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Preliminary communication

^{13}C NMR INVESTIGATION OF THE PROPERTIES OF THE ANION $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ IN SOLUTION

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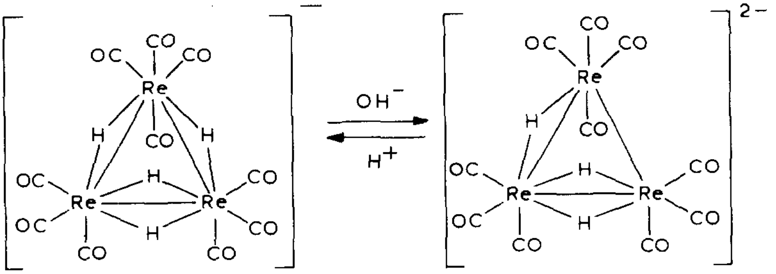
Summary

^{13}C NMR measurements were performed on $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ at various temperatures and field strengths. Selective decoupling allowed assignments of the carbonyl resonances. Spin-lattice relaxation time measurements indicated that two mechanisms, scalar coupling and chemical shielding anisotropy, contribute to the relaxation of carbon-13. Variable temperature experiments revealed that more than one mechanism is responsible for the fluxional behaviour.

We present the results of an NMR study of the properties in solution of the hydridocarbonylrhenium cluster $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ (I) [1], the conjugated base of the monoanion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^{-}$ (II), which was previously the subject of a detailed NMR investigation [2].

Compound II exhibits ^{13}C unusual relaxation properties at room temperature [3], owing to the operation of the scalar coupling mechanism (SC) with



SCHEME 1

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quadrupolar rhenium, whereas at low temperature and at higher fields the chemical shielding anisotropy mechanism (CSA) becomes dominant [4]. In contrast with the majority of the analogous carbonyl clusters, compound II does not show any fluxional behaviour up to 50°C [2], and it seemed of interest to ascertain whether dianion I showed the same type of relaxation behaviour and to study its dynamic properties.

The carbonyl region of the ^{13}C NMR spectrum, at 223 K, of a ^{13}CO-enriched sample of I is shown in the bottom of Fig. 1; there are seven carbonyl resonances at 212.11, 208.03, 205.62, 202.41, 200.87, 198.24, and 192.04 ppm with integrated intensity ratios 2/1/2/1/1/2/1, as expected for C_s symmetry. Assignments were made on the basis of selective irradiation experiments. Figure 2 shows that irradiation of the H^a protons removes coupling from the signals at 212.11 and 200.87 ppm. The signals at 205.62, 198.24, and 192.04 ppm also sharpen, but coupling with H^b is maintained. Saturation of the

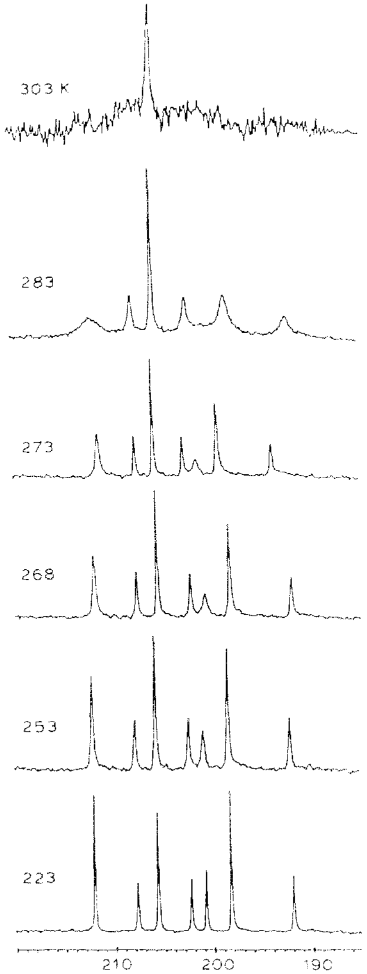

Fig. 1. Carbonyl region of ^{13}C-{^{1}H} NMR spectra of compound I (^{13}CO ca. 30%, 0.05 M in CD$_3$CN/C$_4$D$_8$O 1/1 v/v, 20.15 MHz, Me$_4$Si as internal standard). Spectra recorded at the temperatures (K) shown on a Bruker WP-80 SY spectrometer.

