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PHOSPHIDO COMPLEXES OBTAINED BY REACTION OF (η^5-C_5H_5)Rh(CO)$_2$ WITH DIPHENYLPHOSPHINE. A DETERMINING ROLE OF DIOXYGEN ON THE NATURE OF THE PRODUCTS

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Summary

In aerobic conditions, (η^5-C_5H_5)Rh(CO)$_2$ reacts with diphenylphosphine to give the phosphido complex [Rh(O_2)($PHPh_2$)$_3$$PPh_2$]; under a dinitrogen atmosphere, the same reaction gave [Rh($PHPh_2$)PPh_2]$_3$. A possible scheme for these reactions is proposed.

The complex [Rh(O_2)($PHPh_2$)$_3$$PPh_2$] reacts with halogens or CH_3I giving the corresponding halogen derivatives [Rh(O_2)($PHPh_2$)$_3$X] (X = Cl, Br, I).

Introduction

Secondary phosphines form stable transition metal complexes and their lower steric requirements lead, in some cases, to changes in stoichiometry or structure with respect to those associated with analogous tertiary phosphines [1].

An interesting aspect of the chemistry of secondary phosphines is the possibility of inter- or intra-molecular elimination of HX or H_2 (X = halide) [2—5] and of deprotonation reactions [6] to give complexes derived from the anionic ligand PR_2^-. Reactions of secondary phosphine complexes with metal halide complexes in the presence of $HNEt_2$ or with η-allylmetal complexes are found to give several types of mixed transition metal mono-μ-phosphido complexes [7—8].

Our aim has been to study the effect of the P—H bond of the coordinated secondary phosphine on the η^5-cyclopentadienylrhodium(I) moiety. We have previously observed transfer reactions of hydride ligand from rhodium to the η^5-cyclopentadienyl coordinated group with C_5H_6 elimination [9].

Experimental

(η^5-C_5H_5)Rh(CO)$_2$ and $PHPh_2$ were prepared by published methods [10—11]. Other chemicals were reagent grade and were used without purification. Molecular weights were determined with a Knauer vapour-pressure osmometer. Infrared spectra were recorded with a Perkin—Elmer mod. 457 spectrometer using a polystyrene film for calibration. A Perkin—Elmer R24B at 60 MHz spectrometer was used to obtain ^{1}H NMR spectra. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Preparation of [Rh(O$_2$)(PHPh$_2$)$_3$PPh$_2$]

Diphenylphosphine in heptane was added dropwise under aerobic conditions to a solution of (η^5-C_5H_5)Rh(CO)$_2$ (0.6 g, 2.6 mmol) in the same solvent. The mixture was heated to reflux. The progress of the reaction was followed by IR spectra. After ca. 1 h the addition of diphenylphosphine was stopped owing to disappearance of the ν(CO) bands of the starting compound. The resulting yellow-orange solution was filtered, and, after evaporation of the solvent to a small volume, cooled at —20° C giving a yellow-orange microcrsytalline solid. This was recrystallized from dichloromethane/heptane to give 0.48 g (yield 80%) of product. (Found: C, 65.32; H, 4.93; P, 13.95. $C_{48}H_{43}O_2P_4$Rh calcd.: C, 65.61; H, 4.93; P, 14.10%; molecular weight (CH_2Cl_2 solution): found 849; calcd. 878).

Preparation of [Rh(PHPh$_2$)PPh$_2$]$_3$

To a heptane solution of (η^5-C_5H_5)Rh(CO)$_2$ (0.72 g, 3.21 mmol), diphenylphosphine was added dropwise. The reaction was carried out under nitrogen. The mixture was heated to reflux. The colour of the solution turned from yellow to deep red. The IR spectra of the mixture showed a slow disappearance of the ν(CO) bands of (η^5-C_5H_5)Rh(CO)$_2$ and formation of a new ν(CO) band at 1965 cm^{-1}, which slowly disappeared. After ca. 5 h the IR spectrum did not show ν(CO) bands. The solution was filtered and, after evaporation of the solvent to 10 ml, cooled at —20° C. A red solid was obtained which was crystallized from dichloromethane/heptane to give the product. (Found: C, 61.00; H, 4.78; P, 12.90; $C_{24}H_{22}P_2$Rh calcd.: C, 60.65; H, 4.66; P, 13.03%; molecular weight in CH_2Cl_2 solution: found 1310; calcd. 1425.)

