Carbon-13 Nuclear Magnetic Resonance Evidence of a Relaxation Process dominated by Scalar Coupling with a Quadrupolar Nucleus in $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$†

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Carbon-13 n.m.r. spin–lattice relaxation times of the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ have been determined at various temperatures and field strengths in order to elucidate the different components of the relaxation mechanism. Scalar coupling with the quadrupolar Re isotopes (^{185}Re, ^{187}Re; $I = \frac{5}{2}$) proved to be the main relaxation pathway at room temperature in the range 20—68 MHz. Analysis of the data allowed the estimation of the quadrupolar relaxation time of Re and of the coupling constant $^1J(^{187}\text{Re–C})$. The latter has been determined for the first time.

Four mechanisms can contribute to spin–lattice relaxation of ^{13}C nuclei: dipole–dipole interactions (d.d.), spin rotation (s.r.), chemical shielding anisotropy (c.s.a.), and scalar coupling (s.c.). While the first three are commonly encountered, spin–lattice relaxation is dominated by scalar coupling of the 'second kind'[1a] in only a few systems[2] and this is due to the stringent requirements needed to make this mechanism competitive with the others.

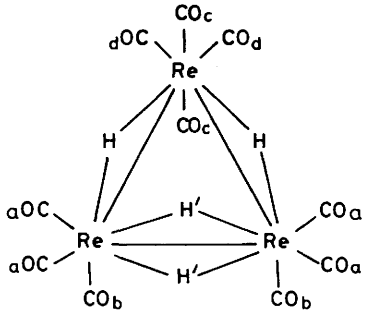
Here we report a study of ^{13}C relaxation properties of the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**) which is the first example, among hydrido-carbonyl metal clusters, in which scalar coupling of the 'second kind' is the dominant relaxation mechanism. Our previous ^{13}C n.m.r. studies[3] on anion (**1**) have shown that the idealized C_{2v} symmetry of the solid-state structure is retained in solution. The four carbonyl resonances observed at 196.7, 187.4, 184.9, and 184.5 p.p.m. (20.15 MHz in [$^2H_8$]tetrahydrofuran, $SiMe_4$ as internal standard, temperature range 183—303 K) with an intensity ratio 2:1:1:1 have been unambiguously assigned on the basis of selective irradiation experiments and of the ^{13}C-^{1}H coupled spectrum to CO_a, CO_b, CO_c, and CO_d, respectively. Investigations on the dynamic behaviour of compound (**1**) did not allow the observation of any scrambling among the ligands up to 303 K and revealed that spin–lattice relaxation times (T_1) were unusually short when compared with those of other metal carbonyls. Indeed, in organometallic compounds, carbonyl T_1 values are usually quite long (up to 200 s, 2.1 T) due to the absence of dipole–dipole interactions with directly bonded hydrogen atoms; shiftless relaxation reagents are often used[4] to get ^{13}C n.m.r. spectra in a reduced time.

The study of the temperature and field dependence of the relaxation times of (**1**) has allowed us to single out which mechanism is operative in our case.

Results and Discussion

The solutions, typically 0.1 mol dm^{-3} in [$^2H_8$]tetrahydrofuran, were prepared using moderately ^{13}C-enriched (*ca.* 20%) samples of compound (**1**) and all the spectra were obtained under full ^{1}H decoupling.

The non-selective inversion-recovery technique[5] was used to determine T_1 of compound (**1**) since previous selective population-transfer experiments ruled out the presence of exchange processes which could affect relaxation rates.[3] The recovery of the magnetization towards its equilibrium value resulted in an exponential behaviour, and the experimental data, analysed by an exponential least-squares fitting, yielded the values reported in Table 1.



(**1**)

The T_1 measurements at 20.15 MHz and 303 K (Table 1) indicated that all the carbons relax very quickly, namely two orders of magnitude faster than those of the analogous osmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (**2**) (25 s at 25.13 MHz, 300 K).[6] On the assumption that the difference in the electrostatic charge between (**1**) and (**2**) should result in a longer correlation time (τ_c) for compound (**1**), some shortening in T_1 values was expected. However, the large observed difference could not be accounted for only by electrostatic solute-ordering effects.[7] In our case intermolecular interactions between the anion and its counter ion did not have a dramatic effect on T_1: diluted samples (0.02 mol dm^{-3}) showed, at 183 K, an increase in T_1 of the order 6—15%.

Relaxation times of compound (**1**) measured at 20.15 MHz, in the temperature range 183—303 K, increase with decreasing temperature (Table 1). This trend is the opposite to that expected if dipole–dipole or chemical shielding anisotropy interactions were dominant. Indeed $T_1^{\text{d.d.}}$ and $T_1^{\text{c.s.a.}}$ have a temperature dependence, expressed through the correlation time, assuming isotropic reorientation, as shown by equations

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† 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-1,2;1,3;2,3;2,3-tetra-μ-hydrido-*triangulo*-trirhenate(1 −).

