CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Complexes of Trivalent Phosphorus Derivatives. V. Photochemical Reactions of Silicon and Tin Derivatives of Cyclopentadienyliron Dicarbonyl with Trivalent Phosphorus Ligands[1,2]

BY R. B. KING[3] AND K. H. PANNELL[4]

Received February 26, 1968

Ultraviolet irradiation of $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si or Sn) with the monodentate trivalent phosphorus ligands PR_3 ($R = C_6H_5$ or OC_6H_5) gives the orange monocarbonyl derivatives $(CH_3)_3EFe(CO)(PR_3)(C_5H_5)$ (E = Si or Sn; $R = C_6H_5$ or OC_6H_5). Similar ultraviolet irradiation of $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si or Sn) with the chelating ditertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ gives the orange carbonyl-free derivatives $(CH_3)_3EFe(diphos)(C_5H_5)$ (E = Si or Sn). The infrared and proton nmr spectra of the new compounds are discussed.

Introduction

Recently reactions of trivalent phosphorus derivatives with σ-bonded alkyl and aryl derivatives of the type $RFe(CO)_2C_5H_5$ have received some attention. Thus the methyl derivative $CH_3Fe(CO)_2C_5H_5$ was found to react with monodentate trivalent phosphorus derivatives of the type R_3P to give either the substituted methyl derivatives $CH_3Fe(CO)(PR_3)(C_5H_5)$ or the substituted acetyl derivatives $CH_3COFe(CO)(PR_3)(C_5H_5)$ depending upon the reaction conditions.[5,6] Reaction of the phenyl derivative $C_6H_5Fe(CO)_2C_5H_5$ with triphenyl phosphite has been reported to remove the phenyl groups as well as the two carbonyl ligands giving the binuclear complex $[C_5H_5Fe[P(OC_6H_5)_3]_2]_2$.[7]

This paper describes the reactions of the compounds $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si or Sn) with representative trivalent phosphorus ligands. This study provides an opportunity to examine the effect of substituting an iron–silicon or an iron–tin σ bond for an iron–carbon σ bond on the course of reactions of $RFe(CO)_2C_5H_5$ compounds with trivalent phosphorus ligands. The phosphorus ligands used were the monodentate tertiary phosphine $(C_6H_5)_3P$, the monodentate tertiary phosphite $(C_6H_5O)_3P$, and the bidentate tertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (designated as "Pf—Pf"), and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (designated as "Pf=Pf").

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratories, Bonn, Germany. Infrared spectra of the new compounds (Table II) were taken in KBr pellets and recorded on a Perkin-Elmer Model 621 spectrometer. In addition, the ν(CO) frequencies of the new carbonyl derivatives prepared during this work were determined in cyclohexane solution. Infrared spectra of some of the reaction mixtures were investigated on this spectrometer in order to follow the course of the reaction by means of the disappearance of the ν(CO) frequencies of the $(CH_3)_3EFe(CO)_2C_5H_5$ starting material. Proton nmr spectra were taken in chloroform-*d* solutions and recorded on a Varian A-60 spectrometer. Ultraviolet irradiations were carried out using a 150-W mercury lamp containing ~7 mm of argon pressure[8] placed in a Pyrex tube immersed in the reaction mixture.

Ligands.—Triphenyl phosphite and triphenylphosphine were commercial samples.[9] Samples of the triphenylphosphine were converted to the chelating ditertiary phosphines *via* lithium diphenyl phosphide in tetrahydrofuran solution using published procedures.[10]

Iron Complexes.[11,12]—Commercial $Fe(CO)_5$ (Antara Division of General Aniline and Film Corp., New York, N. Y.) was converted to $[C_5H_5Fe(CO)_2]_2$ by the published procedure.[13] This was reduced with 1% sodium amalgam in redistilled tetrahydrofuran solution to give orange-brown $NaFe(CO)_2C_5H_5$ which was treated with the appropriate $(CH_3)_3ECl$ derivative. Some details on the isolation of the $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si and Sn) compounds are presented here, since only relatively meager experimental details were presented in the original reports of these compounds.[11,12]

