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PROTONATION OF THE METAL—METAL BOND IN $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ COMPLEXES ($A = A' = SC_6H_5$, $P(C_6H_5)_2$, $P(CH_3)_2$, $A = SC_6H_5$, $A' = P(C_6H_5)_2$; $L = P(C_6H_5)_{3-n}(CH_3)_n$).

III *. EXPERIMENTAL STUDY OF THE INFLUENCE OF THE A AND A' BRIDGES ON THE BASICITY OF THE METAL—METAL BOND **

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Summary

In order to check the influence of the bridges on the basicity of the metal—metal bond in $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ complexes, the compounds with $A = A' = SC_6H_5$, $P(C_6H_5)_2$, $P(CH_3)_2$, $A = SC_6H_5$, $A' = P(C_6H_5)_2$ and $L = P(CH_3)_{3-n}(C_6H_5)_n$ (n = 0—3) have been prepared IR and PMR spectroscopic results are interpreted in structural terms, and show that the $Fe_2(SC_6H_5)(P(C_6H_5)_2)(CO)_4L_2$ complexes are non rigid on the NMR time scale for n = 0, 1 Replacement of the first SC_6H_5 bridge by a $P(C_6H_5)_2$ bridge markedly increase the basicity of the metal—metal bond, but replacement of the second SC_6H_5 bridge has no significant effect

We recently showed that in $(Fe(\mu\text{-}SCH_3)(CO)_2L)_2$ complexes the basicity of the ligand *trans* to the metal—metal bond has a great influence on the nucleophilicity of the metal—metal bond [1] With the aim of determining the bridge influence on the nucleophilic power of the metal—metal bond we have now synthesized $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ complexes with $A = A' = SC_6H_5, P(C_6H_5)_2$, $P(CH_3)_2$, $A = SC_6H_5$, $A' = P(C_6H_5)_2$, $L = P(C_6H_5)_{3-n}(CH_3)_n$, and have investigated their ease of protonation.

Experimental

All reactions were performed under nitrogen. IR spectra were recorded on a Perkin—Elmer 225 apparatus and proton NMR spectra on Varian A60A or

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* For part II see ref 18

** Dedicated to Prof H Normant on the occasion of his 72nd birthday on June 25th 1979

Brucker WH90 spectrometers The ligands $P(CH_3)_3$ [2] $P(CH_3)_2C_6H_5$ [3] $P(C_6H_5)_2CH_3$ [3], $(P(CH_3)_2)_2$ [4], $(P(C_6H_5)_2)_2$ [5] were prepared by literature methods. $P(C_6H_5)_2SC_6H_5$ was prepared from $P(C_6H_5)_2Cl$ and C_6H_5SNa $P(C_6H_5)$ was of commercial origin $(Fe(\mu\text{-}P(CH_3)_2)(CO)_3)_2$ [6] and $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_3)_2$ [7] were prepared according to published procedures $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_6$, previously described by Thompson et al [7] was synthesized by a different method, ultraviolet irradiation with a high pressure mercury vapor lamp (Original Hanau TQ 150) of a mixture of two mol of $Fe(CO)_5$ with one mol of $P(C_6H_5)_2SC_6H_5$ in benzene the dinuclear complex was obtained in 35% yield. $(Fe(\mu SC_6H_5)(CO)_3)_2$ was prepared by treatment of $Fe_2(CO)_9$ with C_6H_5SH in benzene at room temperature [8]

Preparation of $(Fe(\mu\text{-}SC_6H_5)(CO)_2L)_2$ complexes

(a) $L = P(CH_3)_3$ and $P(CH_3)_2C_6H_5$ a stoichiometric amount of L is added to a solution of $(Fe\text{-}\mu\text{-}SC_6H_5(CO)_3)_2$ in benzene and the solution is stirred at room temperature for 1 h The solvent is evaporated and recrystallization from CH_2Cl_2/pentane gives $(Fe(\mu\text{-}SC_6H_5)(CO)_2P(CH_3)_3)_2$ as dark red crystals m p 135°C (80% yield). Anal. Found C, 44.26, H, 4.86, P, 10.46 $C_{22}H_{28}Fe_2O_4P_2S_2$ calcd.: C, 44.44; H, 4.71; P, 10.43%, $(Fe(\mu\text{-}SC_6H_5)(CO)_2P(CH_3)_2C_6H_5)_2$ as dark red crystals, m.p. 115°C (80% yield) Anal Found C, 53.50 H, 4.54 P 8.73 $C_{32}H_{32}Fe_2O_4P_2S_2$ calcd . C, 53.48, H, 4.45, P, 8.63%

