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SYNTHESIS AND STRUCTURE OF NEW DIMETHYL- AND HYDRIDO-IRON CARBONYL COMPOUNDS

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Summary

The preparation of the first iron carbonyl compound, $Fe(CH_3)_2(CO)_2(PMe_3)_2$, to contain two methyl groups bonded to the metal was achieved by two methods: (*a*) alkylation with CH_3Li of the Fe—I bond in $FeI(CH_3)(CO)_2(PMe_3)_2$ and (*b*) oxidative addition of CH_3I to the compound $Na[Fe(CH_3)(CO)_2(PMe_3)_2]$ prepared in situ. The first method also yields, as a side-product, a new hydridoiron carbonyl $FeHI(CO)(PMe_3)_3$. The structure and configuration of both compounds have been determined from their IR and NMR spectra.

Introduction

In a previous study we reported the preparation of $FeI(CH_3)(CO)_3(PMe_3)_3$(I) [1], a stable iron carbonyl compound having one methyl group σ-bonded to the metal. To our knowledge, $Os(CH_3)_2(CO)_4$ [2a] is the only metal carbonyl bearing two alkyl groups. Consideration of the stabilizing effect of PMe_3 compared to other phosphine ligands [1] led us to investigate the possibilities of attaching a second methyl group onto the metal center in I. The isolation of such a compound would be of special interest because of the particular importance of alkylmetal compounds in general and in particular the potential application of σ-bonded iron compounds in organic syntheses [2b]. Alkylation of I with CH_3Li led not only to the expected dimethyl compound $Fe(CH_3)_2(CO)_2(PMe_3)_2$ (II), resulting from simple iodide exchange with an alkyl group, but also to a new hydridoiron complex, $FeHI(CO)(PMe_3)_3$ (III).

Experimental

All reactions were conducted under argon. CH_3Li was purchased from Alfa Inorganics. $FeI(CH_3)(CO)_2(PMe_3)_2$ was prepared as reported earlier [1] by an oxidative addition-elimination reaction between CH_3I and *trans*-$Fe(CO)_3(PMe_3)_2$. It can also be obtained, though in poorer yields (1%) from eqn. 1.

$$FeI_2(CO)_2(PMe_3)_2 + CH_3Li \xrightarrow[-40^\circ C]{Et_2O} FeICH_3(CO)_2(PMe_3)_2 + LiI \qquad (1)$$

Preparation of II

This compound can be obtained by two methods:

(a) Action of methyllithium on I. Methyllithium is slowly added to a solution of I in ether at −40°C in a 1/1 molar ratio (eqn. 2). A green suspension gradually forms.

$$FeI(CH_3)(CO)_2(PMe_3)_2 + CH_3Li \xrightarrow[-40^\circ C]{Et_2O} \underset{(II)}{Fe(CH_3)_2(CO)_2(PMe_3)_2} + LiI \qquad (2)$$

The mixture (A) is stirred for 30 min and then filtered; the filtrate is evaporated to dryness and the residue sublimed under vacuum at 40 °C for 12 h to give colorless prisms of II in 1% yield. (Analysis found: C, 40.37; H, 8.08; P, 20.63. $C_{10}H_{24}FeO_2P_2$ calcd.: C, 40.85; H, 8.17; P, 21.10%.) The compound is insoluble in water, but soluble in all common organic solvents; it is a non-electrolyte in nitrobenzene ($\Lambda = 0.32\ \Omega^{-1}\ cm^2\ mol^{-1}$).

(b) Action of CH_3I on the sodium salt of I. Starting from I, the reaction is carried out in two steps (eqns. 3 and 4).

$$\underset{(I)}{FeI(CH_3)(CO)_2(PMe_3)_2} + 2Na \xrightarrow[THF]{25^\circ C} \underset{(IV)}{Na[Fe(CH_3)(CO)_2(PMe_3)_2]} + NaI \qquad (3)$$

$$IV + CH_3I \xrightarrow[THF]{25^\circ C} \underset{(II)}{Fe(CH_3)_2(CO)_2(PMe_3)_2} + NaI \qquad (4)$$

Na/Hg amalgam is added to a solution of I in THF and the mixture stirred for 30 min. Methyl iodide is then added and allowed to react briefly. The volatile components are then evaporated and the solid residue sublimed under vacuum to yield compound I in 1% yield.

Preparation of III

The hydride $FeHI(CO)(PMe_3)_3$ (III) can be obtained from reaction 2 if the reaction mixture A is treated as follows:

The solvent (ethyl ether) is evaporated to dryness (without filtration) and the green solid residue is transferred to a sublimation tube and heated in an oil bath at 40 °C. The volatile compound II is sublimed off, and the residue extracted with hexane. The extract is colled to −30°C when light brown crystals begin to separate. Yield 0.5%. (Analysis found: C, 27.40; H, 6.45; P, 21.15; I, 28.88. $C_4H_{28}FeIOP_3$ calcd.: C, 27.30; H, 6.37; P, 21.15; I, 28.90%.)