$(CH_3)_3SiFe(CO)_2C_5H_5$.[11]—Reaction of 100 mmol of $NaFe(CO)_2C_5H_5$ with an excess (20 ml, 17 g, 157 mmol) of $(CH_3)_3SiCl$ in 400 ml of tetrahydrofuran gave a brown solution from which the solvent was removed at ~40° (40 mm). The residue was extracted with pentane and solvent removed from the filtered extracts at ~25° (40 mm). Sublimation of the resulting oily residue at 58° (0.2 mm) gave 10.2 g (41% yield) of orange waxy solid $(CH_3)_3SiFe(CO)_2C_5H_5$.

$(CH_3)_3SnFe(CO)_2C_5H_5$.[11,12,14]—The preparation was carried out on a 100-mmol scale like that of its silicon analog using hex-

---

[1] For Part IV of this series see R. B. King and C. A. Eggers, *Inorg. Chim. Acta*, in press.

[2] Portions of this work were presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[3] Fellow of the Alfred Sloan Foundation, 1967–1969.

[4] Postdoctoral research associate supported by Grant GP-7081 of the National Science Foundation, June–Dec 1967.

[5] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

[6] J. P. Bibler and A. Wojcicki, *ibid.*, **5**, 889 (1966).

[7] A. N. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.* (Amsterdam), **9**, 345 (1967).

[8] This ultraviolet irradiation equipment is available from Nester-Faust Manufacturing Corp., Newark, Del. After this work was completed, related experiments were carried out which suggest that in some cases improved results might be obtained by using a more powerful (450-W) mercury lamp available from Englehard-Hanovia, Newark, N. J.

[9] Triphenyl phosphite was purchased from Fisher Scientific Corp. and triphenylphosphine from Eastern Chemical Co., Pequannock, N. J.

[10] For the preparation of these ligands see the following references: (a) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, J. Chatt and F. S. Hart, *J. Chem. Soc.*, 1378 (1960); (b) *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[11] For the original report on $(CH_3)_3SiFe(CO)_2C_5H_5$ see T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwissenschaften*, **43**, 129 (1956).

[12] The compound $(CH_3)_3SnFe(CO)_2C_5H_5$ has been studied by J. Kenney and W. A. G. Graham cited by H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965), and by W. A. G. Graham in papers presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 1965, and at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; see also R. E. J. Bichler, M. R. Booth, and H. C. Clark, *Inorg. Nucl. Chem. Letters*, **3**, 71 (1967).

[13] R. B. King, *Organometal. Syn.*, **1**, 114 (1965).

[14] R. B. King and E. W. Gowling, unpublished results.

TABLE I

NEW COMPOUNDS PREPARED IN THIS WORK

Compound[a]	Color	Mp, °C	Yield,[b] %	Analyses, %									
				C		H		O		P		Other	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(CH_3)_3SiFe(CO)[P(C_6H_5)_3](C_5H_5)$	Orange	163–164	39 (48)[c]	66.9	67.3	6.0	6.4	3.3	3.0	6.4	5.9	5.8	5.8 (Si)
$(CH_3)_3SnFe(CO)[P(C_6H_5)_3](C_5H_5)$	Orange	127–128	40 (16)[d,c]	56.4	56.3	5.1	5.2	2.8	3.0	5.6	5.5	9.7	9.5 (Fe)
$(CH_3)_3SiFe(CO)[P(OC_6H_5)_3](C_5H_5)$	Orange	95–96	12 (96)[d,c,e]	61.0	61.0	5.5	5.8					10.5	11.2 (Fe)
$(CH_3)_3SnFe(CO)[P(OC_6H_5)_3](C_5H_5)$	Orange	99–100	28 (24)[d,c]	52.1	52.5	4.7	5.0	10.3	10.1	5.0	5.0		
$(CH_3)_3SiFe(Pf—Pf)(C_5H_5)$	Orange	179–181 dec	16 (15)[f]	68.8	68.5	6.4	6.6	...	...	10.4	9.9	9.4	9.5 (Fe)
$(CH_3)_3SnFe(Pf—Pf)(C_5H_5)$	Orange	190–200 dec	49 (18)[d]	59.8	59.4	5.6	5.9	...	...	9.1	8.8	8.2	8.4 (Fe)
$(CH_3)_3SiFe(Pf{=}Pf)(C_5H_5)$	Orange	~176 dec	11 (18)[c]	69.1	69.3	6.1	6.5	...	...	10.5	10.2	9.5	8.8 (Fe)
$(CH_3)_3SnFe(Pf{=}Pf)(C_5H_5)$	Red	175 dec	30 (10)[c,c]	59.1	60.2	5.3	5.7	...	...	8.9	8.8	8.1	8.0 (Fe)

