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CHEMISTRY OF MIXED TRANSITION-METAL COMPLEXES II*. PREPARATION OF MIXED TRANSITION-METAL μ-DIPHENYLPHOSPHIDO COMPLEXES

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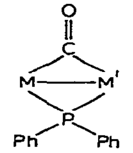
SUMMARY

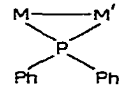
Dehydrohalogenation reactions of $HPh_2PM'(CO)_n$ ($M'=Fe$, $n=4$; $M'=Ni$, $n=3$) with several metal halide complexes in the presence of $HNEt_2$ were carried out and it was found that following three types of mixed transition-metal mono-μ-phosphido complexes are obtained:

Type (1)



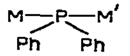
[(II) M = Ni, M' = Fe]

Type (2)



[(VIII) M = Mn, M' = Fe
(IX) M = Co, M' = Fe]

Type (3)



[(V) M = Fe, M' = Ni]

The stepwise formation of a metal–metal bond from the type 3 complex (III: M,M' = Fe) to the type 1 complex (IV: M,M' = Fe) was found.

INTRODUCTION

Numerous mixed transition-metal complexes with metal–metal bonds are known[1] and they are of interest because of possible differences in their reactivity or catalytic behavior, compared with mononuclear transition metal complexes. The complexes known thusfar were mostly mixed metal carbonyls in which metals are

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* For Part I see Ref. 5.

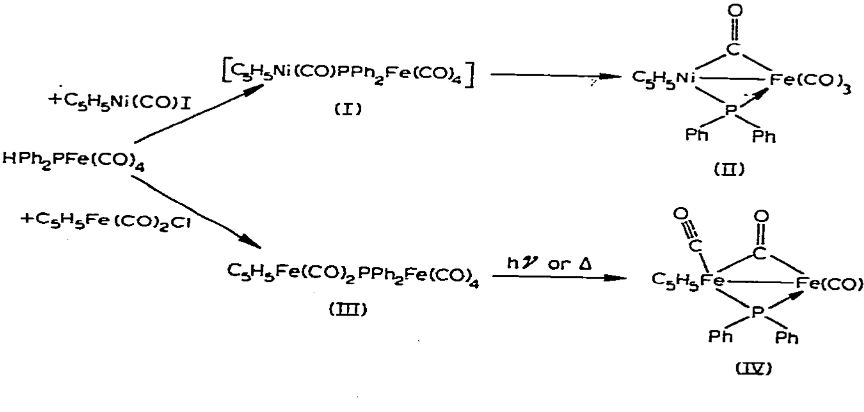
bonded only with a metal–metal bond and in a few instances with additional bridged carbonyls[2,3]. There are no reports about any characteristic behavior of the complexes since the complexes generally dissociate into the respective mono-metallic species in the reaction system. But the appearance of a characteristic reactivity of the mixed transition-metal complexes may be anticipated in cases where the metals are bound more tightly via a suitable bridging group.

Recently, mixed transition-metal complexes with a metal–metal bond and a μ-diphenylphosphido group were prepared by Thompson *et al.* in reactions of π-allyl complexes of palladium, manganese and cobalt with tetracarbonyl(diphenylphosphine)iron[4]. We obtained another type of mixed transition-metal complex with a metal–metal bond, a μ-diphenylphosphido and a bridged carbonyl group by treatment of π-cyclopentadienyl(triphenylphosphine)nickel chloride and the diphenylphosphine iron complex with excess amine[5]. The mono-μ-phosphido dinuclear complexes previously prepared were of the homonuclear type[6,7].

In the present paper, the dehydrohalogenation reaction was extended to several transition metal halide complexes and diphenylphosphine complexes and found to give three types of mixed transition-metal complexes: Type (1) The mixed transition-metal complex joined by a metal–metal bond and a bridged phosphido and a bridged carbonyl group; type (2) the mixed transition-metal complex joined by a metal–metal bond and a bridged phosphido group; and type (3) the mixed transition-metal complex joined only by a μ-phosphido group. The dehydrohalogenation method described seems to be a useful procedure for the preparation of such mixed metal complexes.

