

**^{13}C N.M.R. Spectra of Highly ^{13}CO -enriched Metal Carbonyls:
Observation of $^2J_{\text{CC}}$ *cis* Coupling Constants**

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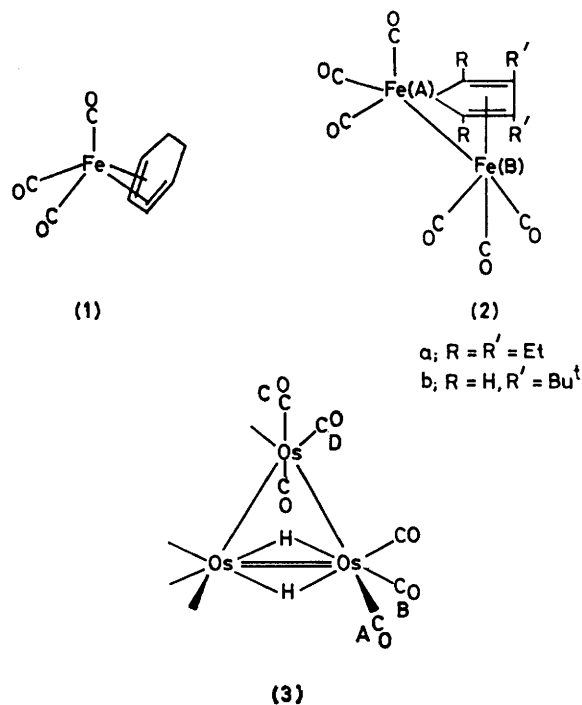
Summary ^{13}C N.m.r. spectra of metal carbonyls (>60% ^{13}CO -enriched) allow the first observation of $^2J_{\text{CC}}$ *cis* values which are an order of magnitude smaller than $^2J_{\text{CC}}$

trans; this technique is also useful in the assignment of CO resonances as is shown in the case of $\text{H}_2\text{Os}_3(\text{CO})_{10}$.

THE advent of Fourier transform n.m.r. techniques has, in general, overcome the difficulties in the observation of ^{13}C resonances due to the low natural abundance and to the low sensitivity of ^{13}C nuclei. The application of ^{13}C n.m.r. spectroscopy to organo transition metal compounds has put a new and very powerful tool in the hands of organometallic chemists. In the last decade additional knowledge has been gained of the structure, chemical bonding and stereochemical non-rigidity of these compounds.¹⁻⁴ In the study of metal carbonyls special techniques are required to overcome additional experimental difficulties.³ ^{13}C O-enrichment of the samples is a common technique, particularly useful in overcoming solubility problems at low temperatures in dynamic n.m.r. studies; the enrichment is usually in the range 10–20% to avoid unwanted broadening of the absorptions due to unresolved J_{CC} coupling. Few $^2J_{\text{CC}}$ are then observed however: between axial carbonyls they are in the range 30–35 Hz⁵ and no evidence for axial-equatorial coupling has been gained.

We report preliminary results on ^{13}C n.m.r. spectra of highly ^{13}C O-enriched (50–80%) metal carbonyl derivatives from which $^2J_{\text{CC}}$ *cis* coupling constants are extractable. An example showing their usefulness in the assignment of CO resonances will also be discussed.

The variable temperature (v.t.) ^{13}C n.m.r. spectra of (1) have already been reported:⁶ the single resonance observed in the carbonyl region at room temperature was ascribed to the fast (on the n.m.r. time scale) rearrangement of the carbonyl groups. This rearrangement is frozen at -90°C ; two peaks (relative intensities 1:2) were observed and assigned to the axial and equatorial CO groups, respectively. In the spectrum at -100°C of a 65% ^{13}C O-



enriched sample of (1), the details of a fine structure are evident for both peaks (Figure 1); the two singlets are split into 5 and 3 lines. The origin of these patterns can be easily explained in terms of the presence of different isotopomers according to the number of ^{13}C O groups

