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Reactions of Fe^{III} with $LiAlH_4$ and $LiBH_4$ in the presence of bis(diphenylphosphino)methane (dppm) and CO. The crystal and molecular structures of *trans*-[Fe(Cl)(CO)(η^2-dppm)$_2$] [$FeCl_4$], *trans*-Fe(H)$_2$(η^2-dppm)$_2$ and *cis*-[Fe(η^2-S_2CH)(η^2-dppm)$_2$]BF_4

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Abstract—Reactions between Fe^{III}, dppm, CO as appropriate and $LiAlH_4$ produce the Fe^{II} complexes *trans*-[Fe(Cl)(CO)(η^2-dppm)$_2$][$FeCl_4$]. (**1a**) *trans*-[Fe(H)$_2$(η^2-dppm)$_2$] (**2**) and *trans*-[Fe(H)(Cl)(η^2-dppm)$_2$] (**3**), depending upon the reaction conditions. The *trans* octahedral structures, with chelating dppm ligands, of **1a** and **2** have been established by X-ray crystallography. Compound **2** reacts with CO to produce the Fe^0 complex Fe(CO)$_3$(η^1-dppm)$_2$ (**4**), identified by NMR spectrometry, and with $H_2/HBF_4 \cdot Et_2O$ to give the dihydrogen complex *trans*-[Fe(H)(η^2-H_2)(η^2-dppm)$_2$]BF_4 (**5**). The dihydrogen can be replaced with, for example, CO and CH_3CN to give *trans*-[Fe(H)(L)(η^2-dppm)$_2$]BF_4 (L = CO, **6**, and L = CH_3CN, **7**, respectively). With CS_2, insertion into the Fe—bond of **5** occurs to produce the dithioformato complex *cis*-[Fe(η^2-S_2CH)(η^2-dppm)$_2$]BF_4 (**8**), the structure of which is also reported. © 1997 Elsevier Science Ltd

Keywords: bis(diphenylphosphino)methane; dihydrogen complex; hydrido complexes; iron(II) complexes; tetrahydroaluminate reductions; X-ray structures.

The great versatility of dppm as a ligand plays an important role in the formation of many metal(I)- and (0)—CO—dppm complexes, which have been obtained from reductions of the +2 states of metals such as Ni [1], Co [2] and Pd [3] by $NaBH_4$ in the presence of CO and dppm. The majority of products which have been isolated are dinuclear (or higher oligomers), the formation of which is made possible by bridging dppm ligands. In almost every case, bis(diphenylphosphino)ethane, dppe, behaves fundamentally differently in the above reactions and acts as a chelating (mostly) or monodentate ligand. Iron(II) is considerably more difficult to reduce than the metal ions mentioned above. For example, reactions between Fe^{II}, dppm and CO result in the formation of Fe^{II} species containing both CO and the phosphine [4] and even reactions of Fe^{II} with $NaBH_4$ in the presence of phosphines lead to no reduction of the Fe [5]. Consequently, the chemistry of Fe^{I} is less well developed than that of the +1 states of the other metals mentioned above and the production of Fe^{I}-phosphine complexes apparently requires the presence of a stronger reducing agent, such as Na [6]. Reducing agents such as Mn [7], ethoxydiethylaluminum [8] and dialkyl magnesium [9] will reduce Fe^{III} and Fe^{II} to Fe^0 in the presence of phosphines and there are numerous reports of Fe^0 complexes of dppm (and other phosphines) and CO formed by substitution reactions of the various iron carbonyls [10].

In general, the complexes obtained from reactions involving $NaBH_4$ contain hydrido and/or dihydrogen

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ligands and such complexes are of considerable current interest [11,12]. We are aware of only one such complex with dppm [12], namely *trans*-$[Fe(H)(\eta^2\text{-}H_2)(\eta^2\text{-dppm})_2]^+[X]^-$, although little is known about its chemistry. We now report results from reactions between Fe^{III} and Fe^{II}, dppm and $LiAlH_4$ or $LiBH_4$, in the presence (or absence) of CO as part of a general plan of assessing the generality of this synthetic route to metal—CO—dppm complexes.

EXPERIMENTAL

Reagents and solvents

$FeCl_2 \cdot 4H_2O$, $FeCl_3$, dppm, $NaBH_4$, $LiAlH_4$, $LiAlD_4$, $HBF_4 \cdot Et_2O$ and $HClO_4$ were obtained from Aldrich. CO was purchased from Matheson. $HBF_4 \cdot Et_2O$ (48%) and $LiBH_4$ were obtained from Strem and the latter was recrystallized according to published procedures [13]. $FeCl_3$ and the reducing agents were stored under nitrogen. When necessary, $FeCl_3$ was purified by heating the hydrated salt under reflux with $SOCl_2$ [14]. Benzene, THF and ether were dried by distillations from Na wire, CH_2Cl_2 and acetone were dried over activated molecular sieves and CH_3CN was distilled from P_2O_5. In addition, all solvents were degassed prior to use.

Physical measurements

Both samples and reagents were handled under an inert atmosphere during weighing and data collection. Microanalyses for C, H and N were acquired in our laboratories using a Control Equipment Corporation model 240XA analyzer using V_2O_5 as a combustion aid. IR spectra (for Nujol mulls between NaCl plates and in solution) were recorded on either a Beckman IR-4250 or a Bruker IFS-66 FT–IR spectrophotometer. ^1H and ^{31}P ^1H NMR spectra were recorded on a Bruker AC-E 200 spectrometer. Chemical shifts are reported as δ values with positive shifts for ^1H downfield of the signal of Me_4Si (TMS) while those for ^{31}P are downfield of the signal of external 85% H_3PO_4. For the ^{31}P NMR spectra, a frequency lock was provided by a coaxial D_2O insert in instances where undeuterated solvents were used.

Synthesis of the compounds

All syntheses were carried out under a flow of either pure nitrogen or carbon monoxide. In the latter case, CO was passed at a rate of approximately 5 bubbles s^{-1}. Reactions involving $LiAlH_4$ were under anhydrous conditions. Isolation and recrystallization procedures were carried out in a nitrogen-filled glove box.

