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Note

Organometallic chemistry of diphosphazanes. Rhodium(I) complexes of $RN(PX_2)_2$ (R=C₆H₅; X=OC₆H₅, OC₆H₄Br-*p*, R=CH₃; X=OC₆H₅)

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Abstract

Reactions of $[Rh(COD)Cl]_2$ with the ligand $RN(PX_2)_2$ (1: $R = C_6H_5$; $X = OC_6H_5$) give mono- or disubstituted complexes of the type $[Rh_2(COD)Cl_2\{\eta^2-C_6H_5N(P(OC_6H_5)_2)_2\}]$ or $[RhCl\{\eta^2-C_6H_5N(P(OC_6H_5)_2)_2\}]_2$ depending on the reaction conditions. Reaction of 1 with $[Rh(CO)_2Cl]_2$ gives the symmetric binuclear complex, $[Rh(CO)Cl\{\mu-C_6H_5N(P(OC_6H_5)_2)_2\}]_2$, whereas the same reaction with 2 ($R = CH_3$; $X = OC_6H_5$) leads to the formation of an asymmetric complex of the type $[Rh(CO)(\mu-CO)Cl\{\mu-CH_3N(P(OC_6H_5)_2)_2\}]_2$ containing both terminal and bridging CO groups. Interestingly the reaction of 3 ($R = C_6H_5$, $X = OC_6H_4Br-p$) with either $[Rh(COD)Cl]_2$ or $[Rh(CO)_2Cl]_2$ leads only to the formation of the chlorine bridged binuclear complex, $[RhCl\{\eta^2-C_6H_5N(P(OC_6H_4Br-p)_2)_2\}]_2$. The structural elucidation of the complexes was carried out by elemental analyses, IR and ³¹P NMR spectroscopic data.

Keywords: Diphosphazane complexes; Chelation; Rhodium complexes

1. Introduction

Previous papers of this series have discussed the reactions of various transition metal derivatives with diphosphazane ligands of the type $RN(PX_2)_2$ ($R = C_6H_5$ or CH_3 ; X = OR', R' = alkyl or aryl). As a continuation of our work [1–10] and for the interest of others [11], we report herein the syntheses and characterization of binuclear rhodium(I) complexes of $RN(PX_2)_2$ (1: $R = C_6H_5$, $X = OC_6H_5$; 2: $R = CH_3$, $X = OC_6H_5$; 3: $R = C_6H_5$, $X = OC_6H_4Br-p$). A preliminary account of the work described in this paper has appeared in the proceedings of two conferences [1,2].

2. Experimental

All manipulations were carried out under dinitrogen by standard Schlenk line techniques. Solvents were dried and distilled prior to use. The light petroleum ether used was the fraction of b.p. 60–80 °C. $X_2PN-(R)PX_2$ (1–3), [3] [Rh(COD)Cl]₂ [12] and [Rh(CO)₂Cl]₂ [13] were prepared according to published procedures. NMR and IR spectroscopic measurements were carried out as described previously [3].

2.1. Preparation of $[Rh(CO)Cl-{\mu-C_6H_5N(P(OC_6H_5)_2)_2}]_2$ (4)

Method 1

A solution of 1 (0.269 g, 0.51 mmol) in benzene (20 ml) was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (0.10 g, 0.25 mmol) also in benzene (10 ml). The reaction mixture was stirred for 1 h. Concentration of the resulting solution under reduced pressure followed by the addition of petrol gave a yellow precipitate which was filtered, washed with petroleum ether and recrystallized from a 1:2 mixture of benzene and petroleum ether to give analytically pure yellow crystals of 4. Yield 80%; m.p. 140–142 °C. Anal. Calc. for $C_{62}H_{50}Cl_2N_2O_{10}P_4Rh_2$: C, 54.2; H, 3.8; N, 2.1. Found: C, 53.8; H, 3.6; N, 2.0%. IR (mull): ν (CO) 2040 cm⁻¹.

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Method 2

A mixture of $[Rh(COD)Cl]_2$ (0.10 g, 0.20 mmol) and 1 (0.213 g, 0.40 mmol) was dissolved in 30 ml of acetonitrile under an atmosphere of CO at 25 °C; CO was bubbled through the solution for 30 min. Stirring was continued for 1 h at 40–45 °C during which time a yellow precipitate was formed. The precipitate was filtered and recrystallized as described above to give 4 in 98% yield.

