

kind of reaction is most probably involved in other organometallic reactions also, such as the formation of diethyl ketone from ethylene and CO with a cobalt catalyst and a hydrogen donor at 350° as reported by Staib, Guyer, and Slotterbeck.<sup>12</sup>

**Acknowledgment.**—The author gratefully acknowledges helpful discussions with Professor S. Winstein and Dr. D. S. Breslow.

(12) J. H. Staib, W. R. F. Guyer, and O. C. Slotterbeck, U. S. Patent 2,864,864 (December 16, 1958).

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PA.]

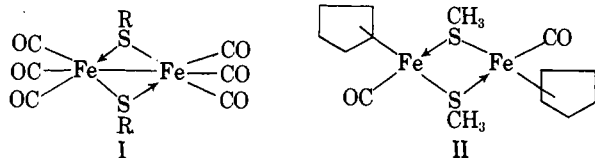
## Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. I. Cyclopentadienyliron Complexes<sup>1</sup>

BY R. G. HAYTER

RECEIVED MAY 20, 1963

The reactions of  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  with tetrasubstituted biphosphines and biarsines,  $\text{R}_4\text{M}_2$  ( $\text{M} = \text{P}, \text{As}$ ;  $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) and of  $\text{Na}[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]$  with  $\text{R}_2\text{MCl}$  have been found to give  $[\text{C}_5\text{H}_5\text{Fe}(\text{MR}_2)(\text{CO})]_2$  and  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2\text{H}(\text{PR}_2)(\text{CO})_2]$ . The infrared and nuclear magnetic resonance spectra of the compounds have been used to show that they contain bridging  $\text{MR}_2$  groups.  $[\text{C}_5\text{H}_5\text{Fe}(\text{MR}_2)(\text{CO})]_2$  has been isolated in both *cis* and *trans* isomeric forms.

In recent years there has been considerable interest in the reactions of organosulfur compounds with metal carbonyls and, as a result, a number of sulfur-bridged, usually binuclear complexes (for example I<sup>2a</sup> and II<sup>2b</sup>), have been prepared containing most of the elements of the first transition series. Comparatively little attention, however, has been given to the study of related complexes containing phosphorus or arsenic as the



bridging atom, although, in general, tertiary phosphine complexes of the metal carbonyls are more stable than those of the substituted sulfides. This neglect may be due to the fact that only recently have good synthetic methods been developed for some of the key methylphosphine intermediates, although the corresponding arsine compounds have been known for some time.

Recent studies have shown the four-membered  $\text{Pd}_2\text{P}_2$  ring in some complexes of Pd(II) to be a stable molecular unit.<sup>3</sup> Unfortunately, the method of preparation (reaction of secondary phosphines with palladium halides, in the presence of a base) does not appear to be one which can be readily applied to a wide range of transition elements. In a search for alternative synthetic methods, we are investigating the reactions of (a) metal carbonyls and their cyclopentadienyl derivatives with tetrasubstituted biphosphines and biarsines ( $\text{R}_4\text{M}_2$ ;  $\text{M} = \text{P}, \text{As}$ ;  $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) and (b) the reactions of the alkali metal salts of suitable metal carbonyl compounds with chlorophosphines and -arsines ( $\text{R}_2\text{MCl}$ ). It was anticipated that in reactions of type a the  $\text{M}-\text{M}$  bond of the ligand would be cleaved to give  $\text{R}_2\text{M}$  radicals, which can act as three-electron bridging groups in linking two metal atoms. In much the same way, I and II are obtained by reaction between  $\text{R}_2\text{S}_2$  and iron pentacarbonyl and  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ , respectively. In b, elimination of sodium chloride, followed by ring closure with loss of carbon monoxide, could also lead to bridged complexes.

In reactions of type a, we have found that, in general, the ease of cleavage of the  $\text{R}_2\text{M}-\text{MR}_2$  or  $\text{RS}-\text{SR}$  ligands increases ( $\text{P} < \text{As} < \text{S}$ ) in the order of decreasing strength of the  $\text{M}-\text{M}$  or  $\text{S}-\text{S}$  bond. The tetrasubstituted biphosphines are thus the most difficult to cleave, although cleavage appears to occur more readily when the metal carbonyl compound contains a metal-metal bond (as in  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  or  $\text{Co}_2(\text{CO})_8$ ) and when  $\text{P}_2(\text{C}_6\text{H}_5)_4$  rather than  $\text{P}_2(\text{CH}_3)_4$  is used. The latter effect may be due to the greater electronegativity of the phenyl group.

### Experimental

**Analyses and Apparatus.**—Microanalyses and molecular weight determinations were by Schwarzkopf Laboratories, Woodside, N. Y.; Huffmann Microanalytical Laboratories, Wheatridge, Colo.; and Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany. Melting points were determined in evacuated capillaries and are uncorrected.

Infrared spectra were measured on a Beckman IR 9 spectrophotometer and the nuclear magnetic resonance spectra on Varian Associates A-60 and HR-60 spectrometers. Unless otherwise stated, the n.m.r. spectra were determined using saturated carbon disulfide solutions and tetramethylsilane as an internal standard. All the compounds described in this paper gave sharp n.m.r. spectra and are thus presumed to be diamagnetic. Resonances due to cyclopentadienyl protons were observed in the range  $\tau = 5.6-6.2$ , methyl protons in the range  $\tau = 8.0-8.8$ , and phenyl protons  $\tau = 2.5-2.9$ .