[a] Pf—Pf = 1,2-bis(diphenylphosphino)ethane, Pf=Pf = *cis*-1,2-bis(diphenylphosphino)ethylene. [b] Purification processes used for product isolation indicated by footnotes in the sequence performed. Reaction time in hours given in parentheses. [c] Recrystallized from hexane. [d] The reaction mixture was chromatographed as described in the Experimental Section. [e] An 8% yield of $\{C_5H_5Fe[P(OC_6H_5)_3]\}_2$, mp 133–134° (lit.[7] mp 131–132°) was also obtained from this reaction. [f] This product was separated from a more strongly absorbed unidentified green material (ν(CO) 1670 cm^{-1}) by chromatography on alumina in CH_2Cl_2 solution.

TABLE II

INFRARED SPECTRA OF COMPOUNDS PREPARED IN THIS WORK[a]

Compounds[b]	ν(CH)	ν(CO)[c]	Other bands
$(CH_3)_3SiFe(CO)[P(C_6H_5)_3](C_5H_5)$	3050 w, 2965 vw, 2948 w, 2890 vw	1916 s	1481 w, 1435 m, 1402 m, 1311 vw, 1255 vw, 1240 m, 1195 sh, 1182 vw, 1160 vw, 1115 vw, 1095 m, 1085 m, 1030 vw, 1013 vw, 1002 w, 845 m, 827 s, 749 sh, 742 m, 699 s, 667 m
$(CH_3)_3SnFe(CO)[P(C_6H_5)_3](C_5H_5)$	3060 vw, 2960 w, 2895 vw	1918 s	1479 w, 1431 m, 1400 m, 1182 w, 1160 vw, 1085 m, 1029 vw, 1012 vw, 999 w, 840 w, 830 m, 743 m, 692 m
$(CH_3)_3SiFe(CO)[P(OC_6H_5)_3](C_5H_5)$	2946 w, 2898 vw	1953 s	1591 m, 1489 s, 1459 w, 1401 w, 1240 m, 1226 m, 1200 s, 1181 s, 1168 m, 1072 w, 1068 sh, 1030 w, 1011 sh, 912 s, 900 s, 872 s, 823 m, 778 m, 766 s, 743 w, 732 w, 722 w
$(CH_3)_3SnFe(CO)[P(OC_6H_5)_3](C_5H_5)$	3061 vvw, 3038 vvw, 2983 vw, 2967 vw, 2901 vw	1949 s	1591 m, 1487 s, 1452 w, 1401 w, 1218 m, 1192 s, 1168 w, 1163 m, 1155 w, 1069 w, 1065 w, 1022 w, 1004 w, 917 s, 909 s, 902 m, 892 s, 873 s, 842 w, 833 w, 778 s, 767 s, 755 m, 723 m, 714 m, 690 m
$(CH_3)_3SiFe(Pf—Pf)(C_5H_5)$	3049 vvw, 2956 vvw, 2926 vw, 2873 vw	...	1483 w, 1438 m, 1404 w, 1266 vw, 1248 vw, 1228 w, 1096 w, 1076 vw, 1030 vw, 1002 vw, 831 m, 810 m, 741 m, 698 s, 678 vw
$(CH_3)_3SnFe(Pf—Pf)(C_5H_5)$	*d*	...	1480 w, 1430 m, 1403 w, 1259 vw, 1148 vw, 1095 w, 1083 m, 1020 vw, 992 w, 867 w, 830 w, 810 w, 801 m, 738 m, 692 s, 675 m
$(CH_3)_3SiFe(Pf{=}Pf)(C_5H_5)$	3074 vvw, 3057 vvw, 2933 vvw, 2883 vvw	...	1482 w, 1434 m, 1406 w, 1249 vw, 1230 w, 1187 vw, 1162 vvw, 1099 w, 1090 w, 1077 w, 1031 vw, 1003 w, 831 m, 813 m, 762 vw, 752 w, 735 m, 722 m, 700 s 644 vw, 614 w, 554 m, 533 w
$(CH_3)_3SnFe(Pf{=}Pf)(C_5H_5)$	3074 vvw, 3055 vw, 2959 vvw, 2900 vvw	...	1482 w, 1434 w, 1409 w, 1306 vw, 1274 vw, 1184 vw, 1160 vw, 1099 w, 1089 w, 1074 w, 1029 vw, 1003 w, 839 w, 815 w, 773 w, 751 m, 727 m, 719 m, 694 s, 554 m, 533 m

