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NEW ACETYL- AND METHYL-IRON COMPLEXES

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SUMMARY

Several oxidative addition reactions of alkyl halides with derivatives of iron carbonyl have been undertaken at varying degrees of substitution, basicity and bulkiness of phosphine ligands. Only trimethylphosphine leads to a stable *trans*-iodo-acetyl derivative which decarbonylates to give the *cis*-iodo-methyl derivative of dicarbonylbis(trimethylphosphine)iron. Methyl migration mechanism to the nearest CO during carbonylation reaction has been confirmed. The experimental evidence suggests that the reactivity of trigonal bipyramidal iron complexes depends on the negative charge associated with the remaining carbonyl ligands, and on the bulkiness of the phosphine ligands.

INTRODUCTION

Considerable interest has been recently shown in transition metal compounds having direct metal-to-carbon σ bonds. Piper and Wilkinson[1] were the first to synthesize the iron methyl complex $C_5H_5Fe(CO)_2(CH_3)$ and more recently the preparation of a variety of alkyl, aryl and acyl derivatives of cyclopentadienyl iron dicarbonyl has been reported[2].

In this paper a new method of preparation is described, based on the oxidative addition of a saturated trigonal bipyramidal iron complex from which the cyclopentadienyl ring is absent, with methyl iodide.

$$trans\text{-}Fe(CO)_3(PMe_3)_2 + ICH_3 \rightleftarrows FeI(COCH_3)(CO)_2(PMe_3)_2 \quad (1)$$

$$FeI(COCH_3)(CO)_2(PMe_3)_2 \rightleftarrows CO + FeI(CH_3)(CO)_2(PMe_3)_2 \quad (2)$$

Many examples can be found in the literature of iron pentacarbonyl and its phosphine-substituted derivatives acting as nucleophilic reagents and undergoing oxidative addition with different electrophilic reagents such as halogens[3,4], liquid HCl[5], strong inorganic acids[6], nitrosyl halides[8], liquid SO_2[9], cyanogen halides[4] and perfluoroalkyl halides[9,10]. A general review of such reactions has recently been presented by Collman and Roper[11]. Apparently the only attempt to react alkyl halides with saturated trigonal bipyramidal d^8 complexes has been that made by Collman and Roper, who reacted tricarbonylbis(triphenylphosphine)ruthenium with methyl iodide[11]. Derivatives of iron pentacarbonyl have not been studied to the same extent as those of ruthenium and osmium, probably because of their lower stability. The choice of phosphine is also important in relation to the reactivity of iron d^8 carbonyl complexes and in this respect trimethylphosphine seems to be a more interesting ligand than the bulkier triphenylphosphine.

EXPERIMENTAL SECTION

Infrared spectra were measured with a Perkin–Elmer Model 225 (region 4000–200 cm^{-1}) and a Beckman FS-720 Spectrophotometer (region 400–40 cm^{-1}). Dipole moments were measured for benzene solutions using the Guggenheim method. The infrared and dipole moment data are reported in Table 1. The starting compound *trans*-$Fe(CO)_3(PMe_3)_2$ was prepared using a previously described method[12]. Although the compounds reported in this paper are reasonably stable in air, all the preparations were carried out under nitrogen.

TABLE 1

INFRARED ABSORPTION BANDS[a] AND DIPOLE MOMENTS[b]