**Starting Materials and Experimental Conditions.**—All reactions and the handling of phosphines and arsines were carried out under nitrogen. The pure crystalline complexes were usually stable to air, but solutions decomposed more or less rapidly on exposure to air. Chromatographic separations were carried out on Merck acid-washed alumina.

Dimethylchlorophosphine was prepared by a modification of Parshall's method,<sup>4</sup> in which diphenylchlorophosphine was substituted for phenyldichlorophosphine in the reaction with tetramethylbiphosphine disulfide. The yields were in the range 51–67%. In some preparations, the distillate (b.p. 70–115°) from the reaction mixture separated into two layers. After removal of the lower layer, the upper layer was almost pure  $(\text{CH}_3)_2\text{PCl}$ , b.p. 74–74.5°. Tetramethylbiphosphine<sup>5</sup> and tetraphenylbiphosphine<sup>6</sup> were synthesized by published methods,  $(\text{C}_6\text{H}_5)_3\text{P}_2$  being prepared as needed from  $(\text{C}_6\text{H}_5)_2\text{PH}$  and  $(\text{C}_6\text{H}_5)_2\text{PCl}$  in toluene or *n*-heptane solution. Dimethylchloroarsine<sup>7</sup> and tetramethylbiarsine<sup>8</sup> were also prepared by well-established methods.

Cyclopentadienyliron dicarbonyl dimer was prepared from iron pentacarbonyl.<sup>9</sup> Sodium cyclopentadienyliron dicarbonyl<sup>10</sup> was

(4) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

(5) G. W. Parshall, *ibid.*, **14**, 291 (1960).

(6) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).

(7) E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen," Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 472.

(8) V. Auger, *Compt. rend.*, **142**, 1153 (1906).

(9) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(10) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

(1) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

(2) (a) R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962), and references therein; (b) R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3600 (1961).

(3) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).

prepared by reaction between  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and about 30% excess of freshly prepared 3% sodium amalgam in dry tetrahydrofuran in a round-bottom reaction flask fitted with a stopcock. When the reaction was complete (after *ca.* 1 hr.), the excess sodium amalgam was drained off through the stopcock.

**Preparation of Cyclopentadienyliron Complexes. Method A.**—In this method,  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (13 mmoles), the biphosphine or biarsine (13 mmoles), and toluene (150–200 ml.) were refluxed together for about 16 hr. (usually overnight). The reaction mixture was then filtered under nitrogen and the filtrate evaporated at 15 mm., leaving a slightly sticky dark brown solid. Since the product was a mixture of compounds, the separation procedures are described below under the reacting ligands.

**Tetramethylbiarsine.**—The product was dissolved in the minimum quantity of warm chloroform and chromatographed on alumina. The column was well washed with hexane and then developed with solutions of benzene in hexane of gradually increasing concentration; 30% benzene–hexane eluted a brown band; evaporation of the eluate left brown crystals which, after washing twice with 5 ml. of hexane, were shown to be pure *trans*- $\mu$ -(*di*-methylarsenido)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 273–277°, yield 34%. The n.m.r. spectrum showed singlet absorption bands at  $\tau = 5.90$  and 8.65 with relative intensities 5:6, respectively.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{22}\text{As}_2\text{Fe}_2\text{O}_2$ : C, 37.8; H, 4.4; Fe, 22.0; O, 6.3; mol. wt., 508. Found: C, 38.0; H, 4.7; Fe, 21.5; O, 6.3; mol. wt. ( $\text{C}_6\text{H}_6$ ), 476.

Further elution of the chromatogram, finally with pure benzene, gave a second brown band and the eluate, on evaporation, afforded brown needles of *cis*- $\mu$ -(*di*-methylarsenido)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 277–278°, yield 16%. The n.m.r. spectrum of the *cis* isomer showed singlet absorptions at  $\tau = 5.93$ , 8.54, and 8.77 with relative intensities 5:3:3, respectively.

*Anal.* Found: C, 38.9; H, 4.5; Fe, 21.7; O, 6.2; mol. wt. ( $\text{C}_6\text{H}_6$ ), 542.

**Tetramethylbiphosphine.**—The crude product was dissolved in hexane and chromatographed on alumina. Elution with hexane gave a yellow band which afforded orange crystals of ferrocene (6% yield), which was identified by comparison of its m.p. and n.m.r. spectrum with that of an authentic specimen. Elution with 30% benzene–hexane gave an orange-brown band, which gave a brown solid on evaporation of the eluate. Sublimation at 90° and 0.2 mm. afforded a low yield of dark brown crystals, which were identical (by n.m.r.) with V which was obtained in higher yield from the reaction between  $(\text{CH}_3)_2\text{PCl}$  and  $\text{Na}[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]$  (see below). Further sublimation at 130° and 0.2 mm. gave orange crystals of *trans*- $\mu$ -(*di*-methylphosphido)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 220–270°, yield 13%. The n.m.r. spectrum shows absorption bands at  $\tau = 5.84$  (triplet,  $J_{\text{HP}} 1.1$  c.p.s.) and 8.44 (triplet,  $J_{\text{HP}} 5.4$  c.p.s.). The integrated relative intensities of these bands are in the ratio 5:6.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{22}\text{Fe}_2\text{O}_2\text{P}_2$ : C, 45.8; H, 5.3; Fe, 26.6; O, 7.6; P, 14.75; mol. wt., 420. Found: C, 45.6; H, 5.3; Fe, 26.55; O, 7.2; P, 14.2; mol. wt. ( $\text{C}_6\text{H}_6$ ), 399.

