# Chemistry of Mixed Transition-metal Complexes. V.[1] The Preparation of Several Mixed Transition-metal Complexes with Two $\mu$-Diphenylphosphido Groups

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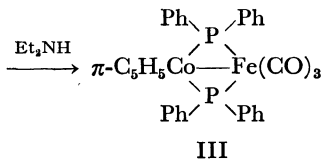
Several mixed transition-metal complexes with two $\mu$-diphenylphosphido groups as bridging ligands were prepared from bis(diphenylphosphine)metal complexes and diiodometal complexes by means of the action of amine or a Grignard reagent.

Homometallic dinuclear complexes with two $\mu$-phosphido groups have been studied extensively,[2] but few of the heterometallic dinuclear complexes are known. Only one patent claim of $(CO)_nM\text{-}(\mu\text{-}PR_2)_2\text{-}M'(CO)_m$ [M=Cr, Mo, W ($n$=4), M'=Fe ($m$=3), R=Ph; M=Cr, M'=Mo ($n$= $m$=4), $R$=$CH_3$,] has been reported.[3] In the previous papers[4,5] of this series, we reported the preparation of mixed transition-metal complexes with one $\mu$-diphenylphosphido group from the diphenylphosphinemetal complexes and the halogenometal complexes by dehydrohalogenation with amines. Now, we wish to report the preparation of several mixed transition-metal complexes with two $\mu$-diphenylphosphido groups from bis(diphenylphosphine)metal complexes and diiodometal complexes; this is as an extension of the previous work.

## Results and Discussion

The treatment of an equimolar mixture of carbonyl-$\pi$-cyclopentadienyldiiodocobalt (I) and tricarbonyl-bis(diphenylphosphine)iron (II) with excess diethylamine in methylene chloride at room temperature gave $\pi$-cyclopentadienylcobalt-bis($\mu$-diphenylphosphido)tricarbonyliron (III) as brown crystals. The mass spectrum shows the molecular ion at $m/e$ 634 and ions corresponding to the successive losses of three carbonyls. The IR spectrum (in benzene) shows $\nu_{C\equiv O}$ at 2000s and 1945s $cm^{-1}$ and indicates that the carbonyls are all of the terminal type.

$\pi$-$C_5H_5Co(CO)I_2$ + $(HPh_2P)_2Fe(CO)_3$
I II




III

A similar treatment of a mixture of I or tetracarbonyl-diiodoiron (IV) with tetracarbonyl-bis(diphenylphosphine)molybdenum[6] failed to give the desired mixed-metal complexes, although the tetracarbonyl-molybdenum-bis($\mu$-diphenylphosphido)tricarbonyliron had been prepared by the reaction of tetracarbonyl-diphenylphosphineiron with pentacarbonyl-chlorodiphenylphosphinemolybdenum.[3]

It is known that bis(triphenylphosphine)-$\pi$-cyclopentadienyl-cobalt and -rhodium, $\pi$-$C_5H_5M(PPh_3)_2$ (M=Co, Rh), can readily be prepared by the treatment of triphenylphosphine-$\pi$-cyclopentadienyl-diiodo-cobalt and -rhodium with isorpopylmagnesium bromide in the presence of triphenylphosphine.[7] We also attempted to prepare new bis(diphenylphosphine)metal complexes of the $\pi$-$C_5H_5M(PPh_2H)_2$ type according to this procedure. The treatment of I, $\pi$-cyclopentadienyl-diiodo-rhodium (V), or -iridium (VI) with an equimolar amount of diphenylphosphine afforded monodiphenylphosphine complexes of the $\pi$-$C_5H_5M(PPh_2H)I_2$ type (VII, M=Co; VIII, M=Rh; IX, M=Ir). The treatment of I or V with two molar equivalents of diphenylphosphine, or the treatment of VII or VIII with one molar equivalent of diphenylphosphine, gave bis-diphenylphosphine complexes of the $\pi$-$C_5H_5M(PPh_2H)_2I_2$ type (X, M=Co; XI, M=Rh). No corresponding iridium complex was obtained. The compounds thus obtained are summarized in Table 1. All the compounds are very stable in air. The solubility of the bis-diphenylphosphine complexes is lower than that of the corresponding mono-diphenylphosphine complexes, probably because of the influence of the partial ionic character.

