



Coordination chemistry of bidentate phosphine ligands with hydrogen-bonding arms: Picket-fence rhodium complexes



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ARTICLE INFO

Article history:

Received 25 September 2013

Accepted 18 November 2013

Available online 4 December 2013

Keywords:

Bidentate phosphine
Secondary interaction
Rhodium complex

ABSTRACT

A bidentate phosphine ligand with two amide arms, designed to form hydrogen bonds with electron-donating moieties, was synthesized and isolated in high diastereomeric excess (95% de). The hydrogen-bonding abilities of the ligand and its diastereomer were demonstrated with two rhodium complexes containing these ligands. The structures of the rhodium compounds are reminiscent of the well-studied picket-fence porphyrin systems.

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1. Introduction

Secondary ligand–ligand and ligand–substrate interactions play important roles in the catalytic transformations promoted by transition metal complexes [1] and as enzymatic models [2]. Among the various types of interactions, hydrogen bonds are useful, or even critical, in many cases of catalysis involving substrates containing oxygen and nitrogen atoms [3]. Given our interest in heterocycle carbonylation [4], we explored along this line in a limited scope. Here, we document the synthesis of a bidentate phosphine ligand with a capacity for hydrogen bonding and its rhodium coordination chemistry. The resultant Rh complexes resemble picket-fence porphyrins [5], which have been used as models for enzymatic active sites and for selective substrate binding.

2. Experimental

2.1. General remarks

All reactions and manipulations were performed under an inert atmosphere. All solvents were anhydrous and purchased from Sigma–Aldrich. NMR spectra were recorded on a Varian 300 MHz spectrometer. Bis(phenylphosphino)ethane, $\text{PhP(H)(CH}_2)_2\text{P(H)Ph}$, was prepared according to a literature procedure [6].

2.2. Synthesis of **1-C₅**

A 50-mL flask was placed in an oil bath at 100 °C. $\text{Ph(H)CH}_2\text{CH}_2\text{-P(H)Ph}$ (1.24 g, 5.04 mmol), AIBN (~50 mg), and $\text{CH}_2 = \text{CHCONH}^i\text{Pr}$ (1.26 g, 11.2 mmol) were added to this flask. The mixture was stirred at 100 °C for 1 h under a nitrogen atmosphere and then under vacuum for 24 h to remove the slightly excess amount of $\text{CH}_2 = \text{CHCONH}^i\text{Pr}$. The resultant oil was dissolved in boiling toluene (20 mL) and filtered while the solution was hot. The filtrate was kept at room temperature (RT) to allow precipitation of a white crystalline solid, which was washed with acetonitrile (2 × 5 mL) and isolated after filtration (yield, 1.08 g, 45% in 95% diastereomeric excess).

¹H NMR (CDCl_3): δ 1.10 (“triplet” arising from two partially overlapping doublets, $J = 7.7$ Hz, 12 H, $-\text{CH}_3$), 1.63–1.75 (m, 4H, $-\text{PCH}_2\text{CH}_2\text{CO}-$), 1.96 (m, 4H, $-\text{PCH}_2\text{CH}_2\text{P}-$), 2.07 (m, 4H, $-\text{CH}_2\text{CO}-$), 4.02 (heptet, $J = 8.1$ Hz, 2H, $-\text{CH}-$), 5.24 (b, 2H, $-\text{NH}-$), 7.34 (m, 6 H, CH_{aryl}), and 7.42 (m, 4H, CH_{aryl}). ¹³C{¹H} NMR (CDCl_3): δ 171.3, 137.1, 132.4, 119.2, 128.5, 41.4, 32.9, 23.5, 23.1, 22.8. ³¹P{¹H} NMR (CDCl_3): δ -19.9.

2.3. Collection of **1-C₅/1-C₂** mixture

The toluene filtrate from the above experiment was kept at -30 °C. A white crystalline solid again formed, and the isolated solid contained a mixture of **1-C₅** and **1-C₂** in about a 1:3 ratio (yield, 0.30 g, 12%).