Elution of the chromatogram with benzene gave an orange band, which, after evaporation of the eluate, afforded orange plate-like crystals of *cis*- $\mu$ -(*di*-methylphosphido)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 275–280°, yield 10%. The n.m.r. spectrum shows peaks at  $\tau = 5.85$  (triplet,  $J_{\text{HP}} 1.0$  c.p.s.), 8.30 (triplet,  $J_{\text{HP}} 5.3$  c.p.s.), and 8.53 (triplet,  $J_{\text{HP}} 5.9$  c.p.s.).

*Anal.* Found: C, 46.1; H, 5.3; Fe, 26.2; O, 7.7; P, 14.8; mol. wt. ( $\text{C}_6\text{H}_6$ ), 423.

**Tetraphenylbiphosphine.**—The crude reaction mixture contained three products with proton n.m.r. bands in the cyclopentadienyl region at  $\tau = 5.80$ , 6.01, and 6.13. The reaction mixture obtained by method B shows the same three peaks and the identity of the compounds having  $\tau = 6.01$  and 6.13 was confirmed by comparison of their m.p.'s and their infrared and n.m.r. spectra after separation by chromatography. The purification procedure was essentially the same as that described under method B for diphenylchlorophosphine.

**Method B.**— $\text{Na}[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]$  (26 mmoles) in tetrahydrofuran was treated dropwise with the monochlorophosphine or -arsine (26 mmoles). After stirring for 1–2 hr., most of the solvent was removed at 15 mm., toluene (150 ml.) added, and the solution refluxed for a further 16 hr. The solution was then cooled, filtered, and evaporated to dryness. The solid residue was redissolved and chromatographed on alumina, with the results given below:

**Dimethylchloroarsine.**—Repetition of the procedure described under method A gave a 42% yield of *trans*- $[\text{C}_5\text{H}_5\text{Fe}\{\text{As}(\text{CH}_3)_2\}(\text{CO})_2]_2$ . Subsequent elution with 50% benzene–hexane gave a broad red-brown band, which, on evaporation of the eluate, gave brown crystals. These were shown by n.m.r. to be a mixture of  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and *cis*- $[\text{C}_5\text{H}_5\text{Fe}\{\text{As}(\text{CH}_3)_2\}(\text{CO})_2]_2$ . The yield of the *cis* isomer corresponded to about 5%.

**Dimethylchlorophosphine.**—The crude product was dissolved in hexane and chromatographed. Elution with hexane gave ferrocene (5% yield); 30% benzene–hexane eluted a brown band and evaporation of the eluate gave brown crystals. These were sublimed at 90° and 0.2 mm. to give dark brown crystals of  $\mu$ -(*di*-methylphosphido)-*hydrido*-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 137–140° dec., yield 13%. The n.m.r. spectrum of this compound consists of doublet bands at  $\tau = 5.64$  ( $J_{\text{HP}} 1.1$  c.p.s.), at  $\tau = 8.01$  and 8.20 (due to two kinds of methyl protons,  $J_{\text{HP}} \sim 0.5$  c.p.s.) and (in benzene solution) at  $\tau = 28.73$  (due to hydrogen directly bonded to iron,  $J_{\text{HP}} 43.5$  c.p.s.). The first three bands have intensities in the ratio 10:3:3, respectively.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{17}\text{Fe}_2\text{O}_2\text{P}$ : C, 46.7; H, 4.8; Fe, 31.0; O, 8.9; P, 8.6; mol. wt., 360. Found: C, 47.1; H, 4.8; Fe, 30.8; O, 9.5; P, 9.1; mol. wt. ( $\text{C}_6\text{H}_6$ ), 275, 266.

The residue from the sublimation was an orange solid which was shown by n.m.r. to be almost pure *trans*- $[\text{C}_5\text{H}_5\text{Fe}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_2]_2$  (8% yield). Continued elution of the chromatogram with benzene gave an orange band due to *cis*- $[\text{C}_5\text{H}_5\text{Fe}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_2]_2$  which was isolated as described in method A in 8% yield.

**Diphenylchlorophosphine.**—The crude product was dissolved in the minimum quantity of chloroform and chromatographed. After washing the column well with hexane, elution with 50% benzene–hexane gave an orange-brown band, which on evaporation of the eluate left a brown oil, which solidified in hexane. Crystallization from hexane containing about 10% benzene gave brown-red crystals of pure *trans*- $\mu$ -(*diphenylphosphido*)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 215–217°, yield 23%. The n.m.r. spectrum showed complex bands at  $\tau = 2.45$  and 2.8 and a band at  $\tau = 6.13$  (triplet,  $J_{\text{HP}} 1.2$  c.p.s.).

*Anal.* Calcd. for  $\text{C}_{35}\text{H}_{30}\text{Fe}_2\text{O}_2\text{P}_2$ : C, 64.7; H, 4.5; Fe, 16.7; O, 4.8; P, 9.3; mol. wt., 668. Found: C, 64.8; H, 4.7; Fe, 16.7; O, 4.8; mol. wt. ( $\text{C}_6\text{H}_6$ ), 702.

