Notes

Carbon-13 Nuclear Magnetic Resonance Study of the Properties of the Unsaturated Anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ at Low Temperature

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The carbonyl resonances of $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ have been assigned and the ^{13}C spin–lattice relaxation times measured at different field strengths (20.15, 50.31, and 75.43 MHz) at 238 K. The results indicate that scalar coupling of the second kind with rhenium isotopes is the dominant relaxation mechanism at this temperature. Values of T_1^Q(Re) and $^1J(^{187}Re–C)$ were calculated. The presence on the $H_2Re(CO)_3(NCMe)$ moiety of a poor π-acceptor ligand doubles $^1J(^{187}Re–C)$ with respect to the unsubstituted $H_2Re(CO)_4$ moiety in the precursor $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$.

Measurements of spin–lattice relaxation times (T_1) and the analysis of the different mechanisms which can operate have provided a great number of data about molecular structure, dynamics, and bonding.[1] Recent studies on carbonyl metal clusters have pointed out that dipolar relaxation with the hydrogen atoms (present in the molecule both as hydrido ligands and/or as part of organic ligands) plays a negligible role[2] in carbon-13 relaxation, the most important mechanism being generally the chemical shielding anisotropy.[2a] In rhenium carbonyl compounds, however, scalar coupling of the 'second kind'[3a] between carbon and quadrupolar rhenium isotopes proved to be operative at room temperature.[2b] The analysis of the field dependence of the relaxation times allowed estimates of the rhenium quadrupolar relaxation time and of the direct coupling constant between carbon and rhenium.

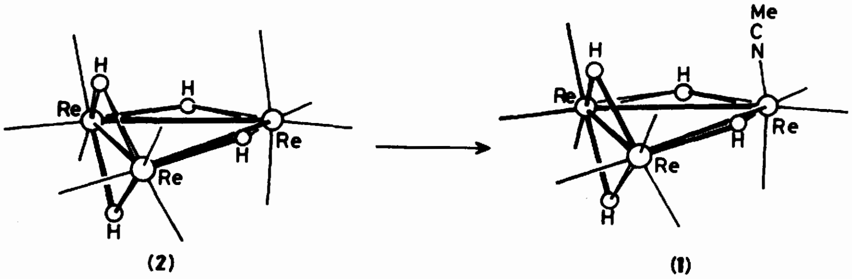
We have recently synthesized[4] the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (**1**) by substitution of a CO ligand in $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**2**) with an acetonitrile (MeCN) molecule (see Scheme) and now we report a carbon-13 n.m.r. spectroscopic study of compound (**1**), with the aim of comparing its properties with those of its precursor (**2**).

Results and Discussion

The substitution shown in the Scheme, removing the equivalence of the H and CO ligands lying on opposite sides of the plane of the metal atoms, lowers the symmetry of the anion from C_{2v}, in compound (**2**), to C_s, in compound (**1**). Accordingly, the carbonyl region of the ^{13}C n.m.r. spectrum of compound (**1**) (238 K, 20.15 MHz, CD_3CN) exhibits [Figure 1(*a*)] five resonances at δ 188.6, 189.4, 192.0, 196.2, and 197.1 p.p.m., respectively, with intensity ratio 2:2:1:2:2, while for compound (**2**) [Figure 1(*b*)] four signals (intensity ratio 4:2:2:2) were observed. Analogously, as already reported,[4] the ^1H n.m.r. spectrum of (**1**) exhibits three resonances [δ −8.21(1), −8.46(1), and −10.64(2); 238 K, 80.13 MHz, CD_3CN] instead of the two resonances {δ −8.50(2) and −13.35(2), 183 K, 80.13 MHz; [$^2H_8$]tetrahydrofuran} observed for compound (**2**). The present study was performed at 238 K since compound (**1**) is fluxional, and at room temperature all the carbon resonances are nearly collapsed. Selective population-transfer (s.p.t.) experiments[5] however, proved that, at 238 K, no magnetization was transferred either between the hydrides or between the carbons. Therefore, at this temperature the exchange was assumed to be slow on the n.m.r. time-scale.