Table 1. Spin–lattice relaxation times (T_1/s)[a] of compound (1)

	20.15 MHz[b]				50.31 MHz[c]	67.88 MHz[d]
	183	233	253	303 K	303 K	303 K
CO_a	0.964	0.636	0.326	0.153	0.339	0.504
CO_b	0.660	0.503	0.262	0.127	0.275	0.418
CO_c	0.500	0.266	0.179	*e*	1.564	2.416
CO_d	0.383	0.192	0.144	*e*	1.128	1.886

[a] Calculated by exponential least-squares fitting. Errors <3%. [b] Using a Bruker WP 80 SY. [c] Using a Varian XL-200. [d] Using a Bruker WP 270 SY. [e] The peaks were unresolved owing to line broadening due to the coupling with Re.

$$\frac{1}{T_1^{\text{d.d.}}} = \frac{\frac{4}{3}\gamma_C{}^2\gamma_X{}^2 S(S+1)\hbar^2}{r_{C\text{-}X}{}^6}\cdot\tau_c \qquad (1)$$

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

(1)[8a] and (2).[8b] All the symbols have their usual meanings, S being the spin quantum number of nucleus X. This allows us to rule out both these mechanisms. Furthermore, nuclear Overhauser effect (n.O.e.) measurements at 20.15 MHz indicated that intramolecular ^{13}C–^{1}H dipole–dipole interactions account for less than 11% of the observed relaxation rates (R^T) at 183 K (Table 2). Indeed they do not contribute significantly to the relaxation at room temperature at any field strength as the nuclear Overhauser enhancement (η) = 0.0 for all the resonances.

Due to the moderate enrichment, the ^{13}C–^{13}C dipole–dipole interactions were also expected to be negligible. An estimation indicated that this contribution is irrelevant even at 183 K ($1/T_1^{\text{d.d.}} = 2.9 \times 10^{-3}$ s^{-1}).* Dipolar interactions between carbon and rhenium were similarly ruled out ($1/T_1^{\text{d.d.}} = 1.1 \times 10^{-2}$ s^{-1}).

The observed field dependence of T_1, resulting in longer T_1 at higher field strength (Table 1), confirmed that, at room temperature, the contribution of chemical shielding anisotropy relaxation is negligible. The observed variations of T_1 with the applied field are also inconsistent with a spin-rotation relaxation, which is not a field-dependent mechanism.[9]

The above results suggest that, at room temperature, the main contribution to relaxation is due to scalar coupling interactions with quadrupolar ^{185}Re (natural abundance 37%, $I = \frac{5}{2}$) and ^{187}Re (natural abundance 63%, $I = \frac{5}{2}$). The requirements for such a mechanism,[10] (*i*) similar Larmor frequencies (ω_0) for the involved nuclei and (*ii*) a quadrupolar nucleus relaxation time (T_1^Q) < 10^{-5} s, are met with in our case. Indeed at 20.15 MHz, $\Delta\omega(^{185}\text{Re}$–$^{13}\text{C}) = 2.11$ MHz, $\Delta\omega(^{187}\text{Re}$–$^{13}\text{C}) = 1.92$ MHz, and T_1^Q(Re) is reported[11] to be less than 10^{-5} s.

The increase in T_1 with the applied field is also consistent with the field dependence of $T_1^{\text{s.c.}}$, according to equation (3),[8] where $A = 2\pi J$, thus confirming the effectiveness of scalar coupling.

$$\frac{1}{T_1^{\text{s.c.}}} = \frac{35}{6}\cdot A^2 \cdot \frac{T_1^Q(\text{Re})}{1 + \Delta\omega^2[T_1^Q(\text{Re})]^2} \qquad (3)$$

Table 2. Nuclear Overhauser measurements* at 20.15 MHz at 183 K

	CO_a	CO_b	CO_c	CO_d
η	0.23	0.16	0.16	0.12
$R^{\text{d.d.}}/R^T$	0.11	0.08	0.08	0.06

* Values were determined from total integrated peak-intensity ratios, which yield $1 + \eta$ values.

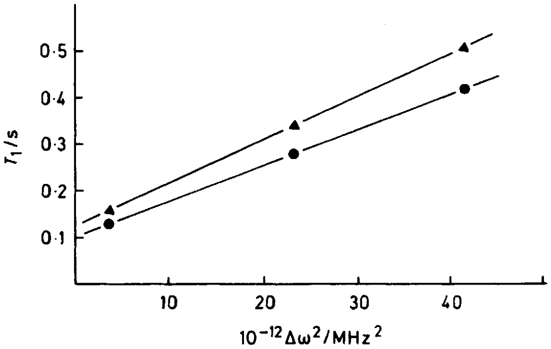

Figure. Plot of T_1 *vs.* $\Delta\omega^2(^{187}\text{Re}$–C); (▲) CO_a, (●) CO_b