Elution of the chromatogram with benzene gave a second brown band. Addition of heptane to the eluate and evaporation at 15 mm. left dark brown crystals. Recrystallization from methylene chloride–pentane gave *cis*- $\mu$ -(*diphenylphosphido*)-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron, m.p. 302–304° with darkening above about 260°, yield 30%. The n.m.r. spectrum showed peaks at  $\tau = 2.7$  (broad) and 6.01 (triplet,  $J_{\text{HP}} 1.0$  c.p.s.).

*Anal.* Found (repeat analyses on two different preparations): C, 64.45, 64.9; H, 4.6, 4.65; Fe, 16.4; O, 5.2, 4.6; P, 9.5; mol. wt. ( $\text{C}_6\text{H}_6$ ), 602.

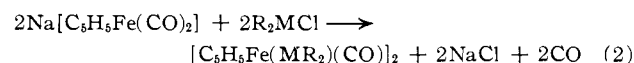
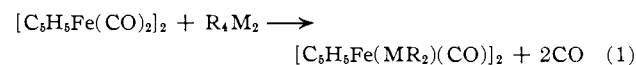
The third component of the crude product was obtained by eluting a fresh chromatogram with 30% benzene–hexane mixture. An orange-brown solution was obtained (*ca.* 750 ml.) which, on evaporation, left a red oil. This was dissolved in hexane (20 ml.), and the solution filtered and cooled to give dark brown crystals (m.p. 153–157°, yield 5%) of  $\mu$ -(*diphenylphosphido*)-*hydrido*-*di*- $\pi$ -cyclopentadienyldicarbonyldiiron.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{21}\text{Fe}_2\text{O}_2\text{P}$ : C, 59.5; H, 4.4; Fe, 23.1; O, 6.6; P, 6.4; mol. wt., 484. Found: C, 60.0; H, 4.6; Fe, 22.6; O, 6.4; P, 6.4; mol. wt. ( $\text{C}_6\text{H}_6$ ), 458.

The n.m.r. spectrum shows complex peaks at  $\tau = 2.5$ , 2.83 and doublets at  $\tau = 5.80$  ( $J_{\text{HP}} 1.3$  c.p.s.) and at  $\tau = 28.67$  (Fe–H hydrogen,  $J_{\text{HP}} 41.0$  c.p.s.) (the last peak being observed in benzene solution). The n.m.r. spectrum confirms the absence of the *cis* and *trans* isomers previously isolated, although the elution of the column with benzene gave no further products, probably owing to decomposition during the unusually long residence time on the column.

## Discussion

The results given in the Experimental section show that reactions 1 and 2 both give products of the same type, whether  $M = \text{P}$  ( $R = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ) or  $\text{As}$  ( $R = \text{CH}_3$ ).



The infrared spectra of the products in carbon disulfide solution (Table I) all show a single absorption band in the region expected for terminal carbonyl groups and no absorption in the bridging carbonyl region. Since the compounds are dimeric and diamagnetic, it is probable that the iron atoms are joined by a double phosphorus (or arsenic) bridge (as in III and IV), in which the bridging atoms each contribute three electrons to the