Preparation of trans-$[Fe(Cl)(CO)(\eta^2\text{-dppm})_2][FeCl_4]$ **(1a)**

(a) From $FeCl_3$, dppm, CO and $LiAlH_4$: Solutions of $FeCl_3$ (0.47 g, 2.9 mmol) in THF (10 cm^3) and dppm (2.2 g, 5.8 mmol) in benzene (15 cm^3) were mixed and CO was bubbled through the resulting dark green solution for 30 min; no visible change was observed. $LiAlH_4$ (0.028 g, 0.72 mmol) was dissolved in THF (3 cm^3) and added to this solution over a period of 2–3 min. The solution foamed vigorously, turned deep red and, when filtered, produced a bright orange solid and a deep red filtrate. The former was recrystallized from acetone/hexanes (1 : 1, 40 cm^3) by slow diffusion over 24 h yielding bright orange crystals suitable for a single crystal X-ray structural determination. Additional crystals appeared in the filtrate over the same time period. The two fractions were combined, washed with hexanes and dried under reduced pressure. Yield 33–38%. IR: ν(CO) 1962 (vs), 1918 (vw, sh); ν(Fe—Cl) 379 (s, br) cm^{-1}. ^{31}P ^1H NMR (25°C, acetone): δ 10.3 (singlet). The ^1H NMR signals (25°C, acetone) were severely broadened due to the presence of paramagnetic $FeCl_4^-$ in solution. Found: C, 56.7; H, 4.1. Calc. for $Fe_2Cl_5P_4OC_{51}H_{44}$: C, 56.5; H, 4.1%.

(b) From $FeCl_2 \cdot 4H_2O$, dppm and CO: Solutions of $FeCl_2 \cdot 4H_2O$ (0.52 g, 2.6 mmol) in THF (10 cm^3) and dppm (2.0 g, 5.2 mmol) in benzene (15 cm^3) were mixed and CO was passed (for 30 min) through the resulting dark green solution which slowly turned deep orange. The solid was isolated as described in (a) above.

(c) From $FeCl_3$, dppm, $LiBH_4$ and CO: This reaction is similar to that described in (a). The Fe : dppm : BH_4^- ratio used was 1 : 2 : 1.5 and the $LiBH_4$ was added as a solution in ether to a THF/benzene mixture of $FeCl_3$ and dppm.

(d) From $FeCl_3$, dppm and CO: The $FeCl_3$ and dppm (1 : 2 molar ratios) solutions [see (a)] were mixed and heated under reflux for 30–45 min under CO. The product was isolated and purified as in (a) in comparable yields.

Preparation of trans-$[Fe(Cl)(CO)(\eta^2\text{-dppe})_2][FeCl_4]$ **(1b)**

Complex **1b** was prepared in a manner similar to that described in (a) above for compound **1a**. Yield: *ca* 24%. IR: ν(CO) 1930 (vs), 1880 (w, sh); ν(Fe—Cl) 379 (s, br) cm^{-1}. ^{31}P ^1H NMR (25°C, acetone): δ 60.1 (singlet). Signals in the ^1H NMR spectrum of **1b** were broadened as observed for **1a**. Found: C, 57.5; H, 4.5. Calc. for $Fe_2Cl_4P_4OC_{53}H_{48}$: C, 57.2; H, 4.4%.

Preparation of trans-$[Fe(H)_2(\eta^2\text{-dppm})_2]$ **(2)**

$FeCl_3$ (0.45 g, 2.8 mmol) and dppm (2.1 g, 5.5 mmol) were dissolved in THF (10 cm^3) and benzene

(15 cm^3), respectively, and mixed to form a dark green solution. $LiAlH_4$ (0.19 g, 5.0 mmol) was dissolved in THF (5 cm^3) and added over a 2 min period. The mixture foamed and turned first light orange and, eventually, deep purple–black after all the reducing agent had been added. The solution was filtered and red crystals formed in the filtrate over a 1–2 day period. These were filtered off, washed successively with 10 cm^3 portions of ether, benzene and again ether before being dried under reduced pressure. Yield: 10–16%. Crystals of **2** produced in this manner were found to be suitable for a single-crystal X-ray structural determination. IR: ν(Fe—H) 1711 (s) cm^{-1}. ^{31}P ^{1}H NMR (25°C, CH_2Cl_2): δ 24 (singlet). ^{1}H NMR (25°C, CH_2Cl_2): δ -7 (Fe—H, broad). Found: C, 72.9; H, 5.6. Calc. for $FeP_4C_{50}H_{46}$: C, 72.7; H, 5.6%. The stability of **2** is very sensitive to the presence of water, but it is stable for long periods in the solid state in a dry, inert, atmosphere and in solution in dry CH_2Cl_2, acetone and benzene for more than 1 h. It decomposes quickly in CH_2CN and THF even when dry.

Preparation of trans-[Fe(H)(Cl)(η^2-dppm)$_2$]·$2C_4H_8O$ (3)

$FeCl_3$ (0.29 g, 1.78 mmol) and dppm (1.37 g, 3.56 mmol) were mixed and dissolved in THF (20 cm^3). A slurry of $LiAlH_4$ (0.068 g, 1.78 mmol) in THF (5 cm^3) was added over 2–3 min causing foaming and forming a deep, dark red (almost black) solution. After filtration, a deep reddish-purple microcrystalline solid was obtained, as a THF solvate, from the filtrate over a 24 h period. The solid was washed successively with 10 cm^3 portions of acetone, ethanol, acetone and, finally, pentane, before drying under reduced pressure. Larger crystals of compound **3** may be obtained (as twinned crystals) from the filtrate (over 24 h) if the $FeCl_3$ and dppm are initially dissolved in a 1 : 1 mixture of THF/benzene (20 cm^3). Yield: 15–21%. Complex **3** is insoluble in aromatic hydrocarbon solvents, alcohols, acetone, THF, CH_3CN and DMSO, and sparingly soluble in halogenated solvents and DMF (**3** has the greatest stability in CH_2Cl_2 and CH_3I, and decomposes rapidly in $CHCl_3$, $C_2H_2Cl_4$, $C_2H_4Cl_2$ and DMF). IR: ν(Fe—H) 1889 (wk, br); ν(Fe—Cl) 370 (wk) cm^{-1}. ^{31}P ^{1}H NMR (25°C, CD_2Cl_2): δ 24.2 (singlet). ^{1}H NMR (25°C, CD_2Cl_2): δ 4.92 and 4.62 (PCH^aH^bP, poorly resolved); δ -21.2 (Fe—H, quintet, $^2J_{PH} = 46$ Hz). Found: C, 69.1; H, 6.0. Calc. for $FeClP_4OC_{58}H_{61}$: C, 69.4; H, 5.6%. The presence of solvent was confirmed spectroscopically.