Assignments	$FeI(COCH_3)(CO)_2(PMe_3)_2$ 3.63 D	$FeI(CH_3)(CO)_2(PMe_3)_2$ 3.25 D
C–H stretch (ligand, acetyl, methyl)	2972.5^c m, 2910.5^c m	2972.0^f m, 2910.5^c m
C–O stretch (terminal CO)	2042.0^d vw A_1, 1961.3^d vs B_1	1998.4^d s A_1, 1939.8^d s B_1
C–O stretch (acetyl group)	1590^e s A_1	
H–C–H bend (ligand, acetyl, methyl)	1433.5^c m, 1422.5^c s, 1416^c sh	1433.5^c m, 1424.5^c s, 1418^c sh
	1328^c m, 1306.5^c m, 1287^c s	1306.5^c m, 1287^c s, 1284^c s
H–C–H sym. bend (methyl)		1174^c m A_1
CH_3 rock (acetyl group)	1064^c m	
CH_3 rock (ligand)	948^e vs, 859^e s, 850^e sh	948^e vs, 862^e sh, 857^e s
C–C stretch (acetyl group)	902^e m	
P–C stretch	732^e s E^g, 672^e s $A_1{}^g$	734^e s E^g, 672^e s $A_1{}^g$
Fe–C–O bend. (terminal CO)	626^e vs, 604^e vs, 573^e m	626^e s, 604^e vs, 571^e s
Fe–C sym. stretch (acetyl group)	523^e s, 529^e sh	
Fe–C asym. stretch (terminal CO)		
Fe–C sym. stretch (methyl group)		522^e s, 527^e sh
Fe–C asym. stretch (terminal CO)		
Fe–C sym. stretch (terminal CO)	464^e m	492^e m
C–P–C bend (ligand)	364^e s $A_1{}^g$, 348^e m, 304^e m, $282^{e,f}$ m E^g	373^e s $A_1{}^g$ $284^{e,f}$ m E^g
Fe–P and Fe–I	232^f m, 194^f w	243^f m, 196^f w
Other low-freq. bands	158^f m, 145^f m, 100^f vs, 74^f sh	137^f m, 118^f m, 110^f m, 97^f m

[a] In cm^{-1}; w=weak; sh=shoulder; m=medium; s=strong; v=very. [b] In Debye. [c] CCl_4 solution. [d] n-Hexane solution. [e] In KBr pellet. [f] In polyethylene pellet. [g] In terms of local symmetry.

Iodoacetyldicarbonylbis(trimethylphosphine)iron, $FeI(COCH_3)(CO)_2(PMe_3)_2$

trans-$Fe(CO)_3(PMe_3)_2$ (2.92 g) was dissolved in 50 ml of methyl iodide and allowed to react at 0° in the dark (reaction 1). No evolution of carbon monoxide was observed. The progress of the reaction was followed spectroscopically in methyl iodide solution; the 1867.4 cm^{-1} band of *trans*-$Fe(CO)_3(PMe_3)_2$ decreasing and the bands at 2040(vw) and 1957(vs) cm^{-1} of $FeI(COCH_3)(CO)_2(PMe_2)_2$ increasing in intensity as the reaction proceeded. After 10 days when all the starting material had apparently reacted, excess methyl iodide was evaporated and the reaction product recrystallised at −10° in n-hexane, when dark-orange well-formed crystals were obtained (yield 90%). These were washed with n-hexane and dried *in vacuo*. (Found: C, 28.35; H, 5.06; I, 29.44; P, 14.57. $C_{10}H_{21}FeIO_3P_2$ calcd.: C, 27.70; H, 4.84; I, 29.26; P, 14.28%.) The compound is soluble in polar and non-polar organic solvents. It is fairly stable in air.

Iodomethyldicarbonylbis(trimethylphosphine)iron, $FeI(CH_3)(CO)_2(PMe_3)_2$

$FeI(COCH_3)(CO)_2(PMe_3)_2$ (4.33 g) was dissolved in 250 ml of boiling n-hexane, and was heated over a period of 5 h under reflux. One mole of carbon monoxide per mole of $FeI(COCH_3)(CO)_2(PMe_3)_2$ was liberated. The progress of the reaction was followed spectroscopically in n-hexane solution, the 2042.0 (vw) and 1961.3 (vs) cm^{-1} bands decreasing in intensity and bands at 1998.4 (s) and 1939.8 (s) cm^{-1} increasing in intensity as the reaction proceeded. Filtration of the reaction mixture, followed by cooling to −10°, afforded the pure compound as dark-red well-formed crystals. Physical constants such as solubility and stability to air were similar to those of the preceeding compound. (Found: C, 27.44; H, 5.23; I, 30.91; P, 14.93; $C_9H_{21}FeIO_2P_2$ calcd.: C, 26.62; H, 5.17; I, 31.27; P, 15.27%.) Yield 90%.