TABLE I  
 INFRARED SPECTRA OF THE PHOSPHORUS- AND ARSENIC-BRIDGED IRON COMPLEXES

Compound	—Absorption bands in the carbonyl region, cm. <sup>-1</sup> —		Other absorption bands, cm. <sup>-1</sup> <sup>a</sup>
	CS <sub>2</sub> soln.	Halocarbon mulls	
<i>trans</i> -[C <sub>5</sub> H <sub>5</sub> Fe{P(CH <sub>3</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1906	1900 (sh), 1888 (vs), 1852 (w)	2972 (w), 2942 (w), 2898 (w), 2884 (w), 1420 (m), 1410 (m), 1278 (w), 1264 (m), 1110 (m), 1060 (w), 1010 (w), 998 (w), 936 (s), 894 (vs), 848 (m), 835 (m), 810 (vs), 711 (w), 708 (s), 672 (s), 613 (m), 566 (vs), 442 (m)
<i>cis</i> -[C <sub>5</sub> H <sub>5</sub> Fe{P(CH <sub>3</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1943	1932 (vs), 1894, 1888, 1856 (all sh)	2968 (m), 2938 (m), 2900 (w), 2882 (m), 1420 (m), 1411 (m), 1285 (m), 1267 (m), 1110 (m), 1062 (w), 1010 (m), 998 (m), 935 (m), 926 (s), 892 (s), 846 (w), 822 (m), 818 (vs), 708 (m), 672 (m), 620 (w), 608 (m), 598 (w), 568 (vs), 442 (m)
<i>trans</i> -[C <sub>5</sub> H <sub>5</sub> Fe{P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1917	1912 (vs), 1900 (vs), 1865 (w), 1856 (w)	3072 (w), 3060 (w), 1474 (w), 1431 (m), 1302 (w), 1270 (w), 1180 (w), 1088 (w), 1071 (w), 1028 (w), 1012 (w), 1000 (w), 868 (w), 845 (m), 833 (w), 822 (w), 812 (w), 752 (m), 745 (m), 741 (m), 705 (sh), 698 (s), 688 (w), 623 (m), 617 (m), 608 (w), 597 (w), 590 (w), 568 (s), 553 (s), 548 (s), 519 (w), 508 (m), 502 (s), 486 (w), 460 (m), 452 (m), 438 (m)
<i>cis</i> -[C <sub>5</sub> H <sub>5</sub> Fe{P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1961	1953 (vs), 1903 (s), 1880 (w), 1872 (w)	3108 (w), 2868 (w), 2850 (m), 2830 (w), 1580 (m), 1472 (m), 1430 (s), 1415 (w), 1362 (w), 1270 (w), 1180 (w), 1114 (w), 1090 (w), 1028 (w), 1018 (w), 1004 (w), 841 (m), 833 (w), 818 (s), 750 (s), 739 (s), 697 (s), 685 (m), 611 (m), 602 (m), 588 (m), 567 (s), 557 (s), 511 (s), 498 (s), 485 (m), 462 (m), 450 (m), 432 (m)
<i>trans</i> -[C <sub>5</sub> H <sub>5</sub> Fe{As(CH <sub>3</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1902	1902 (sh), 1894 (vs), 1882 (sh), 1851 (w), 1846 (w)	2990 (w), 2970 (w), 2900 (w), 1416 (w), 1252 (w), 1231 (m), 1110 (m), 1060 (w), 1012 (m), 998 (m), 918 (w), 890 (s), 844 (s), 834 (s), 822 (s), 812 (m), 790 (m), 608 (s), 588 (m), 570 (vs), 558 (s), 550 (m)
<i>cis</i> -[C <sub>5</sub> H <sub>5</sub> Fe{As(CH <sub>3</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>	1936	1905 (vs), 1870 (vs), 1839 (w)	2960 (w), 2892 (w), 1412 (m), 1232 (w), 1223 (w), 1110 (w), 997 (m), 886 (s), 845 (sh), 838 (s), 820 (s), 802 (s), 780 (m), 604 (m), 600 (m), 571 (vs), 562 (vs)
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sub>2</sub> H{P(CH <sub>3</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>		1915 (vs), 1898 (vs), 1860 (w), 1850 (w)	2980 (w), 2944 (w), 2895 (w), 1428 (m), 1415 (m), 1278 (m), 1265 (m), 1225 (m), 1112 (m), 1061 (w), 1013 (m), 998 (m), 948 (s), 888 (s), 848 (s), 834 (s), 818 (vs), 722 (s), 710 (m), 687 (m), 586 (s), 573 (vs), 553 (s), 498 (m)
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sub>2</sub> H{P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }(CO)] <sub>2</sub>		1932 (s), 1922 (vs), 1911 (vs), 1903 (vs), 1872 (w), 1863 (w)	3060 (w), 3048 (w), 1480 (w), 1433 (s), 1108 (w), 1092 (w), 1066 (w), 1058 (w), 1026 (w), 1010 (w), 998 (w), 834 (m), 820 (m), 751 (m), 738 (m), 700 (s), 586 (m), 560 (s), 552 (s), 524 (w), 507 (w), 498 (w), 482 (m)

<sup>a</sup> Nujol mull 400–1300 cm.<sup>-1</sup>; halocarbon mull 1300–4000 cm.<sup>-1</sup>.

bonding of the two metal atoms.<sup>11</sup> In this way, iron attains an inert gas configuration and the compounds are analogous to [C<sub>5</sub>H<sub>5</sub>Fe(SCH<sub>3</sub>)(CO)]<sub>2</sub>.<sup>2</sup> However, in contrast to the sulfur compound, the phosphorus and arsenic derivatives have been obtained in two isomeric forms, the nature of the isomerism being deduced mainly from the nuclear magnetic resonance spectra.

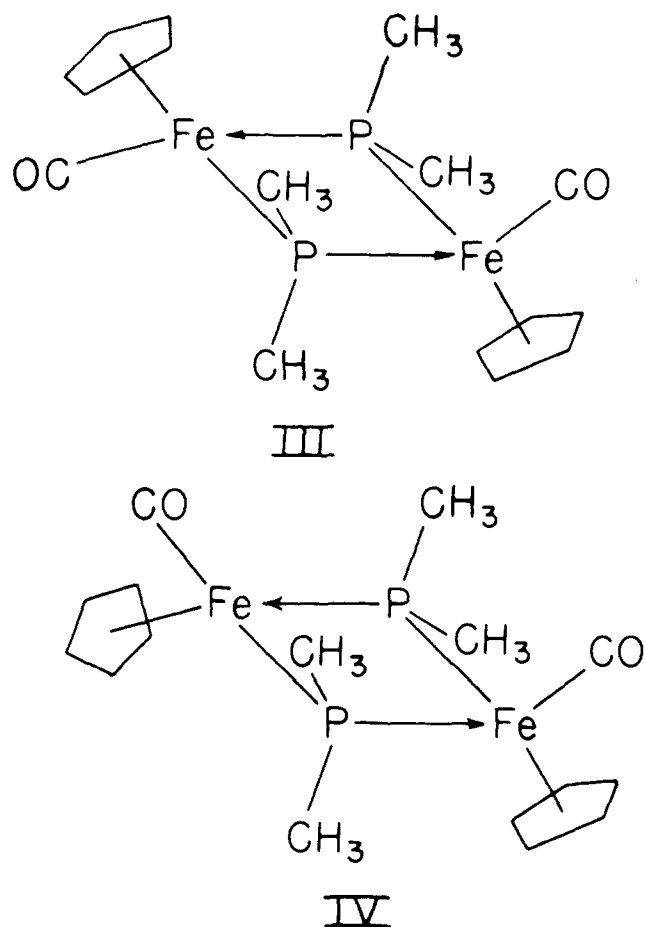
If in compounds of the type [C<sub>5</sub>H<sub>5</sub>Fe(MR<sub>2</sub>)(CO)]<sub>2</sub> an approximately tetrahedral configuration about the iron atoms is assumed, it is evident that two arrangements of the terminal cyclopentadienyl and carbonyl ligands are possible, with like groups lying either on the same or opposite sides of the presumably planar Fe<sub>2</sub>M<sub>2</sub> ring. If on opposite sides, as in III (*trans* isomer), the methyl groups attached to the bridging atom are all equivalent