Though attempts to isolate the $\pi$-$C_5H_5M(PPh_2H)_2$ complexes were not successful, several new mixed transition-metal complexes with two $\mu$-diphenylphosphido groups were obtained by the reaction of the bis-diphenylphosphine complexes, X and XI, with isopropylmagnesium bromide in the presence of some diiodometal complexes. Thus, the treatment of X with excess isopropylmagnesium bromide in the presence of an equimolar amount of IV gave III in a yield comparable with that of the amine method described above. The use of isopropylmagnesium bromide instead of the amine in the reaction of I with II also afforded III. This suggests that the Grignard reagent may act not only as a reducing agent, but also as a base, though no

1) Part IV in this series: K. Yasufuku and H. Yamazaki, *J. Organometal. Chem.*, **38**, 367 (1972).
2) J. P. Candlin, K. A. Taylor, and D. J. Thompson, "Reactions of Transition-metal Complexes," Elsevier, Amsterdam, (1968), p. 375.
3) Neth. Appl., 6,611,373 (1967); *Chem. Abstr.*, **67**, 54266.
4) K. Yasufuku and H. Yamazaki, This Bulletin, **43**, 1588 (1970).
5) K. Yasufuku and H. Yamazaki, *J. Organometal. Chem.*, **28**, 415 (1971).
6) J. G. Smith and D. T. Thompson, *J. Chem. Soc., A*, **1967**, 1694.
7) H. Yamazaki and N. Hagihara, This Bulletin, **44**, 2260 (1971).

Table 1. The diphenylphosphine complexes

| Compound | Color | Yield (%) | Mp (°C) | Analyses (%) Found (Calcd) C | H | I | NMR (τ)[a] π-$C_5H_5$ | P-H | IR ($cm^{-1}$)[c] $\nu_{P-H}$ |
|---|---|---|---|---|---|---|---|---|---|
| VII | black | 73 | 165—166 | 36.22 (36.20) | 3.14 (2.86) | 45.62 (45.00) | 4.78 (s) | 2.50 (d, $J$=417 Hz) | |
| VIII | brown | 77 | 225—228 | 33.68 (33.58) | 2.90 (2.65) | 41.94 (41.74) | 4.41 (d, $J$=2 Hz) | 2.30 (d, $J$=425 Hz) | |
| IX | red | 91 | 242—246 | 29.41 (29.28) | 2.57 (2.31) | 36.31 (36.40) | 4.43 (d, $J$=1.5 Hz) | 1.66 (d, $J$=430 Hz) | |
| X | black | 91 | 157—163 | 45.97 (46.43) | 3.87 (3.63) | 34.19 (33.83) | 4.30 (s) | 2.08[b] (d, $J$=416 Hz) | 2250 |
| XI | red | 84 | 168—172 | 43.96 (43.86) | 3.63 (3.43) | 32.25 (31.96) | 4.01 (t, $J$=1 Hz) | 2.10[b] (d, $J$=428 Hz) | 2270 |

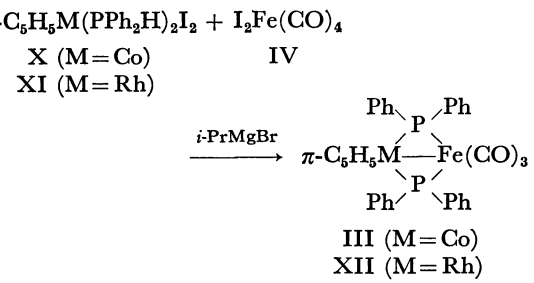
a) Measured in $CDCl_3$.
b) Intensity of the doublet was about one half of expected one.
c) Measured in $C_6H_6$. No P-H stretching absorptions were observed in the cases of VII, VIII, and IX.