2.2. Preparation of $[RHCl(CO)-{\mu-CH_3N(P(OC_6H_5)_2)_2}]_2$ (5)

This was prepared in the same way as in Method 1, from 2 (0.23 g, 0.51 mmol) and $[Rh(CO)_2Cl]_2$ (0.10 g, 0.25 mmol), as a yellow crystalline solid. Yield 68%; m.p. 135 °C dec. *Anal.* Calc. for $C_{52}H_{46}Cl_2N_2O_{10}P_4Rh_2$: C, 50.2; H, 3.8; N, 2.2. Found: C, 49.6; H, 3.6; N, 1.9%. IR (CH₂Cl₂): ν (CO) 2000, 1830 cm⁻¹. ¹H NMR (CDCl₃): δ 3.28 (t, ³*J*(PH) = 10 Hz), 7.15 (m, OPh).

2.3. Preparation of $[RH_2Cl_2(COD) - \{\eta^2 - C_6H_5N(P(OC_6H_5)_2)_2\}]$ (6)

A solution of 1 (0.11 g, 0.20 mmol) in benzene (20 ml) was added dropwise to a solution of $[Rh(COD)Cl]_2$ (0.10 g, 0.20 mmol) also in benzene (10 ml). The reaction mixture was stirred for 30 min at 25 °C. Concentration of the resulting solution under reduced pressure followed by the addition of diethyl ether gave light yellow precipitate of 6. An analytically pure sample was obtained by recrystallizing the crude product in a 1:2 mixture of CH₂Cl₂ and petroleum ether. Yield 62%; m.p. 165 °C dec. *Anal.* Calc. for C₃₈H₃₇Cl₂NO₄P₂Rh₂: C, 51.1; H, 4.1; N, 1.5. Found: C, 50.1; H, 3.9; N, 1.4%.

2.4. Preparation of $[RHCl\{\eta^2 - C_6H_5N(P(OC_6H_5)_2)_2\}]_2$ (7)

A solution of 1 (0.213 g, 0.40 mmol) in benzene (20 ml) was added dropwise to a solution of $[Rh(COD)Cl]_2$ (0.10 g, 0.20 mmol) also in benzene (10 ml). The reaction mixture was stirred for 1 h. The resulting reaction mixture was worked up as described above for 6 to obtain 7 in 65% yield; m.p. 141–143 °C. *Anal.* Calc. for C₆₀H₅₀Cl₂N₂O₈P₄Rh₂: C, 54.3; H, 3.8; N, 2.1. Found: C, 53.6; H, 3.6; N, 2.0%.

2.5. Preparation of $[RHCl\{\eta^2-C_6H_5N-(P(OC_6H_4Br-p)_2)_2\}]_2$ (8)

A solution of 3 (0.41 g, 0.48 mmol) in benzene (15 ml) was added dropwise to a solution of $[Rh(COD)Cl]_2$ (0.095 g, 0.24 mmol) also in benzene (20 ml). The reaction mixture was stirred for 1 h. The resulting reaction mixture was worked up as described above

for 6 to obtain 8 in 68% yield; m.p. 240 °C dec. Anal. Calc. for $C_{60}H_{42}Br_8Cl_2N_2O_8P_4Rh_2$: C, 36,7; H, 2,1; N, 1.4. Found: C, 36.4; H, 2.1; N, 1.3%.

Reaction of **3** (0.50 mmol) with $[Rh(COD)Cl]_2$ (0.25 mmol) under CO atmosphere or with $[Rh(CO)_2Cl]_2$ (0.25 mmol) under similar reaction conditions to those described above gives the same product **8** in 80% yield.

3. Results and discussion

It is well established that the treatment of $[RhX(diene)]_2 (X = Cl, Br or I)$ with tertiary phosphines, L $(L=PPh_3, PMePh_2)$, leads to cleavage of the halide bridges and the formation of complexes of the type [RhX(diene)L] [14,15]. In contrast, a strong π -acceptor tertiary phosphine such as $P(OPh)_3$ has been shown to preferentially displace the diene groups from this dimeric species to afford successively $[Rh_2X_2-(diene)\{P(OPh)_3\}_2]$, $[Rh_2X_2\{P(OPh)_3\}_4]$ and $[RhX-\{P(OPh)_3\}_3]$ [16]. In the present study bis(phosphino)amines behave similarly to $P(OPh)_3$.