Reactions of the acetyl compound

Heating the n-hexane solution of $FeI(COCH_3)(CO)_2(PMe_3)_2$ to 73° gave the methyl derivative $FeI(CH_3)(CO)_2(PMe_3)_2$ with evolution of CO (reaction 2), this being a typical reaction of most acyl derivatives of transition metals[13,14]. Cleavage of the acetyl group from the metal can also be achieved by thermal decomposition. Heating solid $FeI(COCH_3)(CO)_2(PMe_3)_2$ at 180° for 10 min under a stream of nitrogen gave *trans*-$Fe(CO)_3(PMe_3)_2$ and *cis*-$FeI_2(CO)_2(PMe_3)_2$[15].

On exposure of a solution of $FeI(COCH_3)(CO)_2(PMe_3)_2$ in n-hexane to sunlight partial decarbonylation with the formation of $FeI(CH_3)(CO)_2(PMe_3)_2$ (reaction 2) occurred. At the same time the reverse of reaction (1) apparently took place, since *trans*-$Fe(CO)_3(PMe_3)_2$ was found in the reaction mixture.

Reactions of the methyl compound

$FeI(CH_3)(CO)_2(PMe_3)_2$ carbonylates very easily, for on bubbling carbon monoxide through the n-hexane solution of the compound at 25°, the reverse of reaction (2) occurred with formation of the acetyl compound. Cleavage of the methyl group from the metal takes place during thermal decomposition. Only *cis*-$FeI_2(CO)_2(PMe_3)_2$ was found when $FeI(CH_3)(CO)_2(PMe_3)_2$ was heated at 180° for 10 min under a stream of nitrogen.

The methyl group is rapidly removed from the metal at room temperature by reaction of $FeI(CH_3)(CO)_2(PMe_3)_2$ with iodine. This reaction* may be carried out

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* The analogous rection of iodine with $FeI(COCH_3)(CO)_2(PMe_3)_2$ is solvent dependent. If this reaction is carried out in non-polar organic solvents, *e.g.* n-hexane, an unknown ionic precipitate is obtained, which exhibits two carbonyl stretching bands in the IR at 2081 (vw) and 2015 (vs) cm^{-1} (nujol mull). It decomposes in polar organic solvents giving the known *cis*-$FeI_2(CO)_2(PMe_3)_2$. This compound has the formula: [*trans*-$Fe(CH_3)(CO)_3(PMe_3)_2$]I_3.

in solution using polar or non-polar solvents. Only *cis*-$FeI_2(CO)_2(PMe_3)_2$ was found in the reaction mixture. No substitution reaction was observed between $FeI(CH_3)(CO)_2(PMe_3)_2$ and excess of trimethylphosphine even on heating the mixture at the boiling point under 1 atm of nitrogen.

Addition of alkyl halides other than ICH_3

Reaction (1) can be carried out using other alkyl halides but attempts to separate pure products have not been successful. The following compounds were, however, detected spectroscopically in the reaction mixture.