Since all experiments showed an exponential recovery of the magnetization, the contributions of ^{185}Re and ^{187}Re to the relaxation rate must be either comparable or one dominates the other. The relation (4) holds for the two Re isotopes, where γ =

$$\left[\frac{\gamma(^{185}\text{Re})}{\gamma(^{187}\text{Re})}\right]^2 \left[\frac{Q(^{187}\text{Re})}{Q(^{185}\text{Re})}\right]^2 \approx 0.85 \qquad (4)$$

gyromagnetic ratio and Q = quadrupole moment, so that similar values of A and T_1^Q are expected for the two nuclei.[1b]

It is therefore possible to plot our data as T_1 *vs.* $\Delta\omega^2(^{187}\text{Re}$–$^{13}\text{C})$ under the assumption that the relaxation is only due to ^{187}Re (which is more abundant and whose Larmor frequency is closer to that of carbon). The striking linearity observed (Figure)† shows that scalar relaxation is the main contribution even at higher fields. The parameters calculated from this plot led us to determine the quadrupolar relaxation time of ^{187}Re and the coupling constant $^{1}J(^{187}\text{Re}$–C); T_1^Q(Re) has been estimated as 2.7×10^{-7} s. The behaviour of $(T_1^{\text{s.c.}})^{-1}$ *vs.* temperature depends on the relative magnitudes of $\Delta\omega$ and T_1^Q [equation (3)]: at 20.15 MHz, $\Delta\omega^2(T_1^Q)^2 < 1$ and $(T_1^{\text{s.c.}})^{-1}$ will decrease with temperature, in agreement with the observed temperature dependence of T_1. The coupling constants $^{1}J(^{187}\text{Re}$–C), estimated for CO_a and CO_b, are 360 and 397 Hz,

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* The contribution of ^{13}C–X dipole–dipole interactions to the cross-relaxation parameter is given by[8a] $\sigma_{C\text{-}X}{}^{\text{d.d.}} = \frac{1}{2}\gamma_C{}^2\gamma_X{}^2\hbar^2 r_{C\text{-}X}{}^{0-6}\tau_c$, where X is either ^{13}C or ^{187}Re; $\bar{r}_{C\text{-}C} = 2.6$ Å and $\bar{r}_{C\text{-}Re} = 2.0$ Å, from *X*-ray data.[3] The value of $\tau_c = 0.8 \times 10^{-9}$ s was obtained from equation (1) combined with $1/T_1^{\text{d.d.}} = \eta/1.988T_1$, including each possible C–H interaction; C–H distances were calculated by combining *X*-ray data and calculated[3] positions of the hydrogens ($\bar{r}_{Re\text{-}H} = 1.70$, $\bar{r}_{Re\text{-}H'} = 1.94$ Å).

† The standard deviation of the least squares fitting of our data is *ca.* 1% for both the parameters of the two straight lines.

respectively. It should be noted that the values of these coupling constants have never been determined before.

Experimental

Carbon-13 n.m.r. spectra were recorded at different frequencies using Bruker WP 80-SY, Varian XL-200, and Bruker WH 270 spectrometers, operating at 20.15, 50.31, and 67.88 MHz, respectively. Variable-temperature experiments were performed using the B-VT 1000 temperature-control unit of the spectrometer (accuracy ± 1 °C). The samples, contained in 10-mm tubes, were typically 0.1 mol dm^{-3} in deuteriated tetrahydrofuran. Before each experiment, the samples were thoroughly degassed by repeated freeze–thaw cycles. All the spectra were recorded under full proton decoupling. Chemical shifts are reported downfield positive with respect to internal $SiMe_4$.

Carbon-13 spin–lattice relaxation times were measured by the non-selective inversion-recovery technique.[5] In each T_1 measurement the waiting period, T_d, between sequences was always kept longer than $5T_1$. Values of the equilibrium magnetization, M_∞, were measured at the beginning and at the end of each measurement. Values of T_1 were calculated by exponential least-squares fitting using a library program. Those presented here are the average from two or three determinations each employing a total of between 10 and 13 experimental points. Separate experiments were also performed for different carbonyl groups when their relaxation times required different sets of variable delays.

Nuclear Overhauser effects were determined[8b] by recording continuously decoupled (decoupler on 1.5 s before the acquisition) and gated decoupled (decoupler on only during acquisition) ^{13}C spectra using 90° pulses with delays longer than $5T_1$ for the slowest relaxing carbon. The presaturation delay (1.5 s) was calculated from separate experiments of n.O.e. growth. Alternate block acquisition was used to minimize drifts over the whole sequence. Nuclear Overhauser enhancements were calculated from the ratio between the integrated intensities of each peak in the continuously decoupled and gated decoupled spectra.

Compound (**1**) was prepared as previously described[3] from $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ under a high pressure of hydrogen. Moderately enriched (*ca.* 20%) samples were obtained by stirring the rhenium cluster (**1**) in acetone in a ^{13}CO atmosphere (*ca.* 60%) at 35 °C for 24 h.

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