Preparation of trans-[Rh(CO)(PHPh$_2$)$_2$Cl]

[Rh(CO)$_2$Cl]$_2$ (0.5 g, 2.5 mmol) in heptane solution was stirred at room temperature with 0.93 g (5 mmol) of PHPh$_2$. The solution rapidly became colourless and a yellow precipitate separated. This was filtered off, washed with ether, and recrystallized from dichloromethane/heptane to give 0.46 g (yield 92%) of the product. (Found: C, 55.80; H, 4.22; Cl, 6.58. $C_{25}H_{22}P_2$OCl calcd.: C, 55.73; H, 4.11; Cl, 6.58%.)

Reaction of [Rh(O$_2$)(PHPh$_2$)$_3$PPh$_2$] with halogens

An excess of Cl$_2$ in benzene solution was added to a solution of [Rh(O$_2$)-(PHPh$_2$)$_3$PPh$_2$] (0.3 g, 3.4 mmol) in the same solvent (50 ml). The solvent was evaporated to small volume and n-pentane was added to precipitate a yellow solid. This was recrystallized from n-pentane to give 0.28 g of [Rh(O$_2$)-(PHPh$_2$)$_3$Cl] (yield 93%). (Found: C, 59.38; H, 4.61; P, 13.00; Cl, 4.98. $C_{36}H_{33}ClO_2P_3$Rh calcd.: C, 59.32; H, 4.56; P, 12.74; Cl, 4.86%.)

By the same method [Rh(O$_2$)(PHPh$_2$)$_3$I] (90%) and [Rh(O$_2$)(PHPh$_2$)$_3$Br] were obtained from [$Rh(O_2)(PHPh_2)_3PPh_2$] and the appropriate halogens. (Found: C, 56.1; H, 4.51; Br, 10.08; P, 12.21. $C_{36}H_{33}BrO_2P_3Rh$ calcd.: C, 55.91; H, 4.3; Br, 10.33; P, 12.01%.)

Reaction of [$Rh(O_2)(PHPh_2)_3PPh_2$] with CH_3I

[$Rh(O_2)(PHPh_2)_3PPh_2$] (0.25 g, 2.8 mmol) in 5 ml of CH_3I was stirred under reflux for 4 h. The solution became red. Evaporation of the solvent followed by crystallization from ether gave 0.208 g (yield 83%) of [$Rh(O_2)(PHPh_2)_3I$]. (Found: C, 52.48; H, 3.95; P, 11.40; I, 15.50. $C_{36}H_{33}IO_2P_3Rh$ calcd.: C, 52.70; H, 4.05; P, 11.32; I, 15.46%.)

Results and discussion

The reaction of (η^5-C_5H_5)Rh(CO)$_2$ with diphenylphosphine takes a different path under aerobic and anaerobic conditions.

Under aerobic conditions, the complex (η^5-C_5H_5)Rh(CO)$_2$ reacts readily with $PHPh_2$ in refluxing heptane to give a yellow-orange solid, which is indicated by analysis, molecular weight measurement in dichloromethane solution, and spectroscopic properties to be [$Rh(O_2)(PHPh_2)_3PPh_2$] (I). In agreement with this formulation the IR spectrum does not show ν(CO) or ν(P=O) bands, and contains a broad diffuse band at 2280 cm^{-1} due to ν(P—H), consistent with the presence of the secondary phosphine ligands and a band at 855 cm^{-1} which can be attributed to the stretching of the coordinated dioxygen; the ^{1}H NMR spectrum does not contain any signal due to a cyclopentadienyl group; it shows a large complex signal centred at τ 2.75 ppm, which may be assigned to phenyl protons, and three small broad signals at τ 1.95, 4.10 and 5.05 ppm (in $CDCl_3$ solution). The ratio of the sum of the intensities of these broad signals to that of the large signal is approximately 3/40, and so the less intense signals may be assigned to the protons on the phosphorus atoms. These signals may be broadened by coupling of the protons with distant phosphorus nuclei, but they are too small to be resolved satisfactory.