H^b hydride substantially affects all the resonances except those at 212.11 and 200.87 ppm, which are therefore assigned to CO^b and CO^d, respectively. The assignments of the signals at 208.03 and 202.41 ppm to the $Re(CO)_4$ moiety and of the resonance at 192.04 ppm to CO^c are therefore straightforward. The two signals of double intensity at 198.24 and 205.62 ppm are affected by both irradiations: they can be attributed to CO^a and CO^e, respectively, on the basis of the relative effects of the irradiations. The only ambiguity concerns the attribution of the signals at 208.03 and 202.41 ppm to CO^f or CO^g. The analysis of the coupling constants does not help because in this system *cis* and *trans* couplings have almost the same value (Fig. 2b).

^{13}C relaxation time (T_1) measurements were performed at 223 K on accurately degassed solutions of compound I using the non-selective inversion-recovery

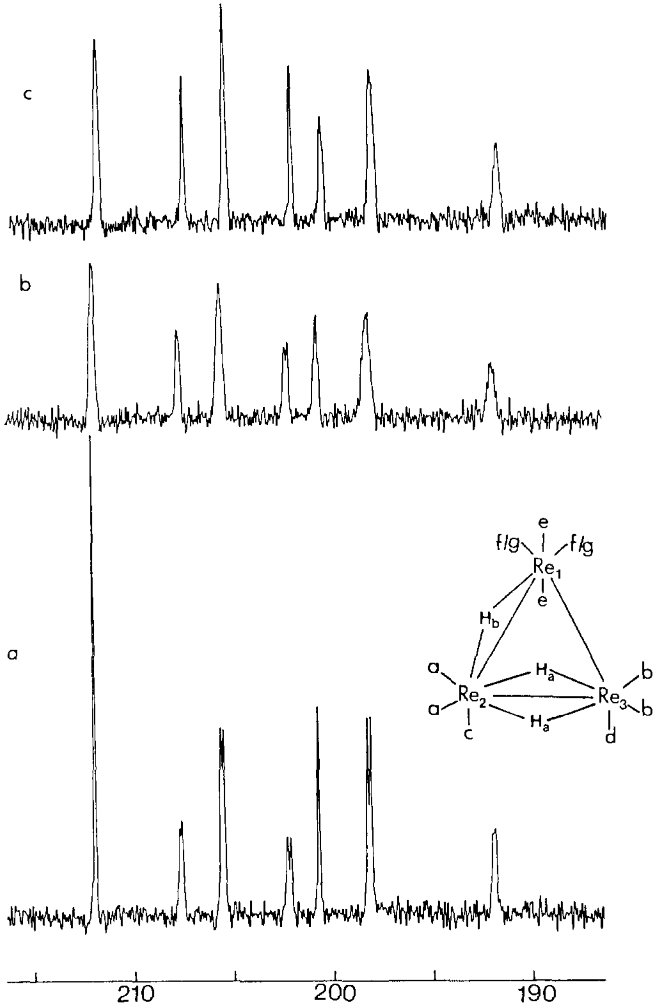

Fig. 2. Selective irradiation experiments recorded on a Bruker WP-80 SY spectrometer operating at 20.15 MHz. Carbonyl region of ^{13}C spectra. (a) on-resonance at H^a frequency (measured coupling constants $^2J(CO^{f,g}—H^b)$ = 2.1 Hz, $^2J(CO^e—H^b)$ = 2.8 Hz, $^2J(CO^{g,f}—H^b)$ = 3.0 Hz, $^2J(CO^a—H^b)$ = 3.2 Hz, $^2J(CO^c—H^b)$ = 3.41 Hz); (b) off-resonance; (c) on resonance at H^b frequency.

TABLE 1

^{13}C SPIN-LATTICE RELAXATION TIMES (T_1/s)^a OF I (223 K)^b MEASURED AT VARIABLE FIELD STRENGTHS

MHz	δ (ppm)						
	212.1	208.0	205.6	202.4	200.9	198.2	192.0
20.15^c	0.697	0.375	0.497	0.258	0.519	0.594	0.495
50.31^d	0.653	0.392	0.472	0.282	0.469	0.550	0.420
67.88^e	0.517	0.361	0.430	0.281	0.453	0.442	0.402

