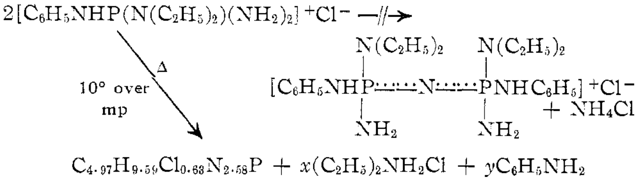
The mass spectra show in each case the presence of the dialkylamine ion, *i.e.* (m/e): $N(CH_3)_2^+$, 44; $N(C_2H_5)_2^+$, 72; $N(n\text{-}C_4H_9)^+$, 128; $N(CH_3)CH_2C_6H_5^+$, 120. Moreover, the mass peak of aniline (m/e 93) can be found in all cases; this is in agreement with the results of the pyrolysis of $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$, where splitting off of the corresponding secondary amine (as diethylammonium chloride) and of aniline could be shown. The mass peak of the mother ion could be found in the mass spectra of compounds II and III.

The aminophosphonium chlorides behave in acetonitrile as 1:1 electrolytes. The Λ_0 and the K_c values at 25° are summarized in Table VII.

Polarographic measurements of $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$ in dimethyl sulfoxide gave the result that the cation is reduced in one step with $E_{1/2} = -2.43$ V (*vs.* the aqueous saturated calomel electrode). The limiting current is diffusion controlled in the investigated concentration range of 5×10^{-4} to 1.2×10^{-3} M. The reduction was found to be irreversible (82 mV) and the diffusion coefficient is $D = 1.5 \times 10^{-6}$ cm^2 sec^{-1} (25°, tetraethylammonium perchlorate), with a diffusion current constant $I = 0.74$. The temperature coefficient of the diffusion current is 0.43%/deg in the investigated temperature range (20–40°).

The thermal condensation reaction and the mass spectra of I–IV indicate that the phosphonium chlorides do not lose NH_4Cl on heating but do lose dialkylammonium chloride and aniline in primarily an intramolecular condensation, where the most basic species are split off



$$2[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^- \not\longrightarrow [C_6H_5NH\overset{N(C_2H_5)_2}{\underset{NH_2}{P}}\cdots N\cdots\overset{N(C_2H_5)_2}{\underset{NH_2}{P}}NHC_6H_5]^+Cl^- + NH_4Cl$$

$$\xrightarrow[\text{10° over mp}]{\Delta} C_{4.97}H_{9.59}Cl_{0.63}N_{2.58}P + x(C_2H_5)_2NH_2Cl + yC_6H_5NH_2$$

It was not possible to assign a definite structural formula to the above pyrolysis product.

Acknowledgments.—We wish to thank Dipl.-Ing. F. Kohlbeck for computing the electric conductance data and Dipl.-Ing. G. Peychal-Heiling (both of Technische Hochschule Wien) for the polarographic measurements.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30601

Complexes of Trivalent Phosphorus Derivatives. IX. Reactions of Cyclopentadienylmetal Carbonyl Halides with Chelating Oligotertiary Phosphines[1]

By R. B. King,[2] L. W. Houk,[3] and K. H. Pannell[3]

Received November 11, 1968

Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with chelating ditertiary phosphines gives the red to orange monocarbonyls $C_5H_5Mo(CO)(diphos)Cl$ which can also be prepared by ultraviolet irradiation of the salts $[C_5H_5Mo(CO)_2(diphos)]Cl$. Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the chelating tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ gives red $C_5H_5Mo(CO)(triphos)Cl$ with one of the three phosphorus atoms not bonded to the metal atom. Ultraviolet irradiation of the halides $C_5H_5Fe(CO)_2X$ (X = Cl or Br) with the chelating ditertiary phosphines in benzene solution gives the black derivatives $C_5H_5Fe(diphos)X$. However, reaction of $C_5H_5Fe(CO)_2I$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$ gives the green binuclear derivative $[C_5H_5Fe(CO)I](CH_3)_2PCH_2CH_2P(CH_3)_2[Fe(CO)IC_5H_5]$ with a bridging ditertiary phosphine ligand. Ultraviolet irradiation of the halides $C_5H_5Fe(CO)_2X$ (X = Cl or Br) with the chelating tritertiary phosphine listed above followed by chromatography on alumina gives yellow salts of the $C_5H_5Fe(triphos)^+$ cation. Reaction of $C_5H_5Co(CO)I_2$ with the chelating ditertiary phosphines at room temperature gives the brown ionic iodides $[C_5H_5Co(diphos)I]I$ which can be converted to the corresponding brown hexafluorophosphates $[C_5H_5Co(diphos)I][PF_6]$. A similar treatment of $C_5H_5Co(CO)I_2$ with the tritertiary phosphines gives the orange ionic diiodide $[C_5H_5Co(triphos)]I_2$ which can be converted to the corresponding yellow bis(hexafluorophosphate) $[C_5H_5Co(triphos)][PF_6]_2$.

The development of the chemistry of cyclopentadienylmetal derivatives containing the strongly π-accepting carbonyl ligands into a major area of transition metal organometallic chemistry makes of interest the development of the chemistry of cyclopentadienylmetal derivatives containing the relatively weakly π-accepting tertiary phosphine ligands. However, compounds containing only π-cyclopentadienyl and tertiary phosphine ligands analogous to the cyclopentadienylmetal carbonyls are unknown. A useful series of intermediates for exploration of this area of chemistry are cyclopentadienylmetal halides containing tertiary phosphine ligands but no carbonyl groups. Known examples of such compounds are $C_5H_5MX_2PR_3$ (M = Co[4]

---

(1) (a) For part VIII of this series see R. B. King and T. F. Korenowski, *J. Organometal. Chem.*, in press. (b) The generic term "oligotertiary phosphine" is used to describe phosphines containing more than one tertiary phosphine group. The more conventional term "polytertiary phosphine" seems inappropriate here since the tertiary phosphines presently under study all contain less than four phosphorus atoms.

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) Postdoctoral fellows supported by the Air Force Office of Scientific Research during the period of this work.

