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Preliminary communication

AN EQUILIBRIUM BETWEEN TWO ISOMERS OF $Ir_4(CO)_{11}PEt_3$ AND THE PATHWAY FOR CARBONYL SCRAMBLING

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Summary

$Ir_4(CO)_{11}PEt_3$ is shown to consist of two isomers in CD_2Cl_2 at low temperatures, the major isomer with the PEt_3 perpendicular to the plane of the carbonyl bridged face and a minor isomer with the PEt_3 in this plane. It is shown that a minor isomer is kinetically more important than the major isomer.

It is extremely unusual to find more than one isomer in polynuclear metal carbonyl compounds where the isomers can interconvert by a carbonyl scrambling mechanism [1]. $Co_2(CO)_8$ is known to exist in solution as a mixture of bridged $(OC)_3Co(\mu\text{-}CO)_2Co(CO)_3$ and unbridged $(OC)_4CoCo(CO)_4$ compounds, and it has been noted that $Ir_4(CO)_{11}PMePh_2$ and $Ir_4(CO)_{11}PMe_3$ exist in solution as a mixture of axial and radial isomers, but no details have been published [3,4].

The 162 MHz ^{31}P NMR spectrum of $Ir_4(CO)_{11}PEt_3$ in CD_2Cl_2 shows a broad signal at δ 9.1 ppm at room temperature. On cooling to −90° C, this signal splits into two at δ 28.7 and 6.0 ppm with an intensity ratio of 1/7. At room temperature using ^{13}CO enriched material, the 100.6 MHz ^{13}C NMR spectrum has a broad signal at δ 173 ppm and a relatively sharp weak signal at δ 161.8 ppm but on cooling two sets of ^{13}CO signals appear in the ratio 1/7, see Fig. 1a. The major species has signals at δ 205.2 (intensity 2), 195.8 (1), m, 173.2 (1), $J(^{31}P, ^{13}C)$ 7 Hz, 170.8 (2), 158.9 (2), 158.1 (2), and 155.9 (1), $J(^{31}P, ^{13}C)$ 23 Hz. These signals are very similar to those previously reported for $Ir_4(CO)_{11}$-$PMePh_2$ [3] and are consistent with structure I. The minor species has signals at δ 207.2 (2) m, 197.8 (1) m, 172.8 (2), $J(^{31}P, ^{13}C)$ 12 Hz, 160.2 (2), 154.8 (1), $J(^{31}P, ^{13}C)$ ca. 30 Hz, 154.6 (2), and 154.0 (1). There are two possible structures for the minor isomer, II and III, the non-bridged structure being

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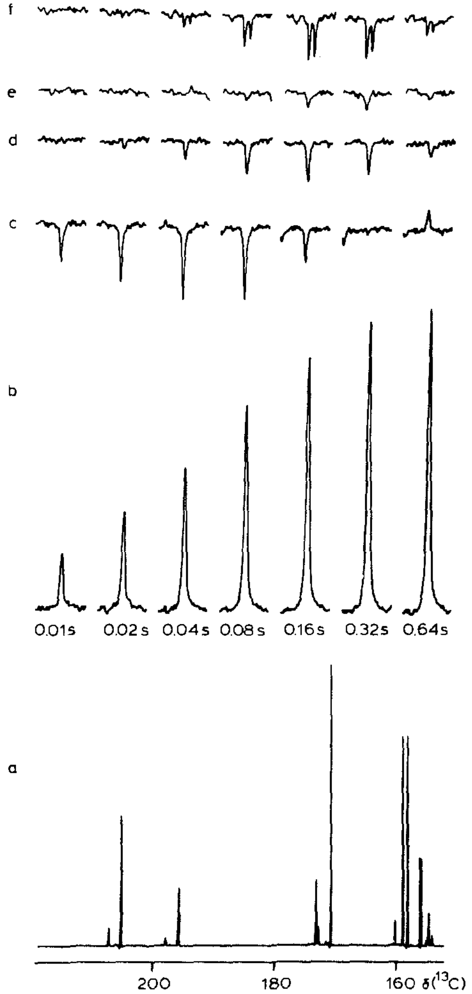
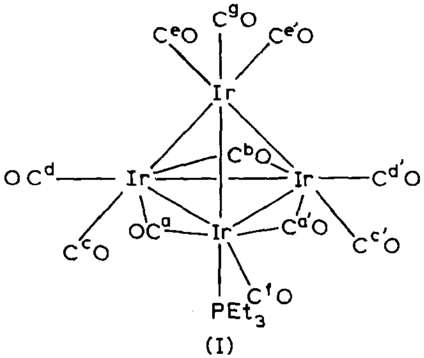
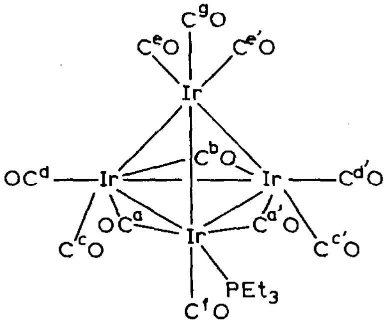


Fig. 1. 100.6 MHz ^{13}C NMR spectra of the carbonyl signals of $Ir_4(CO)_{11}PEt_3$. a. At −90° C. b. At −70° C, the difference signal for the carbonyl at δ 195.8 ppm. A selective 180° pulse is applied to this signal and the spectrum shows the recovery as a function of time by subtracting the spectrum taken after 1 μs from that taken later; the delay time being given below each signal. c. As b showing the magnetisation transfer from δ 195.8 ppm to this signal at δ 170.8. d. As c, but for the signal at δ 205.2 ppm. e. As c, but for the signal at 173.2 ppm. f. As c, but for the signals at δ 158.1 and 158.9 ppm.