(b) $L = PCH_3(C_6H_5)_2$· A solution of $(Fe(\mu\text{-}SC_6H_5)(CO)_3)_2$ (0.2 g) and of $PCH_3(C_6H_5)_2$ (0.16 ml) is refluxed in toluene for 5 h Evaporation of solvent under vacuum and recrystallization from CH_2Cl_2/pentane mixture gives $(Fe(\mu\text{-}SC_6H_5)(CO)_2P(C_6H_5)_2CH_3)_2$ as dark red crystals, m p 160°C (60% yield) Anal. Found C, 59.76; H, 4.41; P 7.58 $C_{42}H_{36}Fe_2O_4P_2S_2$ calcd C, 59.85, H, 4.27; P, 7.36%.

Preparation of $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_2L)_2$ compounds $L = PCH_3(C_6H_5)_2$, $P(C_6H_5)_3$

A solution of $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_3)_2$ and a slight excess of the ligand is irradiated by a water cooled high pressure mercury vapour lamp (Original Hanau TQ 150) and the progress of the reaction is monitored by recording infrared spectra. Recrystallization from CH_2Cl_2/pentane gives·

(i) $Fe(\mu\text{-}P(C_6H_5)_2(CO)_2P(C_6H_5)_2CH_3)_2$ as carmine red crystals solvated by 1 mol of CH_2Cl_2, m.p. 200°C (dec.) (45% yield). Anal. Found C, 61.45, H, 4.46, P, 11.46. $C_{27}H_{23}FeO_4P_2$, CH_2Cl_2 calcd. C, 61.16, H, 4.44, P 11.21%

(ii) $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_2P(C_6H_5)_3)_2$, 0.6 CH_2Cl_2, m p. 95°C (dec) Found C, 66.23, H, 4.42, P, 10.36. $C_{64}H_{50}Fe_2O_4P_4$, 0.6 CH_2Cl_2 calcd C, 66.31, H, 4.37; P, 10.35%

Preparation of $(Fe(\mu\text{-}P(CH_3)_2)(CO)_2P(C_6H_5)_3)_2$ [9]

A solution 0.3 g of $(Fe(\mu\text{-}P(CH_3)_2)(CO)_3)_2$ and 0.39 g of $P(C_6H_5)_3$ in benzene is irradiated with the mercury vapour lamp for one day. The solvent is evaporated and the residue recrystallized from CH_2Cl_2/pentane to give $(Fe(\mu\text{-}P(CH_3)_2)(CO)_2P(C_6H_5)_3)_2$ as brick red crystals in 65% yield

Preparation of $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4L_2$ complexes

The disubstituted compounds can be made in refluxing benzene (L =

$P(CH_3)_3$) and in refluxing toluene (L = $P(CH_3)_2C_6H_5$ and $P(C_6H_5)_2CH_3$). For L = $P(C_6H_5)_3$ photochemical activation is necessary. Recrystallization was from pentane for L = $P(CH_3)_3$ and CH_2Cl_2/pentane for the other compounds.

$Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4(P(CH_3)_3)_2$ dark red crystals, m.p. 140°C (60% yield). Anal. Found: C, 50.27, H, 4.94, P, 13.92, S, 4.68. $C_{28}H_{33}Fe_2O_4P_3S$ calcd.: C, 50.14, H, 4.92, P, 13.88, S, 4.77%.

$Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4(P(CH_3)_2C_6H_5)_2, CH_2Cl_2$, m.p. 95°C (40% yield). Anal. Found: C, 53.20, H, 4.39, P, 10.52, Cl, 7.89. $C_{38}H_{37}Fe_2O_4P_3S, CH_2Cl_2$ calcd.: C, 53.24, H, 4.43, P, 10.35, Cl, 8.07%.

$Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4(P(C_6H_5)_2CH_3)_2$, m.p. 180°C (dec.) (40% yield). Anal. Found: C, 61.68, H, 4.63, P, 10.15. $C_{48}H_{41}Fe_2O_4P_3S$ calcd.: C, 62.74, H, 4.46, P, 10.13%.

$Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4(P(C_6H_5)_3)_2$, m.p. 200°C (dec.) (50% yield). Anal. Found: C, 65.13, H, 4.31, P, 8.89, S, 3.05. $C_{58}H_{45}Fe_2O_4P_3S$ calcd.: C, 66.79, H, 4.31, P, 8.92, S, 3.07.

General procedure for protonation of the complexes

An excess of 60% aqueous perchloric acid is added to a solution of the $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ compound in methanol. The mixture is stirred for 10 min, and deaerated distilled water is added until a precipitate appears. The solution is filtered, and the precipitate washed with water and dried under vacuum. For L = $P(C_6H_5)_2CH_3$ and $P(C_6H_5)_3$ the neutral compounds are not sufficiently soluble in methanol, and CH_2Cl_2 is added to increase the solubility. After addition of perchloric acid and stirring, the solution is under vacuum evaporated to dryness and the residue is dissolved in methanol. The subsequent procedure is as before. Recrystallization was from CH_2Cl_2/diethyl ether. Some of the compounds crystallize with molecules of solvent, the number of which depend on the drying time. In all cases the yield is near 90%.

The analytical and physical data for the protonated complexes are listed in Table 1.

Results and discussion

$Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ complexes

Although the reactions of $Fe_2(SR)_2(CO)_6$ with phosphines are well known (see for instance ref. 10), the chemistry is less developed in the case of PR_2 bridges and has not been explored in the case of the mixed bridge compound $Fe_2(\mu SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_6$. From the point of view of ease of replacement of CO groups this compound is very similar to $Fe_2(SR)_2(CO)_6$ complexes.

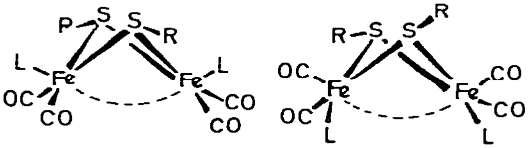
Structure of the $(Fe(\mu\text{-}SC_6H_5)(CO)_2L)_2$ complexes

The replacement of carbonyl groups in $(Fe(\mu\text{-}SC_6H_5)(CO)_3)_2$ by ditertiary phosphines or tertiary phosphines has been extensively studied by the Beer and Haines [11]. They have shown that in the case of tertiary phosphines and phosphites two types of structures exist for the disubstituted complexes (Fig. 1). In Table 2 we list infrared data for the $\nu(CO)$ stretching region and the proton NMR constants of the compounds. We see that when L = $P(CH_3)_3$ there are four infrared active bands which is consistent with structure II. This structure

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE PROTONATED COMPLEXES

Complex	Molecular formula	Colour	M p (°C)	Analysis (Found (calcd)(%))			
				C	H	Cl	P
$[Fe_2(\mu\ SC_6H_5)_2(CO)_4(P(CH_3)_3)_2H]^+[ClO_4]^-$	$C_{22}H_{29}ClFe_2O_8P_2S_2$	orange crystals	122	37 38 (38 01)	4 09 (4 17)	5 95 (5 08)	8 32 (8 92)
$[Fe_2(\mu\ SC_6H_5)_2(CO)_4(P(CH_3)_2C_6H_5)_2H]^+[ClO_4]^-$	$C_{32}H_{33}ClFe_2O_8P_2S_2$	red crystals	93	45 47 (45 60)	4 13 (3 96)	7 39 (7 19)	7 57 (7 27)
$[Fe_2(\mu\ P(C_6H_5)_2)_2(CO)_4(P(C_6H_5)_2CH_3)_2H]^+[ClO_4]^-$	$C_{56}H_{47}ClFeO_8P_4$	orange crystals	165 (expl)	59 19 (59 20)	4 26 (4 29)	3 23 (3 22)	11 10 (11 32)
$[Fe_2(\mu\ P(CH_3)_2)_2(CO)_4(P(C_6H_5)_3)_2H]^+[ClO_4]^-$, 0 1 CH_2Cl_2, 0 25 $(C_2H_5)_2O$	$C_{44}H_{43}ClFe_2O_8P_4$, 0 1 CH_2Cl_2, 0 25 $(C_2H_5)_2O$	yellow orange	130 (dec)	54 00 (54 07)	4 56 (4 51)	4 12 4 13	12 36 (12 28)
$[Fe_2(\mu\ SC_6H_5)(\mu\ P(C_6H_5)_2(CO)_4(P(CH_3)_3)_2H]^+[ClO_4]^-$	$C_{28}H_{34}ClFe_2O_8P_3S$	dark red	115	43 90 (43 60)	4 57 (4 41)	5 44 (4 58)	11 67 (12 07)
$[Fe_2(\mu\ SC_6H_5)(\mu\ P(C_6H_5)_2)(CO)_4(P(CH_3)_2C_6H_5)_2H][ClO_4]^-$	$C_{40}H_{44}ClFe_2O_8P_3S$	orange brown	85	50 83 50 97	4 47 (4 21)	4 05 (3 91)	10 20 (10 38)
$[Fe_2(\mu\ SC_6H_5)(\mu\ P(C_6H_5)_2)(CO)_4(P(C_6H_5)_2CH_3)_2H]^+[ClO_4]^-$, CH_2Cl_2, 0 5 $(C_2H_5)_2O$	$C_{45}H_{46}ClFe_2O_8P_3S$ CH_2Cl_2, 0 5 $(C_2H_5)_2O$	orange	107 (dec)	53 80 (53 66)	4 41 (4 29)	9 28 (9 33)	8 20 (8 15)