(4) (a) R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964); *Inorg. Chem.*, **5**, 82 (1966); (b) R. F. Heck, *ibid.*, **4**, 855 (1965); (c) H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, **38**, 2212 (1965).

and Rh[5]) and $C_5H_5NiXPR_3$.[6] Attempts by previous workers[7,8] to prepare similar compounds of molybdenum and iron by reactions of the cyclopentadienylmetal carbonyl halides $C_5H_5M(CO)_nX$ ($M = Mo$, $n = 3$; $M = Fe$, $n = 2$) with tertiary phosphines have instead led to compounds still containing carbonyl groups of the types $C_5H_5Mo(CO)_n(PR_3)_{3-n}X$ (n = 1 and 2) and $C_5H_5Fe(CO)(PR_3)X$ as well as the metal carbonyl cations $C_5H_5Mo(CO)_n(PR_3)_{4-n}{}^+$ (n = 2 and 3) and $C_5H_5Fe(CO)_n(PR_3)_{3-n}{}^+$ (n = 1 and 2). It appeared possible that substitution of chelating ditertiary and tritertiary phosphines for the monodentate tertiary phosphines used mostly by previous workers[7,8] might enable complete substitution of carbonyl groups in the halides $C_5H_5Mo(CO)_3X$ and $C_5H_5Fe(CO)_2X$ to be achieved. This paper describes reactions of the halides $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I) with the chelating ditertiary phosphines $R_2PCH_2CH_2PR_2$ ($R = CH_3$ or C_6H_5) and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ and the chelating tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$. In the cases of the cyclopentadienyliron dicarbonyl halides complete substitution was achieved to give derivatives of the types $C_5H_5Fe(diphos)X$ and $C_5H_5Fe(triphos)^+$. However, the molybdenum halide $C_5H_5Mo(CO)_3Cl$ gave only additional representatives of the known[7] compound type $C_5H_5Mo(CO)(diphos)Cl$. This paper also describes reactions of $C_5H_5Co(CO)I_2$ with the chelating oligotertiary phosphines to give the novel cations $C_5H_5Co(diphos)I^+$ and $C_5H_5Co(triphos)^{2+}$.

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer. Proton nmr spectra were taken in chloroform-*d* or acetone-d_6 solutions and were recorded on a Varian HA-100 spectrometer at 100 Mc or a Varian A-60 spectrometer at 60 Mc. Melting points were taken of samples in capillaries and are uncorrected. Conductivity measurements (Table I) were taken in acetone solution using an Industrial Instruments Model RC16B2 conductivity bridge. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated vessels. Ultraviolet irradiations were performed by an Englehard-Hanovia water-cooled 450-W mercury lamp.

The chelating ditertiary phosphine ligands were prepared by various published methods[9] all based on the reaction of 1,2-dichloroethane or *cis*-1,2-dichloroethylene with the appropriate alkali metal dialkylphosphide, MPR_2, in liquid ammonia ($R = CH_3$; $M = Na$) or tetrahydrofuran ($R = C_6H_5$; $M = Li$). The chelating tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane was prepared by the published procedure[9a] using the reaction between 1,1,1-tris(chloromethyl)ethane[10] and sodium diphenylphosphide (from $(C_6H_5)_2PH$ and sodium) first in liquid ammonia and then in boiling tetrahydrofuran. The cyclopentadienylmetal carbonyl halides $C_5H_5Mo(CO)_3Cl$, $C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I), and $C_5H_5Co(CO)I_2$ were prepared by various published procedures.[11,12]

Preparation of the Compounds $C_5H_5Mo(CO)(diphos)Cl$.—A small sample (0.2–0.5 g) of $C_5H_5Mo(CO)_3Cl$ was converted to the salt $[C_5H_5Mo(CO)_2(diphos)]Cl$ by reaction with the chelating ditertiary phosphine in benzene solution by the previously described procedure.[12] A suspension of this salt in benzene was exposed to ultraviolet irradiation at room temperature with stirring. The salt gradually dissolved in benzene with gas evolution to give an orange solution. After the salt had dissolved (except for a small intractable residue), the irradiation was discontinued and solvent was removed from the filtered reaction mixture at 25° (40 mm). Recrystallization of the residue from a mixture of dichloromethane and hexane gave red crystals of the $C_5H_5Mo(CO)(diphos)Cl$ derivative.

It was also possible to prepare the $C_5H_5Mo(CO)(diphos)Cl$ derivatives by ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the ditertiary phosphine in benzene solution without isolation of the intermediate $[C_5H_5Mo(CO)_2(diphos)]Cl$ salt similar to the preparation of $C_5H_5Mo(CO)(Pf{—}Pf)Cl$ reported by Haines, Nyholm, and Stiddard.[7]

Preparation of $C_5H_5Mo(CO)(triphos)Cl$.—A mixture of 1.5 g (5.35 mmol) of $C_5H_5Mo(CO)_3Cl$ and 3.33 g (5.34 mmol) of 1,1,1-tris(diphenylphosphinomethyl)ethane in ~250 ml of CP benzene was exposed to ultraviolet irradiation for 10 days. The red solid which precipitated was recrystallized once from a mixture of dichloromethane and hexane. A dichloromethane solution was then chromatographed on a small alumina column. The single orange band was eluted with acetone. Evaporation of this eluate followed by two recrystallizations of the residue from mixtures of dichloromethane and hexane gave ~2.0 g (44% yield) of orange $C_5H_5Mo(CO)(triphos)Cl$, mp 220° dec.

Preparation of the Halides $C_5H_5Fe(diphos)X$.—A mixture of the halide $C_5H_5Fe(CO)_2X$ (X = Br or Cl, 0.2–1.0 g) and an equivalent quantity of the chelating ditertiary phosphine in ~250 ml of CP benzene was exposed to ultraviolet irradiation for 3–6 hr. The black reaction mixture was filtered and the solvent was then removed at ~40° (40 mm). The residue was dissolved in dichloromethane and hexane was added to the filtered solution. Slow evaporation in a stream of nitrogen and cooling to −15° gave black crystals of the pure $C_5H_5Fe(diphos)X$ derivative.

Reaction of $C_5H_5Fe(CO)_2I$ with 1,2-Bis(dimethylphosphino)ethane.—A mixture of 1.0 g (3.39 mmol) of $C_5H_5Fe(CO)_2I$, 0.5 g (3.33 mmol) of 1,2-bis(dimethylphosphino)ethane, and 300 ml of CP benzene was stirred for 24 hr at room temperature. Solvent was removed from the reaction mixture at 25° (40 mm). The greenish residue was dissolved in a minimum of dichloromethane and the solution was chromatographed on an alumina column. The green band was eluted with 1:1 hexane–dichloromethane. Evaporation of the eluate and recrystallization of the residue from a mixture of dichloromethane and hexane gave 0.075 g (6.4% yield) of dark green crystalline $[C_5H_5Fe(CO)I]_2(Pm{—}Pm)$, mp 205°.