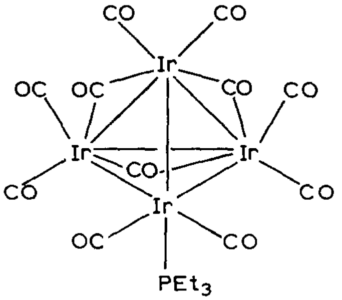
discarded as it would not give signals at ca. δ 200 ppm, which is typical of bridging carbonyls. The signals at δ 170—175 ppm are due to the carbonyls in plane with the bridging carbonyls, and as only one signal of intenstiy 2 is observed in this region, the structure is II, with the assignments δ 207.2 ppm, aa′, 197.8, b, 172.8 dd′, 160.2, ee′, 154.8, g, 154.6, cc′, and 154.0, f. Further information of this assignment comes from the averaged signal at room temperature for the unique carbonyl, g, at δ 161.8 ppm being in a reasonable position for the weighted average of the signal at δ 197.8 ppm in the minor isomer and that at δ 155.9 ppm in the major isomer with a population ratio of 1/7 [4]. These two carbonyls are unique in not being able to exchange with the other ten carbonyls. Significant values of $J(^{31}P, ^{13}C)$ are to be expected in the minor isomer for carbonyls, dd′, and g as observed by comparison with data on $Ir_4(CO)_{10}(PMePh_2)_2$ [3]. The population ratio of 1/7 corresponds to isomer I being 0.8 kcal mol^{-1} more stable than isomer II at −90° C.



(I)



(II)



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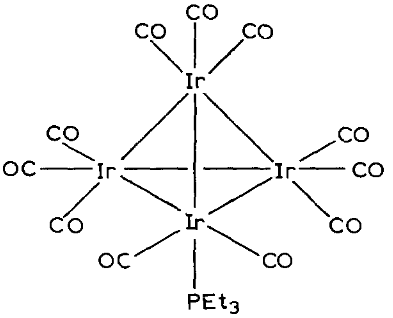

(IV)

The mechanism of carbonyl scrambling in I was investigated at —70°C using selective 180° pulses generated using the DANTE pulse sequence [5]. A selective 180° pulse was applied to the carbonyl b at δ 195.8 ppm, a short time τ waited and then an observing 90° pulse applied. The spectra are displayed as difference spectra {(spectrum with τ) – (spectrum with $\tau = 1$ μs)} in Fig. 1. Figure 1b shows the recovery of carbonyl b due principally to chemical exchange bringing unperturbed nuclei from other sites into site b. This exchange occurs first to carbonyls dd′ at δ 170.8 ppm with maximum transfer occurring after ca 0.06 s, see Fig. 1c. This inverted magnetisation is passed on to carbonyls aa′ at δ 205.2 ppm, see Fig. 1d, 0.16 s, and carbonyls cc′, ee′ at δ 158.9 and 158.1 ppm, see Fig. 1f, 0.2 s. Finally the inverted magnetisation maximises for carbonyl f, δ 173.2, after 0.32 s, see Fig. 1e. The magnetisation transfer b → d → a → f is completely consistent with a Cotton merry-go-round mechanism [6] involving only compound I and the non-bridged intermediate at a rate of ca. 10 s^{-1}, corresponding to $\Delta G^\ddagger$ 10.8 kcal mol^{-1}. The facile magnetisation transfer to carbonyls cc′ee′ can readily be explained by introducing compounds II or III into the mechanism with a rate of ca. 20 s^{-1}, corresponding to $\Delta G^\ddagger$ 10.6 kcal mol^{-1}. Although from Fig. 1 it would appear that migration from dd′ to aa′ and to cc′ee′ all occur at approximately the same rate, the faster rate to cc′ee′ is a consequence of the dd′ → aa′ migration going via one unbridged intermediate, i.e., I → IV → I, while dd′ → cc′ee′ must go via two unbridged intermediates, and one other bridged intermediate, e.g., I → IV → II → IV → I. Thus although II and III are thermodynamically less stable than I, one or both structures provide the faster pathway than I in carbonyl scrambling processes.

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References

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3 (a) G.F. Stuntz and J.R. Shapley, J. Am. Chem. Soc., 99 (1977) 607; (b) J. Organometal. Chem., 213 (1981) 389.
4 This exchange involving the unique carbonyl g has been noted previously and attributed to the presence of isomer II, but isomer II was not observed, see ref. 19 in ref. 3a.
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6 See for example R.D. Adams and F.A. Cotton, in L.M. Jackman and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance, Academic Press, New York, 1975, Chapter 12.

Erratum

The structure and dynamics of rhodium(I) acetylacetonate complexes of monosubstituted olefins. A carbon-13 NMR study; by D. Parker (*J. Organometal. Chem.*, 240 (1982) 83—93)

Page 87, Fig. 3

In all four cases OAc should read CO_2Me.

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