(11) A referee has suggested alternative structures involving a four-membered ring with P–P and Fe–Fe bonds. However, we have found that the methyl resonance in coordination complexes of P<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>, for example C<sub>5</sub>H<sub>5</sub>(CO)Co ← P(CH<sub>3</sub>)<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub> → Co(CO)C<sub>5</sub>H<sub>5</sub>, consists of a doublet with, in some cases, a weak central peak. The methyl resonances in [C<sub>5</sub>H<sub>5</sub>Fe{P(CH<sub>3</sub>)<sub>2</sub>}(CO)]<sub>2</sub> show a different pattern (see below) and structures involving P–P bonds can therefore probably be eliminated. The fact that complexes of type V are also obtained affords direct evidence for cleavage of P–P bonds in reaction I.

and a single methyl resonance in the n.m.r. spectrum will result. If on the same side, as in IV (*cis* isomer), there will be two kinds of methyl group, one of each being attached to each bridging atom, and two methyl resonances will be observed. A similar situation obtains if the iron atom is assumed to have planar coordination or if octahedral coordination is assumed with the cyclopentadienyl rings occupying three coordination positions rather than one.

Since the arsenic compounds give spectra which are not complicated by spin–spin coupling effects involving the arsenic nucleus,<sup>12</sup> these are considered first. In the purification of the products which resulted from either method A or B, the compound which was eluted first from the chromatography column showed a single methyl resonance and hence is *trans*-[C<sub>5</sub>H<sub>5</sub>Fe{As(CH<sub>3</sub>)<sub>2</sub>}(CO)]<sub>2</sub>. The second compound to be eluted showed two methyl resonances of equal intensity and is thus the more polar *cis* isomer. Both compounds gave singlet cyclopentadienyl resonances and the relative

(12) J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).



intensities of these bands and the corresponding methyl bands are consistent with the proposed structures.

The n.m.r. spectra of the corresponding isomeric phosphorus compounds are shown in Fig. 1. In both compounds, the cyclopentadienyl resonances under high resolution are triplets due to coupling of the ten equivalent cyclopentadienyl protons with the two equivalent phosphorus nuclei each of spin  $1/2$ . In the *trans* isomer, a single methyl resonance, in the form of a 1:2:1 triplet, is observed. *cis*-[C<sub>5</sub>H<sub>5</sub>Fe{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>2</sub>] shows two methyl resonances, each in the form of a triplet, which is consistent with the suggestion that like methyl groups are attached one to each phosphorus atom, rather than both to the same atom. It is interesting to note that, in both the phosphorus and arsenic compounds, the methyl resonance in the *trans* isomers occurs very close to the mid-point between the two methyl resonances in the *cis* isomers.

We consider that the triplet patterns can be attributed to the presence of relatively strong phosphorus-phosphorus coupling in the molecule. The methyl groups thus effectively "see" the combined spin states of both phosphorus nuclei. If this is the case, the observed splitting of the methyl resonance is equal to the average of the coupling constants of the methyl protons to the near and far phosphorus nuclei.<sup>13</sup> This type of spectrum is a "deceptively simple"<sup>14</sup> one and explicit values for the individual methyl-phosphorus coupling constants cannot be obtained. However, an approximate limit to the phosphorus-phosphorus coupling constant can be calculated using the condition for the observation of triplets in an A<sub>2</sub>X<sub>2</sub> spectrum<sup>14</sup>; III and IV are A<sub>12</sub>X<sub>2</sub> molecules (if coupling effects involving the cyclopentadienyl protons are neglected), but the

(13) The observed splitting is thus not a true coupling constant, although, for convenience, it is reported as such (see Experimental).