RESULTS AND DISCUSSION

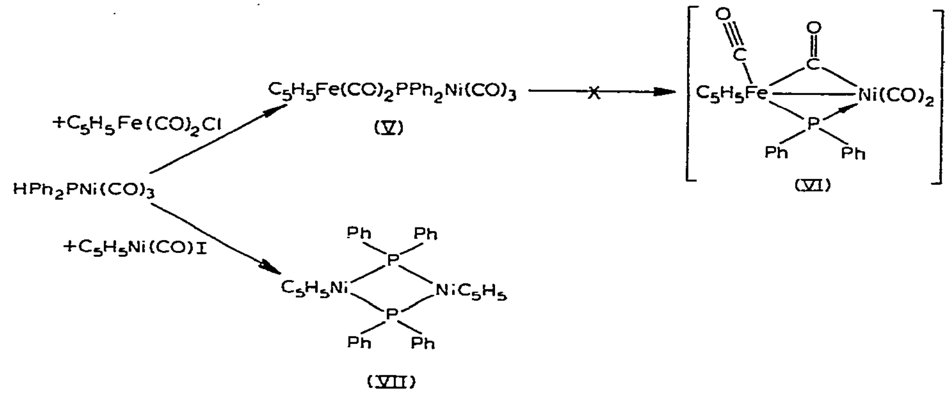
Treatment of the equimolar mixture of $C_5H_5Fe(CO)_2Cl$ and $HPh_2PFe(CO)_4$ with excess diethylamine [that similar as used in the preparation of (tricarbonyliron)-μ-carbonyl-μ-(diphenylphosphido)-π-cyclopentadienylnickel(II)[5] Type (1)] gave (dicarbonyl-π-cyclopentadienyliron)-μ-(diphenylphosphido)tetracarbonyliron(III) as orange crystals in good yield. (III) shows the molecular ion at *m/e* 530, followed by ions corresponding to successive loss of six carbonyls in the mass spectrum. The infrared spectrum shows that the carbonyls are all of the terminal type. The structure found was one in which the dicarbonyl-π-cyclopentadienyliron and the tetracarbonyliron moieties are joined only by a μ-phosphido group [Type (3)].



(III) is stable in air in the crystalline state, but the solution gradually changed from orange to purple even at room temperature under an atmosphere of nitrogen, depositing purple crystals(IV). The latter was obtained almost quantitatively by irradiation of (III), and were less stable than (III). (IV) does not show a clear mass spectrum. The spectrum was contaminated with fragments from [$C_5H_5Fe(CO)$-$PPh_2]_2$ and [$Fe(CO)_3PPh_2]_2$. These were also the products in thermal degradation of (III) and of (IV). The structure analogous to (II), (carbonyl-π-cyclopentadienyl-iron)-μ-carbonyl-μ-(diphenylphosphido)tricarbonyliron, is suggested for (IV) on the basis of the infrared spectrum showing the presence of a bridged carbonyl at 1780 cm^{-1} in CH_2Cl_2 solution.

The cyclopentadienyl proton signal of (III) appears at τ 4.96 as a doublet [J(PH) 1.2 Hz] and that of (IV) at τ 5.13 as a singlet in $CDCl_3$ solution.

From an equimolar mixture of $C_5H_5Fe(CO)_2Cl$ and $HPh_2PNi(CO)_3$, (dicarbonyl-π-cyclopentadienyl)iron-μ-(diphenylphosphido)tricarbonylnickel(V) was obtained as orange yellow crystals. (V) shows bands corresponding to Ni-$K\alpha$ at 36°12′, 43°64′ and 51°34′, to Fe-K_α at 42°32′, 51°36′ and 61°08′, and to P–K_α at 26°38′ and 54°54′ in the X-ray emission spectrum, and ν(C≡O) bands at 2043, 2006 and 1982 cm^{-1} in the infrared spectrum in CH_2Cl_1 solution. The cyclopentadienyl proton signal appears at τ 6.07 as a doublet [J(PH) 1.2 Hz] in C_6D_6 solution*. That the signal of (IV) is a singlet and that those of (III) and (V) are doublets indicates that "terminal" Ph_2P groups lead to P–H coupling on the cyclopentadienyl protons but bridging Ph_2P's do not**.



