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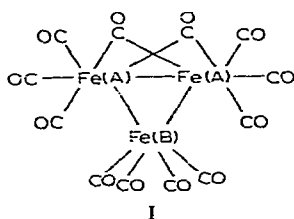
TRIIRON CARBONYL-TRIMETHYL PHOSPHITE COMPLEXES

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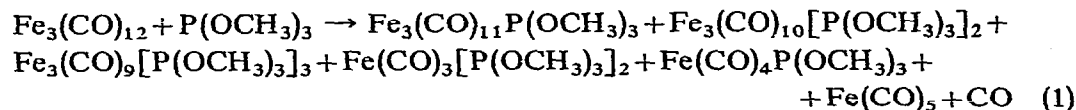
The structure of triiron dodecacarbonyl (I) in the solid has now been elucidated<sup>1</sup>; however, the structure of  $\text{Fe}_3(\text{CO})_{12}$  in solution remains unresolved. Recently, Angelici and Siefert<sup>2</sup> reported the synthesis of  $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$  (II), which, in



the crystal, exists as a mixture of two isomers with the triphenylphosphine replacing a carbonyl group bonded to either iron(A) or iron(B) of I<sup>3</sup>.

Since phosphite esters,  $\text{P}(\text{OR})_3$ , exhibit a greater  $\pi$ -bonding capacity than the phosphines, it seemed reasonable to expect them to replace more than one CO from  $\text{Fe}_3(\text{CO})_{12}$ . Accordingly, in addition to  $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{OR})_3$ , the disubstituted, tri-substituted and, perhaps even more highly substituted triiron carbonyl complexes may be predicted. The synthesis of such derivatives would provide a broader range of closely related compounds with which the interesting problem of structure of the trinuclear  $\text{Fe}_3(\text{CO})_{12-x}\text{L}_x$  could be subjected to additional tests. Reported herein is the preparation of  $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$  (III),  $\text{Fe}_3(\text{CO})_{10}[\text{P}(\text{OCH}_3)_3]_2$  (IV), and  $\text{Fe}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$  (V).

The reaction of triiron dodecacarbonyl with trimethyl phosphite in refluxing cyclohexane for a short period of time (~20 min) yields a mixture of III, IV, and V, in addition to  $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$ ,  $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3$ , and  $\text{Fe}(\text{CO})_5$  (eqn. 1). The trinuclear iron derivatives can be separated cleanly by alumina chromatography



and freed from the phosphite-substituted mononuclear iron carbonyls by sublimation

and/or crystallization. The monosubstituted complex, III, reacts with additional trimethyl phosphite to afford both the di- and trisubstituted triiron carbonyl phosphites. This contrasts the reaction of II with triphenylphosphine which yields only mononuclear iron carbonyls  $\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  and  $\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ .

The triiron carbonyl phosphite complexes form dark green crystals, soluble in organic solvents. Their solubility decreases in the order  $\text{III} > \text{IV} > \text{V}$ . In solution, all three derivatives decompose on storage to  $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3$  and  $\text{Fe}(\text{CO})_5$ , the decomposition becoming pronounced after approximately 2 h. In the solid, partial decomposition is noticeable after a few days; however, this can be almost completely arrested by storage at low temperatures and under nitrogen.

The above mode of decomposition in conjunction with the NMR spectral data furnish good evidence that the phosphite ligands are bonded to different iron atoms in IV and V. Further, the solid state infrared spectra clearly reveal presence of bridging carbonyl groups in each trinuclear complex. In the light of these data it is most likely that the structures of all three compounds are derived from that of  $\text{Fe}_3(\text{CO})_{12}$  by replacement of one, two, or three terminal carbonyl groups with  $\text{P}(\text{OCH}_3)_3$ . The remarkable similarity of the solid phase infrared spectra of II and III (Table 1)

TABLE I

INFRARED CARBONYL STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ ) OF COMPLEXES<sup>a</sup>