Preparation of trans-[Fe(CO)$_3$(η^1-dppm)$_2$] (4)

Compound **2** (0.13 g, 0.16 mmol) was suspended in CH_2Cl_2 (18 cm^3) and CO passed for 30 min, turning the solution dark reddish brown. The reaction solution was filtered and small brown crystals were obtained from the filtrate after 24 h. Yield 17%. The crystals were insoluble in all solvents tried except for dimethylformamide, in which decomposition rapidly occurred. IR (Nujol): ν(CO) 1978 (w), 1882 (w, br), 1868 (w, br). IR (CH_2Cl_2 reaction filtrate): ν(CO) 1985 (s), 1900 (s, sh), 1897 (s, br), 1832 (s) cm^{-1}. ^{31}P ^{1}H NMR (25°C, reaction filtrate): 12 line AA′XX′ pattern centred at δ_A 74.8 (dt) and δ_X -25.5 (dt, coupling constants are from the simulated spectrum using the Bruker PANIC program: $^2J_{AX} = 71.1$ Hz, $^2J_{AA'} = 31.1$ Hz, $^4J_{AX'} = 0.6$ Hz, $J_{XX'} = 0$ Hz).

Preparation of trans-[Fe(H)(η^2-H_2)(η^2-dppm)$_2$][BF_4] (5)

A suspension of finely ground **2** (0.25 g, 0.30 mmol) in dry THF (10 cm^3) saturated with H_2 (*ca* 10 min) was stirred for *ca* 10–20 s under H_2, producing a reddish-purple solution. An excess of $HBF_4 \cdot Et_2O$ (0.1 cm^3, 0.68 mmol) was then added dropwise, with stirring, producing a precipitate within 1–2 min. Ether (10 cm^3) was added and the pure yellow solid was recovered, washed with 3 successive portions of ether (5 cm^3) and then dried briefly under reduced pressure (decomposition occurs over longer periods). Yield 95–100%. IR: ν(Fe—H) 1645 (br, s) cm^{-1}, no ν(HH) was observed. ^{31}P ^{1}H NMR (25°C, CD_2Cl_2): δ 32.5 (singlet); ^{1}H NMR (25°C, CD_2Cl_2): δ -4.0 (broad singlet, Fe—H_2), δ -7.21 (quintet, Fe—H, $^2J_{PH} = 44$ Hz). Found: C, 65.5; H, 5.5. Calc. for $FeF_4P_4BC_{50}H_{47}$: C, 65.7; H, 5.2%. The compound quickly decomposes in acetone, THF, benzene and ethanol and more slowly in CH_2Cl_2 making recrystallization impractical.

Preparation of trans-[Fe(D)(η^2-HD)(η^2-dppm)$_2$][BF_4] (5a)

The procedure is similar to that for **5** except $Fe(D)_2$(η^2-dppm)$_2$ was used as the starting material (prepared as for **2** except that $LiAlD_4$ was used). HD (prepared by reacting NaH with D_2O) was bubbled through THF (10 cm^3) for 5 min. FeD_2(η^2-dppm)$_2$ (0.24 g, 0.288 mmol) was then added and the suspension was stirred under HD for about 1 min. An excess of $HBF_4 \cdot Et_2O$ (0.1 cm^3, 0.679 mmol) was added and the remaining procedure is as described for **5**. ^{31}P ^{1}H NMR (25°C, CD_2Cl_2): δ 32.6. ^{1}H NMR (-25°C, CD_2Cl_2): δ -3.93 (triplet, Fe—HD, $^1J_{HD} = 30.0$ Hz).

Preparation of trans-[Fe(H)(CO)(η^2-dppm)$_2$][BF_4] (6)

The procedure is the same as used for **5** except that the reaction was carried out under CO, yielding a pale yellow solid. Yield: *ca* 100%. IR: ν(CO) 1944 (s), 1904 (wk, sh) cm^{-1}, ν(Fe—H) 1710 (wk) cm^{-1}. ^{31}P ^{1}H NMR (25°C, acetone-d_6): δ 31.6. ^{1}H NMR (25°C, acetone-d_6): δ 5.05 and 4.69 (PCH^aH^bP, poorly resolved); δ -2.03 (Fe—H, quintet, $^2J_{PH} = 44.4$ Hz). Found: C, 65.4; H, 4.4. Calc. for $FeF_4P_4BOC_{51}H_{45}$: C, 65.1; H, 4.8%.

Preparation of trans-[Fe(H)(CH$_3$CN)(η^2-dppm)$_2$][BF$_4$] (7)

Compound **5** (0.037 g) was dissolved in dry CH_3CN (10 cm^3) to form an orange–red solution. Dry ether (50 cm^3) was careful layered over the solution producing crystals over a 24 h period. These were separated, washed with ether and dried under pressure. Yield: 90%. IR: ν(Fe—H) 1880 (wk), ν(CN) 2250 cm^{-1}. ^{31}P ^1H NMR (25°C, CD_2Cl_2: δ 29.8 (singlet). ^1H NMR (25°C, CD_2Cl_2: δ 4.31 and 4.79 (PCH^aH^bP, poorly resolved); δ 1.44 (singlet, Fe—NCCH_3); δ -13.7 (quintet, Fe—H, $^2J_{PH} = 44.0$ Hz). Found: C, 65.5; H, 4.9; N, 1.3. Calc. for $FeF_4P_4BNC_{52}H_{48}$: C, 65.5; H, 5.1; N, 1.5%.

Preparation of cis-[Fe(S$_2$CH)(η^2-dppm)$_2$][BF$_4$] (8)

An excess of CS_2 (40 cm^3) was added to a suspension of **5** (0.13 g, 0.14 mmol) in THF (10 cm^3) and the mixture stirred for 24 h. The solution turned dark violet–red and was evaporated down to dryness under reduced pressure to give a violet residue. Recrystallizing the violet solid by slow diffusion from CH_2Cl_2/hexane (10 and 40 cm^3, respectively) over a 24 h period gave a small quantity of a mixture of crystalline products containing two components; one dark purple (**8**), the other, orange–red and of unknown composition. A crystal of **8**, separated from the mixture by hand, was found to be suitable for a structural determination. Repeated attempts to separate the mixture by fractional crystallization were unsuccessful, as were attempts to isolate sufficient pure **8** manually for satisfactory analysis and more detailed spectroscopic evaluation. IR (mixture, Nujol): ν(CS, due to **8**) 1282 cm^{-1}. The mixture is soluble in CH_2Cl_2 acetone and CH_3CN. ^{31}P ^1H NMR [25°C, $(CD_3)_2CO$]: modified A_2B_2 pattern (see discussion) at δ_A 9.8 and δ_B 14.9 due to **8**; singlet at δ 7.9 due to the unidentified component of the mixture. Integration shows that the two components are present in approximately equal quantities.