$FeI(COC_2H_5)(CO)_2(PMe_3)_2$ showing a strong band at 1956.7 cm^{-1} in ethyl iodide solution; $FeBr(COC_2H_5)(CO)_2(PMe_3)_2$ showing a strong band at 1960.7 cm^{-1} in ethyl bromide solution. Both of these compounds decomposed on heating without yielding the corresponding ethyl to metal derivatives. On the contrary, when methyl chloride was allowed to react with *trans*-tricarbonylbis(trimethylphosphine)iron under pressure in n-hexane solution, it gave not the acetyl compound but a mixture of a methyl-to-metal derivative, $FeCl(CH_3)(CO)_2(PMe_3)_2$ [2000.5 (s) and 1940.0 (s) cm^{-1} in n-hexane] and *cis*-$FeCl_2(CO)_2(PMe_3)_2$. No reaction occurred when methyl iodide was mixed at room temperature with the following complexes: $Fe(CO)_5$; *trans*-$Fe(CO)_4PMe_3$; *trans*-$Fe(CO)_3[P(OMe)_3]_2$; *trans*-$Fe(CO)_3(PPh_3)_2$ and *trans*-$Fe(CO)_3(PEt_3)_2$.

RESULTS AND DISCUSSION

Identification of methyl and acetyl groups

Infrared data in the spectral region 4000 to 40 cm^{-1} of the compounds $FeI(COCH_3)(CO)_2(PMe_3)_2$ and $FeI(CH_3)(CO)_2(PMe_3)_2$ were compared with those of *trans*-$Fe(CO)_3(PMe_3)_2$ and different isomers of its diiodo derivatives $FeI_2(CO)_2(PMe_3)_2$[4].

The acetyl compound exhibited four bands at 1590 (s), 1064 (m), 902 (m) and 529 (sh) cm^{-1} which have also been identified in various other acetyl transition metal compounds by several authors[16,17]. The band at 1590 (s) cm^{-1} may be assigned to CO ketonic stretching. The lowering of this frequency in comparison to those usually found for organic ketones has previously been discussed[16] in terms of partial π bonding from the metal to acetyl group. Bands at 1064 (m) cm^{-1} and 902 (m) cm^{-1} are characteristic of an acetyl group bonded to a transition metal atom, and may be assigned to methyl rocking $\rho(CH_3)$, and to carbon–carbon stretching modes $\nu(C\text{–}CH_3)$ respectively[16].

The spectrum of the acetyl compound exhibited eight bands between 800 and 400 cm^{-1}. Those at 732 and 672 cm^{-1} may be confidently assigned to $\nu(P\text{–}C)$ stretching of E(local) and A_1(local) symmetry respectively. Bands at 626 (s); 604 (s); and 573 (s) cm^{-1} correspond to $\delta(Fe\text{–}C\text{–}O)$ bending modes[15]. The three other bands expected in this region are $\nu(Fe\text{–}C)$ (terminal CO) symmetric and asymmetric stretching modes and one $\nu(Fe\text{–}C)$ (acetyl group) symmetric stretch. The band at 467 cm^1 may be assigned to $\nu(Fe\text{–}C)$ (terminal CO) A_1 stretch, as this is usually found in metal carbonyl compounds[15]. Consequently the two bands at 523 (s) and 529 (sh) cm^{-1} are assignable to $\nu(Fe\text{–}C)$ (terminal CO) asymmetric, and $\nu(Fe\text{–}C)$ (acetyl group) symmetric stretching modes. In confirmation of these assignments, *trans*-$FeI_2(CO)_2$-

(PMe$_3$)$_2$[4] does not show any IR bands between 580 and 500 cm^{-1}, the asymmetric ν(Fe–C) (terminal CO) band being shifted to 492 cm^{-1}.

The methyl compound FeI(CH$_3$)(CO)$_2$(PMe$_3$)$_2$ exhibits two bands at 1174 (m) and 522 (s) or 527 (sh) cm^{-1} in addition to other vibrations due to the methyl group of the trimethylphosphine ligand. The band at 1174 (m) cm^{-1} may be assigned to symmetrical bending of the CH$_3$ bonded to the iron atom; a similar mode occurs at 1190 cm^{-1} for Mn(CO)$_5$CH$_3$[18]. The band at 522 (s) cm^{-1} may be assigned to ν(Fe–CH$_3$) stretching according to the assignments of Adams *et al.*[19] of methyl-to-metal complexes.