[a] These spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer. All reported infrared frequencies are in cm^{-1}. [b] The same abbreviations are used as in Table I, footnote *a*. [c] These frequencies were determined in cyclohexane solution. [d] These frequencies were too weak to be unequivocally observed.

ane rather than pentane for the extraction step. Removal of hexane from the filtered extract gave a liquid which was distilled at 82–84° (0.3 mm) to give 18.5 g (54% yield) of yellow-orange liquid $(CH_3)_3SnFe(CO)_2C_5H_5$, d^{25} 1.71 g./ml. Although liquid at room temperature, this material was solid in a freezer at −10°.

Reactions of $(CH_3)_3EFe(CO)_2C_5H_5$ with Trivalent Phosphorus Derivatives. General Procedure.—A 0.3–1.2-g sample of the $(CH_3)_3EFe(CO)_2C_5H_5$ compound, a quantity of the trivalent phosphorus ligand corresponding to two phosphorus atoms for each iron atom, and 100–200 ml of hexane were exposed to ultraviolet irradiation for several hours. In many cases the course of the reaction was followed by periodic observation of the ν(CO) infrared frequencies. After the reaction period was over, solvent was removed from the reaction mixture at ~35° (40 mm). In most cases the residue was dissolved in a mixture of dichloromethane and hexane and poured down a 15–30-cm alumina chromatography column. Excess ligand was removed by washing the column with 100–200 ml of hexane. The yellow band of product was eluted with a mixture of dichloromethane and hexane. Solvent was removed from the eluate at 35° (40 mm). The solid residue was recrystallized from hexane to give pure product. Dichloromethane was added to the hexane for these crystallizations in cases where hexane was too poor a solvent to use alone.

Discussion

In their reactions with the $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si or Sn) compounds the monodentate ligands PR_3 (R = C_6H_5 or OC_6H_5) replaced one carbonyl group

TABLE III

PROTON NMR SPECTRA[a]