I II

Fig. 1

is also consistent with the fact that the $P(CH_3)_3$ proton resonance is a doublet. For the $P(CH_3)_2C_6H_5$ compounds there are five infrared active bands, which suggests a mixture of two isomers and the proton NMR spectrum shows three signals, one of the $X_6AA'X'_6$ type and two doublets The first signal is consistent with structure I because Haines et al. have shown that virtual coupling occurs [11] The two other doublets of the same intensity are in accord with structure II, since in this case there is no plane of symmetry through the Fe—P bond The same mixture is found for the $P(C_6H_5)_2CH_3$ compound

TABLE 2

IR AND PMR PARAMETERS FOR THE $Fe_2AA(CO)_4L_2$ COMPLEXES

	ν(CO) in hexadecane solution	^{1}H NMR [a]		
		τ(Ph) (ppm)	τ(CH_3) (ppm)	J(PH) (Hz)
$(FeSC_6H_5(CO)_2P(CH_3)_3)_2$	1990m 1952s 1923m 1910w	3	8 5	9
$(FeSC_6H_5(CO)_2P(CH_3)_2C_6H_5)_2$	1994vs 1956vs 1940m 1926s 1912m	2 9	8 2 8 3 8 05	8 5(d) 8(d) 8 [b]
$(FeSC_6H_5(CO)_2P(C_6H_5)_2CH_3)_2$	2000s 1988(sh) 1960s 1945m 1935m 1920w	2 7	7 75 8	7 [b] 8(d)
$(FeP(C_6H_5)_2(CO)_2P(C_6H_5)_2CH_3)_2$	1955m 1920vs 1887s 1875(sh)	3	8 6	8(d)
$(FeP(C_6H_5)_2(CO)_2P(C_6H_5)_3)_2$	1960m 1925s 1885s 1880(sh)			
$(FeP(CH_3)_2(CO)_2P(C_6H_5)_3)_2$	1984s 1975s 1942vs 1926m 1914s		9 1	11(t)
$Fe_2SC_6H_5P(C_6H_5)_2(CO)_4(P(CH_3)_3)_2$	1995m 1980s 1952w 1940(sh) 1933s (br) 1916s 1887w	2 9	8 47 [c]	8(d)
$Fe_2SC_6H_5P(C_6H_5)_2(CO)_4(P(CH_3)_2C_6H_5)_2$	1995s 1977m 1952w, 1940(sh) 1955s (br) 1914m 1890w	2 9	8 3 [c]	7(d)
$Fe_2SC_6H_5P(C_6H_5)_2(CO)_4(P(C_6H_5)_2CH_3)_2$	1986s 1938m 1925s 1990s 1942m 1926m 1885(sh) [a]	2 84	7 97 [c]	6 2 [b]
$Fe_2SC_6H_5P(C_6H_5)_2(CO)_4(P(C_6H_5)_3)_2$	1990s 1947m, 1925m 1905(sh) [a]			

[a] In CH_2Cl_2 solutions [b] $X_nAA'X_n$ type spectra [c] Parameters at 38°C and 60 MHz

Structure of $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_2L)_2$ and $(Fe(\mu\text{-}P(CH_3)_2)(CO)_2P(C_6H_5)_3)_2$ complexes