X-ray crystallography

X-ray crystallographic data collection was carried out on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo-K_α radiation. Unit-cell parameters were obtained by least-squares analysis of 25 low-angle reflections. The stabilities of the crystals, which were protected from atmospheric moisture, were measured by monitoring periodically three standard reflections; no systematic intensity variations were observed. Intensity data were corrected for Lorentz and polarization factors and absorption corrections were applied to **8**.

The Fe atom in each complex was located by direct methods and all remaining atoms were found by cycles of Fourier and difference-Fourier calculations. Calculated ideal positions of the H atoms on the phenyl and methylene C atoms of dppm were included but not refined. The approximate location of the H atom of the dithioformate ligand in **8** was found on the Fourier map. An ideal calculated position was included, but not refined. The hydride ligands in **2** were located in the Fourier map and refined along with other atoms. In **8**, all atoms except H and F were refined with anisotropic thermal displacement parameters and the BF_4^- anion is disordered.

Relevant data concerning the crystals, data collection and structure solution are found in Table 1. Atomic scattering factors were taken from tabulated values [15]. Calculations were performed on a 486 PC using NRCVAX [16] and SHELX [17] programs.

Supplementary X-ray materials, including atomic coordinates and thermal parameters, have been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

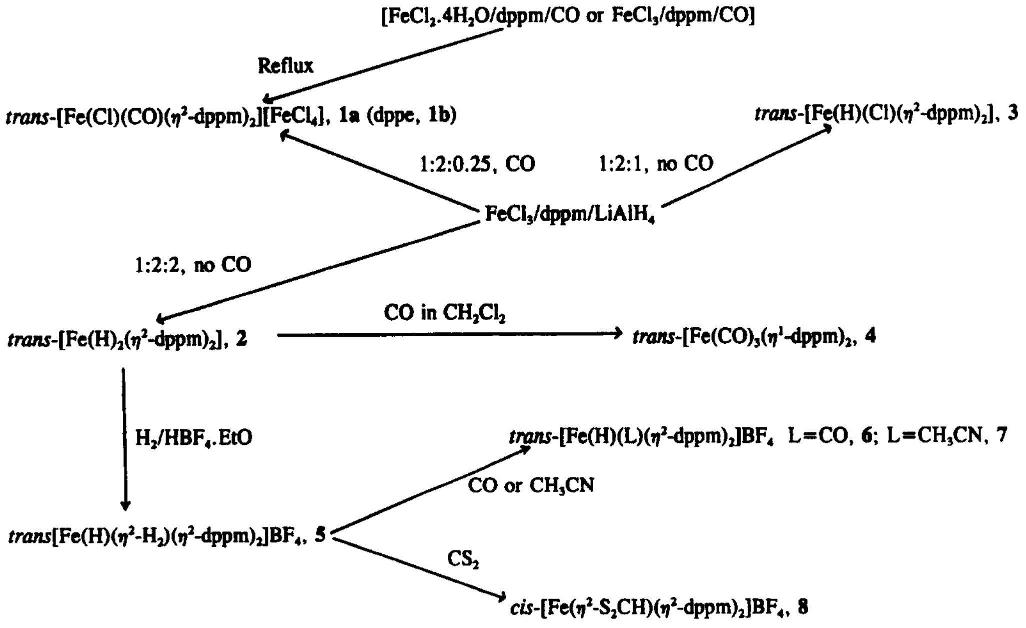
Although $LiBH_4$ and $NaBH_4$ readily reduce Fe^{III} to Fe^{II} (as does CO and dppm), it has proved to be surprisingly difficult to reduce the Fe^{II} and this is fully in keeping with the work of others [5] in related reactions. These reactions, typically between Fe^{II}, phosphine and $NaBH_4$, have generally been very successful in producing Fe^{II} complexes containing coordinated H^-, H_2 or BH_4^- and a variety of phosphines other than dppm. We find that similar reactions involving dppm and either Fe^{III} or Fe^{II} are generally less successful than with other phosphines. For this reason, and in the expectation of further reducing the iron, $LiAlH_4$ was used as the main reducing agent. This has the added advantage of being a better source of H^-, which plays an important role in iron chemistry. It was surprising therefore that no evidence for the reduction of Fe to an oxidation state lower than (II) was observed as a direct result of using this much stronger reducing agent. Some of the preparative chemistry is summarized in Scheme 1. Note that in reactions using $LiAlH_4$, the ratio of Fe:dppm was held constant at 1:2, but that the product formed is dependent upon the amount of reducing agent.

It is interesting that compound **1a** is formed slowly when the (initial) deep green solutions of $FeCl_3$ and dppm are heated under reflux in the presence of CO in the absence of either $LiBH_4$ or $LiAlH_4$. However, when small amounts of $LiBH_4$ or $LiAlH_4$ are added to the $FeCl_3$/phosphine/CO mixtures, there is a smooth and very rapid production of **1a** and **1b**. Although known compounds [18] of the type

Table 1. Crystal data and structure refinement for *trans*-[Fe(Cl)(CO)(η^2-dppm)$_2$][$FeCl_4$] (**1a**), *trans*-Fe(H)$_2$(η^2-dppm)$_2$ (**2**) and *cis*-[Fe(η^2-S_2CH)(η_2-dppm)$_2$]BF_4 (**8**)