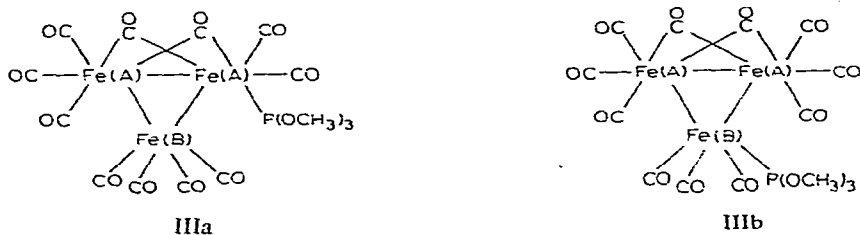
Compound	Terminal CO		Bridging CO	
	Solution	Solid	Solution	Solid
$\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$ <sup>b</sup>	2088 m	2086 m	1825 vw, br	1836 w
	2034 s	2028 s		1815 w
	2013 vs	1995 vs		1795 w
	~1985 w, sh	1949 m		
$\text{Fe}_2(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$	2091 w	2043 s	1855 vw, br	1843 w
	2039 s	2009 vs, br	1830 vw, br	1808 w-m
	2016 vs	1952 s		
	~1995 sh			
$\text{Fe}_3(\text{CO})_{10}[\text{P}(\text{OCH}_3)_3]_2$	2022 vs	2033 m	1840 vw, br	1823 m
	2000 vs	2010 vs, br	1803 vw, br	1788 m
		1958 sh		
$\text{Fe}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$	2048 m	2023 s	1825 vw, br	1821 w-m
	1985 vs, br	1985 vs, br	1782 vw, br	1782 w-m
		1952 sh		

<sup>a</sup> Recorded on a Beckman Model IR-9 spectrophotometer using cyclohexane solutions and KBr pellets. Abbreviations: vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder; br, broad. <sup>b</sup> Data from ref. 2.

indicates that the two compounds undoubtedly possess the same structural features, the latter also being an isomeric mixture. Similar isomerism is very probable for IV but, of course, not possible for V.

The salient feature of the cyclohexane solution infrared spectra of the complexes in the carbonyl stretching region is a very low intensity of the bridging CO bands. A similar phenomenon was reported earlier for I<sup>4</sup> and II<sup>2</sup>. It is possible that

carbonyl bridges are continually being broken and new ones are formed between any two of the metal atoms. If the rate of such process is sufficiently slow, then detection of the isomeric species IIIa and IIIb in solution may become experimentally feasible. Accordingly, we have examined the proton magnetic resonance spectrum of III in



CHF<sub>2</sub>Cl at  $-100^{\circ}$ . However, only one, sharp signal, a doublet, was observed. Inasmuch as the methyl protons may not be sensitive to the chemical nonequivalence of irons (A) and (B), the data do not militate against the possibility of a continuous intramolecular rupture and formation of carbonyl bridges. More definitive experiments aimed at resolving this problem are planned.

#### EXPERIMENTAL

Trimethyl phosphite was purchased from Matheson Coleman and Bell and used without further purification. All solvents, except n-pentane, were reagent grade. Woelm alumina (acid, grade III) was used in chromatography.

All synthetic work, including purification of the products, was carried out under nitrogen. The reported melting points are uncorrected. Proton magnetic resonance spectra were recorded in CDCl<sub>3</sub> solution on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Molecular weight measurements were made on *ca.*  $1 \times 10^{-2}$  M chloroform solutions with a Mechrolab Model 301-A osmometer. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

#### Reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with P(OCH<sub>3</sub>)<sub>3</sub>

Finely powdered Fe<sub>3</sub>(CO)<sub>12</sub><sup>5</sup> (1 g, 2.0 mmoles) and P(OCH<sub>3</sub>)<sub>3</sub> (0.20 g, 1.6 mmoles) in 65 ml of cyclohexane were heated at bath temperature of *ca.* 100° for 20 min. The reaction mixture was allowed to cool to room temperature and then filtered, leaving 0.18 g of pyrophoric material containing some Fe<sub>3</sub>(CO)<sub>12</sub>. Solvent and iron pentacarbonyl were removed from the filtrate under reduced pressure ( $\sim 50$  mm), the oily residue was dissolved in 50 ml of cyclohexane, and the resulting solution was introduced onto a  $2.5 \times 10$  cm chromatographic column. Four dark green bands were developed with cyclohexane.

(a). The first band was eluted off with 25 ml of cyclohexane followed by 25 ml of 4/1 cyclohexane/benzene. Removal of the solvent yielded a mixture of green and white solids. This was placed in a sublimer at 25° and *ca.* 0.1 mm for 6 h. (i) Sublimate (0.23 g): Identified as Fe(CO)<sub>4</sub>P(OCH<sub>3</sub>)<sub>3</sub> by infrared spectroscopy<sup>6</sup>, elemental analyses, and molecular weight. (Found: C, 28.74; H, 2.95; mol. wt., 293. C<sub>7</sub>H<sub>9</sub>FeO<sub>7</sub>P calcd.: C, 28.50; H, 3.08%; mol. wt., 292). M.p. 43° (sealed tube). <sup>1</sup>H NMR:

doublet at  $\tau$  6.26 ppm  $J(\text{P-H})$  12.5 cps. (ii) Residue (0.05 g): Identified by infrared spectroscopy as  $\text{Fe}_3(\text{CO})_{12}$ .