Ultraviolet irradiation of a similar mixture of $C_5H_5Fe(CO)_2I$ and 1,2-bis(dimethylphosphino)ethane in benzene solution at

---

(5) A. Kasahara, T. Izumi, and K. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 699 (1967).

(6) H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **6**, 86 (1966).

(7) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc., A.*, 94 (1967).

(8) (a) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966); (b) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.* (Amsterdam), **7**, 449 (1967).

(9) For the preparations of the chelating ditertiary phosphines see the following references: (a) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: J. Chatt and F. A. 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); (c) $(CH_3)_2PCH_2CH_2P(CH_3)_2$: J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961). However, in this work the $NaP(CH_3)_2$ was obtained by cleavage of $(CH_3)_2P{—}P(CH_3)_2$ with sodium metal in liquid ammonia.

(10) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

(11) For the preparation of the cyclopentadienylmetal carbonyl halides see the following references: (a) $C_5H_5Mo(CO)_3Cl$: T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956) (with minor modifications indicated in ref 12); (b) $C_5H_5Fe(CO)_2Cl$: T. S. Piper, F. A. Cotton, and G. Wilkinson, *ibid.*, **1**, 165 (1955); (c) $C_5H_5Fe(CO)_2Br$: B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956); (d) $C_5H_5Fe(CO)_2I$: T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956); R. B. King, *Organometal. Syn.*, **1**, 175 (1965); (e) $C_5H_5Co(CO)I_2$: ref 4a.

(12) R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).

Table I

New Compounds Prepared in This Work

Compound[a]	Color	Mp, °C	Yield, %	Analyses, %										Molar conductance[b]	Proton nmr, $\tau(C_5H_5)$[c]
				C		H		P		X		Other			
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$C_5H_5Mo(CO)(Pm—Pm)Cl$	Red	208	50	38.4	37.7	5.7	5.6	16.5	17.0	9.4	9.8	4.3 (O)	4.6 (O)	2.8 (1.6)	4.98 s, 5.03 s [C][d]
$C_5H_5Mo(CO)(Pf{=}Pf)Cl$	Red	205	55	61.7	60.5	4.4	4.2							12.4 (0.6)	5.55 s
$C_5H_5Mo(CO)(triphos)Cl$	Red	220 dec	44	66.5	65.6	5.2	5.3			4.2	4.0			4.7 (0.7)	4.67 s [C]
$[C_5H_5Fe(CO)I]_2(Pm—Pm)$	Green	205	6.4	30.8	30.7	3.7	3.8			4.6 (O)	5.1 (O)	15.9 (Fe)	16.6 (Fe)	6.4 (0.8)	5.34 s [C]
$C_5H_5Fe(Pm—Pm)Cl$	Black	205	26	43.1	43.2	6.9	7.0	20.2	20.1	11.6	11.7	18.2 (Fe)	17.9 (Fe)		5.75 s [C]
$C_5H_5Fe(Pf—Pf)Br$	Black	207–215	41	62.3	63.1	4.9	5.4	10.4	10.4			9.4 (Fe)	8.7 (Fe)	2.7 (0.6)	5.8 s [C]
$C_5H_5Fe(Pf—Pf)Cl$	Black	177–178	45	67.1	68.6	5.3	5.9	11.2	11.8					7.5 (0.2)	5.80 s [C]
$C_5H_5Fe(Pf{=}Pf)Br$	Black	220–225	43	62.3	61.8	4.5	4.6	10.4	10.1	13.4	13.1	9.4 (Fe)	9.1 (Fe)	2.6 (0.9)	5.8 s [C]
$C_5H_5Fe(Pf{=}Pf)Cl$	Black	198–202	52	67.1	67.0	5.0	4.8	11.2	11.3	6.4	6.3	10.1 (Fe)	10.1 (Fe)	3.1 (0.7)	5.89 s [C]
$[C_5H_5Fe(triphos)]Cl \cdot 2H_2O$	Yellow	139–141	33	67.5	67.7	5.9	6.3	11.4	11.8	4.3	4.1	3.9 (O)	4.9 (O)	104 ± 4 (0.1–1.3)	
$[C_5H_5Fe(triphos)]Br$	Yellow	127–130	50	66.9	66.2	5.4	5.7			9.7	10.8			114 ± 2 (0.2–1.0)	
$[C_5H_5Fe(triphos)]PF_6$	Yellow	298 dec	93					13.9	14.1	12.8	13.3	6.3 (Fe)	5.5 (Fe)	114 ± 6 (0.2–1.1)	4.94 [A]
$[C_5H_5Co(Pm—Pm)I]I$	Dark green	238 dec	78	25.1	25.2	4.0	4.3			48.1	47.9				
$[C_5H_5Co(Pm—Pm)I]PF_6$	Dark brown	263 dec	100	24.2	25.1	3.9	4.0					10.8 (Co)	10.5 (Co)		4.34 s [A]
$[C_5H_5Co(Pf—Pf)I]I$	Brown	230 dec	100	48.0	48.2	3.8	3.9			32.7	33.4			129 ± 6 (0.4–1.3)	
$[C_5H_5Co(Pf—Pf)I]PF_6$	Dark brown	253 dec	90	46.9	47.6	3.9	3.8			16.0	15.9	14.4 (F)	14.1 (F)	141 ± 3 (0.3–1.1)	4.18 s [A]
$[C_5H_5Co(Pf{=}Pf)I]I$	Brown	261 dec	92	48.1	48.5	3.5	3.4			32.8	32.7			118 ± 6 (0.4–1.2)	
$[C_5H_5Co(Pf{=}Pf)I]PF_6$	Dark brown	279 dec	78	47.0	48.2	3.4	3.6	11.7	12.4	16.0	17.3				4.10 s [A]
$[C_5H_5Co(triphos)]I_2$	Orange	233 dec	100	55.1	53.9	4.4	4.6	9.3	10.7	25.3	25.5				
$[C_5H_5Co(triphos)][PF_6]_2$	Yellow	260–270 dec	82	53.2	52.1	4.3	4.3	14.9	14.7	21.9	19.9			223 ± 29 (0.2–0.9)	