(V) is unstable thermally (dec. >105°), but is stable photochemically and was recovered quantitatively from a solution which was irradiated for several hours under a nitrogen atmosphere. From $HPh_2PNi(CO)_3$ and $C_5H_5Ni(CO)I$, only the known complex (VII)[8] was obtained in ~10% yield.

The reaction of $BrMn(CO)_5$ and $HPh_2PFe(CO)_4$ with the amine gave orange crystals(VIII) in a 22% yield. The X-ray emission spectrum shows bands corresponding to Fe-K_α, to P-K_α and to Mn-K_α (at 46°22′, 56°24′ and 66°54′). The mass spectrum

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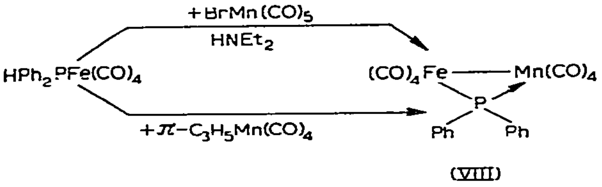
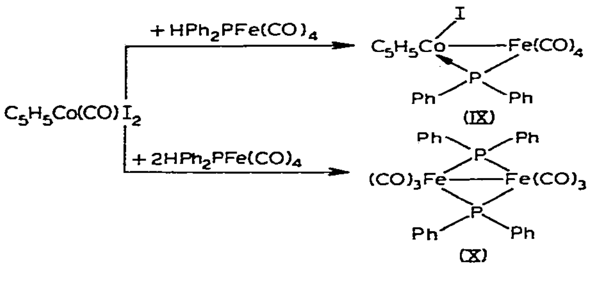
* The signal appears at τ 5.27 as a broad singlet in $CDCl_3$ solution. The broadness is presumably due to partial decomposition of the complex in the chloroform solution.

** We express appreciation to a referee for helpful suggestions.

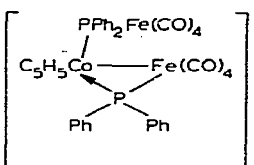
shows the molecular ion at *m/e* 520, followed by ions corresponding to successive loss of eight carbonyls. The infrared spectrum in CH_2Cl_2 solution indicates that the carbonyls are all of the terminal type. Structure (VIII) is thus indicated. The infrared spectrum in KBr disk and the melting point of (VIII) are in good agreement with the complex prepared by Thompson[4] from the reaction of π-$C_3H_5Mn(CO)_4$[4] with $HPh_2PFe(CO)_4$.



A similar treatment of $C_5H_5Co(CO)I_2$ and equimolar $HPh_2PFe(CO)_4$ with excess of the amine gave a green reaction mixture, from which green crystals (IX) were obtained in a 13% yield. (IX) shows the cyclopentadienyl proton signal at τ 5.00 in the nuclear magnetic resonance spectrum in $CDCl_3$ solution and $\nu(C\equiv O)$ bands at 2065, 2000, and 1980 cm^{-1} in the infrared spectrum. The X-ray emission spectrum shows bands corresponding to Fe-K_α, to P-K_α and to Co-K_α (at 39°10′, 47°26′ and 55°58′). The data and the analysis suggest that the structure of (IX) is as shown, (π-cyclopentadienyliodo)cobalt-μ-(diphenylphosphido)tetracarbonyliron, with a cobalt–iron bond. (VIII) and (IX) are complexes of type (2). Complexes of type (2) having a cobalt–iron bond, and a palladium–iron bond had been also obtained by Thompson[4].



