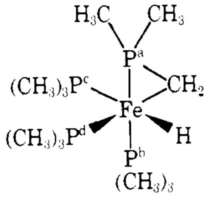
Phosphine Chemistry of Iron(0) and -(II)

Sir:

Recently we[1] described the first example of an iron(0) derivative with all phosphite ligands, $Fe[P(OCH_3)_3]_5$, and showed that a relatively high electron density on the iron atom tends to dominate the chemistry of this type of phosphite complex. In attempting to extend this chemistry to phosphine derivatives we have uncovered a chemistry that is qualitatively different from that of iron–phosphite complexes and one that affords facile access to a variety of new iron(0) and -(II) complexes.

Trimethylphosphine reacted with iron(II) chloride to form $FeCl_2[P(CH_3)_3]_2$.[2a] Reduction of this complex (argon atmosphere) was rapidly effected with sodium amalgam in a tetrahydrofuran medium containing excess trimethylphosphine at 0°. The reduced iron complex, purified by recrystallization from pentane and by vacuum sublimation at 25°, was in the form of yellow crystals[2b] that exhibited high thermal and air reactivity. Mass spectral analysis[2c] established the composition of the gaseous phase to be $Fe[P(CH_3)_3]_4$; major fragment ions were those represented by loss of one and of two trimethylphosphine ligands. The infrared spectrum (Nujol mull) showed a band at 1820 cm^{-1} that could be assigned to an Fe–H stretching vibration.[3] Collectively, ^{31}P and ^{1}H NMR data rigorously established that at least for the solution state the phosphine complex is an iron(II) hydride. There is a metal hydrogen ^{1}H multiplet resonance[5] centered at +13.6 ppm (TMS), a complex CH_3 and CH_2 ^{1}H spectrum,[6] and a four-multiplet ^{31}P spectrum. Inequivalence of all four phosphorus atoms is required by the ^{31}P spectrum; one multiplet resonance at relatively high field with respect to the other three (Figure 1) is assigned to a bridging-$P(CH_3)_2CH_2$-group. These data, in addition to the cryoscopic data that show the complex to be a monomer[7] in benzene, define the structure as shown in **1**; all alternative stereoisomers are inconsistent with the NMR data. This is the first established example of *intra*molecular C–H addition in a trialkylphosphine metal complex, although the closely related[8a] and structurally defined[9] $Ru[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ shows *inter*molecular oxidative addition of a CH bond to give a Ru(II) hydride dimer with a six-membered (alternating Ru, C, P) ring. Basic stereochemistry about Ru is as in **1**. It is not evident why there is a dominant intramolecular mode of addition in one complex and an intermolecular mode in the other.[8b]



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The oxidative addition of the C–H bond in the iron complex showed no evidence of fast (NMR time scale) reversal up to temperatures of ~20° where thermal decomposition ensues. However, we have NMR spectral evidence of a slow equilibrium between the two extreme Fe(0) and Fe(II) structural forms.[10] Moreover, reversibility was evident in reactions of **1** with hydrogen at 25° wherein a high yield (70%) of $H_2Fe[P(CH_3)_3]_4$[4] was realized and with donor ligands wherein more conventional iron(0) complexes of the form $Fe[P(CH_3)_3]_xL_{5-x}$ were generated. An exemplary product of the latter reaction set is $Fe[P(CH_3)_3]_3(PF_3)_2$, a new interesting fluxional molecule which has trigonal bipyramidal ground state form with both PF_3 ligands at equatorial sites.[11] Ligand exchange between **1** and $P(CH_3)_3$ is slow on the NMR time scale at 0°; consistent with this observation of low ligand lability, complex **1** did not isomerize 1-hexene at 25°.

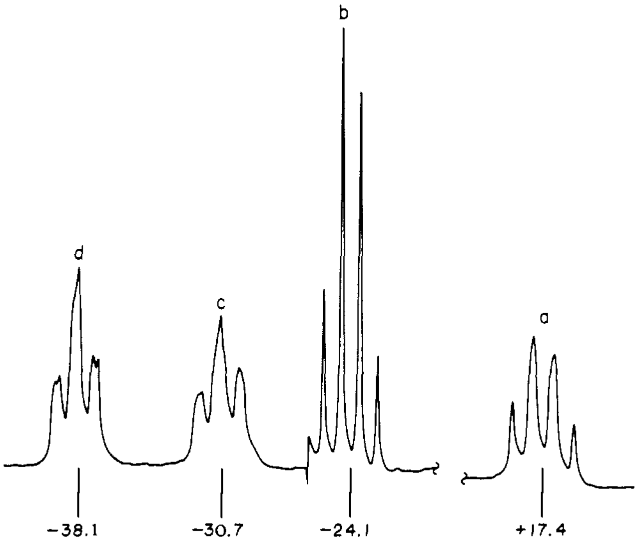
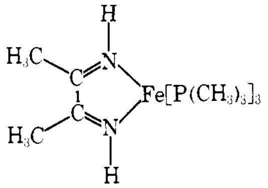


Figure 1. FT $^{31}P\ \{^{1}H\}$ spectrum (36.4 MHz) at −73° for **1** in toluene. The high field multiplet is *tentatively* assigned to a P^a with $J_{P^aP^b} \simeq 34$ Hz, and $J_{P^aP^c} \simeq J_{P^aP^d} \simeq 40$ Hz, the other four-line resonance to P^b with $J_{P^bP^c} \simeq J_{P^bP^d} = 28 \pm 5$ Hz, and the remaining three-line resonances to P^c and P^d (these cannot be distinguished) with $J_{P^cP^d}$ smaller in magnitude than the other five. Chemical shifts are in parts per million from 85% H_3PO_4 (external). The sharp discontinuity to the left of resonance (b) is a machine artifact.