Selective decoupling of the three hydridic resonances was performed at 238 K and the difference spectra, obtained by subtracting the off-resonance spectra from the on-resonance ones, are shown in Figure 2. These experiments allowed the unambiguous assignment of the signal at 189.4 p.p.m. to the carbonyls d, coupled only with the hydrides H_c, and confirmed the straightforward assignment of the unique signal of intensity 1 to the carbonyl e. The resonances of the 'diagonal' carbonyls a and b are expected to occur at similar δ values (as observed for H_a and H_b), so the two signals at lower field can be attributed to them and the highest-field signal to carbonyls c, in agreement also with the values of the chemical shifts found for compound (**2**) (Figure 1). The substitution of an acetonitrile molecule for a carbonyl results therefore in a low-field shift, with respect to compound (**2**), of the resonances of the carbonyls belonging to the '$H_2Re(CO)_3(NCMe)$' moiety (*cf.* 192.0 *vs.* 184.8 for the axial carbonyls and 189.4 *vs.* 184.4 p.p.m. for the equatorial carbonyls) leaving almost unaffected the resonances belonging to the unsaturated unit (*cf.* 197.1—196.2 *vs.* 196.7 and 188.6 *vs.* 187.4 p.p.m. respectively). This deshielding effect was also observed in the ^1H spectrum and it is likely to be related to a change in the paramagnetic contribution to the screening tensor due to increased π back donation to the carbonyls in compound (**1**).

The ^{13}C relaxation times (T_1) were measured at 238 K at 20.15, 50.31, and 75.43 MHz using the non-selective inversion-recovery technique.[6] The values, obtained from a non-linear least-squares fitting of the experimental magnetizations, are reported in the Table. Previous studies on the ^{13}C relaxation properties of compound (**2**)[2b] showed that, at room temperature, the main mechanism is the 'scalar coupling of the second kind'[3a] (s.c.) between carbon-13 and the quadrupolar isotopes of rhenium (^{185}Re, $I = \frac{5}{2}$; ^{187}Re, $I = \frac{5}{2}$; natural abundance 37.07 and 62.93%, respectively), while, at 183 K, the chemical shielding anisotropy (c.s.a) mechanism is dominant.[7] The field dependence of the relaxation rates (R) due to the two mechanisms is expressed through the terms $\Delta\omega^2$ and B_0^2



Scheme.

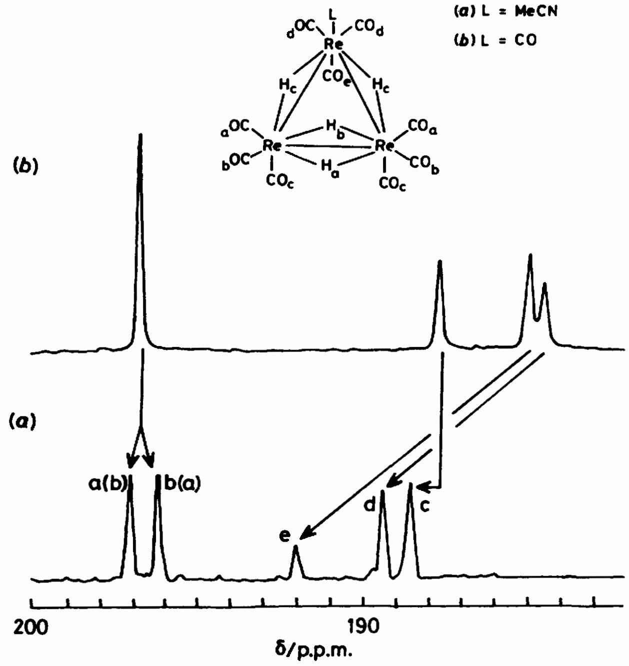


Figure 1. Carbonyl region of the ^{13}C n.m.r. spectra of (*a*) $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (CD_3CN, 20.15 MHz, 238 K), and (*b*) $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ ($[^2H_8]$tetrahydrofuran, 20.15 MHz, 183 K), showing the lowering of symmetry and the deshielding effect caused by the introduction of the nitrile ligand

[equations (1) and (2)],[8] respectively, where S and T_1^{Q} are the spin quantum number and the quadrupolar relaxation time respectively, of the quadrupolar nucleus involved, J is the C–Re

$$(T_1^{\text{s.c.}})^{-1} = R_{\text{s.c.}} = \frac{8}{3}\pi^2 J^2 S(S+1)\cdot\frac{T_1^{Q}}{1+\Delta\omega^2(T_1^{Q})^2} \qquad (1)$$

$$(T_1^{\text{c.s.a.}})^{-1} = R_{\text{c.s.a.}} = 2\gamma^2 B_0^2 \Delta\sigma^2 \tau_c/15 \qquad (2)$$

coupling constant, $\Delta\omega$ is the difference between the Larmor frequencies of carbon and rhenium, B_0 is the external magnetic field, $\Delta\sigma$ refers to the anisotropy of the shielding tensor, γ is the carbon gyromagnetic ratio, and τ_c is the molecular correlation time. Values of T_1 will increase or decrease with the field strength depending on the relative importance of the two mechanisms and, when one of the two is dominant, relaxation times (s.c.) or relaxation rates (c.s.a.) will have a linear dependence *vs.* $\Delta\omega^2$ or B_0^2, respectively. The experimental results (Table) indicate that for compound (**1**), at 238 K, the T_1 values increase with the field and the scalar coupling of the second kind still dominates the chemical shielding anisotropy mechanism.

