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BORON HYDRIDE REDUCTION OF TRANSITION METAL—ACETYL COMPLEXES

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Summary

Acetyl complexes of iron(II) and ruthenium(II) of the type $(\pi\text{-}C_5H_5)(CO)LM(COCH_3)$, where L = PPh_3, $P(OPh)_3$, $P(cyclohexyl)_3$, PMe_2Ph or CO for M = Fe, and PPh_3 for M = Ru, are rapidly reduced to the corresponding ethyl complexes by $BH_3 \cdot THF$ or B_2H_6/C_6H_6. In some cases hydrido complexes of the type $(\pi\text{-}C_5H_5)(CO)LMH$ are also formed. The reaction has been studied by use of ^1H NMR and the spectrum of $(\pi\text{-}C_5H_5)(CO)(PPh_3)FeC_2H_5$, which shows several unusual features, is discussed in detail. It is suggested that the rate of reduction increases with increasing electron density at the metal centre.

Acetyl complexes of other transition metals, i.e. Ir, Pt, Pd, Co and Mo, are also reduced to the corresponding ethyl compounds by B_2H_6/C_6H_6.

Introduction

The reduction of organic molecules by diborane and related compounds has been extensively studied during the last thirty years [1] but diborane has received little attention as a reducing agent in organometallic chemistry. $LiAlH_4$ and $NaBH_4$ are probably the most commonly used reducing agents in transition-metal chemistry, and it has been shown [2] that reductions by these Group III hydride anions tend, at least in organic chemistry, to involve the transfer of a hydride ion from the anion to an electron-deficient centre of the functional group. BH_3 on the other hand is a strong Lewis acid, and reduction by BH_3 appears to involve preferred attack at the centre of highest electron density [3]. We were interested in being able to reduce an acetyl group coordinated to a transition metal, and since it might be expected that such a group would constitute a centre of high electron density, we chose BH_3 as reducing agent.

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TABLE 1

^{1}H NMR DATA FOR SOME COMPLEXES OF THE TYPE (π-C_5H_5)(CO)LMR, WHERE M = Fe OR Ru, R = ACETYL, ETHYL OR HYDRIDE AND L = TERTIARY-PHOSPHINE, TERTIARY-PHOSPHITE OR CARBONYL

Measured at 90 MHz in C_6D_6 containing tetramethylsilane as internal standard.

M	L	Chemical shifts, δ (ppm) and coupling constants [a] (Hz)					
		R = acetyl		R = ethyl		R = hydride	
		π-C_5H_5	acetyl	π-C_5H_5	ethyl	π-C_5H_5	hydride
Fe	PPh_3	4.25(1.2) [b]	2.57(0.8) [b]	4.12(1.0)	[i]	4.27(1.2)	−12.8(75)
Fe	PMe_2Ph	4.08(1.2) [c,b]	2.66(<0.2)	4.05(1.0) [j]	ca. 1.5 [k]	4.20(1.2) [p]	−13.9(79) [p]
Fe	P(cyclohexyl)$_3$	4.39(<0.2) [e]	2.18(<0.2) [e]	4.37(<0.2)	[l]	4.58(<0.2)	−13.7(70)
Fe	$P(OPh)_3$	4.03(0.9) [b]	2.76(0.9) [b]	3.93(0.6)	ca. 1.5 [k]	4.07(0.9)	−12.9(94)
Fe	$PPh(OPh)_2$	4.15(1.2)	2.68(1.0)	4.05(1.0)	ca. 1.6 [k]	4.11(1.0)	−13.2(88)
Fe	$PPh_2(OPh)$	4.13(1.2)	2.30(0.8)	4.07(1.0)	ca. 1.5 [k]	4.12	−13.1(82)
Fe	$PPh_2(CH_2Ph)$	4.05(1.2)	2.57(0.7)	4.01(1.2)	ca. 1.6 [k]	4.14(1.2)	−13.3(80)
Fe	$P(CH_2Ph)_3$	3.90(1.0) [f]	2.75(0.7) [f]	3.85(1.0)	ca. 1.6 [k,l]	3.98(1.0)	−13.8(81)
Fe	CO	4.25 [g]	2.44 [g]	4.80 [m]	[n]	-	-
Fe	CO	4.97 [h]	1.66 [h]	-	-	-	-
Ru	PPh_3	4.79(<0.2) [e]	2.35(<0.2) [e]	4.65(<0.2)	[o]	4.77(<0.2)	−10.9(32)
(π-C_5H_5)(CO)(PPh_3)$FeCD_2CH_3$		-	-	4.12(broad)	1.57(broad)	-	