Table 2. The bis-μ-diphenylphosphido complexes

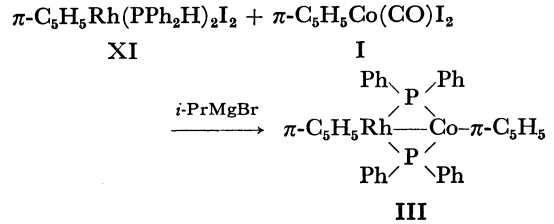
| Compound | Color | Yield (%) | Decomp. Temp. (°C) | Found (Calcd) C | H | NMR[a] (τ) π-$C_5H_5$ |
|---|---|---|---|---|---|---|
| III | dark brown | 17 | 210 | 60.96 (60.60) | 3.93 (3.97) | 5.06 (s) |
| XII | red | 18 | 260 | 56.96 (56.12) | 3.77 (3.57) | 4.54 (s) |
| XIII | black | 25 | 250 | 61.59 (61.65) | 4.60 (4.57) | 4.72 (s) 5.37 (s) |
| XIV | black | 44 | 300 | 66.28 (66.03) | 5.00 (4.89) | 5.32 (s) |
| XV | red | 29 | 300 | 58.23 (57.81) | 4.53 (4.28) | 4.80 (s) |
| XVI[b] | yellow | 1 | 310 | — | — | 4.86 (s) |

a) Measured in $CDCl_3$. Protons of $PPh_2$ appeared in 2.0—3.3 τ as multiplet.
b) No elemental analysis was carried out because of the failure to obtained enough amount.

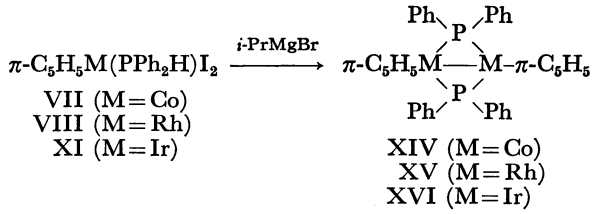
exact mechanism is clear from these observations only. Tricarbonyliron-bis(μ-diphenylphosphido)-π-cyclopentadienylrhodium (XII) was prepared from XI and IV by a similar treatment. The mass spectrum of XII showed a pattern similar to that of III.




The similar treatment of XI with I afforded π-cyclopentadienylcobalt-bis(μ-diphenylphosphido)-π-cyclopentadienylrhodium (XIII).




The homometallic bis-μ-diphenylphosphido complexes of cobalt (XIV) and of rhodium (XV) were obtained by the treatment of the mono-diphenylphosphine complexes, VII and VIII respectively, with isopropylmagnesium bromide. The iridium analogue (XVI) was also obtained from IX, though the yield was very low. The cobalt complex (XIV) is already known,[8] but the other two complexes are new ones. All the compounds are stable in air, and in their mass spectra the parent ion peak is the strongest in every case.




The reaction of an equimolar mixture of the monodiphenylphosphine complexes of cobalt (VII) and rhodium (VIII) with isopropylmagnesium bromide afforded a mixture of XIII, XIV, and XV as the product. A similar treatment of a mixture of the

8) R. G. Hayter, *Inorg. Chem.*, **2**, 103 (1963).

mono-diphenylphosphine complexes of rhodium (VIII) and iridium (IX) gave only a mixture of XV and XVI. The failure to detect a mixed metal complex of rhodium and iridium is probably the result of differences in the reactivities of the mono-diphenylphosphine complexes and/or the stabilities of the reaction intermediates.

The data for the bis($\mu$-diphenylphosphido)metal complexes prepared are collected in Table 2.

## Experimental

The preparations were carried out under an atmosphere of nitrogen. The diphenylphosphine was prepared as has been described in a previous paper,[5] while the tricarbonyl-bis-(diphenylphosphine)iron was prepared by the method of Thompson.[6] The carbonyl-$\pi$-cyclopentadienyl-diiodo-cobalt (I),[9] $\pi$-cyclopentadienyl-diiodo-rhodium (V),[10] and -iridium (VI)[11] were prepared according to the known procedures. The melting points were determined using a Yanaco micro-melting-point apparatus. The spectra were measured with a Perkin-Elmer grating infrared spectrophotometer, Type 521, a JEOL nuclear magnetic resonance spectrometer, Type C-60, and a JEOL mass spectrometer, Type 1S, at 75 eV.