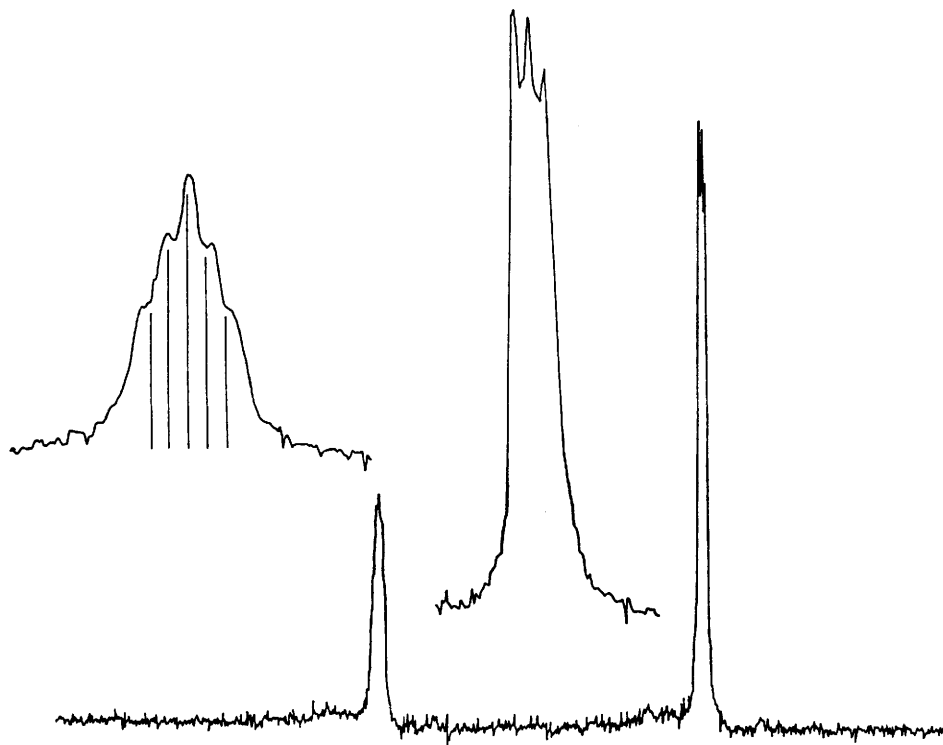


FIGURE 1. ^{13}C N.m.r. spectrum (-100°C) of (1) and expansion of the carbonyl region.

incorporated. Thus, the quintuplet arises by overlap of a singlet (no C-13 in the basal position) with a doublet (one C-13 in the basal position) and with a triplet (two C-13 in the basal position). Analogously, the high-field triplet (corresponding to basal CO groups) arises by overlap of a singlet with a doublet. The inner separation in the doublets and in the triplet corresponds to the ${}^2J_{\text{CC}}$ coupling constant (2.1 Hz). ${}^2J_{\text{CC}}$ *cis* values have also been observed for (2) between the axial and equatorial carbonyl groups bonded to Fe_A . Values of 3.4 and 3.5 Hz have been measured for (2a) and (2b), respectively. These observations suggest that ${}^2J_{\text{CC}}$ *cis* values are an order of magnitude smaller than ${}^2J_{\text{CC}}$ *trans*. A steric dependence seems to hold for ${}^2J_{\text{CC}}$ as has already been established for ${}^2J_{\text{CH}}$ ^{1,7} and ${}^2J_{\text{CF}}$.¹

of a moderately ${}^{13}\text{C}$ -enriched (15%) sample of (3).³ The proton-coupled spectrum as well as the v.t. spectra allowed the assignment of the two high-field peaks to CO_A and CO_B respectively;³ however it was not possible to assign the resonances of CO_C and CO_D . In Figure 2, the low-field signal is a broad envelope whereas the next signal can be analysed in terms of a singlet, a doublet, and a triplet. The inner separation of the doublet and of the triplet is 3.2 Hz. We then associate the five-line signal with CO_C . A fine structure identical to that observed for CO_C should appear for CO_D as well: we suspect that the broad envelope of resonances observed instead is due to a further coupling of CO_D with CO_A ; ${}^3J_{\text{CC}}$ values are expected to be not negligible for carbonyl groups which are three bonds away but

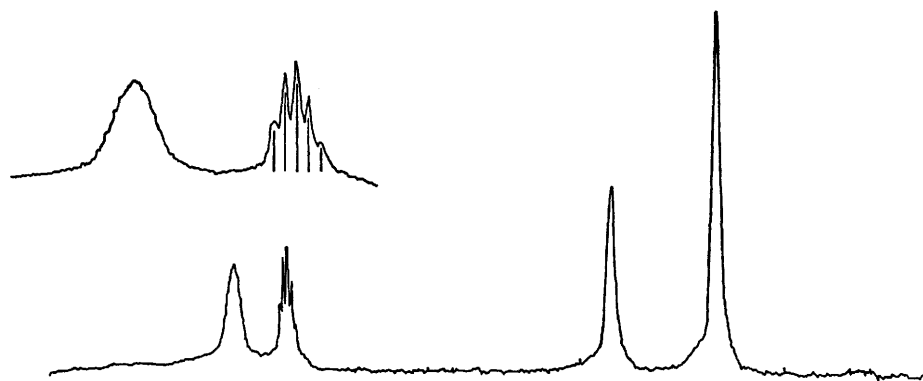


FIGURE 2. Proton-decoupled room temperature ${}^{13}\text{C}$ n.m.r. spectrum of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and expansion of the low-field peaks.

The proton-decoupled ${}^{13}\text{C}$ n.m.r. spectrum of a 60% ${}^{13}\text{C}$ -enriched sample of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (3) is an example of the potential use of the observation of ${}^2J_{\text{CC}}$ in structural assignments (Figure 2). Four singlets with relative intensities from low to high field 2:2:2:4 were observed in the room temperature proton-decoupled ${}^{13}\text{C}$ n.m.r. spectrum

trans-related through a metal-metal bond, as already found for $\text{Ir}_4(\text{CO})_{11}\text{CNBu}^{\text{t}}$.⁸

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