Results and discussion

The procedures which lead to the dimethyl (II) and to the hydrido (III) compounds call for some comments. Whereas method (*b*) leads to compound II exclusively, method (*a*) leads both to compounds II and III, depending on the man-

TABLE 1

INFRARED AND NMR DATA FOR $Fe(CH_3)_2(CO)_2(PMe_3)_2$ AND $FeHI(CO)(PMe_3)_3$ COMPOUNDS

	τ (ppm)[e]	J(P—H) (Hz)	ν(C—O) (cm^{-1})	ν(Fe—H) (cm^{-1})
$Fe(CH_3)_2(CO)_2(PMe_3)_2$	9.00 (t) (P—CH_3)	5	A_1 1976.5 s[b]	
	10.30 (t) (Fe—CH_3)	10	B_1 1912.5 s[b]	
$FeHI(CO)(PMe_3)_3$	8.42 (t) (P—CH_3)	4[a]	1896.0 s[c]	1824 m[c]
	8.70 (d) (P—CH_3)	6		
	20.90 (Fe—H)[d]	68 (*cis*)		
		54 (*trans*)		

[a] In C_6D_6. [b] In hexane. [c] CsI pellets. [d] Doublet of triplets. [e] TMS: τ = 10 ppm.

ner in which the reaction mixture is treated. The filtrate from A does not contain any hydrido compounds as is shown by infrared measurements. Although the conditions under which the latter compound is formed are not clear, an intramolecular rearrangement could have taken place on heating the green solid. Abstraction of both methyl and CO groups could result and replacement by a phosphine ligand, which is always present in the free state, and by a proton, the origin of which cannot be indicated without further evidence.

The molecular structures of II and III were determined from the infrared and NMR data (Table 1). For compound II two infrared CO bands of equal intensity together with the NMR coupling patterns ($X_nAA'X'_n$) [5,6] of PCH_3 protons with phosphorus in phosphine ligands exclude four out of the five possible isomers, so that the structure a is assigned (Fig. 1). Structure b of compound III is assigned on the basis of its NMR spectrum. The high field signal of the hydrido proton is split into a doublet of triplets (Fig. 2), due to coupling with two phosphorus nuclei in the *cis* position and to one in the *trans* position. The PCH_3 protons signal (a triplet and a doublet) indicates a meridional configuration for the phosphine ligands [6]. This gives for the Fe—H proton a J'(P—H) *trans* $<$ J'(P—H) *cis*, an order which is the reverse of that observed for the ruthenium analog $RuHI(CO)(PR_3)_3$ [7]. Finally the ν(Fe—H) stretch has been assigned at 1824 cm^{-1}, and the ν(C—O) at 1896.0 cm^{-1}; the latter value is close to 1926 cm^{-1} for ν(C—O) in $FeI_2(CO)L_3$ [8], a compound of analogous configuration.

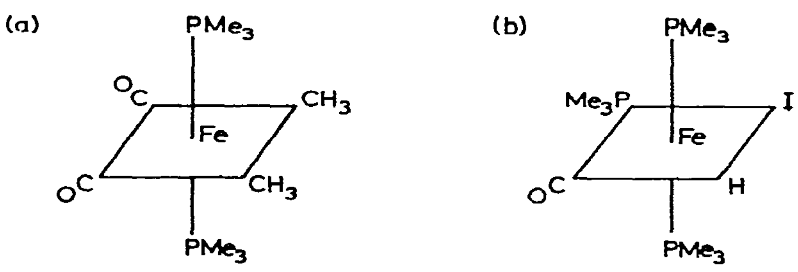

Fig. 1.

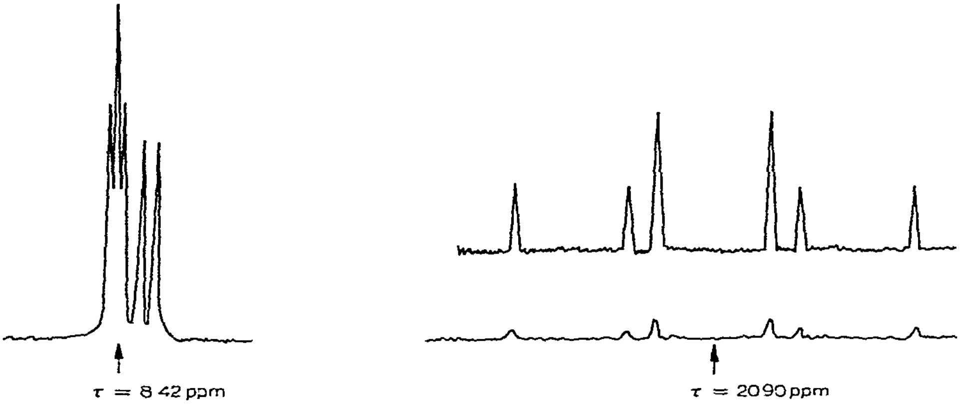

Fig. 2. Proton NMR spectrum of $FeHI(CO)(PMe_3)_3$.

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