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Stereochemically Non Rigid Acetylenic Carbonyl Complexes of Iron and Cobalt*

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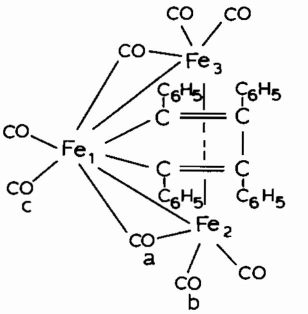
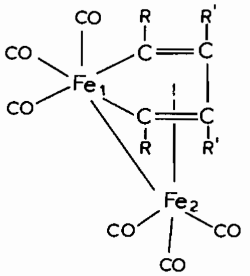
The role of differential opening of asymmetric carbonyl bridges in promoting stereochemical non rigidity in polynuclear carbonyl clusters has been shown by ^{13}C n.m.r. spectra at variable temperature in $RhCo_3(CO)_{12}$[1] and $H_2FeRu_3(CO)_{13}$.[2] We have examined the fluxional behaviour of two polynuclear carbonyl complexes having acetylenic ligands. The ^{13}C n.m.r. spectrum at –64 °C of the dark green isomer $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$ (I)[3] exhibits three signals in the carbonyl region at 255.1, 205.8 and 204.2 pp, positive downfield TMS with integrated intensities 2:4:2 (Fig. 1). The multiplicity and intensity of the CO are in precise accord with the expectations based on the solid state structure of (I).[4] The low field resonance is straightforwardly assigned to the unsymmetrical CO_a bridges. Spectra at higher temperatures show that the two resonances at 255.1 and 205.8 ppm are broadening whereas the upfield one remains sharp; the large chemical shift difference prevented the observation of the average peak up to +90 °C where decomposition of the sample occurs. The results are interpreted in terms of exchange between CO_a and CO_b with the opening of the longer bond of the asymmetric CO bridges and rotation of the $Fe_{2,3}(CO)_3$ moieties. The resonance remaining sharp throughout the temperature range is associated with CO_c.





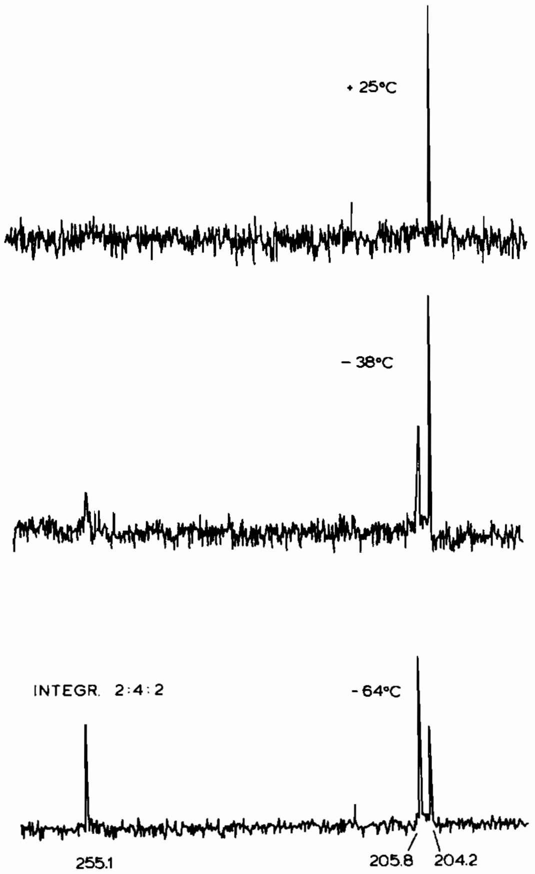


Figure 1. Variable temperature ^{13}C n.m.r. spectra of $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$ (I) in the carbonyl region in CD_2Cl_2 solution.