The reaction of $[Rh(COD)Cl]_2$ with 1 in 1:1 and 1:2 mole ratio in benzene leads to the successive replacement of the diene ligands and the formation of 6 and 7, respectively, as shown in Scheme 1. In these complexes bis(phosphino)amines exhibit a chelating mode of coordination. They are moderately stable to air in the solid state but decompose slowly in solution. The reaction of two equivalents of 1 with $[Rh(CO)_2Cl]_2$ in benzene results in the formation of the binuclear rhodium complex 4 which is analogous to the Ph₂PCH₂PPh₂ (dppm) complex, $[Rh(CO)Cl{\mu-dppm}]_2$ [17,18]. Complex 4 can also be prepared by the reaction of 1 with $[Rh(COD)Cl]_2$ in 2:1 molar ratio under CO atmosphere in benzene or acetonitrile. The yield is quantitative. Similarly the reaction of 2 with $[Rh(COD)Cl]_2$ affords



Table 1 ³¹P NMR^a spectroscopic data for ligands 1-3 and their complexes

Compound	δP (ppm)	¹ J(RhP) (Hz)
$C_6H_5N(P(OC_6H_5)_2)_2$ (1)	127.7	
$CH_3N(P(OC_6H_5)_2)_2$ (2)	135.1	
$C_{6}H_{5}N(P(OC_{6}H_{4}Br-p)_{2})_{2}$ (3)	130.5	
$[Rh(CO)Cl{\mu-C_{c}H_{5}N(P(OC_{c}H_{5})_{2})_{2}]_{2}$ (4)	112.9(d)	214
$[Rh(CO)Cl{\mu-CH_3N(P(OC_6H_5)_2)_2]_2}$ (5)	114.0(d)	187.7
$[Rh_2Cl_2(COD){\eta^2-C_6H_3N(P(OC_6H_3)_2)_2}]$ (6)	88.8(d)	282.5
$[RhCl{\eta^2-C_6H_5N(P(OC_6H_5)_2)_2]_2$ (7)	86.1(d)	284
$[RhCl{\eta^2-C_6H_5N(P(OC_6H_4Br-p)_2)_2]_2$ (8)	90.2(d)	281.2

* All spectra in CDCl₃; ppm vs. 85%H₃PO₄; d=doublet.





the binuclear complex 5, a product of similar stoichiometry, but whose IR spectrum reveals the presence of bridging as well as a terminal carbonyl group indicating that it has an unsymmetrical structure (see Scheme 1).

The bis(phosphino)amine 3 behaves somewhat differently with rhodium derivatives. Reaction of 3 with either $[Rh(CO)_2Cl]_2$ or $[Rh(COD)Cl]_2$ leads only to the formation of the chloro bridged complex 8, analogous to 7. Reaction of 3 with $[Rh(COD)Cl]_2$ under CO atmosphere also leads to the formation of complex 8.

3.1. Spectroscopic aspects

The IR spectrum of complex 4 shows a strong absorption at 2020 cm⁻¹ characteristic of CO *trans* to Cl with *trans*-bridging diphosphine ligands [18,19]. The IR spectrum of complex 5 shows the presence of a bridging as well as a terminal carbonyl group (IR (mull or CH₂Cl₂): ν (CO) = 2000, 1830 cm⁻¹) suggesting an unusual asymmetric structure analogous to [RhCl(CO){ μ -(P(OCH₃)₂)₂NC₂H₅}]₂ [20],the structure of which has been confirmed by single crystal X-ray analysis.

The ³¹P NMR data for diphosphazanes and their complexes are listed in Table 1. The ³¹P NMR spectra of complexes 6 and 7 show doublets centered at 88.7 and 86.1 ppm with ¹J(RhP) couplings of 282 and 284 Hz, respectively. Complex 4 also shows a doublet at

112.9 ppm with a ¹J(RhP) coupling of 214 Hz. The ³¹P NMR spectrum of complex 5 show a major doublet at 114 ppm with a ¹J(RhP) value of 187.5 Hz attributed to the symmetric isomer. This indicates that the asymmetric complex 5 is in equilibrium with the symmetric structure in solution through a fluxional process involving exchange of the terminal and bridging carbonyl groups (Scheme 2). The ³¹P NMR data clearly indicate that in solution the equilibrium is shifted towards the symmetric isomer 5a. In addition to the major doublet attributed to 5a, the spectrum shows other less intense signals which are not resolved. These signals may be due to the presence of isomer 5 which would be anticipated to give rise to a complex AA'BB'XY type of spectrum. Variable temperature NMR measurements at high field are required to throw further light on the fluxional process.

The ³¹P NMR spectrum of complex 8 is similar to that of the complex 7 which shows a doublet at 90.2 ppm with a very large ${}^{1}J(RhP)$ coupling of 281 Hz.

4. Conclusions

The reactions of various diphosphazanes with rhodium(I) derivatives have led to the formation of different types of complexes depending upon the influence of substituents on both the phosphorus and nitrogen atoms on the coordinating phosphorus centers. This clearly demonstrates the versatility of diphosphazanes. Thus functionalities with a wide range of steric and electronic attributes can be introduced at both trivalent phosphorus and nitrogen centers which can cause dramatic changes in their coordination behaviour [8]. These results also suggests that the bite angle is not the only factor which decides the coordination behaviour of bisphosphines.

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