A red-orange solid was obtained on treating (η^5-C_5H_5)Rh(CO)$_2$ with $PHPh_2$ under dinitrogen in refluxing heptane. The analyses and the (osmometric) molecular weight in dichloromethane support the formulation of the compound as [$Rh(PHPh_2)PPh_2$]$_3$ (II). In the molecule the phosphido groups must be bonded to two rhodium atoms, giving a six-membered ring, and metal—metal bonds are probably present. This formulation must, however, be regarded with caution as the X-ray structure could not be determined, owing to bad quality of the crystals; IR and ^{1}H NMR spectra do not give conclusive information. It is interesting to observe that II failed to take up dioxygen or carbon monoxide. We have attempted the formation of II by treating [$Rh(CO)_2Cl$]$_2$ with $PHPh_2$; these attempts were unsuccessful, *trans*-[$Rh(CO)(PHPh_2)_2Cl$] being formed instead. This new compound is a yellow solid and shows ν(CO) at 1965 cm^{-1} and ν(Rh—Cl) at 315 cm^{-1}, as expected for a chloride in *trans* position to CO in a rhodium(I) complex. Although four-coordinated complexes of rhodium(I) with secondary phosphines are known, neutral carbonyl complexes have not been reported [12—14].

In the absence of kinetic data, we cannot with certainty define the steps involved in the formation of I and II. However, some information was obtained by following the reaction by monitoring the IR spectra in the carbonyl stretching region. Under aerobic conditions, only a decrease in the intensity of ν(CO) of the starting material $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ was observed. In contrast under anaerobic conditions, the decrease of the ν(CO) of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ is associated with the appearance of a new ν(CO) band at 1965 cm^{-1}, which disappears as the reaction on progresses. $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ reacts with tertiary phosphines PR_3 giving initially $(\eta^5\text{-}C_5H_5)Rh(CO)PR_3$ and, more then slowly $(\eta^5\text{-}C_5H_5)Rh(PR_3)_2$ [15]. It is reasonable to assume that in the reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with $PHPh_2$, the intermediate $(\eta^5\text{-}C_5H_5)Rh(CO)(PHPh_2)$ is initially formed; the presence of this species was detected by IR spectroscopy with a sample obtained under anearobic conditions. The intermediate, reacts rapidly in presence of dioxygen while under anaerobic conditions a slow carbon monoxide substitution occurs. The dioxygen probably interacts with $(\eta^5\text{-}C_5H_5)\text{-}Rh(CO)(PHPh_2)$, giving, in equilibrium conditions, a labile dioxygen rhodium(III) adduct, which in turn undergoes carbon monoxide substitution and C_5H_6 elimination in fast steps. The sequence proposed is in contrast to low tendency shown by rhodium(I) complexes to take up dioxygen, though dioxygen adducts of rhodium complexes have been reported [16—17]. Under anaerobic conditions the intermediate $(\eta^5\text{-}C_5H_5)Rh(CO)(PHPh_2)$ probably reacts to give $(\eta^5\text{-}C_5H_5)\text{-}Rh(PHPh_2)_2$ (a slow disappearance of the ν(CO) was observed in the IR spectrum) which in turn undergoes a fast rearrangement involving inter- or intra-molecular C_6H_5 elimination and formation of the trinuclear compound.

In accord with its formulation as a rhodium(III) complex, oxidative addition reactions are not observed with I, and on treating I with halogen (X_2 or CH_3I) it gives the corresponding halogen derivatives:

$$[Rh(O_2)(PHPh_2)_3PPh_2] + X_2 \rightarrow [Rh(O_2)(PHPh_2)_3X] + PXPh_2$$

$$[Rh(O_2)(PHPh_2)_3PPh_2] + CH_3I \rightarrow [Rh(O_2)(PHPh_2)_3I] + P(CH_3)Ph_2$$

The new neutral rhodium(III) dioxygen adducts are yellow or yellow-orange solids, stable to air and in refluxing benzene.

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