BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2260—2261 (1971)

Bis(triphenylphosphine)-π-cyclopentadienyl-cobalt(I) and -rhodium(I)[1]

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(Received January 18, 1971)

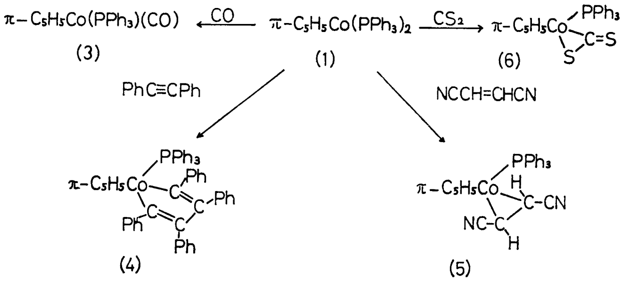
Previously, we have reported the reaction of triphenylphosphine-π-cyclopentadienylcobalt diiodide with isopropylmagnesium bromide in the presence of diphenylacetylene; this afforded acetylene complexes with a π-$C_5H_5Co(PPh_3)$ moiety.[2] In our further study of this reaction, we have found that bis(triphenylphosphine)-π-cyclopentadienylcobalt(I) was the product when the reaction was carried out in the absence of diphenylacetylene.

A recent paper of Rinze *et al.*[3] describes the isolation of the same compound from the reaction of $H_3Co(PPh_3)_3$ or $HN_2Co(PPh_3)_3$ with cyclopentadiene. This report has prompted us to publish our results on the preparation and some reactions of bis(triphenylphosphine)-π-cyclopentadienylcobalt(I) and on the preparation of an analogous rhodium complex.

When triphenylphosphine-π-cyclopentadienylcobalt diiodide in benzene - ether was treated with isopropylmagnesium bromide, favorably in the presence of triphenylphosphine, a red solution resulted. Air-sensitive dark red crystals were isolated from the solution. They melted at 140—143°C with decomposition in a nitrogen-filled capillary tube. The proton NMR spectrum in C_6D_6 showed a singlet at τ 5.55 which was assigned to the five equivalent cyclopentadienyl protons, and complex bands at τ 2.1—3.2 which were assigned to the aromatic protons. On the basis of the elemental analysis, the compound was formulated as π-$C_5H_5Co(PPh_3)_2 \cdot C_6H_6$ (**1**). The inclusion of a benzene molecule was confirmed by gas chromatography.

The similar treatment of triphenylphosphine-π-cyclopentadienylrhodium diiodide with isopropylmagnesium bromide in the presence of triphenylphosphine gave dark brown crystals. They are air stable in the solid state and melt at 190°C with decomposition. The infrared spectrum of the compound is almost identical with that of cobalt analogue. The proton NMR spectrum in C_6D_6 showed a singlet at τ 4.96 which was assigned to the five equivalent π-cyclopentadienyl protons and complex bands at τ 2.1—3.1 which were assigned to the aromatic protons. The detailed spectrum of the π-cyclopentadienyl protons consisted of a 1 : 3 : 3 : 1 quartet (J=0.6 Hz) showing the equivalence of ^{31}P and ^{103}Rh nuclei to couple with the protons. Elemental analysis suggested the compound to be π-$C_5H_5Rh(PPh_3)_2 \cdot C_6H_6$ (**2**), analogous with the cobalt complex. Upon heating at 140°C for ten minutes under reduced pressure, the crystals turned pale brown and lost a benzene molecule to give an exact analysis for π-$C_5H_5Rh(PPh_3)_3$.

The compound (**1**) readily exchanges one triphenylphosphine with another ligand (L) and gives a complex of the type π-$C_5H_5Co(PPh_3)(L)$. When carbon monoxide was passed through the benzene solution of **1**, triphenylphosphine-carbonyl-π-cyclopentadienylcobalt (**3**)[4] was formed almost immediately; this was also described by Rinze *et al.*[3] The reactions with excess diphenylacetylene and with fumaronitrile afforded triphenylphosphine-π-cyclopentadienyl(tetraphenylcobaltacyclopentadiene) (**4**)[2] and triphenylphosphinefumaronitrile-π-cyclopentadienylcobalt (**5**)[2] respectively.



With carbon disulfide, air-stable dark red crystals with the empirical formula of π-$C_5H_5Co(PPh_3)(CS_2)$ were obtained. In the infrared spectrum of the compound, the ν(C=S) appeared at 1170 and 1155 cm^{-1}, suggesting a structure (**6**) which consists of the bonding of a type similar to that of known carbon disulfide complexes of transition metals.[5]

Studies of the reaction of rhodium compound, **2**, will be described separately.

Experimental

All the reactions were carried out in a nitrogen atmosphere. The melting points were determined on a Yanagimoto hot-stage apparatus unless otherwise stated. The proton NMR spectra were obtained on a Hitachi-Perkin Elmer R-20 spectrometer, with tetramethylsilane as the internal standard. The infrared spectra were obtained with a Jasco DS-402G spectrophotometer.