Compound[b]	Chemical shifts,[c] τ C_6H_5	π-C_5H_5	PCH[d]	$(CH_3)_3E$	$J(Sn-CH_3)$, cps
$(CH_3)_3SnFe(CO)_2(C_5H_5)$	...	5.32 s	...	9.68	47
$(CH_3)_3SnFe(CO)[P(OC_6H_5)_3](C_5H_5)$	2.78	5.95	...	9.69	44
$(CH_3)_3SnFe(CO)[P(C_6H_5)_3](C_5H_5)$	2.7	5.80 d (1.2)	...	10.11	39
$(CH_3)_3SnFe(Pf{=}Pf)(C_5H_5)$	2.6, 2.8	5.81 t (1.3)	*e*	10.67	35
$(CH_3)_3SnFe(Pf{-}Pf)(C_5H_5)$	2.6, 2.7	5.82 t (1.3)	7.63 d (12)	10.55	35
$(CH_3)_3SiFe(CO)_2(C_5H_5)$	...	5.36 s	...	9.61	...
$(CH_3)_3SiFe(CO)[P(OC_6H_5)_3](C_5H_5)$	2.76	5.84 d (1.5)	...	9.59	...
$(CH_3)_3SiFe(CO)[P(C_6H_5)_3](C_5H_5)$	2.5, 2.7	5.83	...	9.99	...
$(CH_3)_3SiFe(Pf{=}Pf)(C_5H_5)$	2.6, 2.8	5.80 t (1.2)	*e*	10.57	...
$(CH_3)_3SiFe(Pf{-}Pf)(C_5H_5)$[f]	2.6–2.8	5.85	7.6	10.47	...

[a] These spectra were taken in chloroform-*d* solutions. [b] Pf—Pf = 1,2-bis(diphenylphosphino)ethane; Pf=Pf = *cis*-1,2-bis(diphenylphosphino)ethylene. [c] s, singlet; d, doublet; t, triplet; separation in cps given in parentheses. [d] CH_2 protons of Pf—Pf; CH=CH protons of Pf=Pf. [e] Not unequivocally observed because of its weakness.

whereas the chelating bidentate ligands $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ replaced both carbonyl groups. Prolonged irradiation of $(CH_3)_3EFe(CO)_2C_5H_5$ with excess of the monodentate PR_3 ligands failed to replace the second carbonyl group. On the other hand, there was some evidence for the production of a monocarbonyl $(CH_3)_3EFe(CO)(L)(C_5H_5)$ intermediate in the reaction between $(CH_3)_3EFe(CO)_2C_5H_5$ and the chelating ditertiary phosphines. Thus the infrared spectrum of the solution obtained after irradiating a mixture of $(CH_3)_3SnFe(CO)_2C_5H_5$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ for 8 hr exhibited a band at 1918 cm^{-1} corresponding to the ν(CO) frequency of an intermediate monocarbonyl derivative presumably either $(CH_3)_3SnFe(Pf{=}Pf)(CO)(C_5H_5)$ with one uncoordinated phosphorus atom or $(CH_3)_3SnFe(CO)(C_5H_5)(Pf{=}Pf)Fe(CO)(C_5H_5)Sn(CH_3)_3$ with a bridging ditertiary phosphine ligand. In the case of the irradiation of $(CH_3)_3SiFe(CO)_2C_5H_5$ with $(C_6H_5)_2PCH_2P(C_6H_5)_2$, a dirty yellow, sparingly soluble solid was isolated with a single ν(CO) frequency at 1900 cm^{-1} (KBr pellet). Analyses suggested this to be impure $(CH_3)_3SiFe(CO)(C_5H_5)(Pf{-}Pf)Fe(CO)(C_5H_5)Si(CH_3)_3$.