Empirical formula	$C_{51}H_{44}Cl_5Fe_2OP_4$ (**1a**)	$C_{50}H_{46}FeP_4$ (**2**)	$C_{51}H_{45}BF_4FeP_4S_2$ (**8**)
Formula weight	1085.69	826.60	988.53
Temperature (K)	293(2)	293(2)	293(2)
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pcab*	$P2_1/c$	*Cc*
Unit Cell dimensions	$a = 20.12(2)$ Å $b = 20.214(5)$ Å $c = 25.159(7)$ Å	$a = 18.541(4)$ Å $b = 9.984(2)$ Å, $\beta = 90.82(3)^\circ$ $c = 22.410(4)$ Å	$a = 26.352(5)$ Å $b = 11.799(2)$ Å, $\beta = 132.98(3)^\circ$ $c = 21.924(4)$ Å
Volume ($Å^3$)	10232(11)	4148.0(14)	4987(2)
Z	8	4	4
Density (calculated) (g cm^{-3})	1.410	1.324	1.317
Absorption coefficient (mm^{-1})	0.990	0.553	0.563
F(000)	4440	1728	2040
Crystal size (mm)	$0.10 \times 0.25 \times 0.55$	$0.10 \times 0.30 \times 0.55$	$0.78 \times 0.73 \times 0.36$
Theta range for data collection (°)	1.62–23.97	1.10–24.05	1.9–27.97
Index ranges	$0 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 23$, $0 \leqslant l \leqslant 28$	$-21 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 25$	$-25 \leqslant h \leqslant 34$, $-15 \leqslant k \leqslant 15$, $-28 \leqslant l \leqslant 0$
Reflections collected	7982	6511	6162
Independent reflections	7982 ($R_{int} = 0.0000$)	6511 ($R_{int} = 0.0000$)	6162 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7982/0/568	6511/0/504	6162/44/558
Goodness-of-fit on F^2	0.938	0.805	1.011
Final *R* indices[a]	$R_1 = 0.0678$, $wR_2 = 0.1273$ $[4311 F_o > 4\sigma(F_o)]$	$R_1 = 0.0507$, $wR_2 = 1218$ $[4322 F_o > 4\sigma(F_o)]$	$R_1 = 0.0754$, $wR_2 = 0.1865$ $[4374 F_o > 4\sigma(F_o)]$
R indices (all data)	$R_1 = 0.1281$, $wR_2 = 0.1470$	$R_1 = 0.0836$, $wR_2 = 0.1392$	$R_1 = 0.1040$, $wR_2 = 0.2063$
Largest difference peak and hole (e $Å^{-3}$)	0.368 and -0.371	0.582 and -0.490	0.863 and -0.565

[a] $R_1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.



Scheme 1.

$FeCl_2(phosphine)_2$ (green) were neither isolated nor observed in ^{31}P NMR spectra of solutions containing Fe^{III} and phosphines (due to paramagnetism), it is not unreasonable that they are intermediates in the formation of **1a** and **1b**.

An ORTEP drawing of the structure of the cation component of **1a** is shown in Fig. 1. There is also an $FeCl_4^-$ anion, which is not shown. The cation contains a six-coordinated Fe^{II} atom in the plane of the four P atoms of two dppm ligands, with a Cl and a CO in the axial positions. Selected bond lengths and angles are shown in Table 2. The P—Fe—P angles in the chelating dppm ligands are only *ca* 74° and illustrates the considerable flexibility of dppm and the strain imposed on the four-membered Fe—P—C—P ring. The almost linear Cl—Fe—C—O arrangement is close to being orthogonal to the FeP_4 plane. Bond lengths are normal. The compound is analogous to well known complexes of the type $[Fe(H)(Y)(dppe)_2][X]$ (Y = CO, N_2, Me_2CO, MeCN, X = ClO_4, BPh_4 [19]; or Y = CNR, X = BF_4, PF_6 [20]) although these, apart from the complex in which Y = H_2 [21], have not been structurally characterized.

The strong absorptions in the IR spectra at 1962 (**1a**) and 1930 (**1b**) cm^{-1} are typical of terminally bound CO. Both complexes show peaks in the far IR at 379 (**1a**) and 386 (**1b**) cm^{-1} due [22] to $FeCl_4^-$, but the Fe—Cl vibration in each of the cations could not be assigned. The ^{31}P NMR spectra show singlets at δ 10.3 (**1a**) and δ 60 (**1b**) due to the chelating dppm and dppe ligands, respectively [23], but proton NMR signals were broad due to the presence of the paramagnetic $FeCl_4^-$.

When the Fe : dppm : $LiAlH_4$ ratio is increased from 1 : 2 : 0.25 (for **1a**) to 1 : 2 : 1, in the presence or absence of CO, a different product, identified as *trans*-$[Fe(H)(Cl)(\eta^2\text{-}dppm)_2]$, **3** (as a THF solvate), is formed (see Scheme 1). The IR spectrum of **3** shows a weak signal at 1889 cm^{-1}, which is comparable to that recorded for the Fe—H vibration in analogous complexes containing a variety of bidentate phosphines, including dppe [5a]. The presence of chelating dppm ligands and a *trans* stereochemistry of **3** in solution is supported by the following facts: (a) a singlet at δ 24.2 in the ^{31}P ^1H NMR spectrum, (b) signals (poorly resolved) of equal area at δ 4.92 and δ 4.62 in the ^1H NMR spectrum, due to the two inequivalent methylene protons of the dppm ligands and (c) a well resolved quintet at δ −21.2 ($^2J_{PH}$ = 46 Hz) in the ^1H NMR spectrum of **3**. Thus, **3** is analogous to the known dppe complex [5a,24].

By increasing the amount of $LiAlH_4$ even further (to 1 : 2 : 2 ratios) in these reactions, the deep purple complex *trans*-$[Fe(H)_2(\eta^2\text{-}dppm)_2]$ (**2**), is produced (see Scheme 1). It is an example of numerous complexes of the same type [5a,19,25,26]; of these, the dppe complex is prepared by the reaction of Fe^{II} with $NaBH_4$ in the presence of dppe [5a]. Once isolated, **2** is reasonably stable in the dry solid state but, in solution, it is very sensitive to traces of water and dry CH_2Cl_2 is the only solvent in which it is both soluble and stable. Crystals suitable for structural analysis

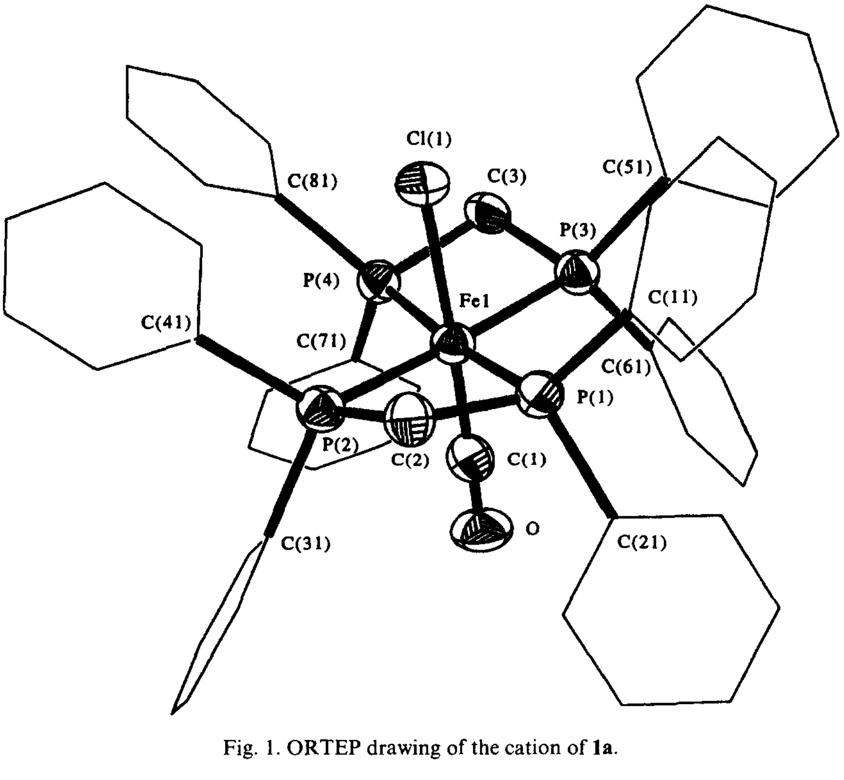


Fig. 1. ORTEP drawing of the cation of **1a**.