For L = $P(C_6H_5)_2CH_3$ and $P(C_6H_5)_3$ the two complexes have four infrared active (Table 2) bands, which is consistent with a structure of type II This is confirmed by the H NMR spectrum of the $P(C_6H_5)_2CH_3$ complex which shows a doublet for the methyl resonance

The $(Fe(\mu\text{-}P(CH_3)_2)(CO)_2P(C_6H_5)_3)_2$ compound shows five infrared active bands (Table 2), which suggests the presence of isomers The proton NMR spectrum shows only one triplet at 60 MHz for the $P(CH_3)_2$ resonance These two observations can be only explained if the molecule is non rigid on the NMR time scale, as was recently observed for $Fe_2(\mu\text{-}PR_2)_2(CO)_5PR_3$ [12] and $Fe_2(\mu\text{-}PR_2)_2(CO)_6$ complexes [13], but its low solubility precludes variable temperature proton NMR studies.

Structure of $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2(CO)_4L_2$ complexes

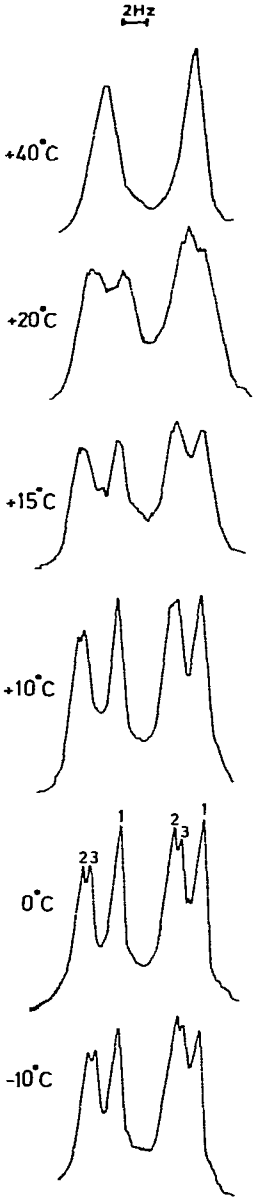
The complexes with L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$ have complex infrared spectra in the ν(CO) stretching frequencies region (Table 2) which suggests a mixture of isomers. At room temperature the 60 MHz PMR spectrum in the PCH_3 region shows a broad doublet for each compound The discrepancy between these two observations can be explained by the presence of non rigid molecule on the NMR time scale, and we carried out a variable temperature proton NMR study.

In the case of L = $P(CH_3)_3$ three doublets appear near 0° C (Fig 2). This can be explained either by the presence of two isomers one of which has two non equivalent ligands or by the presence of three isomers The first hypothesis seems unrealistic because in all the isomers known for $Fe_2A_2(CO)_4L_2$ compounds, the monodentate ligands are always symmetrically disposed [10]. With the second possibility one isomer would be of type I and the two other isomers of type II, with the $P(CH_3)_3$ ligands in one case *trans* to the $P(C_6H_5)_2$ bridge and in the other *trans* to the SC_6H_5 bridge

For L = $P(CH_3)_2C_6H_5$ the phenomenon is complicated by the dissymmetry of the ligand but the variation of the proton NMR signals with temperature suggests that only two isomers are present in this case (Fig 3) For L = $P(C_6H_5)_2CH_3$ the complex shows three infrared active bands in accord with a rigid structure of type I. This is corroborated by the proton NMR spectrum which shows a $X_3AA'X'_3$ pattern for the CH_3 resonance. For L = $P(C_6H_5)_3$, the complex is too insoluble to be examined in hexadecane solution. The infrared spectra in CH_2Cl_2 of the complexes with L = $P(C_6H_5)_2CH_3$ and $P(C_6H_5)_3$ show the same pattern and a structure of type I is suggested for the latter compound

In summary, the $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4L_2$ complexes are non rigid on the NMR time scale for L = $P(CH_3)_3$ and $P(CH_3)_2C_6H_5$. This phenomenon has been observed for $Fe_2(\mu\text{-}A)_2(CO)_6$ complexes with A = $P(CH_3)_2$, $As(CH_3)_2$ [13], S-t-C_4H_9 [14]: but this is the first example for distributed $Fe_2A_2(CO)_2$-L_2 molecules. Unfortunately the presence of phenyl groups on sulfur and phosphorus bridges prevents the study of their exchange behaviour even though the phenyl resonance signals are also temperature dependent.

