Two-dimensional Nuclear Magnetic Resonance for the Analysis of the Carbon-13 Spectra of Carbonyl Groups in Metallocarbonyls

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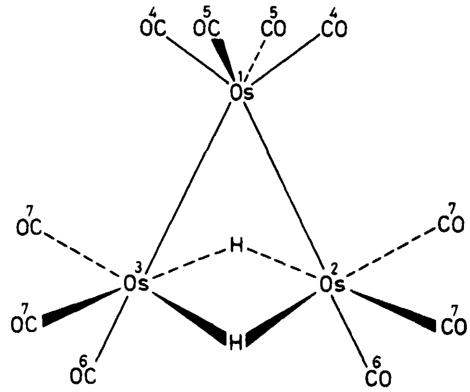
The ^{13}C homonuclear two-dimensional n.m.r. shift correlation experiment COSY on the ^{13}C-enriched complex $[Os_3H_2(CO)_{10}]$ established the presence of two- and three-bond scalar couplings which partially invalidates previous assignment of the ^{13}C spectrum. A related two-dimensional experiment (NOESY) was used to detect slow localised carbonyl group exchange. The exchanging system was treated as a three-site problem (two of which are equivalent) and intensities of the slowly exchanging peak and the associated correlation peak in the NOESY experiment were analysed quantitatively to yield ^{13}C spin-lattice relaxation rates and a value for the exchange rate constant (1.21 s^{-1}).

Carbon-13 enrichment of CO groups in metallocarbonyls has been used at the 10—20% level to facilitate the observation of the ^{13}C resonances, and at higher levels ($\geqslant$40%) to yield[1,2] ^{13}C–^{13}C couplings, in particular $^2J_{CC}$ *trans* (30—35 Hz) and $^3J_{CC}$ *trans* (11.5 Hz). We report here the use of two-dimensional spectra to (*i*) detect the presence of $^2J_{CC}$ and $^3J_{CC}$ and (*ii*) measure quantitatively the intramolecular CO exchange. The compound studied was $[Os_3H_2(CO)_{10}]$ (**1**) at high ^{13}C enrichment (*ca.* 75%).

Results and Discussion

Previous ^{13}C n.m.r. studies showed four resonances at δ 175.2, 176.3, 181.8, and 182.7 (relative intensities 2:1:1:1) for $[Os_3H_2(CO)_{10}]$ (**1**) (*ca.* 75% ^{13}C). The two lowest frequency resonances (175.2, 176.3) were definitely assigned[3] to carbonyls 7 and 6 respectively on the basis of relative intensities, ^1H coupling, and variable-temperature spectra. The assignment of the high-frequency peaks was less clear: 181.8 to CO(5) and 182.7 to CO(4) on the basis of the following observations and assignments.[4] The peak at 181.8 showed a complex structure arising from the mixture of isotopomers but which included a 3.2 Hz doublet splitting from a $^2J_{CC}$ *cis* coupling between carbonyls 4 and 5. The peak at 182.7 was broader and the extra width was assumed to arise from $^3J_{CC}$. Since $^3J_{CC}$ *trans* is expected to be larger than $^3J_{CC}$ *cis* the peak at 182.7 was assigned to the resonance of CO(4) since it is *trans* to carbonyl 6, and there is a nearly linear arrangement[5] for the CO(4)–Os–Os–CO(6) fragment. Two-bond coupling between 7 and 6 was inferred from the widths of the resonances at δ 175.2 and 176.3.

A relatively straightforward method for the determination of scalar coupling connectivities is the so-called COSY-45 two-dimensional correlation.[6] The lower right half of Figure 1 is a contour plot of such an experiment on 75% ^{13}C-enriched (**1**), in which the diagonal peaks represent the normal ^{13}C spectrum and the off-diagonal peaks the scalar coupling connections. The presence of the two-bond couplings is confirmed within the two sets of carbonyls (6,7 and 4,5). The three-bond coupling is now found to be between CO groups giving the resonances at δ 182.7 and 175.2 [CO(7)], *not* at δ 176.3 [CO(6)]. Therefore the assignment of CO(4) and CO(5) remains in doubt and the previous assumption[4] that a *trans* arrangement is necessary for $^3J_{CC}$ to be observed is not substantiated. Therefore the interpretation of $^3J_{CC}$ in structural terms must await the collection of a greater body of data.