[a] The following abbreviations are used: Pf—Pf = $(C_6H_5)_2PCH_2CH_2P(C_8H_5)_2$· Pf=Pf = *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$; Pm—Pm = $(CH_3)_2PCH_2CH_2P(CH_3)_2$; triphos = $CH_3C[CH_2P(C_6H_5)_2]_3$. [b] These molar conductance values were obtained from acetone solutions. The concentrations ($\times 10^{-3}$ *M*) are given in parentheses. [c] The proton nmr spectra were run in chloroform-*d* (designated as [C]) or acetone-d_6 (designated as [A]) solutions. In addition to the π-C_5H_5 resonances the expected resonances arising from the protons of the chelating polytertiary phosphine ligands were observed; s = singlet. [d] In addition to these two π-C_5H_5 resonances of $C_5H_5Mo(CO)(Pm—Pm)Cl$, the resonances arising from the CH_3 or CH_2 protons of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ were observed as single sharp lines at τ 8.17, 8.26, 8.33, 8.39, 8.44, 8.60, 8.85, and 8.98 in a spectrum taken at 60 Mc.

room temperature for 6 hr also gave green $[C_5H_5Fe(CO)I]_2$(Pm—Pm) rather than C_5H_5Fe(Pm—Pm)I.

Preparation of C_5H_5Fe(triphos) Salts. (a) The Halides $[C_5H_5Fe(\text{triphos})]X$.—A mixture of the corresponding $C_5H_5Fe(CO)_2X$ (X = Cl or Br) derivative (1.0 g) and 1,1,1-tris(diphenylphosphinomethyl)ethane (X = Cl, 2.9 g; X = Br, 2.14 g) in 250 ml of CP benzene was exposed to ultraviolet irradiation for 12–20 hr. The filtered black reaction mixture was evaporated at ~25° (25 mm). Crystalline C_5H_5Fe(triphos)X derivatives could not be obtained from the resulting black residue by using mixtures of dichloromethane and hexane and a crystallization procedure similar to that described above for the C_5H_5Fe(diphos)X derivatives. Therefore a concentrated dichloromethane solution of this black residue was chromatographed on a 2 × 50 cm alumina column. The chromatogram was developed with dichloromethane. The first purple band was eluted with dichloromethane. This eluate contained only traces of noncrystalline iron complexes which were not characterized. After removal of the purple band, a yellow band appeared. This band was also eluted with dichloromethane. Evaporation (~25° (40 mm)) of the eluate gave a yellow solid. Further purification of this material by chromatographing a second time by a similar procedure and/or by recrystallization from a mixture of dichloromethane and hexane gave the yellow $[C_5H_5Fe(\text{triphos})]X$ salts.

(b) The Hexafluorophosphate $[C_5H_5Fe(\text{triphos})][PF_6]$.—An acetone solution of the bromide $[C_5H_5Fe(\text{triphos})]Br$ (0.3 g, 0.36 mmol) was treated with excess of a concentrated aqueous solution of ammonium hexafluorophosphate. Slow removal of the acetone at ~25° (40 mm) gave a yellow precipitate which was purified by recrystallization from a mixture of acetone and benzene to give 0.3 g (93% yield) of yellow solid $[C_5H_5Fe(\text{triphos})][PF_6]$.

Preparation of $C_5H_5Co(\text{diphos})I^+$ Salts. (a) The Iodide $[C_5H_5Co(\text{diphos})I]I$.—A mixture of equivalent quantities of $C_5H_5Co(CO)I_2$ (~0.8 g) and the chelating ditertiary phosphine was stirred in benzene solution at room temperature. A brown precipitate formed. After 1–12 hr this precipitate was filtered off, washed with diethyl ether, and dried to give the brown to green $[C_5H_5Co(\text{diphos})I]I$ derivative.

(b) The Hexafluorophosphate $[C_5H_5Co(\text{diphos})I][PF_6]$.—A filtered acetone solution of 0.6 g of the iodide $[C_5H_5Co(\text{diphos})I]I$ was treated with excess of a concentrated aqueous solution of ammonium hexafluorophosphate. Slow removal of the acetone at ~25° (40 mm) gave a brown precipitate. This precipitate was removed by filtration and recrystallized from a mixture of acetone and benzene to give the dark brown solid hexafluorophosphate $[C_5H_5Co(\text{diphos})I][PF_6]$.

Preparation of $C_5H_5Co(\text{triphos})^{2+}$ Salts. (a) The Iodide $[C_5H_5Co(\text{triphos})I_2$.—A mixture of 0.6 g (1.47 mmol) of $C_5H_5Co(CO)I_2$ and 0.92 g (1.47 mmol) of 1,1,1-tris(diphenylphosphinomethyl)ethane in 100 ml of CP benzene was stirred for 12 hr at room temperature. Solvent was removed from the reaction mixture at ~40° (40 mm) to give 1.5 g (100% yield) of crude orange $[C_5H_5Co(\text{triphos})]I_2$. The analytical sample was obtained by recrystallization of some of this material from a mixture of dichloromethane and hexane.

(b) The Hexafluorophosphate $[C_5H_5Co(\text{triphos})][PF_6]_2$.—An acetone solution of 0.61 g (0.61 mmol) of $[C_5H_5Co(\text{triphos})]I_2$ was treated with a concentrated aqueous solution of ammonium hexafluorophosphate. Acetone was then removed slowly at ~25° (40 mm). The yellow precipitate (0.52 g, 82% yield) of the crude hexafluorophosphate was filtered and treated again with excess of concentrated aqueous ammonium hexafluorophosphate to ensure complete conversion of the iodide. The analytical sample was purified by two recrystallizations from mixtures of acetone and benzene.

Infrared Spectra.—The following ν(CO) frequencies (cm^{-1}; all very strong) were obtained from dichloromethane solutions of the new metal carbonyl derivatives described in this paper: $C_5H_5Mo(CO)$(Pm—Pm)Cl, 1846; $C_5H_5Mo(CO)$(Pf=Pf)Cl, 1855; $C_5H_5Mo(CO)$(triphos)Cl, 1844; $[C_5H_5Fe(CO)I]_2$(Pm—Pm), 1955. The remaining regions of the infrared spectra of these compounds as well as the infrared spectra of the remaining carbonyl-free derivatives reported in this paper were taken in potassium bromide pellets in the 4000-600-cm^{-1} region and are reported below. In order to conserve space, the infrared spectrum of only one salt of each of the new cations is given. The infrared spectra of all of salts of a given cation were quite similar except for the presence in the spectra of the hexafluorophosphates of the usual extremely strong band in the range 820–835 cm^{-1} arising from the ν(PF) frequency of the PF_6^- anion.