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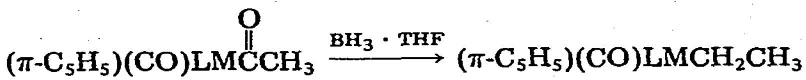
[a] $J(^{31}P$—$H)$ given in parentheses after chemical shifts. [b] 60 MHz ^{1}H NMR spectrum previously reported [6]. [c] Methyl protons of PMe_2Ph; two doublets at δ 1.50 ppm, $^2J(^{31}P$—$H) = 10$ Hz and δ 1.21 ppm, $^2J(^{31}P$—$H) = 10$ Hz. [d] ^{1}H NMR spectrum in CS_2 previously reported [7]. [e] ^{1}H NMR spectrum in $CDCl_3$ previously described [8], although no $J(^{31}P$—$H)$ reported. [f] Benzyl CH_2 protons of $P(CH_2Ph)_3$ give rise to a doublet at δ 3.14 ppm, $^2J(^{31}P$—$H) = 9$ Hz. [g] Measured in acetone-d_6; previously reported [9] in $CDCl_3$. [h] Measured in tetrahydrofuran-d_8. [i] CH_2 protons give rise to two signals at δ 1.08 ppm, $^3J(^{31}P$—$H) = 12$ Hz and δ 1.88 ppm, $^3J(^{31}P$—$H) = 2$ Hz. The CH_3 protons give rise to an adsorption at δ 1.59 ppm, $^4J(^{31}P$—$H) = 2$ Hz. All three signals are mutually coupled: $^3J(H$—$H) = 7.5$ Hz, $^2J(H$—$H) = 9$ Hz. (See text.) [j] Methyl protons of PMe_2Ph; doublet at δ 1.17 ppm, $^2J(^{31}P$—$H) = 9$ Hz. [k] Unresolved multiplet. [l] Not observed since overlapping signals arise from the cyclohexyl protons of L. [m] Measured in tetrahydrofuran-d_8. [n] Complex A_2B_3 pattern (see ref. 10). [o] CH_2 protons give rise to multiplets at δ 2.13 ppm and δ 1.3 ppm; CH_3 protons give triplet at δ 1.71 ppm. $^3J(H$—$H) = 7$ Hz. [p] Methyl protons of PMe_2Ph give rise to a doublet at δ 1.29 ppm, $^2J(^{31}P$—$H) = 9$ Hz.

Results and discussion

Reduction of acetyl complexes of iron and ruthenium

Addition of $BH_3 \cdot THF$ to an acetyl complex of type I resulted in a rapid (ca. 2 min at 20°C) reduction of the coordinated acetyl to a coordinated ethyl:



$$(\pi\text{-}C_5H_5)(CO)LM\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{BH_3 \cdot THF} (\pi\text{-}C_5H_5)(CO)LMCH_2CH_3$$

(I) (II)

(a) M = Fe; L = PPh_3, PMe_2Ph, P(cyclohexyl)$_3$, $P(OPh)_3$, $PPh(OPh)_2$, $PPh_2(OPh)$, $P(CH_2Ph)_3$, or CO.
(b) M = Ru; L = PPh_3.

We have followed this reaction using ^1H NMR spectroscopy. The addition of BH_3 (B_2H_6) to a solution of the acetyl complex I in C_6D_6 (see Experimental section) resulted in the disappearance of the signal(s) due to the methyl protons of the acetyl group with the concurrent appearance of signals assigned to the newly formed ethyl complex. The NMR data for the acetyl and ethyl complexes are given in Table 1. In two cases, i.e. with M = Fe and L = PPh_3 or CO, we confirmed the presence of the iron—ethyl compound by independent synthesis of the complex and comparison of the ^1H NMR spectra.