(14) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

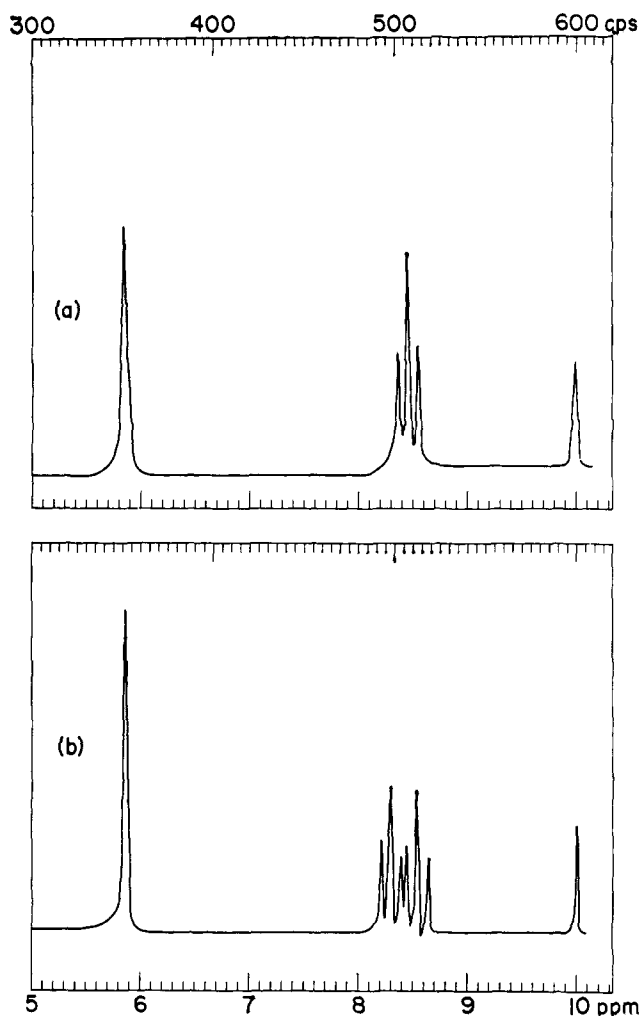


Fig. 1.—Proton n.m.r. spectra of (a) *trans*-[C<sub>5</sub>H<sub>5</sub>Fe{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>2</sub>] (III) and (b) *cis*-[C<sub>5</sub>H<sub>5</sub>Fe{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>2</sub>] (IV). The cyclopentadienyl resonances (triplets under higher resolution) occur at about 5.85 p.p.m. and the methyl resonances in the range 8.2–8.7 p.p.m. The peak at 10 p.p.m. is due to the internal reference, tetramethylsilane.

same condition is valid for the A nuclei (protons of the methyl groups)

$$L^2/2M < \Delta\nu_{1/2}$$

( $L = J_{HP} - J'_{HP}$ ;  $M = J_{PP} - J_{HH}$ ;  $\Delta\nu_{1/2}$  is the half-height width of the component lines, and was found to be about 1 c.p.s. in the spectra under consideration).

In order to simplify the expression, it is assumed that the longer range couplings ( $J'_{HP}$ ,  $J_{HH}$ ) are small compared with the shorter range couplings ( $J_{HP}$ ,  $J_{PP}$ ). The condition for triplet formation thus becomes

$$J_{PP} > 1/2 J_{HP}^2$$

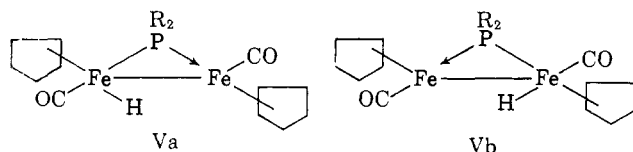
The lower limit of  $J_{PP}$  is thus very sensitive to  $J_{HP}$ , which apparently lies in the range 5–8 c.p.s. in the bridged complexes;  $J_{PP}$  therefore must exceed 13–32 c.p.s. This does not seem to be an unreasonable condition, although there are few phosphorus-phosphorus coupling constants available in the literature for comparison.<sup>15</sup> The observation of a triplet allows either or both of the following deductions to be made: (a)  $J_{HP}$  or, more strictly, ( $J_{HP} - J'_{HP}$ ) is small. Accurate values of  $J_{HP}$  in the bridged complexes are not available since, as already stated above, the observed splitting of

(15)  $J_{PP}$  is 108 c.p.s. in P<sub>4</sub>H<sub>4</sub> (R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961)), 17 c.p.s. in some polyphosphate anions, and 86 c.p.s. in P<sub>4</sub>S<sub>4</sub> (C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957)).

the methyl resonances equals  $1/2(J_{HP} + J'_{HP})$ , and the estimates of  $J_{HP}$  may thus be high. It is also possible, although not likely, that  $J'_{HP}$  is not negligible. (b) A mechanism may exist within the molecule for the strong transmission of coupling effects between the phosphorus atoms. It is possible that such transmission could occur through the filled d-orbitals of the iron atoms and would be aided by the well-known ability of phosphorus to form  $d_{\pi}$ - $d_{\pi}$  bonds with transition metals. Attempts are being made to distinguish between these two effects.

Two isomers of  $[C_5H_5Fe\{P(C_6H_5)_2\}(CO)]_2$  have also been prepared, although their n.m.r. spectra do not allow them to be assigned *cis* or *trans* structures, owing to the complexity of the phenyl absorption. However, it has previously been observed,<sup>16</sup> and our present observations agree, that *trans* isomers are eluted before *cis* from a chromatography column, and a tentative assignment of structure is made on this basis. Both *cis*- and *trans*- $[C_5H_5Fe\{P(C_6H_5)_2\}(CO)]_2$  show triplet cyclopentadienyl resonances in their n.m.r. spectra and appear to be quite analogous to the methyl compounds.

During the preparation of the phosphorus-bridged complexes, a second type of complex of structure Va,b ( $R = CH_3, C_6H_5$ ) has also been isolated. The infrared spectra of these compounds show only terminal car-



bonyl absorption and hence phosphorus, rather than a carbonyl group, must occupy the bridge position. It is necessary to postulate a metal-metal bond in order to account for the diamagnetism of the compounds and to allow each metal atom to achieve an inert gas configuration. The presence of hydrogen directly bonded to iron is an interesting feature of these compounds<sup>17</sup> and was confirmed by the observation of absorption bands in the region of the n.m.r. spectra expected for transition metal hydrides.<sup>18</sup> These absorptions occur at  $\tau = 28$ - $29$  in the form of a doublet, arising from spin-spin coupling between the Fe-H hydrogen atom and the phosphorus nucleus. It is interesting that the related compound  $[Mn_2H\{P(C_6H_5)_2\}(CO)_3]$ <sup>19</sup> shows absorption due to Mn-H hydrogen at  $\tau = 26.8$  (doublet,  $J_{HP}$  32 c.p.s.).