A. $C_5H_5Mo(CO)$(Pm—Pm)Cl.—ν(CH) frequencies at 3067 (vw), 2956 (w), and 2890 (w) cm^{-1}; other bands at 1410 (m), 1291 (w), 1275 (w), 1266 (w), 1128 (w), 1100 (w), 1085 (w), 1058 (w), 1005 (w), 987 (w), 929 (s), 908 (m), 888 (m), 828 (w), 804 (w), 786 (m), 718 (m), 693 (m), and 638 (m) cm^{-1}.

B. $C_5H_5Mo(CO)$(Pf=Pf)Cl.—ν(CH) frequencies too weak to be unequivocally observed; other bands at 1474 (w), 1428 (m), 1177 (m), 1147 (m), 1110 (m), 1087 (m), 937 (vw), 898 (w), 790 (vw), 722 (m), and 682 (s) cm^{-1}.

C. $C_5H_5Mo(CO)$(triphos)Cl.—ν(CH) frequencies at 3040 (vw), 2950 (vvw), and 2888 (vvw) cm^{-1}; other bands at 1483 (w), 1433 (m), 1412 (w), 1395 (w), 1326 (vw), 1305 (vw), 1262 (vw), 1255 (vw), 1194 (m, sh), 1185 (m), 1155 (w), 1111 (m), 1084 (w), 1066 (w), 1048 (vw), 1020 (vw), 1001 (vvw), 990 (vw), 920 (vw), 836 (m), 816 (w), 796 (w), 744 (m), 731 (s), 722 (w), 704 (w), and 685 (s) cm^{-1}.

D. $[C_5H_5Fe(CO)I]_2$(Pm—Pm).—ν(CH) frequencies at 3078 (vvw), 2957 (vvw), and 2891 (vw) cm^{-1}; other bands at 1420 (w), 1409 (m), 1354 (vw), 1290 (w), 1278 (m), 1170 (w), 1090 (m), 1046 (vw), 1000 (w), 989 (w), 928 (m), 890 (s), 840 (w), 827 (m), 810 (m), 730 (m), 715 (m), 694 (w), 664 (w), and 659 (w) cm^{-1}.

E. C_5H_5Fe(Pm—Pm)Cl.—ν(CH) frequencies at 2961 (vw), 2949 (vw), 2912 (vvw), and 2890 (w) cm^{-1}; other bands at 1412 (m), 1292 (vw), 1287 (vw), 1278 (w), 1227 (vvw), 1097 (w), 1072 (vw), 998 (vw), 986 (w), 932 (m), 921 (m), 897 (w), 882 (w), 830 (w), 821 (w), 772 (w), 724 (w), 711 (w), 700 (w), 686 (w), and 638 (w) cm^{-1}.

F. C_5H_5Fe(Pf—Pf)Br.—ν(CH) frequencies at 3058 (vw), 3038 (w), 3030 (w, sh), and 2940–2890 (vw, br) cm^{-1}; other bands at 1478 (m), 1428 (s), 1403 (m), 1299 (vw), 1177 (vw), 1087 (s), 1057 (w), 1016 (vw), 999 (vw), 987 (w), 850 (vw), 835 (vw), 820 (vw), 801 (w), 773 (w), 730 (m), 688 (s, sh), 682 (s), 655 (m), and 642 (w) cm^{-1}.

G. C_5H_5Fe(Pf—Pf)Cl.—ν(CH) frequencies too weak to be unequivocally observed; other bands at 1482 (w), 1432 (s), 1092 (m), 992 (w), 853 (w), 804 (w), 779 (w), 746 (m), 737 (m), 695 (s, sh), 688 (s), 660 (m), and 645 (w) cm^{-1}.

H. C_5H_5Fe(Pf=Pf)Br.—ν(CH) frequencies too weak to be unequivocally observed; other bands at 1477 (m), 1427 (s), 1301 (w), 1264 (w), 1175 (w), 1150 (w), 1087 (m), 1060 (w), 1016 (vw), 989 (w), 829 (vw), 796 (w), 765 (vw), 720 (s), and 682 (s) cm^{-1}.

I. C_5H_5Fe(Pf=Pf)Cl.—ν(CH) frequencies too weak to be unequivocally observed; other bands at 1475 (w), 1429 (m), 1394 (w), 1176 (w), 1090 (w, sh), 1082 (m), 1059 (vw), 993 (w), 830 (vw), 796 (w), 770 (m), 742 (s), 721 (s), 705 (m), 692 (s, sh), and 684 (s) cm^{-1}.

J. $[C_5H_5Fe(\text{triphos})]Br$.—$\nu$(CH) frequencies at 3037 (w) and 2908 (w) cm^{-1}; other bands at 1610 (w), 1567 (w), 1476 (m), 1427 (s), 1402 (sh), 1320 (vw, sh), 1305 (w), 1260 (w), 1208 (vw), 1177 (w), 1148 (vw), 1077 (s), 1016 (vw), 989 (w), 824 (m), 807 (m), 732 (sh), 719 (s), and 684 (vs) cm^{-1}.

K. $[C_5H_5Co$(Pm—Pm)I]I.—ν(CH) frequencies at 3082 (vw), 3046 (w), 2942 (w), and 2880 (w) cm^{-1}; other bands at 1424 (s), 1407 (s), 1354 (w), 1351 (vw, sh), 1300 (m), 1282 (s), 1232 (w), 1197 (vw), 1125 (w), 1076 (w), 1046 (w), 1012 (w), 983 (w), 942 (vs), 913 (s), 902 (m), 864 (m), 846 (s), 832 (s), 823 (m), 781 (vw), 738 (m), and 711 (s) cm^{-1}.

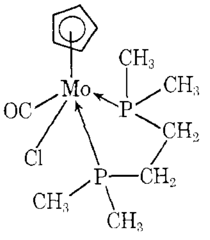
L. $[C_5H_5Co$(Pf—Pf)I]I.—ν(CH) frequencies at 3070 (vw), 3043 (w), and 2900 (vw) cm^{-1}; other bands at 1479 (w), 1432 (s), 1415 (m), 1328 (vw, sh), 1307 (w), 1186 (vw), 1156 (vw), 1090 (m), 1067 (w), 1052 (vw), 1019 (vw), 1009 (vw), 992 (w), 878 (vw), 861 (w), 837 (m), 821 (w), 779 (w), 744 (m), 739 (m), 703 (m), 687 (s), and 665 (m) cm^{-1}.