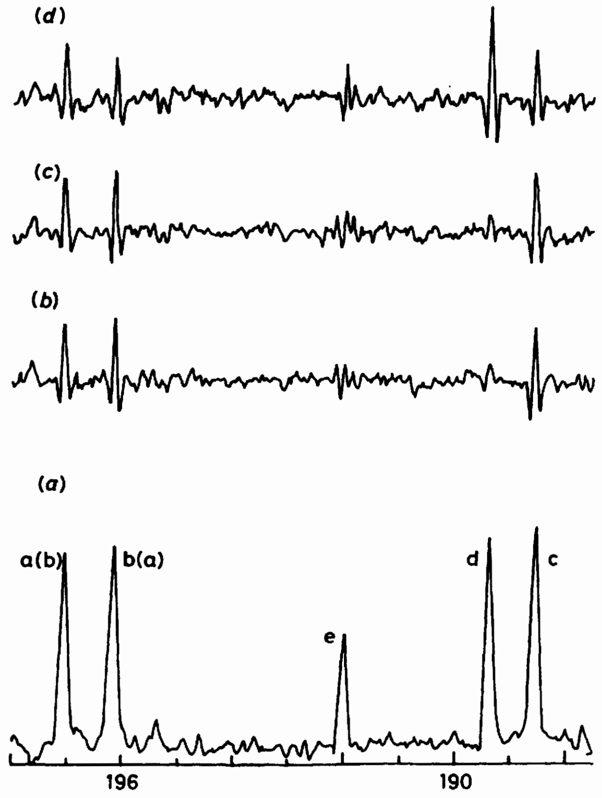


Figure 2. Selective decoupling experiments performed on $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (**1**) (carbonyl region, CD_3CN, 75.43 MHz, 238 K), assignments as in Figure 1. (*a*) Off-resonance spectrum, (*b*) difference spectrum after irradiation of H_a, (*c*) difference spectrum after irradiation of H_b, and (*d*) difference spectrum after irradiation of H_c

Table. Carbonyl ^{13}C spin–lattice relaxation times (T_1/s)[a] of compound (**1**)

	T_1/s				
	20.15	50.31	75.43 MHz	$^1J(^{187}Re\text{–}C)$/Hz	$10^8T_1^{Q}(Re)$/s
CO_a	0.32	0.36	0.40	1 085	1.2
CO_b	0.29	0.35	0.41	1 018	1.5
CO_c	0.28	0.36	0.37	*b*	*b*
CO_d	0.19	0.28	0.43	970	2.8
CO_e	0.18	0.28	0.39	1 003	2.5

[a] Errors < 3%. [b] Not calculated owing to the poor correlation coefficient.

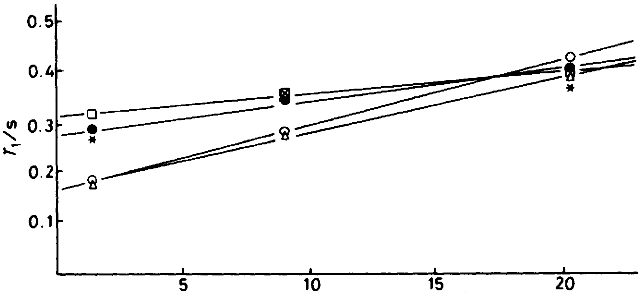


Figure 3. Plot of T_1 *vs.* $\Delta\omega^2(^{187}Re–C)$: (□) CO_a, (●) CO_b, (✱) CO_c, (○) CO_d, and (△) CO_e. The line relating to CO_c has not been drawn due to its low correlation coefficient

The plot of the measured relaxation times *vs.* $\Delta\omega^2(^{187}Re–^{13}C)$ (Figure 3) results in a linear dependence for carbonyls a, b, d, and e, thus indicating the major contribution of the scalar coupling mechanism; for carbonyls c there is an unquestionable contribution from the c.s.a. mechanism at 75.43 MHz. No attempt was made to separate the contributions of the two isotopes of rhenium to $T_1^{s.c.}$. Indeed, rhenium-185 and -187 have similar gyromagnetic ratios and quadrupolar moments, therefore they are expected to have similar quadrupolar relaxation times and similar coupling constants with carbon-13,[3b] while the $\Delta\omega^2$ terms are within 10%. Rhenium-187 was chosen since it is the most abundant isotope and the one whose Larmor frequency is closer to that of carbon. The same procedure performed using the values for the rhenium-185 isotope or a weighted-mean value of $\Delta\omega^2$ led to the same results within experimental error.