Using B_2H_6/C_6H_6 in place of $BH_3 \cdot THF$ resulted in a slower reduction, as would be expected in view of lower Lewis acidity of B_2H_6/C_6H_6 relative to $BH_3 \cdot THF$. This was especially marked for the complexes with L = CO. Thus, for complex I with M = Fe and L = CO no reduction was observed with B_2H_6/C_6H_6 even after several hours at room temperature. We suggest that this may be ascribed to the lower electron density on the metal resulting from the replacement of the tertiary-phosphine by a carbonyl ligand. Since reductions with BH_3 or B_2H_6 probably involve electrophilic attack at the centre of highest electron density [3], decreasing the electron density in the acetyl group would be expected to lead to a decrease in the rate of reduction.

There have been two reports of the reduction of complexes containing groups related to acetyl: the reduction of the salt $[(\pi\text{-}C_5H_5)(CO)(PPh_3)Fe\{C(OEt)CH_3\}]BF_4$ with $NaBH_4$ in ethanol gives $[(\pi\text{-}C_5H_5)(CO)(PPh_3)Fe(C_2H_5)]$ together with $\{(\pi\text{-}C_5H_5)(CO)(PPh_3)Fe\{CH(OEt)CH_3\}]$ [4]; and treatment of compounds of the type $RC(O)CCo_3(CO)_9$ with Et_3SiH/CF_3CO_2H in tetrahydrofuran (THF) results in a smooth reduction to the corresponding alkylidynetricobalt nonacarbonyl $RCH_2CCo_3(CO)_9$ [5]. However, the reaction reported here represents the first example of the direct reduction of a metal-coordinated acetyl group.

In addition to the ethyl complexes II, $BH_3 \cdot THF$ reduction of I gives rise to hydrido complexes of type III, the NMR data for which are given in Table 1.

$(\pi\text{-}C_5H_5)(CO)LMH$

(III)

The percentage of hydride formed, relative to ethyl complex, is dependent on the nature of L, being ca. 5% for L = $P(OPh)_3$ and ca. 25% for L = PPh_3. We suggest that III is formed via BH_3 attack at the metal centre. An alternative route to III would involve β-hydrogen elimination from the ethyl group of II, giving ethylene and III. We have demonstrated that this does not play a major role by carrying out the reduction of I (M = Fe, L = PPh_3) with B_2D_6 in C_6D_6. The major products obtained were $(\pi\text{-}C_5H_5((CO)(PPh_3)FeCD_2CH_3$ and $(\pi\text{-}C_5H_5)(CO)(PPh_3)$-FeD. Further, under the reaction conditions used (25°C in either benzene or toluene) the ethyl complex II with L = PPh_3 and M = Fe is stable for several hours. In order to effect β-elimination a temperature of ca. 100°C (45 min in $C_6D_5CD_3$) is required. Under these forcing conditions II is smoothly converted into III with elimination of ethene.

We attempted to effect this reduction using:

(i) Group IV metal hydrides, e.g. Et_3SiH/CF_3COOH, Ph_3GeH, Ph_2SnH_2 or Ph_3SnH;

(ii) $NaBH_4$ or $LiAlH_4$;

(iii) Transition metal-hydride complexes, e.g. $HCo(CO)_4$, $H_2Fe(CO)_4$ or $H_5Ir(PEt_2Ph)_2$;

(iv) Molecular hydrogen in the presence of a transition metal hydrogenation catalyst.

TABLE 2

ATTEMPTED REDUCTION OF $[(\pi\text{-}C_5H_5)(CO)\{P(CYCLOHEXYL)_3\}Fe(ACETYL)]$

Conditions: 24 h at ambient temperature. Unless otherwise stated the starting material was recovered unreacted.

