift anisotropy of 383 ± 50 p.p.m. This is similar to the values reported for [Ni(CO)$_4$] and [Fe(CO)$_5$] of 440 and 408

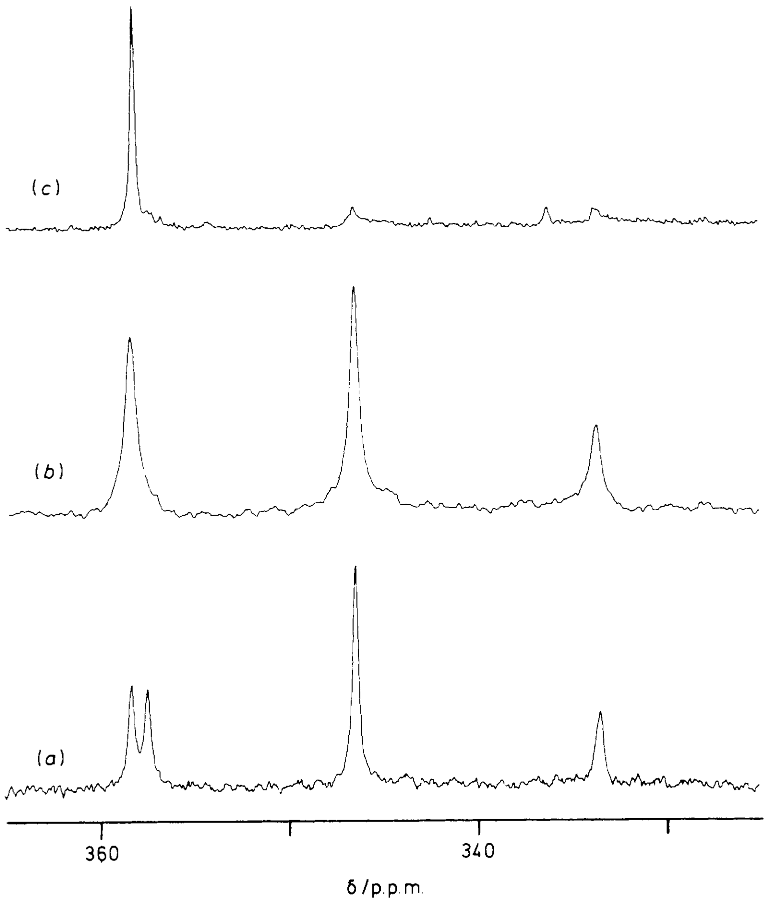


Figure 4. 54.25-MHz ^{17}O spectra of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$; (*a*) at 300 K in $CDCl_3$ solution; (*b*) at 343 K in $[^2H_8]$toluene solution; (*c*) as (*b*) but with selective saturation of the resonance at 346.5 p.p.m.

p.p.m. respectively.[14] The dominance of the c.s.a. mechanism * for ^{13}C relaxation will clearly be important in determining the sensitivity of long-term spectral accumulations of metallocarbonyl samples run on high-field spectrometers.

The relatively sharp ^{17}O resonances from the carbonyl groups in the osmium compounds studied here clearly have their origin in the low values of the electric quadrupole couplings. We have shown elsewhere that this is true for many other metallocarbonyls as well.[17,18]

Experimental

The ^{17}O spectra were obtained on a Bruker WH-400 spectrometer operating at 9.4 T and 54.25 MHz. The sample was contained in a 10-mm tube, the 90° pulse width was 42 μs and $CDCl_3$ provided the lock signal. Shifts are reported relative to an external water sample.

The ^{13}C spectra were obtained on a Bruker WH-400 (100.6 MHz), a Bruker WM-250 (62.9 MHz), and a JEOL FX-100 (25.13 MHz) spectrometer. ^{13}C Shifts are reported relative to $SiMe_4$. For the selective inversion experiments [13] with the WH-400 spectrometer a train of 75 on-resonance pulses of 1 μs duration spaced by 1 ms produced the best inversion, whereas with the WM-250 the selective inversion was achieved by adjusting an attenuator (to 10 dB) on the pulse to give a train of 120 pulses each of 1 μs, spaced by 1 ms. Typically the degree of selective inversion achieved was *ca.* 75% (WH-400) and *ca.* 60% (WM-250).

The computer program for the multi-parameter fit was generously provided by Dr. K. D. Sales (Queen Mary College) and was executed using the ICL 2980 computer at Queen Mary College.

The complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ was prepared according to the literature method,[19] starting from a ^{13}CO-enriched (75%) sample of $[Os_3(CO)_{12}]$. The enrichment of $[Os_3(CO)_{12}]$ was achieved by exchange between the natural abundance sample and ^{13}CO (Prochem., 99%) in n-octane contained in sealed vials (4 d at 110 °C). The same procedure was used for production of the ^{17}O-enriched sample (~15%) starting from $C^{17}O$ (Prochem, 35%).

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* *Note added at proof:* a recent article (J. W. Gleeson and R. W. Vaughan, *J. Chem. Phys.*, 1983, **78**, 5384) reported the application of solid-state ^{13}C n.m.r. techniques to the measurement of the ^{13}C c.s.a. for a range of metal-bound terminal CO groups. They found essentially axial symmetry for the shielding tensors with anisotropy values in the region 380 ± 60 p.p.m., in good agreement with the values found in this solution study for (1) ($\Delta\sigma = 383 \pm 50$ p.p.m.).

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