Configurations of the acetyl and methyl complexes

These two compounds were found to be diamagnetic, and to be non-electrolytes in nitrobezene. These observations strongly support the view that they are hexacoordinated complexes of a formally bivalent iron in a d^6 configuration at the center of an octahedron.

The assignment of their molecular configuration was based on:

(*a*) infrared data in the carbonyl region, and

(*b*) dipole moment measurements (see Table 1).

Six stereoisomers are possible and estimates of their dipole moments are given in Fig. 1.

(*a*). Considerations based on the intensity of carbonyl stretching bands[20] suggest that two bands of equal intensity should occur in the infrared spectra of the *cis* complexes [steroisomers (III) to (VI), Fig. 1], which is observed in the case of the methyl compound FeI(CH$_3$)(CO)$_2$(PMe$_3$)$_2$; and that only one band should occur (eventually another weak band) for the *trans* complexes [stereoisomers (I) or (II), Fig. 1), which is observed in the case of the acetyl compound FeI(COCH$_3$)(CO)$_2$-(PMe$_3$)$_2$.

(*b*). The static electric dipole moments (Fig. 1) were estimated assuming that the bond moments in the two complexes are approximately the same as in similar transition metal complexes such as *cis*-FeI$_2$(CO)$_4$ 3.69 D[21], *trans*-Fe(CO)$_4$PEt$_3$ 5.38

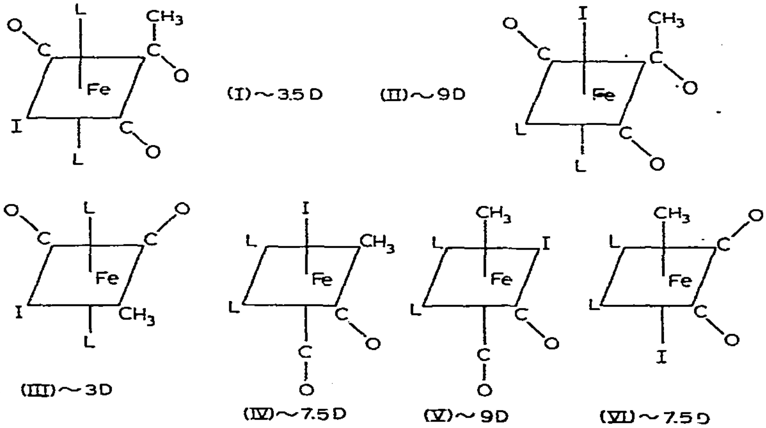

Fig. 1. Stereoisomers of acetyl and methyl compounds together with estimates of their dipole moments (L = trimethylphosphine).

D[22], $Mn(CO)_5(CH_3)$ 0.79 D[23], $Mn(CO)_5(COCH_3)$ 2.27 D[23], and *trans*-$PtI(COCH_3)(PEt_3)_2$ 3.15 D[14].

Thus (I) would have a dipole moment almost identical with that of *trans*-$PtI(COCH_3)(PEt_3)_2$, and the observed value of 3.63 D found for $FeI(COCH_3)(CO)_2(PMe_3)_2$ leads to the rejection of the only other possible configuration (II). In the same way the methyl compound must have configuration (III).

Fe–C and C–O bonds of the acetyl group

The average C–O stretch (2001 cm^{-1}) of $FeI(COCH_3)(CO)_2(PMe_3)_2$ is considerably displaced in comparison to the average* C–O stretch (1907 cm^{-1}) of *trans*-$Fe(CO)_3(PMe_3)_2$. This difference of 94 cm^{-1} cannot be solely ascribed to the electron withdrawing property of iodine but must also be due to that of the acetyl group (the $COCH_3$ group being slightly less electron-withdrawing than iodine). This is illustrated when the average carbonyl frequency of *trans*-$FeI_2(CO)_2(PMe_3)_2$ (D_{2h} symmetry) (2017 cm^{-1}) is compared with that of *trans*-$FeI(COCH_3)(CO)_2(PMe_3)_2$ (2001 cm^{-1}). A similar comparison may be made between the average carbonyl frequency of $FeI(CH_3)(CO)_2(PMe_3)_2$ (1969 cm^{-1}) and the value for the acetyl compound (2001 cm^{-1}).