M. **[$C_5H_5Co(Pf{=}Pf)I$]I.**—ν(CH) frequencies at 3087 (vw, br), 3060 (vw), 3037 (vw), 3007 (vw), and 2936 (w) cm^{-1}; other bands at 1481 (m), 1431 (s), 1422 (m), 1410 (m), 1359 (vw), 1327 (w), 1302 (w), 1183 (w), 1150 (w), 1096 (m, sh), 1087 (s), 1064 (w), 1048 (w), 1022 (w), 1005 (w), 990 (m), 935 (vw), 874 (w), 839 (m), 818 (m), 757 (m), 738 (s), 728 (vs), 687 (vs), 679 (vs), and 607 (w) cm^{-1}.

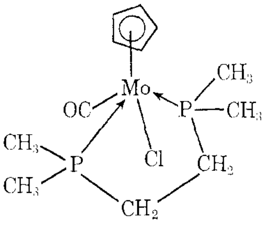
N. **[C_5H_5Co(triphos)]I_2.**—ν(CH) frequencies at 3042 (vw), 2946 (vvw), and 2909 (vvw) cm^{-1}; other bands at 1481 (w), 1433 (s), 1401 (w), 1393 (w), 1335 (vw), 1309 (w), 1284 (vw), 1218 (vw), 1185 (w), 1154 (w), 1083 (m), 1018 (vw), 1010 (vw), 994 (w), 830 (w), 819 (w), 735 (m), and 687 (s) cm^{-1}.

Discussion

A. Molybdenum Derivatives.—Haines, Nyholm, and Stiddard[7] have previously reported the ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the bidentate ligands 1,2-bis(diphenylphosphino)ethane and *o*-phenylenebis(dimethylarsine) to give the corresponding monocarbonyl compounds $C_5H_5Mo(CO)$(bidentate)Cl. The new compounds $C_5H_5Mo(CO)$(diphos)Cl (diphos = *cis*-1,2-bis(diphenylphosphino)ethylene or 1,2-bis(dimethylphosphino)ethane) prepared in this work are further representatives of this type. All of the $C_5H_5Mo(CO)$(diphos)Cl derivatives are red to orange solids exhibiting a single ν(CO) infrared frequency around 1840 cm^{-1} and a low conductance (2–13 ohm^{-1} cm^2 mol^{-1}) in acetone solution in accord with the expected nonionic formulation. The proton nmr spectrum of the compound $C_5H_5Mo(CO)$(Pm—Pm)Cl exhibited two cyclopentadienyl resonances at τ 4.98 and 5.03 as well as eight lines in the region τ 8.0–9.1 arising from the CH_2 and CH_3 protons of the 1,2-bis(dimethylphosphino)ethane ligand. This observation may be explained by the presence of the two isomers Ia and Ib in approximately equal quantities. This suggests that bidentate chelating ligands can bridge not only lateral positions (Ia) but also diagonal positions (Ib) in $C_5H_5ML_4$ derivatives in contrast to the situation in octahedral derivatives ML_6 where bidentate chelating ligands can bridge *cis* positions but not *trans* positions. However, it is also possible to have isomers of $C_5H_5Mo(CO)$(Pm—Pm)Cl differing only in the conformation of the five-membered chelate ring.



Ia



Ib

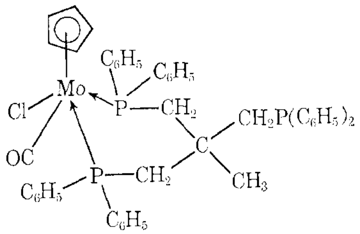
The reaction between $C_5H_5Mo(CO)_3Cl$ and chelating ditertiary phosphines in benzene solution at room temperature in the *absence* of ultraviolet irradiation has been reported[12] to give the ionic benzene-insoluble chlorides [$C_5H_5Mo(CO)_2$(diphos)]Cl, isolated as monohydrates. Exposure of benzene suspensions of these chloride salts to intense ultraviolet irradiation caused them to dissolve with gas evolution to give an orange solution from which the corresponding nonionic $C_5H_5Mo(CO)$(diphos)Cl derivative could be isolated. These observations suggest that the photochemical reaction of $C_5H_5Mo(CO)_3Cl$ with chelating ditertiary phosphines to give $C_5H_5Mo(CO)$(diphos)Cl derivatives proceeds according to the scheme

$$C_5H_5Mo(CO)_3Cl + \text{diphos} \longrightarrow C_5H_5Mo(CO)_2(\text{diphos})^+ + Cl^- + CO \quad (1)$$

$$C_5H_5Mo(CO)_2(\text{diphos})^+ + Cl^- \longrightarrow C_5H_5Mo(CO)(\text{diphos})Cl + CO \quad (2)$$

The first step of this scheme involves displacement of chloride and one carbonyl group from $C_5H_5Mo(CO)_3Cl$ with the chelating ditertiary phosphine ligand. The second step involves displacement of one carbonyl group from the $C_5H_5Mo(CO)_2(\text{diphos})^+$ cation with the chloride ion liberated in the first step. The practice[8] of adding aluminum chloride to reaction mixtures of the halides $C_5H_5Mo(CO)_3X$ or $C_5H_5Fe(CO)_2X$ with Lewis bases in order to promote the formation of ionic products thus depends on the ability for aluminum chloride to complex with the halide ion liberated in the first step of a reaction scheme similar to that given above. This makes the halide ion unavailable for destruction of the formed carbonyl cation derivative by reactions analogous to the second step of the scheme given above. In cases where the rate of the second step is slow relative to that of the first step because of the reaction conditions, the metal carbonyl halide used, and/or the ligand used, an ionic product will be obtained even if aluminum chloride is not added.