In the reaction of $CH_3Fe(CO)_2C_5H_5$ with triphenylphosphine, carbonyl insertion into the methyl–iron bond occurred[5,6] resulting in the acetyl derivative $CH_3COFe(CO)P(C_6H_5)_3(C_5H_5)$. However, in the reactions of the compounds $(CH_3)_3EFe(CO)_2C_5H_5$ (E = Si and Sn) with trivalent phosphorus derivatives, analogous carbonyl insertion reactions to give $(CH_3)_3ECO$ derivatives were never observed. Apparently the silicon–iron and tin–iron bonds are so stabilized by $d\pi$–$d\pi$ bonding that they cannot be broken by a carbonyl ligand as is required for the insertion reaction. The tin–iron bond appears to be more stable than the silicon–iron bond in compounds of the type $(CH_3)_3EFeL_2C_5H_5$ (E = Si or Sn; L = CO, R_3P, etc.). In none of the reactions of $(CH_3)_3SnFe(CO)_2C_5H_5$ were products isolated where the tin–iron bond had been broken. However, in the photochemical reaction of $(CH_3)_3SiFe(CO)_2C_5H_5$ with triphenyl phosphite, an 8% yield of the silicon-free derivative $[C_5H_5Fe[P(OC_6H_5)_3]_2]_2$ was obtained in addition to a 12% yield of the substitution product $(CH_3)_3SiFe(CO)[P(OC_6H_5)_3](C_5H_5)$. The formation of the silicon-free derivative clearly must involve cleavage of the silicon–iron bond. Silicon–iron bond cleavage also occurred during the ultraviolet irradiation of $(CH_3)_3SiFe(CO)_2C_5H_5$ with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)$ since a green silicon-free unidentified cyclopentadienyliron carbonyl complex was produced with a characteristic ν(CO) frequency at 1670 cm^{-1}. The same green complex was obtained by ultraviolet irradiation of $[C_5H_5Fe(CO)_2]_2$ with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. The greater stability of the tin–iron bond relative to the silicon–iron bond is also suggested by the consistently higher product yields in reactions of $(CH_3)_3SnFe(CO)_2C_5H_5$ with the tricovalent phosphorus derivatives than in the corresponding reactions of the silicon analog. The tin–iron derivatives gave better quality nmr spectra than the silicon–iron derivatives indicative of less decomposition to paramagnetic impurities in solution.

The absence of carbonyl groups in the compounds $(CH_3)_3EFe(diphos)(C_5H_5)$ was confirmed by the absence of ν(CO) frequencies in their infrared spectra. The infrared spectra of the monocarbonyl derivatives $(CH_3)_3EFe(CO)(PR_3)(C_5H_5)$ in cyclohexane solution exhibited the expected single strong ν(CO) frequency at 1917 ± 1 cm^{-1} for the triphenylphosphine derivatives and at 1951 ± 2 cm^{-1} for the triphenyl phosphite derivatives. The lower value of the ν(CO) frequency in the triphenylphosphine derivatives relative to that in the triphenyl phosphite derivatives is a consequence of the poorer π-acceptor strength of triphenylphosphine. Triphenylphosphine therefore removes less electron density from the iron atom leaving more available for $d\pi$–$p\pi$ bonding with the carbonyl group. This increases the carbon–iron bond order and hence reduces the carbon–oxygen bond order thus accounting for the decrease in ν(CO) frequency in going from the triphenylphosphite derivatives to corresponding triphenylphosphine derivatives.

The proton nmr spectra of the new complexes (Table III) exhibited the expected features. Thus broad resonances were observed in the range τ 2.6–2.8 from the slightly nonequivalent aryl protons of the phenylphosphorus ligands. The π-C_5H_5 resonances were sharp. However, in the better resolved spectra they were split into a doublet or triplet (J = ~1 cps) by interaction with the one or two phosphorus atoms of the coordinated phosphorus ligands. The chemical shifts of the π-C_5H_5 protons occurred in the range τ 5.8–5.9 and were thus appreciably higher than those in the unsubstituted compounds $(CH_3)_3EFe(CO)_2C_5H_5$. Replacement of carbonyl groups with the more weakly π-accepting trivalent phosphorus ligands would be expected to increase the electron density on the metal atom. Some of this electron density can be transferred to the antibonding orbitals of the π-C_5H_5 ring. This would be expected to increase the shielding of the protons of the π-C_5H_5 ring and hence raise their chemical shift. The fact that the chemical shifts in all of the trivalent phosphorus derivatives in Table III are the same regardless of the π-accepting qualities of the phosphorus ligand and of the remaining number of carbonyl groups can be attributed to the fact that replacement of one carbonyl group in the $(CH_3)_3EFe(CO)_2C_5H_5$ compounds with a more weakly π-accepting phosphorus ligand increases the electron density in the π-C_5H_5 antibonding orbitals to near the saturation point. Additional electron density obtained either by substitution of the second carbonyl group with a more weakly π-accepting ligand or by use of still more weakly π-accepting phosphorus ligands is not fed into the π-C_5H_5 antibonding orbitals. Instead this extra electron density appears to be fed into the $(CH_3)_3E$ group by increased dπ–dπ bonding between the iron atom and the silicon or tin atom. This suggestion is supported by the steady increase in the nmr chemical shifts of the $(CH_3)_3E$ protons of the $(CH_3)_3EFeL_2C_5H_5$ compounds with the following variation of the L ligands: 2CO (least) $\sim$ CO, $P(OC_6H_5)_3$ $<$ CO, $P(C_6H_5)_3$ $<$ diphos (greatest). Except for the first approximate equality, this sequence corresponds to decreasing π-acceptor ability of the L ligands. Increasing the dπ–dπ bonding between the iron atom and the silicon or tin atoms increases the negative charge on the silicon or tin atom and hence decreases its electronegativity. Prior data[15] suggest that a decrease in the electronegativity of an atom increases the chemical shift of an attached methyl group.