Complex (m*M*)	Reductor [a]	Solvent [b]
	Attempted reduction using metal-hydride complexes	
0.1	$IrH_5(PEt_2Ph)_2$ (0.1) [c]	C_6D_6 (0.5)
0.5	$Na_2Fe(CO)_4 \cdot 1\frac{1}{2}$ dioxane (1.0), trifluoroacetic acid (2)	n-hexane (5)
0.5	$[Co(pyr)_6][Co(CO)_4]_2$ (2.4), trifluoroacetic acid (5)	n-heptane (20)
0.5 [d]	$NaBH_4$ (30)	absolute ethanol
0.2 [e]	$LiAlH_4$ (5)	Et_2O (10)
0.1	Ph_2SnH_2 (0.1)	C_6D_6 (0.5)
	Attempted reduction using H^+/H^- system	
0.1 [f]	trifluoroacetic acid (0.4, isopropanol (0.2)	$CDCl_3$ (0.5)
0.1	trifluoroacetic acid (0.4), triphenylmethane (0.1)	$CDCl_3$ (0.5)
0.5	trifluoroacetic acid (0.7), hydrogen (1 atm)	C_6H_6 (5)
0.1 [g]	trifluoroacetic acid (0.4), Et_3SiH (0.2)	$CDCl_3$ (0.5)
	Attempted reduction with molecular hydrogen	
0.5	H_2 (1 atm)	CH_2Cl_2 (25)
0.5	H_2 (1 atm)	C_6H_6 (5)
0.5	H_2 (1 atm); Pd/C, 10% (110 mg)	C_6H_6 (5)
0.5	H_2 (1 atm); Pt/C, 10% (110 mg)	C_6H_6 (5)
0.5	H_2 (1 atm), $[Rh(norbornadiene)(PMe_2Ph)_3]PF_6$ (0.5)	CH_2Cl_2 (5)
0.5	H_2 (1 atm), $RhCl(PPh_3)_3$ (0.1)	C_6H_6 (5)

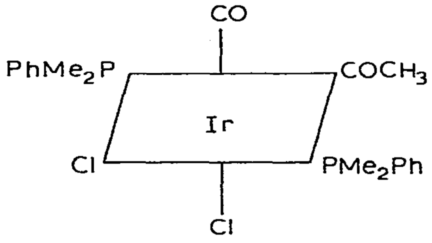
[a] Concentration (m*M*) of reductor given in parentheses. [b] Volume (ml) given in parentheses. [c] Iridium-hydrido complex decomposed under reaction conditions; iron—acetyl complex remained unchanged. [d] Ten min under reflux followed by 3 h at 20°C. [e] Tricyclohexylphosphine ligand of iron—acetyl complex replaced by dimethylphenylphosphine ligand. Reaction conditions ($\frac{1}{2}$ h at 20°C) resulted in complete destruction of iron—acetyl complex. [f] Isopropyl trifluoroacetate formed. [g] $Et_3SiC(O)CF_3$ formed together with a small amount of paramagnetic material.

However, our attempts met with no success; we observed either no reaction or decomposition of the acetyl complex (see Table 2).

Reduction of other transition metal—acetyl complexes

In order to investigate the generality of this reaction we have made a brief study of BH_3 reduction of other transition metal—acetyl complexes.

(a) Action of B_2H_6 on IV in benzene gave rise to the corresponding ethyl derivative (NMR evidence). Decomposition of this complex with $[PdCl_2(PhCN)_2]$ produced a solution containing ethane and ethene. This is further evidence for the formation of an iridium—ethyl complex [11].



(IV)

(b) B_2H_6/C_6H_6 reduction of *trans*-$[PtCl(COCH_3)(PEt_3)_2]$ gave *trans*-$[PtCl(C_2H_5)(PEt_3)_2]$. However, with *trans*-$[PtI(COCH_3)(PMe_2Ph)_2]$ we observed no reduction of the acetyl ligand.

(c) Addition of B_2H_6/C_6H_6 to *trans*-$[PdBr(COCH_3)(PMe_2Ph)_2]$ resulted in a rapid reaction. The ^1H NMR spectrum of the resulting mixture contained no resonances due to the original acetyl group. Although several new resonances were present in this spectrum we were unable, owing to signal overlap and decomposition, to assign one or more of these signals unambiguously to a palladium—ethyl group. However, the addition of $PdCl_2(PhCN)_2$ to this mixture resulted in the formation of ethane and ethene, indicating the presence of a palladium—ethyl complex [11].