For L = $P(C_6H_5)_2CH_3$ and $P(C_6H_5)_3$ the complexes are rigid at room temperature on the NMR time scale. This difference is attributed to steric crowding with the last two ligands.



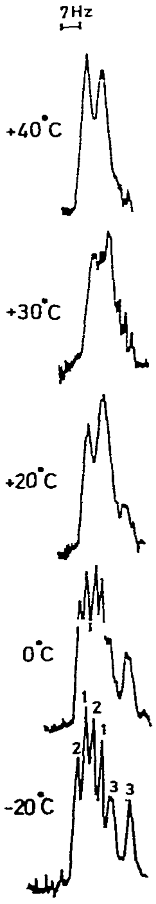


Fig 2 Variable temperature 60 MHz proton NMR spectra of $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4\text{-}(P(CH_3)_3)_2$($PCH_3$ resonance) at various temperatures

Fig 3 Variable temperature 60 MHz proton NMR spectra of $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4\text{-}(P(CH_3)_2C_6H_5)_2$ (PCH_3 resonance) at various temperatures

Structure of the protonated complexes

The infrared spectra for the ν(CO) stretching region and the proton NMR data are listed in Tables 3 and 4 The protonated derivatives of $(Fe(\mu\text{-}SC_6H_5)(CO)_2P(C_6H_5)_2CH_3)_2$, $(Fe(\mu\text{-}P(C_6H_5)_2)(CO)_2P(C_6H_5)_3)_2$ and

TABLE 3

IR AND PMR PARAMETERS FOR THE $[Fe_2(\mu\text{-}A)_2(CO)_4L_2H]^+$ COMPLEXES

A	L	^1H NMR in CH_2Cl_2 solution (ppm)					CO frequencies (cm^{-1}) (CH_2Cl_2 solution)
		$\tau(PC_6H_5)$	τ(PCH)	$J(PCH_3)$ (Hz)	τ(H)	J(PH) (Hz)	
SPh	PMe_3	2 7	8 25(d)	10	24 63(t)	4	2046s 2029m 1949s
SPh	PMe_2Ph	2 7	8(d)	10	25 91(t)	4 4	2045s 2029m 1994s
SPh	$PMePh_2$	2 65	7 74(d)	9 5	25 96(t)	4 4	2047s 2030m 1995s
PPh_2	$PMePh_2$	2 47	8 43(d)	8 8	24 33(tt)	50(J_2) 15 5(J_1)	2030(sh) 2015s 1971s
PPh_2	PPh_3	2 41			23 99(tt)	50 7(J_2) 12 7(J_1)	2030(sh) 2020s 1972s
PMe_2	PPh_3	2 5	7 91 ^{a} 9 08 ^{a}	11 0 12 50	25 74(tt)	48 5(J_2) 14 7(J_1)	2030(sh) 2016s 1970s

^{a} X part of X_n AA X_n spin system

$Fe_2(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}SC_6H_5)(CO)_4(P(C_6H_5)_3)_2$ complexes have not been isolated, the usual isolation procedure giving only the starting material. In these cases the spectroscopic properties of the protonated forms were determined in a mixture of CH_2Cl_2 and CF_3COOH

All the protonated complexes show a signal in the τ 23—27 range characteristic of a hydride in bridging position [15] For the $(Fe(\mu\text{-}A)(CO)_2L)_2$ complexes the resonance appears as a triplet for A = SC_6H_5 or a triplet of triplets for A = $P(C_6H_5)_2$ or $P(CH_3)_2$ (Fig. 4) as a result of the coupling with two equivalent nuclei of phosphorus (A = SC_6H_5) or two sets of two equivalent nuclei of phosphorus (A = PR_2). Furthermore the infrared spectra in the ν(CO) stretching region show three bands consistent with a C_{2v} symmetry for the molecule We suggest for these $[(Fe(\mu\text{-}A)(CO)_2L)_2H]^+$ complexes the structure we pro-

TABLE 4

IR AND PMR PARAMETERS FOR $[Fe_2(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}SC_6H_5)(CO)_4L_2H]^+$