Modification of the reduction course for $FeCl_2[P(CH_3)_3]_2$ can be effected by the presence of additional coordinating ligands. For example, the above described reduction in the presence of butadiene yielded the novel η^4-$C_4H_6Fe[P(CH_3)_3]_3$[12] complex. One of the most interesting modifications was that achieved with acetonitrile[13] to give a blue-black crystalline solid (30% yield) that readily sublimes under vacuum at 25°. NMR, infrared, and mass spectral data[14] defined the heterocyclic diimine[15] complex **2**. The N–H protons were derived from acetonitrile as shown by the synthesis of $(C_4D_8N_2)Fe[P(CH_3)_3]_3$[12] from the reduction scheme using CD_3CN. (In the analogous reduction in the phosphite system, $Fe[P(OCH_3)_3]_5$[1] was formed.) Reduction of the iron chloride–phosphine complex in the presence of 2-butyne generated (~40% yield), the novel iron(II) heterocycle[12] **3** which is a blue, highly volatile solid of high thermal reactivity. Purification was achieved by vacuum sublimation at 40°. Hexamethylbenzene was also produced in the reduction scheme. Possi-



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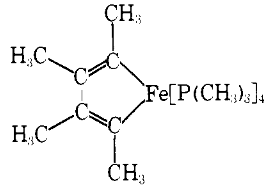

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ble involvement of **1** and/or **3** in this scheme is indicated by the finding that **1** catalyzed the trimerization of 2-butyne as well as oligimerization to tetra-, penta-, and hexamers which remain to be fully characterized structurally.

NOTE ADDED IN PROOF. Through private communications, we have learned that compound **1** has been prepared in other laboratories: H. F. Klein and H. Schmidbaur (personal communication from H. Schmidbaur) and by Dr. S. Ittel (personal communication from S. Ittel).

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References and Notes

(1) E. L. Muetterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).

(2) (a) Very pale green needles; identified by complete elemental analysis; (b) 70% yields; (c) electron and chemical ionization mass spectra.

(3) We found no evidence in our product for $H_2Fe[P(CH_3)_3]_4$,[4] a compound that has a similar physical appearance, volatility, and infrared Fe–H stretch.

(4) H. F. Klein, *Angew. Chem.*, **82**, 885 (1970).

(5) At 90 MHz, the spectrum may be described as a doublet of triplets with the triplets further split into doublets. *Tentative* assignments of H(Fe–H)–P coupling constants for **1** are $J_{HP_a} = 70$ Hz, $J_{HP_b} \simeq J_{HP_d} = 56$ Hz, and $J_{HP_c} = 26$ Hz.

(6) At 90 MHz, the unique CH_2 resonance (**1**) and four CH_3 resonances (doublets) were resolved.

(7) Macroscale cryoscopic molecular weight determination with benzene solvent in a Vacuum Atmospheres "Dri Lab" with an argon atmosphere (Theory: 360, Found: 328, 370).

(8) (a) J. Chatt and J. N. Davidson, *J. Chem. Soc.*, 843 (1965). (b) The molecular weight in benzene (ebullioscopic) was reported as slightly higher than theory for a monomer.

(9) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J. Chem. Soc., Chem. Commun.*, 755 (1974).

(10) When the NMR spectrum of **1** was examined in the presence and absence of *internal* $P(CH_3)_3$, there was no detectable difference in line shapes of the resonances characteristic of **1**. However, the internal $P(CH_3)_3$ resonance broadened in the higher temperature ranges ($>-50°$) and was slightly shifted from the normal $P(CH_3)_3$ position. In contrast, the $^{31}P\{^1H\}$ spectrum of $P(CH_3)_3$ alone in toluene remained sharp over this temperature range. We tentatively propose that there is an equilibrium of the type $\mathbf{1} \rightleftharpoons Fe[P(CH_3)_3]_4$ which shifts to the right as T increases, with k_f small with respect to the NMR time scale and small with respect to k_b (K small). We further propose that the equilibrium $P(CH_3)_3 + Fe[P(CH_3)_3]_4 \rightleftharpoons Fe[P(CH_3)_3]_5$ extant with rates large with respect to the NMR time scale and with the equilibrium shifting to the *right* with temperature decrease. The four- and five-coordinate species in the latter equilibrium would be probably paramagnetic (T_d) and definitely diamagnetic (D_{3h}), respectively. A paramagnetic species, $Fe[P(CH_3)_3]_4$, present in low concentrations could account for broadening and shifting of the $P(CH_3)_3$ resonance.