(d) Although the acetyl ligand of $[Co(COCH_3)(CO)_2(PPh_3)\{P(OMe)_3\}]$ was readily reduced by B_2H_6/C_6H_6, that of $[Co(COCH_3)(CO)_2\{P(OMe)_3\}_2]$ was not. Substitution of a trimethylphosphite ligand for the triphenylphosphine ligand would result in a decrease in electron density in the carbonyl ligand, possibly decreasing its susceptibility to reduction.

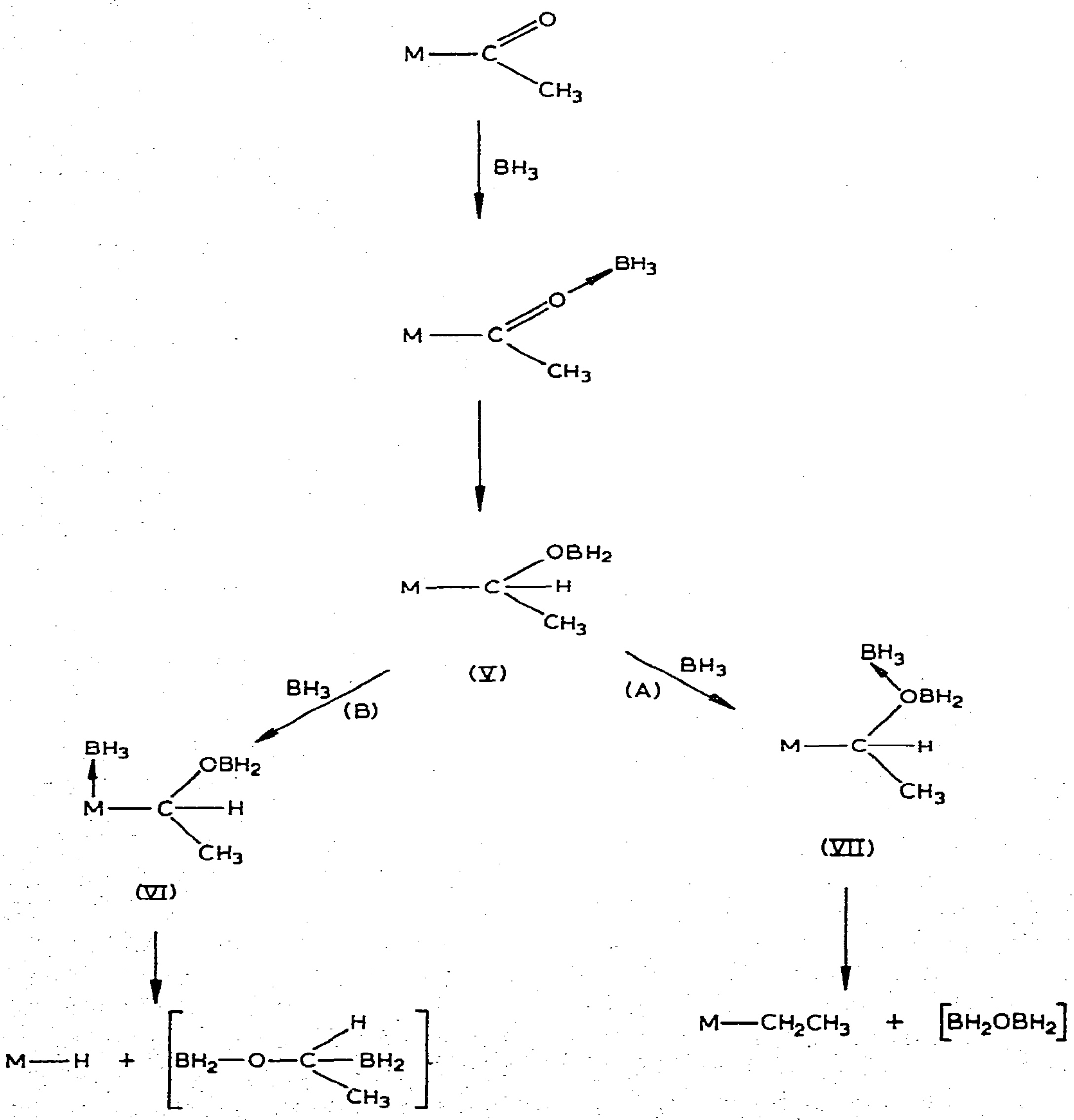
(e) The ^1H NMR spectrum of $[(\pi\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COCH_3)]$ in C_6D_6 consists of, apart from the resonances due to the triphenylphosphine ligand, a doublet at δ 5.03 ppm, $J(^{31}P\text{—}H) = 1.2$ Hz, assigned to the cyclopentadienyl protons, together with a singlet (i.e. no ^{31}P—H coupling observed) at δ 2.62 ppm, assigned to the acetyl protons. Addition of B_2H_6 to this solution resulted in the disappearance of these signals and the appearance of four new signals: a doublet at δ 4.51 ppm, $J = 1.4$ Hz, and a broad signal at δ 1.96 ppm, assigned to the ethyl complex, $[(\pi\text{-}C_5H_5)(CO)_2(PPh_3)MoC_2H_5]$; together with a singlet at δ 4.75 ppm and a doublet at δ —5.1 ppm, $J = 49$ Hz, assigned to the hydrido complex, $[(\pi\text{-}C_5H_5)(CO)_2(PPh_3)MoH]$. Thus, in the presence of B_2H_6/C_6H_6 the molybdenum complex $[(\pi\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COCH_3)]$ undergoes smooth reduction to the analogous ethyl complex with, as found for the iron and ruthenium complexes, concurrent hydrido formation.