(b). The second band was eluted off with 25 ml of 4/1 cyclohexane/benzene followed by 25 ml of 3/2 cyclohexane/benzene. Removal of the solvent afforded an oil, which upon addition of *ca.* 5 ml of *n*-pentane and evaporation gave dark green crystals. These were placed in sublimator at  $25^\circ$  and *ca.* 0.1 mm for 12 h. (i) Sublimate (0.08 g):  $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3$ . (ii) Residue (0.12 g): Purified by dissolution in a minimum amount of *n*-pentane, filtration, cooling to  $-78^\circ$ , and collecting the dark green crystals of  $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$  on a filter. Yield 10%. (Found: C, 28.09; H, 1.31; Fe, 27.89; mol. wt., 591.  $\text{C}_{14}\text{H}_9\text{Fe}_3\text{O}_{14}\text{P}$  calcd.: C, 28.04; H, 1.51; Fe, 27.94%; mol. wt., 600.) M.p.  $67^\circ$  (sealed tube).  $^1\text{H}$  NMR: doublet at  $\tau$  6.22 ppm;  $J(\text{P-H})$  11.0 cps.

(c). The third band was eluted off with 50 ml of 2/3 cyclohexane/benzene and the eluate was evaporated to an oily residue. Addition of *ca.* 5 ml of *n*-pentane followed by removal of the solvent yielded dark green crystals. The product was placed in a sublimator at  $60^\circ$  and *ca.* 0.1 mm for 24 h. (i) Sublimate (0.06 g): Identified as  $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$  by infrared spectroscopy<sup>6</sup>, elemental analyses, and molecular weight. (Found: C, 28.06; H, 4.70; mol. wt., 371.  $\text{C}_9\text{H}_{18}\text{FeO}_9\text{P}_2$  calcd.: C, 27.86; H, 4.68%; mol. wt., 388.) M.p.  $72^\circ$  (sealed tube).  $^1\text{H}$  NMR: 1/2/1 triplet at  $\tau$  6.26 ppm;  $J(\text{P-H}) \sim 11$  cps. (ii) Residue (0.21 g): Purified by dissolution in a minimum amount of chloroform, filtration, addition of 6–8 times this volume of *n*-pentane, cooling to  $-78^\circ$ , and filtering off the dark green crystals of  $\text{Fe}_3(\text{CO})_{10}[\text{P}(\text{OCH}_3)_3]_2$ . Yield 15%. (Found: C, 27.47; H, 2.59; mol. wt., 689.  $\text{C}_{16}\text{H}_{18}\text{Fe}_3\text{O}_{16}\text{P}_2$  calcd.: C, 27.62; H, 2.61%; mol. wt., 696.) M.p.  $105^\circ$  (sealed tube).  $^1\text{H}$  NMR: doublet at  $\tau$  6.26 ppm;  $J(\text{P-H})$  11 cps.

(d). The final band was eluted off with 50 ml of benzene and the eluate was evaporated to a viscous oil. Addition of *ca.* 5 ml of *n*-pentane followed by removal of the solvent yielded 0.06 g (3.8%) of dark green crystals of  $\text{Fe}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$ . (Found: C, 27.22; H, 3.41; Fe, 20.99; mol. wt., 736.  $\text{C}_{18}\text{H}_{27}\text{Fe}_3\text{O}_{18}\text{P}_3$  calcd.: C, 27.30; H, 3.44; Fe, 21.16%; mol. wt., 792.) M.p.  $107^\circ$  (sealed tube).  $^1\text{H}$  NMR: doublet at  $\tau$  6.29 ppm;  $J(\text{P-H})$  11 cps.

#### Reaction of $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$ with $\text{P}(\text{OCH}_3)_3$

One gram (8.1 mmoles) of  $\text{P}(\text{OCH}_3)_3$  and 0.38 g (0.63 mmole) of  $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$  in 50 ml of cyclohexane were heated at bath temperature of  $100^\circ$  for *ca.* 5 min. The reaction mixture was cooled to room temperature and then filtered. The residue was washed with 10 ml of benzene, and the wash and the filtrate were combined and chromatographed using a  $2.5 \times 10$  cm column. Development of the chromatogram with cyclohexane yielded two dark green bands. These were eluted off and the eluates treated in a manner similar to that described above for the last two bands from the reaction of  $\text{Fe}_3(\text{CO})_{12}$  with  $\text{P}(\text{OCH}_3)_3$ . The yields: 0.11 g (25%) of  $\text{Fe}_3(\text{CO})_{10}[\text{P}(\text{OCH}_3)_3]_2$  along with 0.07 g of  $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$  and a trace of  $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3$  from band one and 0.21 g (43%) of  $\text{Fe}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$  from band two.

#### ACKNOWLEDGEMENT

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