We feel that the simplest explanation for the non-participation of the $Fe_1(CO)_2$ moiety in the CO scrambling process is the high coordination of Fe_1 and the formation of two σ bonds between the metal and the ligand. This observation is consistent with the stereochemical rigidity of the $Fe_1(CO)_3$ moiety in the dinuclear complex $Fe_2(CO)_6(C_2RR')_2$.[5]

We have also studied the fluxional behaviour of a related molecule, $Co_4(CO)_{10}C_2(C_6H_5)_2$ (II)[6] which has two unsymmetrical carbonyl bridges and an acetylene σ and π bound to the metal atoms. Recently variable temperature ^{13}C n.m.r. spectra have been reported for (II) suggesting the presence of a two-step exchange process. Before delocalized exchange takes place, interchange of CO_a with CO_c occurs.[7] In addition to the two steps already reported[7] we were able to detect a further step in the intramolecular exchange. This step is noticeable in the range of temperatures –90 - –60 °C. Thus three

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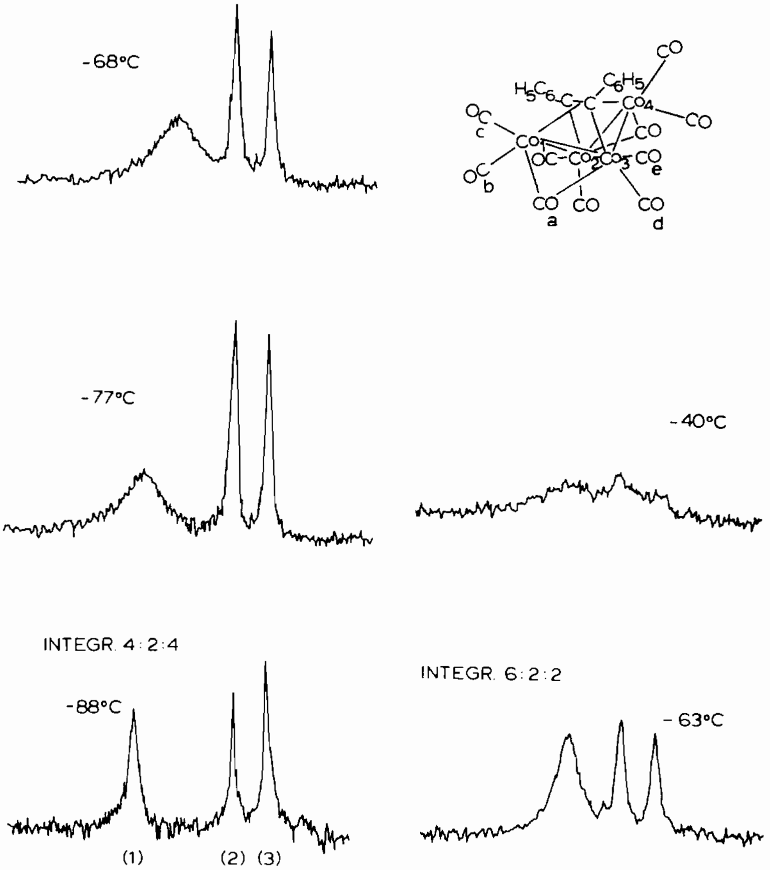

Figure 2. Variable temperature ^{13}C n.m.r. spectra of $Co_4(CO)_{10}C_2(C_6H_5)_2$ (II) in the carbonyl region in CD_2Cl_2 solution.

lines are observed in the −88 °C spectrum at 211.6, 197.2 and 192.2 ppm in integrated intensities 4:2:4 (Fig. 2). As the temperature is increased the lowfield resonance broadens and sharpens again in a small range of temperature to an upfield position at 205 ppm. This shift is in good accord with the weighted average of resonance (1) (weight 4) and resonance (3) (weight 2). In the −63 °C spectrum the integrated intensities are 6:2:2. The first step is ascribed to interchange of CO_a and CO_c while the other carbonyls are rigid. Resonance (3) is due to casual superposition of two non-equivalent pairs of carbonyls (CO_b and CO_d or CO_e). The increase in the temperature allows interchange of CO_b and CO_c in addition to the first exchange process. The final step requires the opening of both sides of the unsymmetrical CO bridges and rotation of the $Co_{2,3}(CO)_2$ moieties to lead to delocalized scrambling.

References

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