

New Octahedral, Asymmetric Iron Carbonyl Complexes

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Summary Isomerization of the prochiral octahedral complex $[\text{FeMe}(\text{CO})_2(\text{PMe}_3)_2(\text{PMe}_2\text{Ph})]^+[\text{BPh}_4]^-$ (CO-CO *cis*, PMe_3 - PMe_3 *trans*) leads exclusively to a new chiral molecule by permutation of PMe_2Ph with one of the PMe_3 ligands.

THERE is considerable interest in the reactivity of asymmetric transition-metal complexes and their role as stereo-

specific catalysts is well recognized.¹ However, recent work in this field deals almost exclusively with tetrahedral systems. The only asymmetric octahedral complexes recently reported^{2,3} bear chelating ligands. We report here the first synthesis of an asymmetric, octahedral iron complex with monodentate ligands.

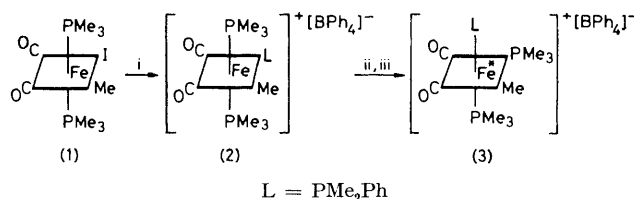
Treatment of $\text{FeIme}(\text{CO})_2(\text{PMe}_3)_2$ (**1**)⁴ in MeOH at -30°C with PMe_2Ph in the presence of NaBPh_4 yields, quantita-

TABLE. Spectral data for compounds (2) and (3).

Compound	$\nu_{\text{CO}}/\text{cm}^{-1}$	^1H and ^{31}P n.m.r. ^b		
		PMe_2Ph	PMe_3	Fe-Me
(2)	2018.0s A' 1961.0s A'	δ_{H} 1.64(d), $^2J_{\text{PH}}$ 7.9 $\delta_{^{31}\text{P}}$ 14.6	δ_{H} 1.29(t), N^c 7.9 $\delta_{^{31}\text{P}}$ 9.2	δ_{H} -0.10(dt) $\left\{ \begin{array}{l} ^3J_{\text{PH}} 9.6(\text{d}) \\ ^3J_{\text{PH}} 8.6(\text{t}) \end{array} \right.$
(3)	2018.0s A' 1961.0s A'	δ_{H} $\left\{ \begin{array}{l} 1.79(\text{d}), ^2J_{\text{PH}} 8.1 \\ 1.74(\text{d}), ^2J_{\text{PH}} 8.7 \end{array} \right.$ $\delta_{^{31}\text{P}}$ 21.3	δ_{H} $\left\{ \begin{array}{l} 1.47(\text{d}), ^2J_{\text{PH}} 8.6 \\ 1.13(\text{d}), ^2J_{\text{PH}} 8.3 \end{array} \right.$ $\delta_{^{31}\text{P}}$ $\left\{ \begin{array}{l} 14.7 \\ 7.4 \end{array} \right.$	δ_{H} -0.14(dt) $\left\{ \begin{array}{l} ^3J_{\text{PH}} 11.0(\text{d}) \\ ^3J_{\text{PH}} 7.8(\text{t}) \end{array} \right.$

^a Perkin Elmer 325, solvent CH_2Cl_2 . ^b Varian XL-100, solvent CD_2Cl_2 , δ_{H} relative to tetramethylsilane, $\delta_{^{31}\text{P}}$ relative to external H_3PO_4 (85%) in p.p.m.; J in Hz. ^c $N = |^2J_{\text{PH}} + ^4J_{\text{PH}}|$.

tively, the cationic complex $[\text{FeMe}(\text{CO})_2(\text{PMe}_3)_2(\text{PMe}_2\text{Ph})]^+[\text{BPh}_4]^-$ (2) which precipitates as white crystals (Scheme). The complex (2) is stable in the solid state at room temperature and in solution (CH_2Cl_2) below -30°C .



SCHEME. Reagents: i, L + NaBPh_4 ; ii, CD_2Cl_2 solvent; iii, $T > -30^\circ\text{C}$.