Owing to some unusual features of V, the remainder of the n.m.r. spectra cannot be unambiguously interpreted at the present time. The location of the Fe-H hydrogen atom is uncertain and it may be undergoing rapid exchange between equivalent positions on the iron atoms (for example, between Va and Vb) or it may be part of a bent three-center bond involving both iron atoms and possibly also the electrons of the metal-metal bond. A similar situation obtains in some of the protonated species, for example  $[(C_5H_5)_2Fe_2H(CO)_4]^+$ , recently investigated by Davison, *et al.*<sup>20</sup>

(16) G. B. Kaufman, R. B. Pinnell, and L. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962).

(17) The origin of this hydrogen is at present unknown and is the subject of further investigation. This may be another case of hydride ion abstraction from the solvent by a transition metal. For previous examples, see J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 290 (1961); L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 4989 (1962).

(18) M. L. H. Green, *Angew. Chem.*, **17**, 719 (1960).

(19) M. L. H. Green and J. T. Moelwyn-Hughes, *Z. Naturforsch.*, **17b**, 788 (1962). We have recently suggested that this compound may in fact be  $[Mn_2H\{P(C_6H_5)_2\}(CO)_3]$  (R. G. Hayter, *ibid.*, **18b**, 581 (1963)).

From an n.m.r. study of the related tungsten cation  $[(C_5H_5)_2W_2H(CO)_6]^+$ , these authors concluded that the single hydrogen atom is associated with both metal atoms, probably by rapid intramolecular exchange, although a bridging hydrogen was not definitely excluded.<sup>20</sup> Unfortunately a similar study is not possible with the iron compounds since none of the isotopes of iron have suitable nuclear properties.<sup>20</sup> It can therefore only be inferred that the iron protonated species and probably also the neutral compounds V behave similarly. In V ( $R = CH_3, C_6H_5$ ), the cyclopentadienyl resonance appears as a doublet and this may be due to spin-spin coupling between the cyclopentadienyl protons and either the phosphorus or the Fe-H hydrogen nucleus, probably the former since no splitting of the cyclopentadienyl resonance was reported for the protonated species derived from  $[C_5H_5M(CO)_2]_2$  ( $M = Fe, Ru$ ) or  $[C_5H_5M(CO)_3]$  ( $M = Mo, W$ ).<sup>20</sup>

In the aliphatic proton region, the n.m.r. spectrum of V ( $R = CH_3$ ) shows two resonances each in the form of a doublet. These are probably due to two nonequivalent methyl groups attached to phosphorus, the splitting being due to spin-spin interaction between the methyl protons and the phosphorus nucleus. The nonequivalence of the methyl groups may arise in either of two ways, depending on the spatial characteristics of the metal-metal bond. If the bond is of the linear  $\sigma$ -type (as in  $Mn_2(CO)_{10}$ ), then V ( $R = CH_3$ ) has the *cis* configuration, and the methyl groups have different environments with respect to the terminal carbonyl and cyclopentadienyl groups, as in *cis*- $[C_5H_5Fe\{P(CH_3)_2\}(CO)]_2$ . If the metal-metal bond is bent, as has been recently found in  $[Fe(SC_2H_5)(CO)_3]_2$ ,<sup>21</sup> then the methyl groups are distinguishable by their different orientations with respect to the metal-metal bond irrespective of the relative positions of the terminal ligands. It is not possible on the basis of the presently available evidence to differentiate between these two possibilities. It is also conceivable that the two methyl groups are equivalent and that the observed pattern arises from the methyls coupling unequally with the phosphorus and the Fe-H hydrogen. This alternative was rejected since no fine structure corresponding to  $J_{H-CH_3}$  was found in the Fe-H absorption doublet.<sup>21a</sup>

Transition metal hydride complexes usually show absorption in the 1700-2300  $cm^{-1}$  region of their infrared spectra due to metal-hydrogen stretching vibrations.<sup>18,22</sup> In the case of V ( $R = CH_3, C_6H_5$ ), this region of the spectrum is dominated by the intense  $\nu_{CO}$  absorptions, and these may obscure  $\nu_{M-H}$ . However, in the phenyl compound it is possible that the two bands on the high frequency side of the very strong  $\nu_{CO}$  band may be associated with metal-hydrogen stretching vibrations.

**Acknowledgments.**—The author thanks Drs. R. K. Harris and P. Lauterbur for discussions of the nuclear magnetic resonance spectra, Mr. F. Dickson for the measurement of the spectra at high field, and Mr. F. S. Humiec for experimental assistance.

(20) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3658 (1962).

(21) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(21a) NOTE ADDED IN PROOF.—Our most recent view is to regard the methyl resonance as centered at  $\tau = 8.11$  with splittings of 12.1 and 0.5 c.p.s. The larger splitting is due to  $J_{HP}$  and the smaller splitting is due either to coupling with the Fe-H hydrogen or, more likely, to the slightly different environments of the methyl groups arising from one of the two causes discussed above.

(22) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 5507 (1961)