The reaction between $C_5H_5Mo(CO)_3Cl$ and the chelating tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane was investigated in an attempt to prepare a completely substituted derivative of the type $C_5H_5Mo(PR_3)_3Cl$. This was unsuccessful. Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the tritertiary phosphine in hexane solution for 1 hr gave an orange precipitate exhibiting very strong ν(CO) frequencies at ~1960 and ~1860 cm^{-1}. This indicated a dicarbonyl derivative probably of the type $[C_5H_5Mo(CO)_2Cl]_n$(triphos) (n = 1, 2, and/or 3). This product, obviously not the material being sought, was not investigated in detail. Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the tritertiary phosphine in benzene solution for 10 days gave an orange solution from which orange $C_5H_5Mo(CO)$(triphos)Cl was isolated. The presence of one carbonyl group in this complex was confirmed by the presence of a single strong ν(CO) frequency at 1844 cm^{-1}. This is



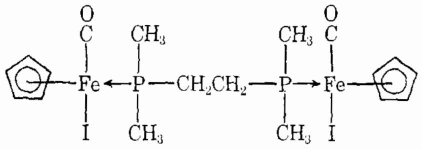
II

the same region where the ν(CO) frequencies in the $C_5H_5Mo(CO)(diphos)Cl$ complexes appear. The low conductance ($\sim$5 ohm^{-1} cm^2 mol^{-1}) supports a nonionic formulation for $C_5H_5Mo(CO)(triphos)Cl$. These data are all consistent with formulation of $C_5H_5Mo(CO)(triphos)Cl$ as II[13] with one of the phosphorus atoms of the chelating tritertiary phosphine not bonded to the molybdenum atom.

B. Iron Derivatives.—Reactions of the halides $C_5H_5Fe(CO)_2X$ with tertiary phosphines have been described[8a] but the only reported completely substituted derivative appears to be the triphenyl phosphite complex $C_5H_5Fe[P(OC_6H_5)_3]_2X$.[14] However, the chelating ditertiary phosphines used in this work readily replaced both carbonyl groups in the halides $C_5H_5Fe(CO)_2X$ (X = Br or Cl) upon ultraviolet irradiation in benzene solution to give the black crystalline complexes $C_5H_5Fe(diphos)X$. The formulation of these complexes as nonionic disubstituted $C_5H_5Fe(CO)_2X$ derivatives is supported by their low conductances in acetone solution and by the lack of ν(CO) frequencies in their infrared spectra.

The reaction of $C_5H_5Fe(CO)_2I$ with the very reactive 1,2-bis(dimethylphosphino)ethane followed a different course even under ultraviolet irradiation. The green product was indicated by analyses and the single ν(CO) frequency at 1955 cm^{-1} in the infrared spectrum to be $C_5H_5Fe(CO)I(Pm—Pm)Fe(CO)IC_5H_5$ (III) with a bridging rather than chelating 1,2-bis(dimethylphosphino)ethane ligand. The failure to obtain $C_5H_5Fe(Pm—Pm)I$ even when ultraviolet irradiation is used may be attributed to the ease of formation of III from the very reactive ditertiary phosphine Pm—Pm and to the difficulty of breaking the bridge in III once formed.

Ultraviolet irradiation of the $C_5H_5Fe(CO)_2X$ (X = Br or Cl) halides with the tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane in benzene solution gave a black solution resembling those obtained from the $C_5H_5Fe(CO)_2X$ (X = Br or Cl) halides and the chelating ditertiary phosphines. However, black crystalline $C_5H_5Fe(triphos)X$ derivatives could not be isolated from these reaction mixtures by using techniques effective for the isolation of the $C_5H_5Fe(diphos)X$ derivatives. Chromatography of dichloromethane solutions of the $C_5H_5Fe(CO)_2X$–triphos reaction mixtures indicated the major component to give a *yellow* band from which the yellow solids $[C_5H_5Fe(triphos)]X$ (X = Cl or Br) could be isolated by elution, evaporation, and recrystallization. These $[C_5H_5Fe(triphos)]X$ derivatives are formulated as salts of the $C_5H_5Fe(triphos)^+$ cation for the following reasons: (1) high conductivities in acetone solution; (2) conversion of the bromide to the corresponding yellow hexafluorophosphate $[C_5H_5Fe(triphos)][PF_6]$ by a metathetical reaction with ammonium hexafluorophosphate; (3) yellow color of the $[C_5H_5Fe(triphos)]X$ derivatives suggesting the absence of iron–halogen covalent bonds by comparison with the much deeper colors of the $C_5H_5Fe(CO)_2X$ and $C_5H_5Fe(diphos)X$ halides which have iron–halogen covalent bonds. The high solubility of the $C_5H_5Fe(triphos)^+$ salts in noncoordinating organic solvents such as benzene and dichloromethane and the ability to chromatograph these salts on alumina in dichloromethane solution probably arise from the large organic bulk of the tritertiary phosphine ligand which has 41 carbon atoms. The $C_5H_5Fe(triphos)^+$ cation may be regarded as derived from the known[15] $C_5H_5Fe(CO)_3^+$ cation by complete substitution of the three carbonyl groups with tertiary phosphine ligands.



III

C. Cobalt Derivatives.—The chelating ditertiary phosphines react rapidly with $C_5H_5Co(CO)I_2$ at room temperature in the absence of ultraviolet irradiation to give green to brown salts formulated as $[C_5H_5Co(diphos)I]I$ on the basis of their high conductance in acetone solution and their metathetical reactions with excess ammonium hexafluorophosphate to give the corresponding dark brown hexafluorophosphate $[C_5H_5Co(diphos)I][PF_6]$. These reactions are thus completely analogous to the reactions of $C_5H_5Co(CO)I_2$ with 2,2-bipyridyl and with *o*-phenanthroline under similarly mild conditions to give the salts $[C_5H_5Co(bidentate)I]I$.[4a,b] Furthermore, the perfluoroalkyl derivatives $C_5H_5Co(CO)R_fI$ (R_f = *n*-C_3F_7 and *n*-C_7F_{15}) have been recently reported to react with the chelating ditertiary phosphines to give the yellow salts $[C_5H_5Co(diphos)R_f]I$.[16] The brown color of the $C_5H_5Co(diphos)I^+$ salts as contrasted with the much paler yellow color of the $C_5H_5Co(diphos)R_f^+$ salts is a further indication of the auxochromic effect of metal–halogen covalent bonds.