(1)

A two-dimensional n.m.r. experiment which is related to the scalar coupling correlation is the NOESY experiment,[7] wherein the intramolecular correlation is established by cross-relaxation leading to nuclear Overhauser enhancement (n.O.e.) connectivities, or by magnetisation transfer and slow chemical exchange. In a previous quantitative study of the ^{13}C relaxation and exchange dynamics of (**1**) we have shown[8] that localised slow exchange occurs *only* between CO(6) and CO(7) at 300 K, and that for ^{13}C observation at 100.6 MHz ^{13}C–^{13}C cross-relaxation and hence n.O.e. effects are negligible. The result of the NOESY experiment on (**1**) is shown in the upper left half of Figure 1 wherein the single off-diagonal peak demonstrates this slow exchange between CO(6) and CO(7). The pulse sequence for the NOESY experiment is $(t_r - \frac{\pi}{2} - t_e - \frac{\pi}{2} - t_m - \frac{\pi}{2}\ \text{acquire})_n$ where $\frac{\pi}{2}$ is the non-selective ^{13}C pulse, and the times t_r, t_e, and t_m are respectively a relaxation delay, the incremented evolution period, and the mixing period during which exchange occurs.† Jeener *et al.*[7] have shown how *quantitative* relaxation and exchange rate data may be obtained † for the two-site problem ($A \leftrightarrows B$) by analysing the

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† We have successfully combined the COSY and NOESY experiments by acquiring the COSY data during the NOESY mixing time with the second pulse of the NOESY sequence being 45°. Related combinations of these experiments have also been reported: C. A. G. Haasnoot, F. J. M. Van de Ven, and C. W. Hilbers, *J. Magn. Reson.*, 1984, **56**, 343; A. Z. Gurevich, I. L. Barsukov, A. S. Arseniev, and V. F. Bystrov, *ibid.*, p. 471.

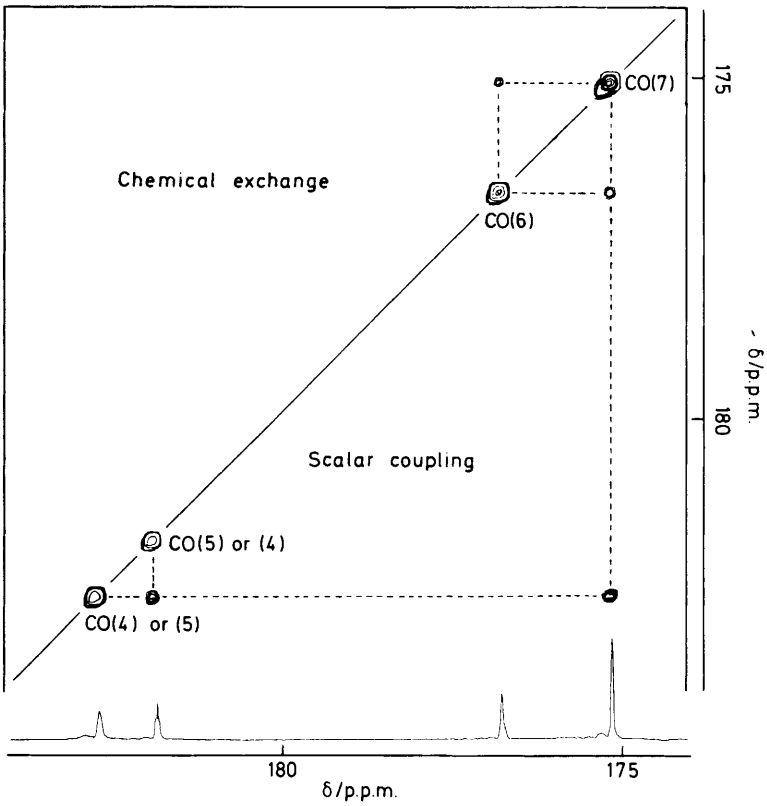

Figure 1. Two-dimensional homonuclear ^{13}C scalar coupling (COSY) and chemical exchange (NOESY) correlations for $[Os_3H_2(CO)_{10}]$ (**1**). These data are the result of two separate experiments, with t_m = 1 s for the NOESY experiment