Table 2. Selected bond lengths (Å) and angles (°) for **1a**, **2** and **8**

For **1a**			
Fe(1)—C(1)	1.750(7)	C(1)—Fe(1)—P(1)	93.5(2)
Fe(1)—P(1)	2.290(2)	C(1)—Fe(1)—P(3)	92.6(2)
Fe(1)—P(3)	2.295(3)	P(1)—Fe(1)—P(3)	103.75(8)
Fe(1)—P(4)	2.299(2)	C(1)—Fe(1)—P(4)	92.0(2)
Fe(1)—Cl(1)	2.298(2)	P(1)—Fe(1)—P(4)	174.06(7)
Fe(1)—P(2)	2.316(3)	P(3)—Fe(1)—P(4)	73.65(7)
		C(1)—Fe(1)—Cl(1)	177.3(2)
		P(1)—Fe(1)—Cl(1)	88.88(7)
		P(3)—Fe(1)—Cl(1)	88.07(8)
		P(4)—Fe(1)—Cl(1)	85.71(7)
		C(1)—Fe(1)—P(2)	92.0(2)
		P(1)—Fe(1)—P(2)	73.97(7)
		P(3)—Fe(1)—P(2)	174.96(7)
		P(4)—Fe(1)—P(2)	108.17(7)
		Cl(1)—Fe(1)—P(2)	87.39(7)
For **2**			
Fe—P(2)	2.153(2)	P(2)—Fe—(P3)	175.88(7)
Fe—P(3)	2.160(2)	P(2)—Fe—P(1)	75.63(6)
Fe—P(1)	2.167(2)	P(3)—Fe—P(1)	104.39(6)
Fe—P(4)	2.172(2)	P(2)—Fe—P(4)	104.36(6)
Fe—H(1)	1.56(8)	P(3)—Fe—P(4)	75.85(6)
Fe—H(2)	1.50(8)	P(1)—Fe—P(4)	176.73(7)
		P(2)—Fe—H(1)	88(3)
		P(3)—Fe—H(1)	88(3)
		P(1)—Fe—H(1)	96(3)
		P(4)—Fe—H(1)	87(3)
		P(2)—Fe—H(2)	95(3)
		P(3)—Fe—H(2)	89(3)
		P(1)—Fe—H(2)	82(3)
		P(4)—Fe—H(2)	95(3)
		H(1)—Fe—H(2)	176(4)
For **8**			
Fe—P(2)	2.263(2)	P(2)—Fe—P(4)	102.22(10)
Fe—P(4)	2.270(2)	P(2)—Fe—P(3)	100.13(9)
Fe—P(3)	2.272(2)	P(4)—Fe—P(3)	74.49(9)
Fe—P(1)	2.274(2)	P(2)—Fe—P(1)	73.50(9)
Fe—S(2)	2.304(3)	P(4)—Fe—P(1)	174.26(9)
Fe—S(1)	2.317(3)	P(3)—Fe—P(1)	102.24(9)
S(1)—C(3)	1.656(14)	P(2)—Fe—S(2)	94.84(11)
S(2)—C(3)	1.661(14)	P(4)—Fe—S(2)	90.04(10)
		P(3)—Fe—S(2)	160.37(10)
		P(1)—Fe—S(2)	94.11(10)
		P(2)—Fe—S(1)	162.36(10)
		P(4)—Fe—S(1)	91.37(10)
		P(3)—Fe—S(1)	94.27(10)
		P(1)—Fe—S(1)	93.60(10)
		S(2)—Fe—S(1)	73.71(11)
		C(3)—S(1)—Fe	86.3(4)
		C(3)—S(2)—Fe	86.6(4)
		S(1)—C(3)—S(2)	113.3(6)

were obtained from the reaction filtrate. An ORTEP view of the molecule is shown in Fig. 2 and selected bond lengths and angles are shown in Table 2. The main features of the structure are an almost planar arrangement of the FeP_4(methylene C$)_2$ unit and an essentially linear H—Fe—H group [176(4)°] perpendicular to the former plane. The P—Fe—P angles in the chelating ligands are 75–76°, similar to those in **1a**. The average Fe—P bond length of 2.163 Å is considerably shorter (by 0.137 Å) than the corresponding average in **1a** and possibly reflects the greater ability of the $2H^-$ groups to withdraw electron density from the Fe^{II} centre compared with one Cl and one CO. Alternatively, it may simply be the small size of the hydride ligands, which is responsible for Fe—P bond contraction.

Complex **2** is only slightly soluble in dichloromethane and shows a sharp singlet at δ 24 in the ^{31}P ^{1}H NMR spectrum consistent with chelating dppm [23] and a *trans* arrangement of the hydride ligands. This arrangement, creating a strong *trans* effect, is probably responsible for the low value (1711 cm^{-1}) for ν(Fe—H) observed in the solid-state FT-IR spectrum.

It should be noted in passing that **2** differs from most similar dihydrides which assume *cis* geometries in the solid state. Another exception to this generally *cis* geometry is [27] *trans*-FeH_2(*meso*-tetraphos) which is similar in properties to **2**.