The very low ketonic ν(C–O) stretch frequency of 1590 cm^{-1} and the relatively high ν(Fe–C) sym. stretch frequency of 492 cm^{-1} in the acetyl compound when compared to the ν(Fe–C) symmetric stretch frequency of terminal carbonyls of 464 cm^{-1} underline the attractive character of the $COCH_3$ group, which arises through the existence of an important π component in the Fe–C acetyl-to-metal bonding.

Carbonylation and decarbonylation reactions

Reaction (1) is apparently the first example of an oxidative addition of ICH_3 to an iron carbonyl complex yielding an iodo-acetyl derivative. The acetyl group derives its CO from one of the terminal carbonyls of the initial reactant while the iodine atom and the acetyl group occupy mutually *trans* positions. The compound is quite stable.

The complex obtained by decarbonylation contains an iodine atom and a methyl group in mutually *cis* positions, whereas oxidative addition of ICH_3 to square complexes of other Group VIII elements gives compounds with the iodine atom and the methyl group in a mutually *trans* position.

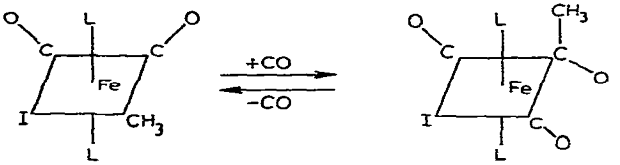

Fig. 2. Carbonylation and decarbonylation reactions (L=trimethylphosphine).

The mechanism of CO fixation by methyl-to-metal carbonyl complexes has been studied by many authors[2,25] and the methyl migration pathway is now widely accepted. A methyl migration mechanism is also most probable in the present case (Fig. 2).

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* This value was calculated using data from ref. 24.

If a CO molecule from the gas phase were inserted into the Fe–CH_3 bond, the resulting $FeI(COCH_3)(CO)_2(PMe_3)_2$ would have the terminal groups in a mutually *cis* position; if on the other hand ketonic CO was evolved during decarbonylation the resulting $FeI(CH_3)(CO)_2(PMe_3)_2$ would have the two CO groups *trans* to each other, which is not observed.

Thus, if the hypothesis of an intermediate isomerisation during reaction (2) (Fig. 2) is rejected, the insertion mechanism should also be rejected, leaving only a methyl migration mechanism to fit the experimental results. Further this system shows that the methyl group goes to the nearest CO ligand.

No reaction was observed when the starting compound (reaction 1) *trans*-$Fe(CO)_3L_2$ contained triethylphosphine instead of trimethylphosphine. This could have been due to steric effects, the bulkiness of triethylphosphine, in comparison to trimethylphosphine[26], making the approach of ICH_3 to the reactant more difficult. It is suggested that the existence of two isomers of triethylphosphine, which exchange very rapidly, increase the effective bulkiness of this ligand[27]. A similar argument may be used to explain the non-reactivity of the *trans*-$Fe(CO)_3(PPh_3)_2$ with methyl iodide, but here the basicity of the ligand may also interfere.

$Fe(CO)_5$, *trans*-$Fe(CO)_4PMe_3$ and *trans*-$Fe(CO)_3[P(OMe)_3]_2$ do not react with ICH_3; possibly the negative charge on the metal which is shared with the carbonyl ligands plays an important role in this case. If this is so, the presence of a weak negative charge would prevent the addition of methyl iodide. These results agree with Chatt's observations[28] concerning the basicity of the ligands of some rhodium complexes during the activation of molecular hydrogen.

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