The above results indicate that although B_2H_6/C_6H_6 reduction of a coordinated acetyl group is a fairly general reaction, its efficiency is strongly dependent on the nature of the other ligands present in the complex.

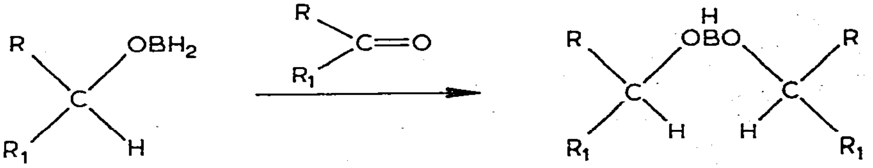
Discussion of the BH_3/B_2H_6 reduction

In organic chemistry, in all but a few cases [12] reduction of an acetyl-containing compound by $BH_3 \cdot THF$ yields, after hydrolysis, the expected alcohol. The reduction reported here is unusual in that (a) it involves no hydrolysis stage and (b) it results in the direct reduction of an acetyl to an ethyl group. A possible reaction scheme is shown in Scheme 1.

SCHEME 1



We suggest that the initial interaction involves BH_3 coordination at the carbonyl oxygen followed by hydride migration to give V, a sequence analogous to that proposed [3] for the BH_3 reduction of an aliphatic aldehyde or ketone. At this stage we propose that a second BH_3 molecule becomes coordinated, either at the BH_2-substituted oxygen atom (route A) or at the metal centre (route B). The metal—ethyl complex could then be formed by decomposition of either VI or VII, and the observed metal-hydrido complex could be produced from VI via a hydride shift to the metal centre. This behaviour contrasts with that observed [3] with an aliphatic aldehyde or ketone in that in the latter cases the labile monoalkoxyborine (VIII) undergoes further reaction either to form a polymer or, via interaction with a second carbonyl compound, to produce the dialkoxyborine (IX):



(VIII) (IX)

R = alkyl; R_1 = alkyl or H

The presence of the metal centre, together with its associated ligands, in V makes reaction with a second coordinated carbonyl to give a complex analogous to IX extremely unlikely on steric grounds. Further, it creates new reaction possibilities by either providing an alternative site for BH_3 coordination (route B), or increasing the electron density at the carbonyl oxygen to such an extent as to enable it to coordinate a second BH_3 unit (route A). Although there are, as yet, no reports of metal—acetyl—BH_3 complexes, it has been shown [13] that Group VII metal-carbonyl anions of the type $[M(CO)_5]^-$, M = Re or Mn, and $[Mn(CO)_4PPh_3]^-$ interact with BH_3 to give monoborane complexes in which the BH_3 is coordinated to the metal. Further, it has been found [11] that these monoborane complexes are readily hydrolysed in water or dilute acid to give boric acid and $HM(CO)_5$.