The linear least-squares fitting of the experimental data gave correlation coefficients better than 0.995 in each case, except for carbonyls c (0.86). The analysis of the slopes and intercepts of the lines relative to carbonyls a, b, d, and e allowed us to calculate the quadrupolar relaxation time of rhenium and the $^1J(^{187}Re–C)$ values (Table). These results show that the different field dependence of the resonances belonging to the apical moiety and those of the unsaturated moiety is mainly due to a difference in $T_1^Q(Re)$ rather than different coupling constants. The quadrupolar relaxation times calculated for rhenium in compound (**1**) are shorter than those reported for compound (**2**),* their difference being due to the longer molecular correlation time at lower temperature.

For the parent anion (**2**) the coupling constants, calculated for the carbonyls of the unsaturated moiety, are *ca.* 1 000 Hz,* while for the apical moiety a rough estimate,† using the procedure described above, led to $^1J(^{187}Re–C) = 550$ and 423 Hz for the equatorial and axial carbonyls, respectively. On the contrary, in compound (**1**) the calculated constants are *ca.* 1 000 Hz for all the carbonyls belonging both to the apical and to the unsaturated moieties (Table). The substitution of a carbonyl with a ligand with poor π-acceptor properties results therefore in a stronger carbon–metal interaction of the remaining carbonyls and an increase in the value of the direct coupling constants, which, in the present case, double on going from compound (**2**) to compound (**1**).

Experimental

N.m.r. samples (0.1 mol dm^{-3} solution) of moderately ^{13}C-enriched (*ca.* 20%) compound (**1**) dissolved in CD_3CN in 10-mm outside diameter tubes were carefully degassed by repeated freeze–pump–thaw cycles. Carbon-13 n.m.r. spectra were obtained on Bruker WP 80-SY, Varian XL-200, and Varian XL-300 spectrometers operating in the Fourier-transform mode at 20.15, 50.31, and 75.43 MHz, respectively. All the spectra were recorded under full proton decoupling and the chemical shifts are reported downfield positive with respect to internal $SiMe_4$. Sample temperatures were calibrated using methanol solutions by recording the proton spectrum *via* the decoupling coils of the ^{13}C probe. Temperatures were then controlled by using the temperature-control units of the spectrometers with an accuracy of ± 1 °C. Selective-decoupling experiments were performed on the Varian XL-300 spectrometer; alternate acquisition of eight on- and off-resonance transients was used in order to minimize drifts over the whole sequence and the difference spectra were obtained by subtracting the off-resonance f.i.d. (free induction decay) from the on-resonance f.i.d. Carbon-13 spin–lattice relaxation times were determined by using the non-selective inversion-recovery technique.[6] A waiting time, T_d, much longer than $5T_1$ was utilized. Values of the equilibrium magnetization, M_∞, were measured at the beginning and end of each measurement. Thirteen different pulse intervals were utilized in each individual run to ensure that a minimum of ten data points was used for each T_1 calculation.

Acknowledgements

The authors thank the Centro C.N.R. Sintesi e Struttura Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione for financial support.

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Received 6th October 1986; *Paper* 6/1960

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* The values of $^1J(^{187}Re–C)$ and of $T_1^Q(Re)$ previously reported[2b] were incorrectly calculated: the parameters of the lines in the plot T_1 *vs.* $\Delta\omega^2(Re–C)$ in ref. 2*b* must be rectified by a $4\pi^2$ factor. The final values, corrected accordingly, are $^1J(^{187}Re–C) = 906$ Hz for carbonyls a and 998 Hz for carbonyls b, and $T_1^Q(Re) = 4.4 \times 10^{-8}$ s.

† This estimate (based only on the data corresponding to 50.31 and 67.88 MHz) is however supported by the longer T_1 (*ca.* five times) measured[2a] in compound (**2**) for the apical carbonyls with respect to those of the unsaturated moiety.