L	^1H NMR in CH_2Cl_2 solution (ppm)					CO frequencies (cm^{-1}) (CH_2Cl_2 solution)
	τ(Ph)	τ(PCH)	$J(PCH_3)$ (Hz)	τ(H)	J(PH) (Hz)	
PMe_3	2 54	8 11(d)	9 5	24 34(dt)	37 9(J_2) 2 0(J_1)	2040m 2020s 1982s
		8 37(d)	10 0	26 26(d)	45 8(J_2)	
PMe_2Ph	2 45	8.15(d)	9.5	24 15(dt)	37 5(J_2) 20(J_1)	2037m 2020s 1984s
		8 17(d)	9 5			
		8 21(d)	8 8	26 63(d)	44 8(J_2)	
		8 30(d)	10			
$PMePh_2$	2 59	8 16	8 8	23 47(dt)	38 9(J_2) 19 1(J_1)	2040m, 2022s 1985s
PPh_3	2 63			23 38(dt)	38 2(J_2) 16 9(J_1)	2040m(sh) 2025s, 1985s

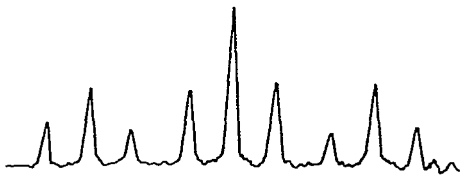


Fig 4 Hydride resonance of [(Fe$_2$(μ-P(CH$_3$)$_2$)$_2$(CO)$_4$(P(C$_6$H$_5$)$_3$)$_2$H]$^+$

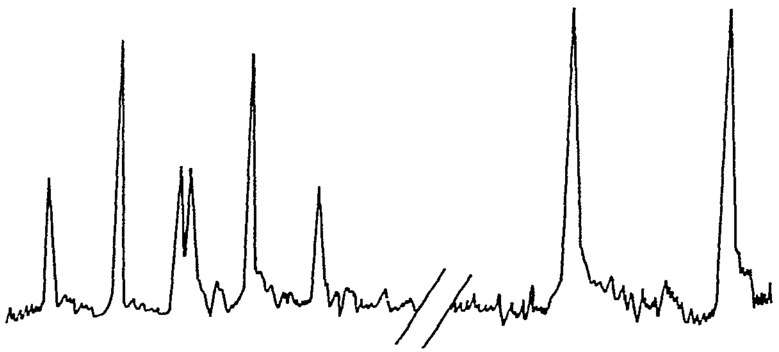
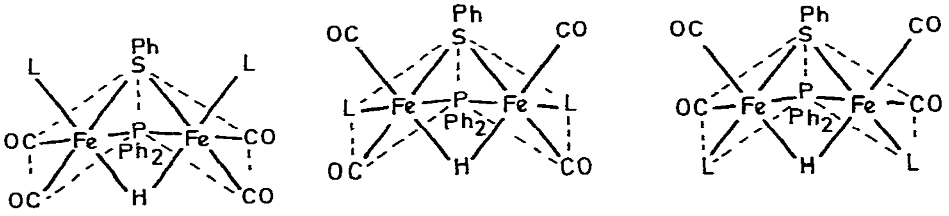


Fig 5 Hydride resonance of [Fe$_2$(μ-SC$_6$H$_5$)(μ-P(C$_6$H$_5$)$_2$(CO)$_4$ (P(CH$_3$)$_3$)$_2$H]$^+$



I IIa IIb

Fig 6 Proposed structures for the Fe$_2$(μ-SC$_6$H$_5$)(μ-P(C$_6$H$_5$)$_2$(CO)$_4$L$_2$ complexes (L = P(CH$_3$)$_3$ P(CH$_3$)$_2$C$_6$H$_5$)

TABLE 5

RESULTS OF THE PROTONATION OF Fe$_2$(μ-A)(μ-A')(CO)$_4$L$_2$ COMPLEXES ((+) IRREVERSIBLE, (—) REVERSIBLE)

	PMe$_3$	PMe$_2$Ph	PMePh$_2$	PPh$_3$
A = A = SCH$_3$	+	+	—	—
A = A' = SC$_6$H$_5$	+	+	—	—
A = SC$_6$H$_5$ A = P(C$_6$H$_5$)$_2$	+	+	+	—
A = A' = P(C$_6$H$_5$)$_2$			+	—
A = A' = P(CH$_3$)$_2$				+

posed for $[(Fe(\mu\text{-}SCH_3)(CO)_2L)_2H]^+$ from spectroscopic data [1] This structure was corroborated by X-ray structural analysis [16] for $L = P(CH_3)_2C_6H_5$ In this structure the hydride bridges the two iron atoms and the L ligands are *trans* to the M—H—M bond.