The chelating tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane also reacts with $C_5H_5Co(CO)I_2$ at room temperature in the absence of added ultraviolet irradiation to give a mixture from which orange solid $[C_5H_5Co(triphos)]I_2$ can be isolated. This material is formulated as the diiodide salt of the $C_5H_5Co(triphos)^{2+}$ dication for the following reasons: (1) high conductivity in acetone solution; (2) conversion of the diiodide to the yellow bis(hexafluorophosphate) $[C_5H_5Co(triphos)][PF_6]_2$ by repeated treatment with ammonium hexafluorophosphate; (3) orange color of $[C_5H_5Co(triphos)]I_2$ as contrasted with the much deeper brown color of the $[C_5H_5Co(diphos)I]I$ salt discussed. The much lighter color of $[C_5H_5Co(triphos)]I_2$ suggests the absence of a cobalt–iodine covalent bond. The

---

(13) An alternative formulation $C_5H_5Mo(CO)(triphos)Cl$ with the two "arms" of the chelating tritertiary phosphine bonding to diagonal (*cf.* Ib) rather than lateral (*cf.* Ia) positions of the square of the four ligands is also possible.

(14) A. N. Nesmeyanov, Yu. A. Chapovskii, and Yu. A. Ustynyuk, *J. Organometal. Chem.* (Amsterdam), **9**, 345 (1967).

(15) E. O. Fischer and K. Fichtel, *Ber.*, **94**, 1200 (1961); A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961); R. B. King, *Inorg. Chem.*, **1**, 964 (1962).

(16) R. B. King, R. N. Kapoor, and L. W. Houk, *J. Inorg. Nucl. Chem.*, in press.

cyclopentadienyltricarbonylcobalt dication, $C_5H_5Co(CO)_3^{2+}$, isoelectronic with the $C_5H_5Co(triphos)^{2+}$ dication remains unknown, possibly owing to insufficient electron density from the cobalt atom in the relatively high formal +3 oxidation state to form the necessary $d\pi$–$p\pi$ bonds for stabilization of bonds with *three* carbonyl groups; the reported[17] monocation $C_5H_5Co(CO)_2R_f^+$ with only two carbonyl groups bonded to cobalt(III) is already rather unstable. However, the known[18] yellow dication $C_5H_5CoC_6H_6^{2+}$ is isoelectronic with $C_5H_5Co(triphos)^{2+}$. The related dication $C_5H_5Co(tripy)^{2+}$ has also been prepared from $C_5H_5Co(CO)I_2$ and 2,2′,2′′-terpyridyl[4a,19] but this material has not been obtained as a completely pure salt.

Acknowledgment.—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68.

---

[17] P. M. Treichel and G. Werber, *Inorg. Chem.*, **4**, 1098 (1965).

[18] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16b**, 556 (1961).

[19] (a) R. B. King, unpublished results, 1964; (b) R. F. Heck, private communication, 1965.

CONTRIBUTION FROM LABORATORIO CHIMICA RADIOELEMENTI CNR PADOVA
AND ISTITUTO DI CHIMICA ORGANICA INDUSTRIALE, THE UNIVERSITY, BOLOGNA, ITALY

Reduction of Olefins by Means of an HA-Platinum(II) Hydride System

BY MARIO GIUSTINIANI, GIULIANO DOLCETTI, ROSARIO PIETROPAOLO, AND UMBERTO BELLUCO

Received January 13, 1969

The present work reports on hydrogenation reactions of linear and/or cyclic unsaturated hydrocarbons in the presence of *trans*-$Pt(P(C_2H_5)_3)_2HCl$ and hydrochloric or perchloric (HA) acid in ethanol. Reactions proceed under ambient conditions leading to saturated hydrocarbons and *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$. The olefins investigated are 1-hexene, cyclohexene, 1-octene, and 2-methyl-2-butene. Electronegatively substituted olefins such as acrylonitrile and *trans*-dichloroethylene do not react under these experimental conditions. The pseudo-first-order rate constants depend upon the concentrations of olefin, mineral acid, and chloride ion. The following conceivable reaction mechanisms are discussed: (i) olefin insertion across the Pt–H bond followed by cleavage of the ensuing platinum(II)–alkyl complex by hydrochloric acid aid and (ii) formation of a platinum(IV) dihydride with subsequent hydrogenation of the olefin to the corresponding hydrogenated hydrocarbon.

In the present work we report a reduction reaction of linear and cyclic olefins with hydrochloric or perchloric acid in the presence of *trans*-$Pt(P(C_2H_5)_3)_2HCl$ in ethanol at room temperature. The reactions studied are

$$trans\text{-}Pt(P(C_2H_5)_3)_2HCl + RCH{=}CHR' \xrightarrow{HCl} trans\text{-}Pt(P(C_2H_5)_3)_2Cl_2 + RCH_2CH_2R'$$

where olefin = 1-hexene, cyclohexene, 1-octene, or 2-methyl-2-butene. All of the reactions were carried out in 99.5% ethanol. We established that under the experimental conditions used, the olefins investigated did not react separately with either hydrochloric acid or the platinum hydride. On the other hand, the complex *trans*-$Pt(P(C_2H_5)_3)_2HCl$ reacts very slowly with HCl yielding $Pt(P(C_2H_5)_3)_2Cl_2$ and molecular hydrogen.[1] We did not succeed in detecting any reaction intermediates. All of the reactions go to completion.

A kinetic investigation has been carried out under pseudo-first-order conditions by using an excess of all other reactants with respect to the metal complex concentration. Values of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), at various concentrations of reactants are reported in Table I. Figure 1 shows the plot of k_{obsd} *vs.* LiCl concentration. There is a linear dependence on $[Cl^-]$ with a nonzero intercept, corresponding to the rate of reaction of the hydride complex with 1-hexene in the presence of perchloric acid alone. Runs 9, 10, and 18 (Table I) show a dependence of the rate on the acid concentration. A wider range of acid concentrations was not examined to avoid the presence of ionic pairs in solution.

These kinetic data indicate that pseudo-first-order rate constants depend on the concentration of mineral acid, chloride ion, and olefin. Although a detailed kinetic investigation of these reactions could not be carried out, we could establish that the reaction rates depend also upon the nature of the olefin. However, we found that the rates of reduction of cyclohexene are of the same order of magnitude as those of 1-hexene.

These olefin reduction reactions display also the following features. (i) No isomerization occurs during the process. In fact, no hexene-2 is formed during the course of a reduction. If isomerization takes place *before* the material is reduced, it is of no consequence since the final products are the saturated hydrocarbons. (ii) The reduction reactions occur also with cyclohexene and 2-methyl-2-butene, although preparation of secondary alkylplatinum(II) derivatives has always been difficult.[2] (iii) Electronegatively substituted olefins such as acrylonitrile and *trans*-dichloroethylene do not react under the above experimental conditions.

---

[1] U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.*, **89**, 6494 (1967).

[2] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968), and references therein.