On the other hand, when two molar equivalents of $HPh_2PFe(CO)_4$ were allowed to react with $C_5H_5Co(CO)I_2$, the reaction mixture turned immediately from green to red and none of the expected mixed transition-metal complex was isolated. The only isolable product after chromatography was the known di-iron complex (X)[9]. A reaction system of (IX) and $HPh_2PFe(CO)_4$ with $HNEt_2$ gave the same result. As it is known that rather severe conditions are necessary for the preparation of (X), the formation of (X) under the milder conditions suggests that a bis(μ-(diphenylphosphido)tetracarbonyliron) complex (XI) might be formed in the red reaction mixture intermediately and that this then decomposed to (X), accompanied by an intramolecular coupling of the (μ-diphenylphosphido)tetracarbonyliron group.



(XI)

Similar reactions of $(C_5H_5)_2TiCl_2$, $C_5H_5Cr(NO)_2Cl$, $(Ph_3P)_2NiCl_2$, $C_5H_5Ru(CO)_2Cl$, $(Ph_3P)_2PdCl_2$, $(Ph_3P)_2Pd(CH_3)I$, and $(Ph_3P)_2Pt(CH_3)I$ were attempted, but the only isolable product was (X) in all of these cases.

With respect to metal–metal bond formation, Graham[10] reported that a quick addition of $Na[Co(CO)_4]$ to $(Acac)_2SnCl_2$ afforded μ-carbonyl-μ-(diacetylacetonato)tin-bis(tricarbonylcobalt) with a cobalt–cobalt bond (XII). On the other hand, slow addition did not afford (XII). Instead *trans*-bis(tetracarbonylcobalt)-(diacetylacetonato)tin was formed which was not convertable to (XII) with a metal–metal bond formation. O'Brien[11] also reported that metal–metal bond formation in bis(tetracarbonylcobalt)diphenylgermane (XIII) to form μ-carbonyl-μ-(diphenylgermyl)bis(tricarbonylcobalt) (XIV) did not occur, although conversion of (XIV) to (XIII) with addition of one mole of carbon monoxide was possible. (XIII) and (XIV) were obtained separately through different routes. The preparation of (IV) from (III) seems to be the first evidence for the stepwise formation of the metal–metal bond. This fact suggests that a complex (I) of type (3) may be an intermediate present prior to the formation of (II). Any attempt to obtain a complex such as (VI) with metal–metal bond formation from (V) was unsuccessful.

EXPERIMENTAL

Preparations were carried out under an atmosphere of nitrogen. Diphenylphosphine was prepared by hydrolysis of lithium diphenylphosphide prepared from triphenylphosphine and lithium in tetrahydrofuran[12]. Tetracarbonyl(diphenylphosphine)iron was prepared by the method of Thompson[13]. Melting points were determined using a Yanaco micro melting point apparatus. Spectra were measured with Perkin–Elmer grating infrared spectrophotometer Type 521, JEOL nuclear magnetic resonance spectrometer Type C-60, JEOL mass spectrometer Type 1S at 75eV, and JEOL primary X-ray analyzer Type JPX-3 with KAP.

Preparation of the complex (III)

π-$C_5H_5Fe(CO)_2Cl$ (0.3 g, 1.5 mmole) and 0.5 g of $HPh_2PFe(CO)_4$ (1.4 mmole) were stirred in 10 ml of benzene–ether mixture (5/2) with 0.3 ml of $HNEt_2$ at room temperature for two days. The reaction mixture was evaporated under reduced pressure and the residue dissolved in benzene was chromatographed on a silica gel column (Wakogel C-200) using hexane/methylene chloride mixture (4/1) as an eluent. From the dark-red band, 0.53 g of red-purple crystals of (III) were obtained. The mass spectrum of (III): M^+ at *m/e* 530 (relative intensity 8), $[M-(CO)]^+$ at 502 (22), $[M-2(CO)]^+$ at 474 (24), $[M-3(CO)]^+$ at 446 (31), $[M-4(CO)]^+$ at 418 (38), $[M-5(CO)]^+$ at 390 (66), $[M-6(CO)]^+$ at 362 (100), $[M-6(CO)-H_2]^+$ at 360 (38), $[M-6(CO)-Fe]^+$ at 306 (13), $[M-6(CO)-H_2-Fe]^+$ at 304 (8), $[M-6(CO)-C_6H_6]^+$ at 284 (40), and $[M-6(CO)-C_6H_8]^+$ at 282 (23).

