

Preliminary communication

ON THE USE OF ^{13}C — ^{13}C COUPLING IN ESTABLISHING INTRAMOLECULAR VERSUS INTERMOLECULAR CO LIGAND REARRANGEMENT PROCESSES IN METAL CARBONYL DERIVATIVES

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Summary

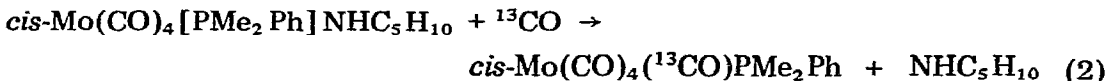
^{13}C — ^{13}C spin—spin coupling between axial and equatorial CO ligands in $\text{M}(\text{CO})_5\text{L}$ (M = Group VIB metal) derivatives is employed in establishing intramolecular versus intermolecular axial—equatorial carbon monoxide ligand exchange pathways.

In previous publications we have demonstrated that octahedral metal carbonyl complexes of the types $\text{M}(\text{CO})_5\text{L}$ and *cis*- $\text{M}(\text{CO})_4\text{L}_2$ (M = Group VIB metal, L = phosphine or phosphite) often undergo ligand rearrangements by a non-dissociative intramolecular mechanism [1–4]. The criterion used in these studies has been the lack of ligand replacement, either CO or L, occurring on the same time scale as the ligand scrambling process. For example, when reaction 1 was carried out in a ^{13}CO atmosphere it did not afford either more highly ^{13}CO -labelled parent species or $\text{W}(\text{CO})_6$. Analogous observations were made using stereoselectively oxygen-18 labelled derivatives, where the oxygen-18 isotope shift on the ^{13}C NMR of the carbonyl ligands was em-



ployed as the probe [3]. An additional rule, which is often simpler to test experimentally, for providing definitive information regarding the molecularity of reactions such as that described in eq. 1 is presented herein based on ^{13}C — ^{13}C spin—spin coupling studies.

A stereoselectively, equatorially ^{13}C -labelled $\text{Mo}(\text{CO})_5\text{PMe}_2\text{Ph}$ derivative was prepared according to eq. 2 at 65°C in hexane and its ^{13}C NMR spectrum in CDCl_3 is shown in Figure 1A. The sample of *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PMe}_2\text{Ph}$