The methyl resonances of the trimethyltin derivatives exhibited satellites corresponding to coupling of the methyl protons with the magnetically active tin isotopes ^{117}Sn and ^{119}Sn. The resolution of the spectra did not permit unequivocal separation of the coupling with the two different tin isotopes which differ by only about 4%. The values given in Table III may be regarded as an average of these two coupling constants. Progressive substitution of carbonyl groups in $(CH_3)_3SnFe(CO)_2C_5H_5$ with more weakly π-accepting trivalent phosphorus ligands lowers the $J(Sn\text{–}CH_3)$ coupling constant. The increased dπ–dπ iron–tin bonding which occurs upon substitution with more weakly π-accepting ligands increases the involvement of the d orbitals in the bonding of the tin atom which may lower the s character of the tin orbitals bonding to the methyl groups. Flitcroft and Kaesz[16] indicate that a reduction in the s character of the tin orbital in the $Sn\text{–}CH_3$ bond leads to a reduction in the $J(Sn\text{–}CH_3)$ coupling constant in agreement with our observations.

Acknowledgment.—We are indebted to the National Science Foundation for generous support of this work under Grant GP-7081. We are also indebted to Dr. William Atwell of Dow-Corning Corp. for generous samples of trimethylchlorosilane and to Dr. William Considine of M and T Chemical Corp. for generous samples of trimethyltin chloride.

---

[15] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

[16] N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

CONTRIBUTION FROM THE RESEARCH CENTER OF HERCULES INC.,
WILMINGTON, DELAWARE 19899

Cyclopentadienylcobalt Derivatives of Chelating Aromatic Ligands

BY RICHARD F. HECK

Received March 1, 1968

A series of five-coordinate cyclopentadienylcobalt complexes has been prepared by allowing diiodocarbonylcyclopentadienylcobalt(III) to react with *ortho*-substituted benzene derivatives containing phenolic, amino, and thiophenolic groups, in the presence of a base. The products are probably best formulated as cobalt(I) derivatives with *o*-quinoidal-type ligands rather than as five-coordinate cobalt(III) complexes.

Introduction

Stable coordination complexes of group VIII metal ions with the dianions of toluene-3,4-dithiol, catechol, *o*-phenylenediamine, and related derivatives have recently been reported by Balch, Röhrscheid, and Holm.[1] *o*-Phenylenediamidocyclopentadienylcobalt(III) was also reported recently from the reaction of *o*-phenylenediamine with dicarbonylcyclopentadienylcobalt(I) and oxygen.[2] These reports prompted us to attempt to prepare the complete series of related chelates with oxygen

---

[1] A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

[2] T. Joh, N. Hagihara, and S. Murahashi, *Bull. Chem. Soc. Japan*, **40**, 661 (1967).