From the i.r. and low-temperature ^1H n.m.r. spectra structure (2) was assigned to this complex. The observation of two i.r. active bands of equal intensity in the carbonyl region (Table) indicates that the two CO ligands are in mutually *cis*-positions, as previously found for the complex (1).⁴ ^1H N.m.r. spectra (CD_2Cl_2 , -30°C) show that the two PMe_3 ligands are isochronous, as their resonance gives a 'filled-in' doublet ($A_nXX'A_n'$ spectrum),⁵ indicating their mutually *trans*-positions. The structure (2) is confirmed by the presence of a low-field doublet for the methyl groups of the equatorial dimethylphenylphosphine ligand and a high-field doublet of triplets for the methyl group bonded to iron.

^{31}P Chemical-shifts determined by double resonance $^1\text{H}\{^{31}\text{P}\}$ experiments indicate that, as expected, the two equivalent ^{31}P signals of the axial PMe_3 groups are more shielded than the ^{31}P signal of the equatorial PMe_2Ph ligand.

A slow isomerization of complex (2) occurs in solution above -30°C leading to the complex (3) (Scheme), whose formation is almost complete within 1 h at $+32^\circ\text{C}$. I.r. data of compound (3) indicate that, as previously found for the complex (2), the two CO ligands remain in mutually *cis*-positions.

The isomerization of complex (2) \rightarrow (3) can be followed by the changing ^1H n.m.r. spectra (Figure). They show a progressive disappearance of the 'filled-in' doublet and the concomitant appearance of two distinct doublets of equal intensity, due to the resonance of two anisochronous PMe_3 groups. Furthermore, the methyl groups of the PMe_2Ph ligand give rise to two distinct doublets of equal intensity. This result indicates that the two diastereotopic methyl

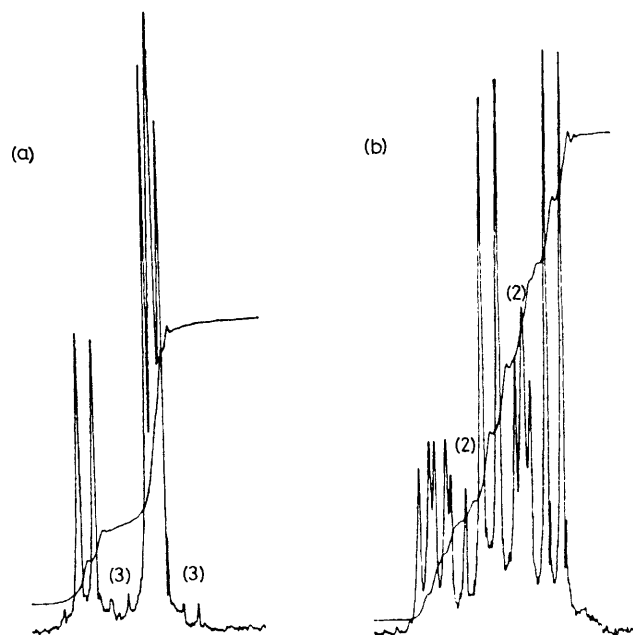


FIGURE. Partial ^1H n.m.r. spectra (Me-P region): (a) Complex (2), -30°C , with traces of (3); (b) complex (3), $+32^\circ\text{C}$, with a small amount of (2).

groups of the PMe_2Ph ligand become non-equivalent in the structure (3).

The assignment of the different signals of complex (3) is confirmed by ^{31}P noise irradiation, as each multiplet collapses to a singlet. Selective ^{31}P irradiation experiments show the presence of three different ^{31}P nuclei in (3). Therefore, spectral data emphasize the absence of any elements of symmetry in the molecule (3), where the metal centre is chiral.

Some complexes similar to complex (2) which are substituted by other equatorial phosphorus ligands such as $\text{P}(\text{OMe})_2\text{Ph}$ or PEtPh_2 have been examined. No isomerization is observed in the first case while a total switch occurs in the second. These preliminary results indicate that steric strain is the essential driving force which induces permutation of a bulky equatorial ligand with one of the PMe_3 axial ligands. The final, chiral molecule has a lower steric interaction.

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¹ H. B. Kagan and J. C. Fiaud, *Top. Stereochem.*, 1978, **10**, 175.

² H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 152.

³ P. W. Jolly and R. Mynott, *Adv. Organomet. Chem.*, 1981, **19**, 290.

⁴ M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, 1971, **30**, 227.

⁵ R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.