When a suspension of **2** in CH_2Cl_2 is saturated with CO, compound **4**, believed to be $Fe(CO)_3(\eta^1\text{-dppm})_2$, is formed in a reaction which has proved difficult to reproduce consistently. The product appears to be particularly difficult to crystallize and, while it is quite soluble in the reaction medium, it is extremely difficult to redissolve once the solid is formed. Good analytical data have not been obtained and the existence in solution of **4** is based on compelling NMR and IR data. The IR spectra of both the reaction filtrate and the isolated solid show (experimental) four peaks due to vibrations of terminally bound CO groups. The ^{31}P ^{1}H NMR spectrum (CH_2Cl_2) displays an AA′XX′ pattern of two six-line multiples (doublets or triplets) at δ_A 74.8 and at δ_X −25.5 ($^2J_{AX}$ = 71.1, $^2J_{AA'}$ = 31.1, $^4J_{AX'}$ = 0.6, $^6J_{XX'}$ = 0 Hz) consistent with two monodentate dppm ligands. This is generally a clean spectrum, although the solution sometimes exhibits a singlet at δ 14 due to the presence of an unknown species. There are several known complexes of the type $Fe(CO)_3(P)_2$ (P = η^1-dppe [10d,28]; PR_3 with R being alkyl or aryl groups [29a]), which are *trans* in the solid state [29b], and the splitting patterns and coupling constants for **4** are similar to those observed for the dppe complex [10d]. These compounds have been prepared either from Fe^0 carbonyls [10d,28] or from Fe^{II} reductions with a combination of CO under high pressure and PhLi [28]. In the case of **4** a possible mechanism for its formation (note that $LiAlH_4$ is not required in its synthesis) could involve the elimination of H_2 from **2** by CO. The above NMR data are therefore consistent with an iron coordinated by two monodentate dppm and three CO ligands. It has been proposed [30] that for d^8 transition metal complexes with D_{3h} symmetry, strong σ-donor phosphine ligands will tend to occupy axial positions, whereas strong π-acceptor CO ligands will generally occupy equatorial sites. $^2J_{\mathrm{P\,M\,P}}$ coupling constants for *trans* P atoms are

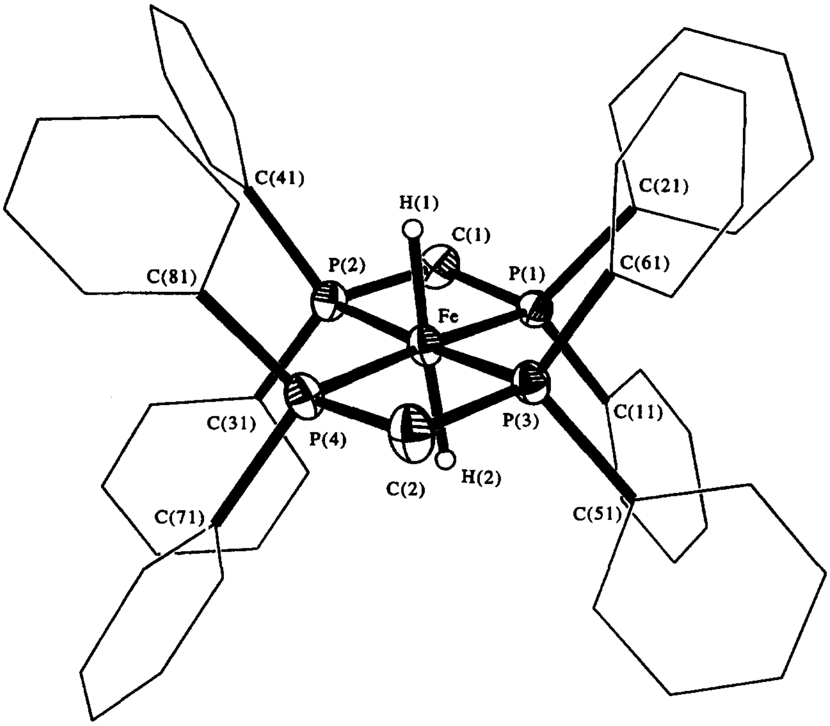


Fig. 2. ORTEP drawing of **2**.

normally significantly greater than for *cis* P atoms [31]. Thus, while a J_{PP} of 31.1 Hz for **4** compares with 30.4 Hz for the corresponding dppe complex (assigned a *trans* structure [10d]) these values might seem unusually low for such a structure. However, it has been observed [27] that for iron complexes, it is not unusual for *trans* P—P couplings to be smaller than the *cis* couplings.

Compound **2** undergoes additional interesting reactions. For example, it reacts with H_2/HBF_4 to produce *trans*-[Fe(H)(η^2-H_2)(η^2-dppm)$_2$][BF_4] (**5**), which has been reported briefly previously [12,32]. There are many known examples of coordinated H_2 complexes and this chemistry has been reviewed [11,12], with the dppe analog of **5** being particularly well studied. The ^{31}P ^{1}H NMR spectrum of **5** shows a singlet at δ 32.5, consistent with a *trans* arrangement of the dppm ligands in solution. (Care is necessary to ensure that the sample is not contaminated with **2**, δ 24.) The room temperature (298 K) ^{1}H NMR spectrum of **5** shows a broad singlet corresponding to the M—H_2 moiety (δ −4.0) and a quintet which corresponds to the terminal hydride ligand (δ −7.2), coupled with four equivalent phosphorus atoms ($^2J_{PH}$ = 44 Hz). Similar results, together with a somewhat different synthesis of the precursor **2**, have been reported elsewhere [32]. Between 298 and 200 K, the broadening of the dihydrogen signal is due to a decrease in T_2 [12]. There is no rapid intramolecular exchange between the H_2 and H^- at room temperature, which is somewhat unusual since in most cases, intramolecular exchange is usually frozen out at temperatures much lower than 293 K. Attempts to measure the coalescence temperature (when intramolecular exchange occurs between the H_2 and the H^- ligand) were unsuccessful because of the decomposition of **5** as the temperature was raised. Coupling between the H^- and the four P atoms was lost at about 310 K.

The $^1J_{HD}$ coupling constant for **5a**, containing the *trans*-[Fe(D)(η^2-HD)] unit, is 30.0 Hz, and the broad resonance of the dihydrogen ligand is now replaced with a 1 : 1 : 1 triplet. The chemical shift for this triplet (δ −3.93) is slightly downfield of the multiplet observed for the cation containing *trans*-[Fe(H)(η^2-HD)] (prepared in a similar fashion), found at δ −4.17, with a $^1J_{HD}$ of 28.1 Hz. This is consistent with the higher *trans* influence of D relative to H [12]. Correlation of J_{HD} with the H—H distance using the recently published [33] relationship $d(HH) = -0.0167J_{HD} + 1.42$ gives a calculated value of 0.92 Å. In fact, these results are quite similar to those obtained for the analogous dppe complex and its deuterium substituted derivatives [12]. In general, ν_{HH} is not observed in the IR spectra of dihydrogen complexes, as in the case with **5**.

The dihydrogen ligand of **5** is labile and can be replaced by a variety of other ligands (Scheme 1) to form complexes of the type *trans*-[Fe(H)(L)(η^2-dppm)$_2$][BF_4] (L = CO, **6**; L = CH_3CN, **7**). These appear to be simple substitution products and analogous dppe complexes are known [12].

