New Octahedral, Asymmetric Iron Carbonyl Complexes

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Summary Isomerization of the prochiral octahedral complex $[FeMe(CO)_2(PMe_3)_2(PMe_2Ph)]^+[BPh_4]^-$(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 stereospecific 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.

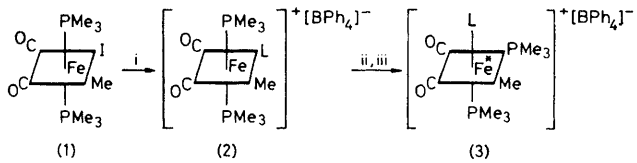
Treatment of $FeIMe(CO)_2(PMe_3)_2$ (**1**)[4] in MeOH at -30 °C with PMe_2Ph in the presence of $NaBPh_4$ yields, quantita-

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

Compound	ν_{CO}/cm^{-1}	^1H and ^{31}P n.m.r.[b] PMe$_2$Ph	PMe$_3$	Fe–Me
(**2**)	2018·0s A′ 1961·0s A′	δ_H 1·64(d), $^2J_{PH}$ 7·9 $\delta_{^{31}P}$ 14·6	δ_H 1·29(t), N^c 7·9 $\delta_{^{31}P}$ 9·2	δ_H −0·10(dt) {$^3J_{PH}$ 9·6(d); $^3J_{PH}$ 8·6(t)}
(**3**)	2018·0s A′ 1961·0s A′	δ_H {1·79(d), $^2J_{PH}$ 8·1; 1·74(d), $^2J_{PH}$ 8·7} $\delta_{^{31}P}$ 21·3	δ_H {1·47(d), $^2J_{PH}$ 8·6; 1·13(d), $^2J_{PH}$ 8·3} $\delta_{^{31}P}$ {14·7; 7·4}	δ_H −0·14(dt) {$^3J_{PH}$ 11·0(d); $^3J_{PH}$ 7·8 (t)}

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

tively, the cationic complex $[FeMe(CO)_2(PMe_3)_2(PMe_2Ph)]^+$-$[BPh_4]^-$ (**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.



L = PMe$_2$Ph

SCHEME. *Reagents:* i, L + NaBPh$_4$; ii, CD_2Cl_2 solvent; iii, $T >$ − 30 °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 $^1H\{^{31}P\}$ 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$_2$Ph 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 °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**) → (**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$_2$Ph ligand give rise to two distinct doublets of equal intensity. This result indicates that the two diastereotopic methyl groups of the PMe$_2$Ph ligand become non-equivalent in the structure (**3**).

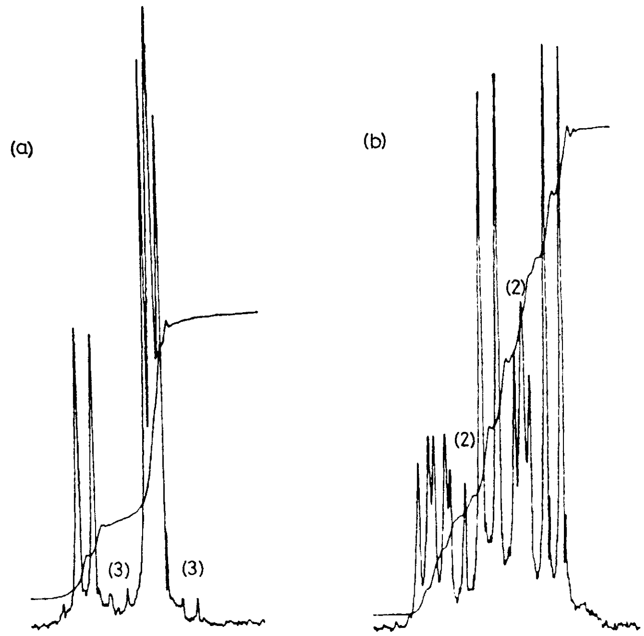


FIGURE. Partial ^1H n.m.r. spectra (Me–P region): (*a*) Complex (**2**), −30 °C, with traces of (**3**); (*b*) complex (**3**), +32 °C, with a small amount of (**2**).

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 P(OMe)$_2$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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