^1H *NMR spectra of complexes of the type* $(\pi\text{-}C_5H_5)(CO)LFeC_2H_5$*, where L = tertiary-phosphine or tertiary-phosphite*

The ^1H NMR spectra of the iron—ethyl complexes merit further comment, as striking differences in these spectra are observed as a function of the ligand L. With the ligands L = PMe_2Ph, $P(OPh)_3$ or $P(CH_2Ph)_3$ the protons of the ethyl group appear as one unresolved multiplet at about 1.5 ppm; whereas with L = PPh_3 the spectrum of the ethyl group consists of three perfectly resolved multiplets arising from proton A, the CH_3 group and proton B at 1.88, 1.59 and 1.08 ppm, respectively (see Fig. 1). A difference between the chemical shifts of the methylene protons is to be expected as they are adjacent to a chiral centre. However, the magnitude of the difference in coupling constant between the two methylene protons and the phosphorus nucleus of the PPh_3 [$^3J(^{31}P\text{—}H_A) = 2$ Hz and $^3J(^{31}P\text{—}H_B) = 12$ Hz] is, at first sight, somewhat surprising.

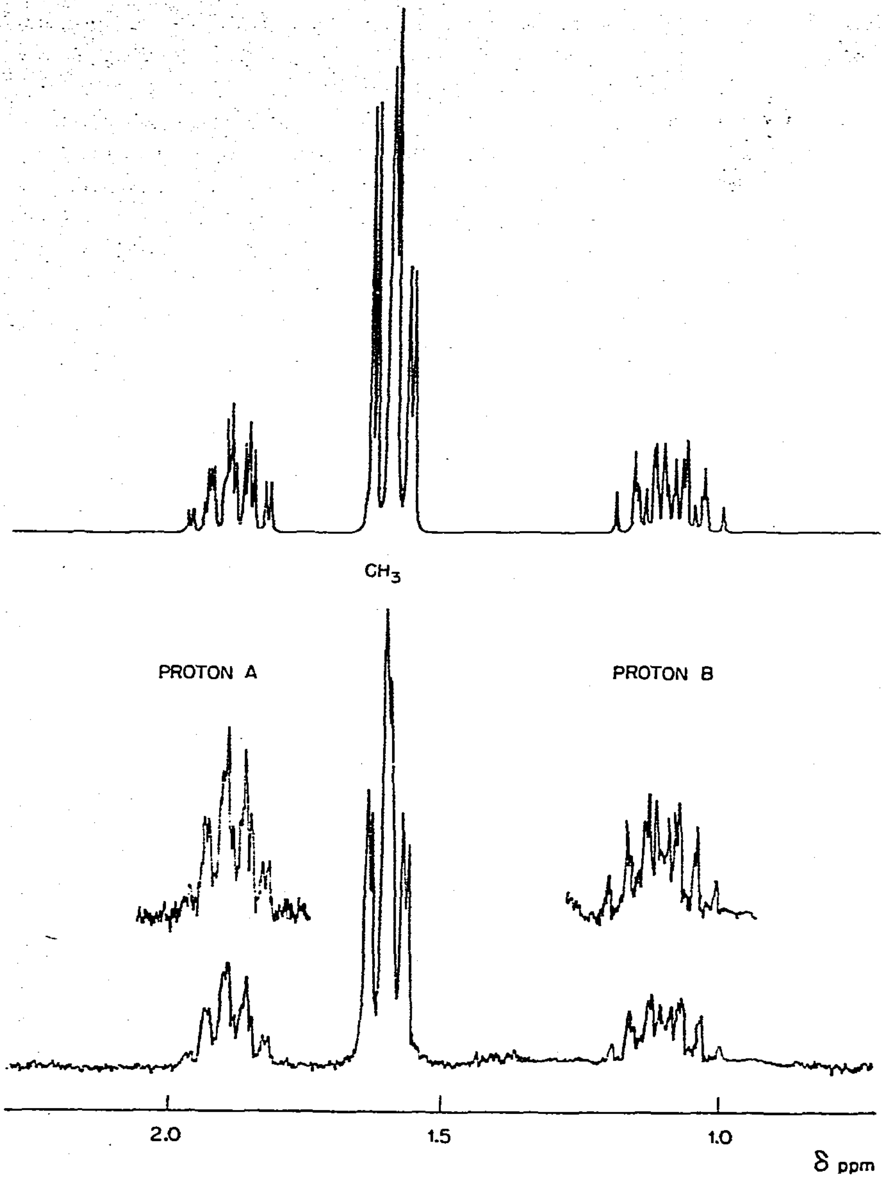
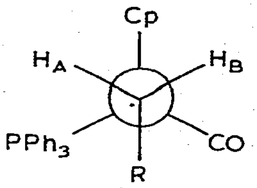
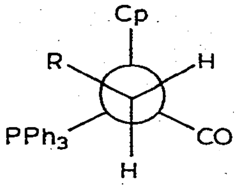