When a suspension of **5** in THF is treated with a large excess of CS_2, a dark purple complex **8** is formed in small quantities together with approximately equal amounts (^{31}P NMR) of an as yet unidentified second component. Attempts to separate the mixture by a variety of approaches were unsuccessful but a crystal of **8**, shown by crystallography to be *cis*-[Fe(η^2-S_2CH)(η^2-dppm)$_2$][BF_4], was isolated by handpicking from the mixture. Crystal, data collection and refinement details and relevant bond lengths and angles to define the Fe centre are contained in Tables 1 and 2. An ORTEP drawing (Fig. 3) shows the three chelating ligands about a six-coordinated Fe atom. The BF_4^- anion in **8** is disordered. As in **1a** and **2**, it is clear that deviations from an octahedral geometry are due to the small angles within the chelating ligands, 74.49(9) and 73.50(9)° (PFeP), and 96.0(4) and 95.8(4)° (PCP) for the two dppm ligands and 73.7(1) (SFeS) and 113.3(6)° (SCS) for the S_2CH ligand. These in turn cause distortions of the angles across the octahedron, i.e. 174.26(9) for P(1)—Fe—P(4), 160.4(1) for P(3)—Fe—S(2) and 162.4(1) for P(2)—Fe—S(1). The Fe—P(1)—P(2)—C(1) and Fe—(P3)—(P4)—C(2) atoms of each dppm and the Fe—S(1)—S(2)—C(3) grouping of atoms is almost planar (rms deviations of each set of atoms from planarity are 0.067, 0.009 and 0.005 Å, respectively). The three characteristic planes of an octahedron containing Fe—P(1)—P(2)—S(1)—P(4), Fe—P(2)—P(3)—S(1)—S(2) and Fe—P(3)—P(4)—P(1)—S(2) deviate further from planarity, with an rms for each set of five atoms from their respective plane of 0.137, 0.230, and 0.142 Å, respectively.

Insertion of CS_2 into Fe—H [34a] and Fe—R [34b] bonds has been reported and the Fe—S bond lengths and angles in the FeSCS four-membered rings in **8** are similar to those observed previously in compounds of the type $C_5H_5Fe(dppm)S_2CR$ [34b].

The ^{31}P ^{1}H NMR spectrum of the mixture shows signals due to the non equivalent P atoms of the *cis* dppm ligands in **8** which approximates to an A_2B_2 pattern (δ 9.8 and 14.9; $^2J_{PP} = 51$ Hz) with further small splittings such that the signals show some of the characteristics of an AA′BB′ pattern. Therefore, the distortions from an ideal octahedral arrangement, arising from the presence of three four-membered rings, which are present in the solid state as shown by X-ray analysis, appear to persist in solution. A further singlet at δ 7.9 due to the second component of the mixture is also observed.

It is clear that reactions involving M^{x+}, dppm, CO and reducing agents are greatly dependent on the metal ion. For example, when $M^{x+} = Ni^{2+}$ [1], Co^{2+} [2] or $Pd^{2+,4+}$ [3] the major products involve either bridging or monodentate dppm and, usually, reduction to metal(0). There are also very significant differences when dppm is replaced by dppe. We have now shown that when $M^{x+} = Fe^{3+}$, dppm readily acts as a chelating ligand producing four-membered ring systems which are quite strained and that reduction of the Fe^{3+} stops at Fe^{2+}, at least with $LiAlH_4$. Furthermore, there is a remarkable similarity between the syntheses and formulations of the dppm complexes reported here and known dppe and dmpe complexes (made from reactions between Fe^{II}, phosphine and

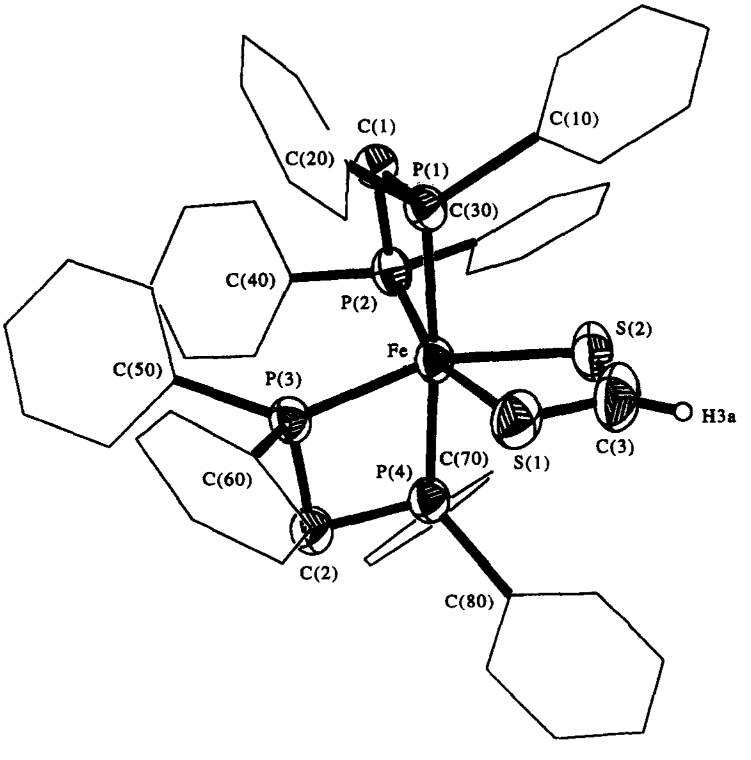


Fig. 3. ORTEP drawing of the cation of **8**.

$NaBH_4$ [5a] and between $FeCl_2(dmpe)_2$ and $LiAlH_4$ [18a]). While it is conceivable that Fe^0 is produced *in situ* and then undergoes oxidative addition, we have seen no evidence (^{31}P NMR) in the reaction solutions or filtrates for the formation of any of the known Fe^0/CO/dppm complexes [10] or of any other compounds except those identified.

Clearly some complexes (**1a** and **1b**) can be formed by reduction of Fe^{III} by the phosphine and CO. There are several known [18a,35] green complexes of the type $FeCl_2(diphosphine)_2$. Although no specific complex has been isolated [35b] from the dark green solutions containing $FeCl_3$ and dppm, it is likely that a similar compound is produced initially. $LiAlH_4$ simply increases the rate of reduction of the Fe^{III} and also reacts with residual water producing Al^{3+} which can then compete for Cl^- from the Fe (or from intermediate $FeCl_2$ complexes). In addition it is the source of H^- in the complexes formed in reactions where its concentration has been increased.

Additional reactions of **5** are under investigation.

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