For the $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4L_2$ compounds the results are more complex. With $L = P(CH_3)_3$ and $P(CH_3)_2C_6H_5$ the high field resonance appears as two signals (Fig 5) (1) a double triplet, which can be explained by coupling with the two equivalent nuclei of the phosphine ligands and the nucleus of the bridging phosphorus (2) a doublet which only can be explained if we assume the presence of a second isomer in which the phosphorus ligand is only weakly coupled to the bridge hydride. This is confirmed by the fact that the methyl resonances appear as two doublets for $L = P(CH_3)_3$ and two sets of two doublets for $L = P(CH_3)_2C_6H_5$. Thus we propose the three structures for the protonated complexes (Fig 6). For the second isomer, it is difficult to choose between IIa or IIb, but on steric grounds IIa seems more probable

For $L = PCH_3(C_6H_5)_2$ and $P(C_6H_5)_3$, as with the neutral complexes there only is one isomer, and the hydride resonance appears as a double triplet The coupling between the bridge phosphorus and the hydride is greater than that with the phosphorus ligands, and so for the symmetrical $(Fe(\mu\text{-}PR_2)(CO)_2L)_2$ complexes we assign J_1 to coupling between the hydride and the phosphorus ligands and J_2 to coupling with the phosphorus bridges.

Nucleophilicity of the metal—metal bond and nature of the bridging ligands

In Table 5 we summarize the data on reversibility of the protonation of complexes $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$. These show that replacement of one SC_6H_5 bridge by one $P(C_6H_5)_2$ bridge markedly increase the basicity of the metal—metal bond. It is relevant to note that the increase in basicity of the $Fe_2(\mu\text{-}SC_6H_5)(\mu\text{-}P(C_6H_5)_2)(CO)_4L_2$ complexes leads to stabilization of the isomers with the phosphine ligands *cis* to the M—H—M bond However replacement of the second SC_6H_5 bridge by $P(C_6H_5)_2$ has no significant effect Only the $P(CH_3)_2$ bridges are sufficient basic to give a stable protonated form from $(Fe(\mu\text{-}P(CH_3)_2)(CO)_2P(C_6H_5)_3)_2$. These results are in good agreement with an electrochemical study of $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_6$ complexes [17] which shows that the ease of electrochemical oxidation increases from $A = A' = SC_6H_5$ to $A = A' = P(CH_3)_2$.

References

1 K. Fauvel, R Mathieu and R Poilblanc, Inorg Chem 15 (1976) 976
2 F G. Mann and A F. Wells J Chem. Soc , (1938) 702
3 P.R. Blomfield and K. Parvin, Chem. Ind. (London) (1959) 541
4 G.W. Parshall, J. Inorg. Nucl Chem 14 (1960) 291
5 W. Kuchen and H. Buchwald, Chem. Ber , 91 (1958) 2871.
6 R.G. Hayter, Inorg. Chem , 3 (1964) 711.
7 B.E. Job, R.A.N. McLean and D T. Thompson J. Chem. Soc , Chem Commun (1966) 895
8 J.A de Beer and R J Haines, J Organometal Chem , 24 (1970) 757
9 D.T. Thompson, J Organometal Chem , 4 (1965) 74
10 J.A. de Beer, R.J. Haines, R. Greatrex and N.N. Greenwood, J. Chem. Soc A (1971) 3271 and ref therein.
11 J.A. de Beer and R.J. Haines J. Organometal. Chem 36 (1972) 297

12 T C Flood F J Disanti and K D Campbell Inorg Chem 17 (1978) 1643
13 R D Adams F A Cotton W R Collen D L Hunter and L Mihichuck Inorg Chem 14 (1975) 1395
14 G Natile L Maresca and G Bor Inorg Chim Acta 23 (1977) 37
15 H D Kaesz and R B Saillant Chem Rev 72 (1972) 231
16 J M Savariault J J Bonnet R Mathieu and J Galy C R Acad Sci Ser C (1977) 663
17 R Mathieu R Poilblanc P Lemoine and M Cross J Organometal Chem 165 (1979) 343