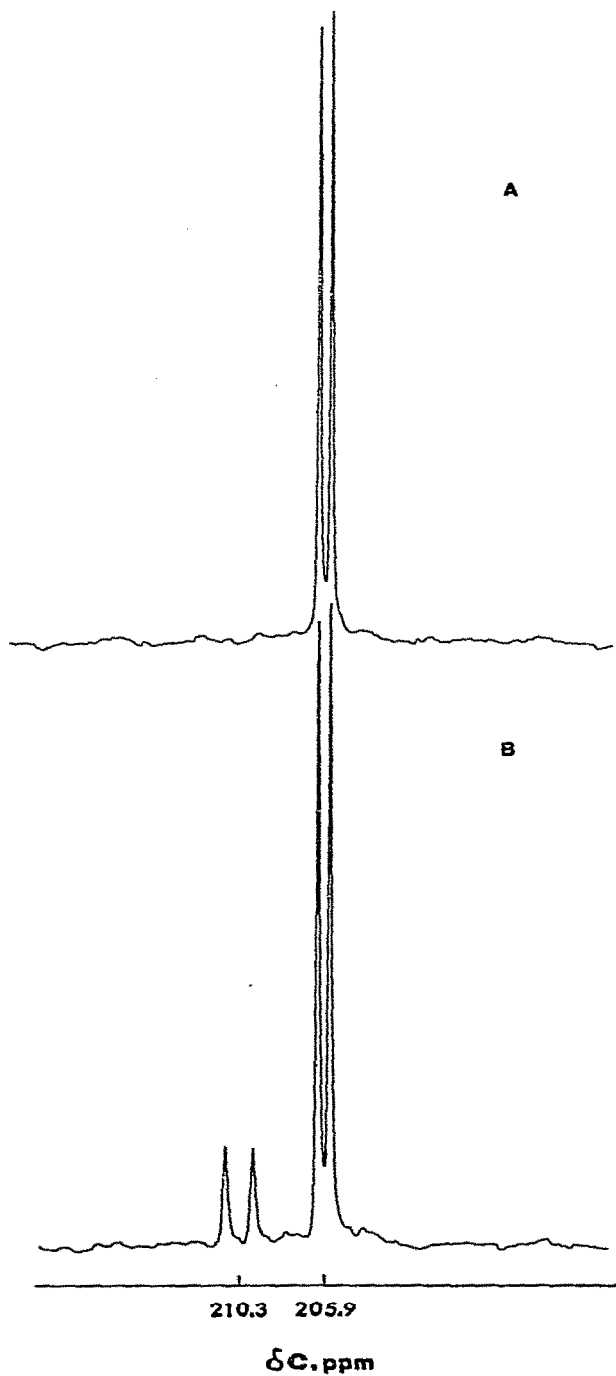


Fig. 1. ^{13}C NMR spectra of $\text{Mo}(\text{CO})_2\text{PMe}_2\text{Ph}$ in CDCl_3 . (A) Stereoselectively ^{13}C -labelled *cis*- $\text{Mo}(\text{CO})_2(^{13}\text{CO})\text{PMe}_2\text{Ph}$ species, $\delta(\text{C}_{\text{cis}})$ 205.9 ppm ($J(\text{P}-\text{C})$ 9.3 Hz). (B) *cis*- $\text{Mo}(\text{CO})_2(^{13}\text{CO})\text{PMe}_2\text{Ph}$ after being heated in heptane at 75°C for 12 h, $\delta(\text{C}_{\text{trans}})$ 210.3 ppm ($J(\text{P}-\text{C})$ 21.5 Hz).

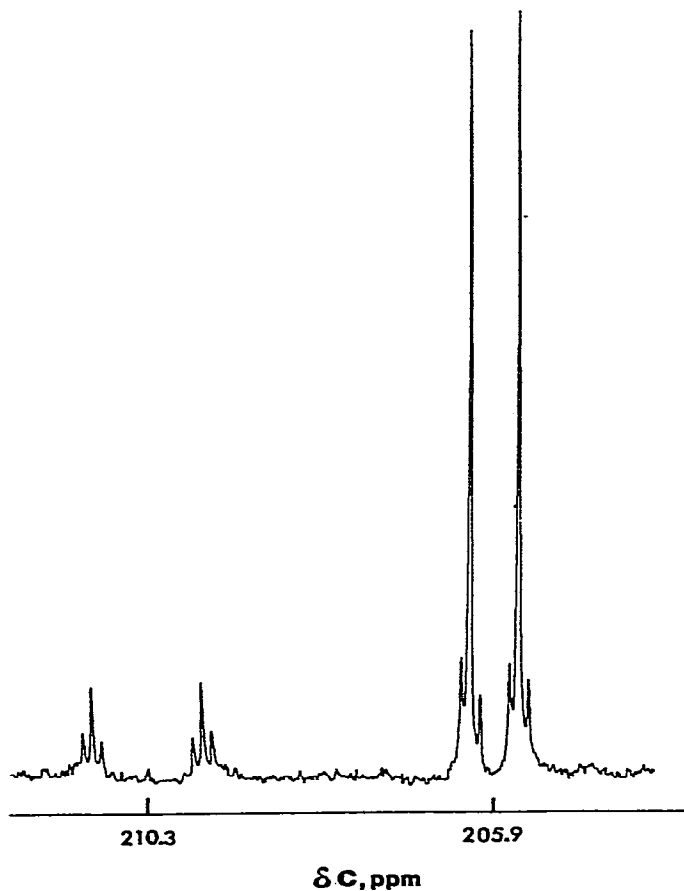


Fig. 2. Same as in Figure 1B determined at higher resolution.

was isolated and purified by recrystallization from chloroform/methanol. Upon heating this stereoselectively ^{13}C -enriched sample at 75°C in heptane for 12 h, followed by isolation and redissolution in CDCl_3 , the ^{13}C NMR spectrum seen in Fig. 1B was obtained. As noted in Fig. 1B, the carbonyl resonance for the axial CO ligand is now in evidence, indicating a thermal redistribution of the ^{13}C label has occurred. Further scrutinizing of the ^{13}C NMR spectrum of this species under higher resolution (Fig. 2) reveals ^{13}C — ^{13}C spin—spin coupling between axial and equatorial CO ligands, where $J(\text{C}—\text{C})$ 3.68 Hz. Hence, the presence of molecules possessing two labelled ^{13}C ligands is indicative of rearrangement via an intermolecular pathway.

On the other hand during the stereomobility of the ^{13}C ligand in *cis*- $\text{W}(\text{CO})_4(^{13}\text{C})\text{P}(\text{OMe})_3$, prepared from *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OMe})_3]\text{Cl}^-$ and ^{13}C , as depicted in eq. 1, no axial—equatorial ^{13}C — ^{13}C spin—spin coupling was observed. This is of course the result anticipated for an intramolecular rearrangement process. It is important to point out that we have noted ^{13}C — ^{13}C spin—spin coupling constants in a variety of $\text{M}(\text{CO})_5\text{L}$ species and these values generally lie in the range of 2–4 Hz. In general, the technique

described here should be applicable to any metal carbonyl species containing magnetically different CO groups which has been labelled initially with one ^{13}C O ligand, and for which the $J(\text{C}-\text{C})$ is observable.

The energetic and molecularity of the pathways for ligand stereomobility in metal carbonyl derivatives as a function of the metal and the substituted ligand is an area of continuing investigation in our laboratories.

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References

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