TABLE 1

Compound	Color	Yield (%)	M.p. (°C)	Analyses, found (calcd.) (%)				$\nu(C\equiv O)^a$ (cm^{-1})	$\tau(\pi\text{-}C_5H_5)^b$ (ppm)
				C	H	Fe[e]	Ni[f]		
(II)	Brown	25	150–152	52.93 (52.90)	3.30 (3.17)	11.7 (11.7)	12.1 (12.3)	2032s 1984(sh) 1970s 1820s	4.58
(III)	Orange	80	175–178(dec.)	52.10 (52.12)	2.76 (2.85)	21.6 (21.1)		2028s 2012s 1987s 1955s 1923s 1918 1910	4.96 d (J(PH) 1.2 Hz)
(IV)	Purple	~100	120–125(dec.)	52.93 (52.64)	3.18 (3.01)	22.4 (22.2)		2015s 1970s 1950s 1780s	5.13
(V)	Yellow-orange	77	~105(dec.)	52.40 (52.55)	3.10 (3.00)	11.0 (11.1)	11.4 (11.6)	2043s 2006s 1982vs	6.07[c] d (J(PH) 1.2 Hz)
(VIII)	Orange	22	164–165	46.55 (46.19)	2.48 (1.98)	11.0 (10.7)		2080s 2022s 2000s 1960s 1940s	
(IX)	Green	13	~110(dec.)	42.00 (41.62)	3.20[d] (2.83)	9.8 (9.2)		2065s 2000s 1980s	5.00

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] Measured in C_6D_6 solution. In $CDCl_3$ solution, the signal appears at τ 5.27 as a broad singlet. [d] Found: I, 20.85. Calcd.: I, 20.94%. [e] Determined by the thiocyanate colorimetric method. [f] Determined by the dimethylglyoxime colorimetric method.

The preparation of the complexes (V), (VIII) and (IX) were carried out similarly except that a methylene chloride/ether mixture (3/1) was used as solvent for the preparation of (VIII) and (IX). Concentration of the eluted solutions followed by storage of the residues in a refrigirator over one or two days generally gave crystals. $C_5H_5Ni(CO)I$ was used as the solution prepared by the method of Schropp[14]. $HPh_2PNi(CO)_3$ was used as the concentrated reaction mixture of HPh_2P with excess $Ni(CO)_4$ in ether at room temperature for two h.

The yields, the analyses, the melting points, the infrared spectra in region of the $\nu(C{\equiv}O)$, and the nuclear magnetic resonance spectra for protons of π-cyclopentadienyl groups are shown in Table 1. The mass spectrum of (VIII): M^+ at m/e 520 (36), $[M-(CO)]^+$ at 492 (11), $[M-2(CO)]^+$ at 464 (15), $[M-3(CO)]^+$ at 436 (33), $[M-4(CO)]^+$ at 408 (60), $[M-5(CO)]^+$ at 380 (40), $[M-6(CO)]^+$ at 352 (100), $[M-7(CO)]^+$ at 324 (92), and $[M-8(CO)]^+$ at 296 (81).

Preparation of the complex (IV)

A solution of 0.15 g of (III) in 10 ml of benzene was irradiated for two h at 0° in a quartz tube with a high pressure, Ushio 450 W mercury lamp at a distance of 10 cm. The reaction mixture was chromatographed on a silica gel column using hexane/benzene mixture (1/1) as an eluent. Concentration of the eluted solution followed by addition of hexane gave purple crystals.

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