[a] Measurements performed under full proton decoupling conditions. The waiting time, T_d, was kept longer than $5T_1$ of the longest relaxing carbonyl, thirteen variable delays were employed for each measurement. Errors < 7%. [b] Calibrated using methanol solutions and controlled by the control-units of the spectrometers with an accuracy of ±1°C. [c] On a Bruker WP-80 SY spectrometer. [d] On a Varian XL-200 spectrometer. [e] On a Jeol GX-270/89 spectrometer.

technique [5], and the values, obtained from the exponential least-squares fitting of the experimental data, are shown in Table 1. Carbonyl spin-lattice relaxation times in metal carbonyls are usually quite long at low fields (ca. 30 s at 2.1 T, 303 K) owing to the absence of dipole—dipole interactions with directly bonded hydrogens. The short relaxation times, observed for compound I at 20.15 MHz and at 223 K, are nearly equal to those for compound II under the same conditions [3], indicating that there is effective scalar coupling with quadrupolar rhenium isotopes ^{185}Re and ^{187}Re (natural abundance 37.07 and 62.93%, respectively, $I(^{185}\mathrm{Re}) = 5/2$ and $I(^{187}\mathrm{Re}) = 5/2$). The requirements [6] for this mechanism to operate are satisfied: the Larmor frequencies of carbon and rhenium isotopes are close to 20.15 MHz ($\Delta\omega(^{185}\mathrm{Re{-}C})$ 2.11 MHz, $\Delta\omega(^{187}\mathrm{Re{-}C})$ 1.92 MHz) and $T_1^{Q}(\mathrm{Re}) < 10^{-7}$ s [2]. Indeed at 303 K only for CO^e could T_1 be measured (0.147 s), because the dianion I is fluxional and all the other resonances are collapsed. The observed decrease of the CO^e relaxation time on increasing the temperature is consistent with the temperature dependence of a scalar coupling mechanism provided that $\Delta\omega^2(T_1^{Q})^2 < 1$, as is the case*.

For the monoanion II we observed that at room temperature, where the SC mechanism is dominant, the values of T_1 increase with increase in the field strength, whereas the opposite trend was observed at 183 K, in agreement with the CSA field dependence. The T_1 values of $[\mathrm{Re_3(\mu\text{-}H)_3(CO)_{10}}]^{2-}$, measured at 223 K, (Table 1) show only a minor decrease on increasing the field strength, and this is attributable to competition between the two mechanisms, SC and CSA, which, having opposite field dependence, compensate each other. The low solubility of I in polar solvents suitable for low temperatures precluded experiments below 223 K, preventing quantitative estimation of the chemical shielding anisotropy parameters.

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[*] Scalar coupling relaxation rate obeys the equation:

$$R^{\mathrm{SC}} = (T_1^{\mathrm{SC}})^{-1} = \frac{2}{3} S(S+1)A^2 \; \frac{T_1^{Q}}{1 + \Delta\omega^2 (T_1^{Q})^2}$$

where S and T_1^{Q} are the spin quantum number and the quadrupolar relaxation time of the nucleus (Re) involved in the scalar coupling with carbon, $A = 2\pi J(\mathrm{C{-}Re})$, and $\Delta\omega$ is the difference between the Larmor frequencies of rhenium and carbon. When $\Delta\omega^2(T_1^{Q})^2 < 1$, T_1^{SC} is proportional to τ_c through T_1^{Q} [7].

The results of variable temperature experiments (20.15 MHz) are shown in Fig. 1. The available range of temperatures is limited by the instability of I above 303 K. It is noteworthy that the absence of a hydride ligand bridging the Re^1—Re^3 bond strongly modifies the dynamic properties of the dianion with respect to the monoanion. At 253 K the major broadening is observed for CO^b and CO^d, whereas at higher temperatures all the other carbonyls except CO^e undergo an exchange process. It is evident that the dynamic process with the lowest activation energy is the localized scrambling of CO^b and CO^d. A mutual exchange between H^a and H^b was ruled out on the basis of ^1H selective population transfer experiments. The behaviour at higher temperatures can therefore be explained in terms of a migration of H^b from the Re^1—Re^2 to the Re^1—Re^3 edge, which would equalize the CO^a/CO^b, CO^c/CO^d and CO^f/CO^g pairs. However, more accurate analysis of the spectra shows that the signal of CO^a broadens before the others, suggesting that some other process may be present in addition to the two mentioned. Work is in progress to elucidate all the possible pathways of the exchange and to make quantitative kinetic measurements.

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