(11) Fully defined by the DNMR ^{31}P spectra.

(12) Mass spectral and NMR characterization.

(13) Wherein an intermediate $Fe[P(CH_3)_3]_3(CH_3CN)_3{}^{2+}FeCl_4{}^{2-}$ is tentatively proposed as indicated by analysis of the intermediate.

(14) ^1H NMR $(CH_3)_4Si$ reference: C–CH_3, −1.95 (S, 6); N–H, −6.73 (broad, 2 H); and P–CH_3, −1.23 (m, 27 H). Inequivalence of P atoms was not seen at −110 to +20° so the molecule is fluxional. Infrared C═N stretch 1560 cm^{-1}. Phosphine ligands are tightly bound; there is no fast ligand exchange (NMR time scale) between **2** and $P(CH_3)_3$ in toluene at 80°.

(15) An analogous *linear* diimine metal complex has been described recently. P. A. Finn, M. S. King, P. A. Kilty, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 220 (1975).

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New Peripheral Metal Complexes Related to Chlorophyll

Sir:

Coordination of metal ions to the four central nitrogen atoms of the porphyrin tetrapyrrole macrocycle has been the generally recognized mode of metal complex formation in chlorophyll and related compounds.[1] We report here new metal complexes of the chlorophyll macrocycle in which the metal is bound to the β-ketoester system of ring V and which we therefore term peripheral complexes.

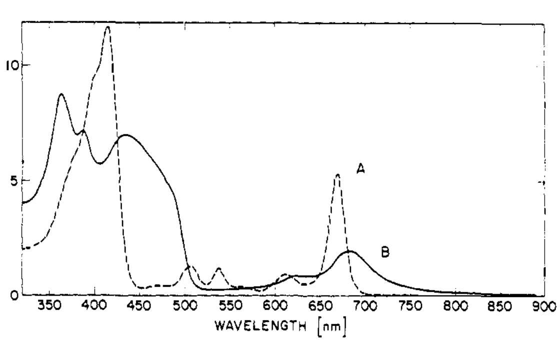
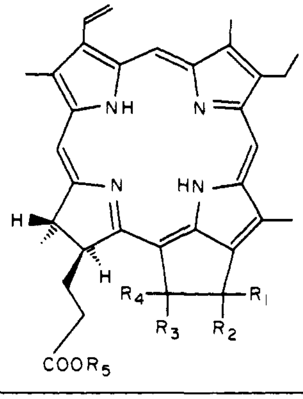


Figure 1. Uv-visible absorption spectra of pheophytin a (**1**) in dry pyridine (A, - - -), and its peripheral magnesium complex (**7**) (B, —) in dry pyridine, saturated with anhydrous $Mg(ClO_4)_2$. Spectrum A is the typical chlorin spectrum.

During metalation studies of pheophorbides of the a series to the respective chlorophyllides by the method of Baum et al.,[2] we noticed that the substrates can be divided into two classes on the basis of their spectral response to Mg^{2+}. Compounds of the first class dissolve in pyridine saturated with $Mg(ClO_4)_2$ to give brown solutions with the uv-visible spectrum typical of pheophorbides (i.e., Figure 1A). Compounds of the second class, by contrast, give under the same conditions bright green solutions in which the red band is broadened and shifted to significantly longer wavelengths and the Soret band is split into two complex band systems extending from 350 to 500 nm (Figure 1B).

The spectral response to pyridine–Mg^{2+} is determined by whether or not the pheophorbides contain an enolizable β-ketoester system in ring V. Pheophytin a (**1**) and methylpheophorbide a (**2**) form green solutions, and similar pronounced spectral changes are observed in pheophytin b, and bacteriopheophytins a and b.[3] These compounds all contain an intact ring V β-ketoester system capable of enolization. However, pyromethylpheophorbide a (**3**),[4] 9-desoxo-9-hydroxymethylpheophorbide a (**4**),[5] and 10-methoxymethylpheophorbide a (**5**)[6] give brown solutions in pyridine with spectra unaffected by the presence or absence of $Mg(ClO_4)_2$. In the latter compounds, ready enolization of the β-ketoester system is prevented by elimination of either the C-10 ester C═O or the C-9 keto C═O functions or by substitution of the enolizable 10-H by an alkoxy group. We conclude from this chemical evidence that the observed



No.	Compound	R_1, R_2	R_3	R_4	R_5
1	Pheophytin a	=O	H	$COOCH_3$	phytyl
2	Methylpheophorbide a	=O	H	$COOCH_3$	CH_3
3	Pyromethylpheophorbide a	=O	H	H	CH_3
4	9-Desoxo-9-hydroxy-methylpheophorbide a	H,OH	H	COOCH	CH_3
5	10-Methoxy-methylpheophorbide b	=O	OCH_3	$COOCH_3$	CH_3