Fig. 1. 220 MHz ^{1}H NMR spectrum of the ethyl protons of (π-C_5H_5)(CO)(PPh_3)$FeCH_AH_BCH_3$ in C_6D_6 together with the simulated spectrum obtained using the data given in Table 1.

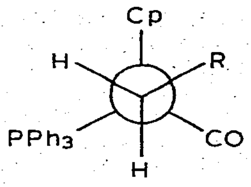
By direct analogy with the extensive work of Baird et al. [14] on systems of type (π-C_5H_5)(CO)$LFeCH_2R$ (L = phosphine donor; R = Ph, $SiMe_3$, 1-naphthyl) we suggest that these differences arise from hindered rotation about the iron—carbon bond; and that of the three possible conformations (X, XI and XII) X is favoured, with H_B (*trans* to PPh_3) giving rise to the larger P—H coupling constant (12 Hz for R = CH_3 and 10 Hz for R = Ph). We exclude XI on steric grounds, and XII on the basis of the observed differences in P—H coupling constants.



(X)



(XI)



(XII)

Cp = π-C_5H_5 ; R = CH_3 or Ph

With the other complexes examined, i.e. with L = PMe_2Ph, $P(OPh)_3$ or $P(CH_2Ph)_3$, we suggest that as a consequence of the lower steric requirements of these ligands compared to PPh_3 there is free rotation about the iron—ethyl bond leading to an "averaged" ^1H NMR spectrum at ambient temperature. Our attempts to "freeze out" this rotation by decreasing the temperature proved unsuccessful; we observed no significant changes in the NMR spectrum within the temperature range +25 to —50°C.

Experimental

The complexes used in this study were prepared by previously reported methods [6,8,9,15-24]. B_2H_6 and B_2D_6 were prepared by the action of either $NaBH_4$ or $NaBD_4$, respectively, on $BF_3 \cdot Et_2O$ in diglyme [25]. ^1H NMR spectra were recorded using either a Bruker WH 90 or a Varian 220 HR spectrometer. Reduction of the acetyl complexes was carried out in an NMR tube either by passing B_2H_6 through a solution of the acetyl complex in tetrahydrofuran-d_8 or benzene-d_6, or by adding a $BH_3 \cdot$ THF solution to the acetyl complex. Details are given below.

Reductions in benzene-d_6 or tetrahydrofuran-d_8

$NaBH_4$ (152 mg, 4 mmoles) in diglyme (4 ml) was added slowly to $BF_3 \cdot Et_2O$ (1 ml, 5 mmoles). The resulting gas was passed via a trap at —80°C through a solution of the acetyl complex (0.1 mmole) in either benzene-d_6 or tetrahydrofuran-d_8 (0.5 ml). The ^1H NMR spectrum of the resulting mixture showed formation of the ethyl complex with, in some cases, concurrent hydrido formation (see above).

Reductions with THF $\cdot$ BH_3

THF $\cdot$ BH_3 (0.5 ml, 0.1 *M* soln. in THF) was added to the acetyl complex (0.1 mmole) in an NMR tube. The ^1H NMR spectrum of the resulting mixture showed the degree of acetyl reduction.

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