*Preparation of Diphenylphosphine Complexes.* To a solution of I (2.0 g, 4.9 mmol) in $CH_2Cl_2$ (50 ml) was added diphenylphosphine (1.0 g, 5.4 mmol) under magnetic stirring. After the evolution of gas had ceased, the solution was concentrated. The subsequent addition of hexane gave black crystals of VII (2.3 g). For analytical purposes, the compound was purified by chromatography on a silica-gel column (Wakogel C-200).

In the case of the preparation of the rhodium and iridium analogues (VIII and IX), the reactions were continued until all of the almost-insoluble V and VI disappeared.

For the preparation of the bis-diphenylphosphine complexes (X and XI), two molar equivalents of diphenylphosphine to V or VI were employed.

The results are summarized in Table 1.

*Preparation of $\pi$-$C_5H_5M(\mu$-$PPh_2)_2Fe(CO)_3$ (III, M=Co; XII, M=Rh).* *Method (a)*: I (0.10 g, 0.25 mmol) and II (0.12 g, 0.23 mmol) were stirred in THF (12 ml) with diethylamine (0.3 ml) at room temperature for two days. The reaction mixture was then evaporated under reduced pressure, and the residue dissolved in benzene was chromatographed on a silica-gel column. From the brown fraction eluted with a hexane–benzene mixture (1/1), dark brown crystals of III (0.024 g) were obtained.

*Method (b)*: To a solution of X (0.23 g, 0.31 mmol) and IV (0.15 g, 0.35 mmol) in THF (20 ml) and benzene (10 ml) was added isopropylmagnesium bromide (5 ml) in ether (5 ml). The reaction mixture was hydrolyzed with aqueous ammonium chloride, and the organic layer was dried with sodium sulfate. After concentration, the residue was chromatographed on a silica-gel column and eluted by a benzene–hexane mixture (1/1). From the brown eluate, dark brown crystals of III (0.033 g) were obtained.

By the same procedure, the rhodium-iron complex, XII (0.039 g), was obtained from XI (0.24 g, 0.30 mmol) and IV (0.13 g, 0.31 mmol).

*Mcthod (c)*: I (0.10 g, 0.25 mmol) and II (0.12 g, 0.23 mmol) were treated in THF (10 ml) and benzene (5 ml) with isopropylmagnesium bromide (2 mmol) in ether (2 ml) at 0 °C for 5 hr. A procedure similar to that used in the (b) method gave III (0.018 g).

*Preparation of $\pi$-$C_5H_5Co(\mu$-$PPh_2)_2Rh$ $\pi$-$C_5H_5$ (XIII).* To a solution of XI (0.26 g, 0.33 mmol) and I (0.41 g, 0.10 mmol) in THF (15 ml) and benzene (30 ml) was added isopropylmagnesium bromide (6 mmol) in ether (6 ml) at 0 °C. After several minutes, the reaction mixture was hydrolyzed with aqueous ammonium chloride and the organic layer was dried with sodium sulfate. After concentration, the residue was chromatographed on an alumina column and eluted by a benzene–hexane mixture (1/1). From the brown eluate, black crystals of XIII (0.054 g) were obtained.

*Preparation of $\pi$-$C_5H_5M(\mu$-$PPh_2)_2M$ $\pi$-$C_5H_5$, (XIV, M=Co; XV, M=Rh; XVI, M=Ir).* A solution of VII (0.56 g, 1.0 mmol) in benzene (20 ml) was treated, drop by drop with isopropylmagnesium bromide (5 mmol) in ether (5 ml) at 0 °C. By a procedure similar to that presented above, black crystals of XIV (0.14 g) were obtained. Similarly, XV and XVI were prepared. All of the bis-$\mu$-phosphido complexes thus prepared are summarized in Table 2.

9) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y. (1965), p. 118.

10) A. Kasahara, T. Izumi, and K. Tanaka, This Bulletin, **40**, 699 (1967).

11) H. Yamazaki, *ibid.*, **44**, 582 (1971).