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[1] Presented at the 21st Annual Meeting of The Chemical Society of Japan, Suita, Osaka, April 3, 1968 (Preprints, III, p. 1972), and at the Symposium of Organometallic Compounds, Osaka, October 16, 1968 (Preprints, p. 123).

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[5] M. C. Baird and G. Wilkinson, *J. Chem. Soc.*, *A*, **1967**, 865; M. C. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*. **1967**, 92; T. Kashiwagi, N.Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, This Bulletin, **41**, 296 (1968); A. J. Deeming and B. L. Shaw, *J. Chem. Soc.*, *A*, **1969**, 1128.

The compounds π-$C_5H_5Co(PPh_3)I_2$[6] and π-$C_5H_5Rh(PPh_3)I_2$[7] were prepared according to the method described in the literature.

Bis(triphenylphosphine)-π-cyclopentadienylcobalt (**1**). A slurry of π-$C_5H_5Co(PPh_3)I_2$ (3.2 g) in ether (20 m*l*) and benzene (20 m*l*) was treated with isopropylmagnesium bromide (15 m*l* of a 1-mol ether solution) at room temperature. The resulting red solution was hydrolyzed with aqueous ammonium chloride, and the organic layer was dried with sodium sulfate. After filtration, the solution was concentrated and hexane was added. When the solution was kept in a refrigerator overnight, dark red crystals (1.1 g) were formed.

Found: C, 77.64; H, 5.74%. Calcd for $C_{47}H_{41}P_2Co$ (including a benzene molecule): C, 77.68; H, 5.69%.

In the presence of triphenylphosphine (1.3 g), **1** was obtained in a better yield (1.4 g) by the same procedure.

Bis(triphenylphosphine)-π-cyclopentadienylrhodium (**2**). According to a procedure similar to that described above, the title compound (1.3 g) was obtained from the reaction of π-$C_5H_5Rh(PPh_3)I_2$ (1.4 g) with isopropylmagnesium bromide (10 m*l* of a 1-mol ether solution) in the presence of triphenylphosphine (1.0 g) and in a mixture of benzene and tetrahydrofurane (1/1, 40 m*l*).

Found: C, 73.15; H, 5.30%. Calcd for $C_{47}H_{41}P_2Rh$ (including a benzene molecule): C, 73.24; H, 5.36%.

The crystals turned pale brown with the loss of the benzene when heated at 140°C under reduced pressure.

Found: C, 71.22; H, 5.15%. Calcd for $C_{41}H_{35}P_2Rh$: C, 71.10; H, 5.09%.

The Reaction of **1** *with Carbon Monoxide.* Carbon monoxide was passed through the solution of 1 (0.5 g) in benzene (15 m*l*) at room temperature. The red color immediately turned brown. The solution was chromatographed on alumina, with a benzene - hexane as the eluent. The red brown eluate was then concentrated to give red brown crystals of π-$C_5H_5Co(PPh_3)(CO)$ (**3**); mp 142—144°C (in a nitrogen-filled capillary tube (0.1 g). IR (Nujol): ν_{CO} 1915 cm^{-1}. NMR (τ in C_6H_6): 5.38 (singlet, π-C_5H_5).

Found: C, 69.91; H, 4.90%. Calcd for $C_{24}H_{20}OPCo$: C, 69.57; H, 4.87%.

The Reaction of **1** *with Excess Diphenylacetylene.* A mixture of **1** (1.0 g) and diphenylacetylene (0.9 g) in benzene (20 m*l*) was heated at 60°C for 10 min. The solution was chromatographed on alumina, with benzene as the eluent. The red eluate was then concentrated, and hexane was added to give red-brown crystals (0.9 g). The infrared spectrum of the crystals was identical with that of π-$C_5H_5Co(PPh_3)(PhC{\equiv}CPh)_2$(**4**).

The Reaction of **1** *with Fumaronitrile.* To a solution of **1** (0.4 g) in benzene (30 m*l*), fumaronitrile (0.1 g) was added at room temperature. After 10 min., the solution was concentrated and chromatographed on alumina, with a benzene - ethyl acetate mixture (**2**/**1**) as the eluent. After the evaporation of the solvent, the residue was recrystallized with benzene - hexane to give dark red crystals (0.19 g). The infrared spectrum of the crystals was identical with that of π-$C_5H_5Co(PPh_3)(NCCH{=}CHCN)$ (**5**).

The Reaction of **1** *with Carbon Disulfide.* To a solution of **1** (0.65 g) in benzene (10 m*l*), carbon disulfide (1 m*l*) was added. The resulting dark brown solution was concentrated and chromatographed on alumina, with benzene as the eluent. The chocolate-brown eluate was then concentrated, and hexane was added to give black crystals (0.18 g) of π-$C_5H_5Co(PPh_3)(CS_2)$ (**6**); mp 137—138°C (with decomp.).

Found: C, 62.33; H, 4.36; S, 13.87%. Calcd for $C_{24}H_{20}S_2PCo$: C, 62.55; H, 4.30; S, 13.63%. NMR (τ in $CDCl_3$): 5.50 (singlet, C_5H_5); 2—3 (complex bands, C_6H_5).

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