integrated intensities of the peaks due to the slowly exchanging sites and the associated off-diagonal peak as a function of t_m. The relevant equations * may be applied to the localised three-site problem for CO(6) and CO(7), since two of the sites are equivalent.[8] The kinetic matrix used in ref. 8 to describe the exchange process is (*a*), whereas the Jeener *et al.*[7] analysis uses (*b*), with $k_{AB} = 2k/3$, where k is the exchange rate constant. As

$$\begin{bmatrix} -2k' & 2k' \\ k' & -k' \end{bmatrix} \qquad \begin{bmatrix} -k_{AB} & k_{BA} \\ k_{AB} & -k_{BA} \end{bmatrix}$$

(*a*) (*b*)

(*a*) and (*b*) are equivalent, the values of k derived herein are three times the k' of ref. 8. The NOESY experiment was repeated for six values of t_m and the derived peak intensities were analysed as described above, with the simplification [8] of negligible ^{13}C–^{13}C cross relaxation. A non-linear least-squares optimisation technique [9] was used to yield best fit values for the spin-lattice relaxation rates (R_1) of the ^{13}C nuclei, and the exchange rate constant (k). The values obtained were $R_1(6) = 0.34$, $R_1(7) = 0.21$ s^{-1}, and $k = 1.21$ s^{-1} (see Figure 2), which are in good agreement with the previous values [8] of 0.24, 0.26, and 1.08 s^{-1} (*i.e.*, 3 × 0.36 s^{-1}) respectively.

The previous quantitative study [8] on (**1**) employed the method of selective inversion of either resonance due to CO(6) or CO(7) followed by monitoring of the return of the resonances to equilibrium. The values for R_1 and k from that study were obtained more economically in terms of

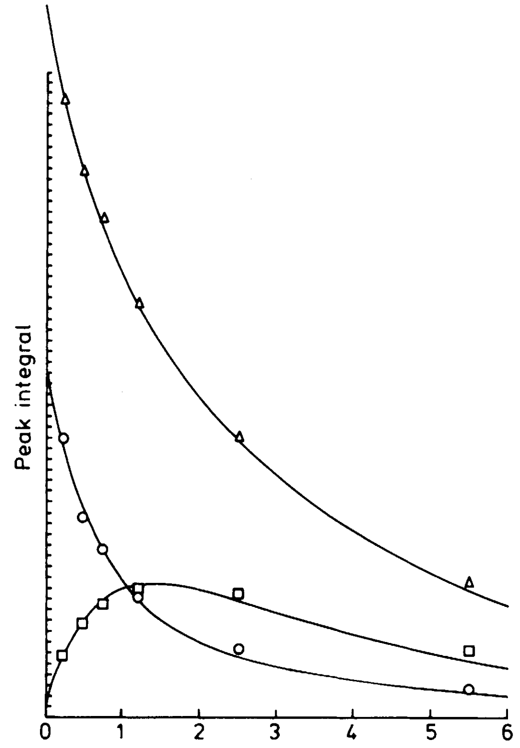

Figure 2. Plots of optimised best-fit peak integrals (continuous lines) *vs.* experimental integrals for the diagonal [CO(6) (○) and CO(7) (△)] and off-diagonal (□) peaks in the NOESY experiment as a function of mixing time (t_m)

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* See equations 22—25 of ref. 7.

spectrometer time. However we foresee advantages for the two-dimensional NOESY method over one-dimensional methods when applied to multi-site exchange situations, in the same way that the advantages of two-dimensional COSY and NOESY n.O.e. correlations are now evident for the unravelling of complex ^{1}H n.m.r. spectra of proteins.[10]

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Received 29*th March* 1984; *Paper* 4/514