¹H NMR (CDCl_3): δ 1.10 (“triplet” arising from two partially overlapping doublets, $J = 7.7$ Hz), 1.62–1.77 (m, $-\text{PCH}_2\text{CH}_2\text{CO}-$), 1.96–1.99 (m, $-\text{PCH}_2\text{CH}_2\text{P}-$), 2.05–2.12 (m, $-\text{CH}_2\text{CO}-$), 3.97–4.05

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(m, –CH–), 5.25 (b, –NH–), 7.34 (m, CH_{aryl}), and 7.39–7.43 (m, CH_{aryl}). ³¹P{¹H} NMR (CDCl₃): δ –19.9 (s), –20.0 (s).

2.4. Synthesis of **2**

To a stirred solution of [(CO)₂RhCl]₂ (100 mg, 0.257 mmol) in CH₂Cl₂ (10 mL) was added a solution of ligand **1-C_s** (488 mg, 1.028 mmol) in CH₂Cl₂ (5 mL) at RT. A drop of PEt₃ (~50 mg) was added to the above solution, which was refluxed with stirring overnight. After all of the volatile compounds were removed under vacuum, the residue was washed with ether to give a bright yellow powder (yield, 0.50 g, 90%). Analytically pure crystals were obtained by layering ether on top of a concentrated CH₂Cl₂ solution of the product.

Anal. Calc. for C₅₂H₇₆ClN₄O₄P₄Rh: C, 57.64; H, 7.07; N, 5.17. Found: C, 58.02; H, 6.69; N, 4.87%. ¹H NMR (CDCl₃): δ 1.23 (“triplet” arising from two partially overlapping doublets, *J* = 7.7 Hz, 24 H, –CH₃), 1.90 (m, 8H, –PCH₂CH₂P–), 2.32 (m, 4H, –PCH₂CH₂CO–), 2.76 (m, 4H, –PCH₂CH₂CO–), 2.86 (m, 4H, –PCH₂CH₂CO–), 3.01 (m, 4H, –PCH₂CH₂CO–), 4.13 (h, 4H, –CH–), 7.06 (“t”, 8H, CH_{aryl}), 7.26–7.16 (m, 12H, CH_{aryl}), 8.68 (d, *J* = 8.9 Hz, 4H, –NH–). ¹³C{¹H} NMR (CDCl₃): δ 170.1, 133.9, 131.2, 130.1, 128.4, 41.7, 31.1, 28.7, 23.4, 22.6. ³¹P{¹H} NMR (CDCl₃): δ 57.3 (d, ¹*J*_{Rh–P} = 128 Hz).

2.5. Reaction of **1-C_s**/**1-C₂** Mixture with [(CO)₂RhCl]₂

The reaction between the **1-C_s**/**1-C₂** mixture and [(CO)₂RhCl]₂ was carried out in the same manner as described above. Judging from the ¹H NMR spectrum, the product was a complex mixture. However, single crystals of **3** were obtained by diffusion of diethyl ether into a solution of the reaction mixture.

2.6. X-ray data collection and structural analysis

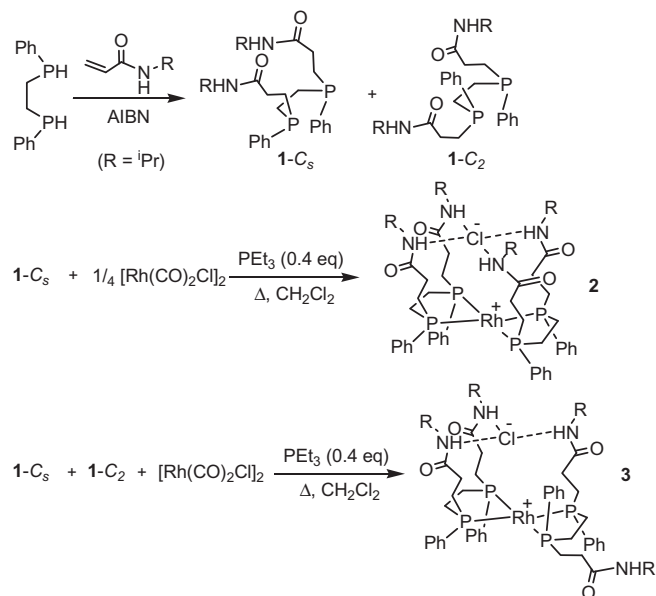
Single crystals of **2** were grown by layering diethyl ether on top of a dichloromethane solution of **2** and allowing diffusion to occur at RT. Single crystals of **3** were grown by layering diethyl ether on top of a dichloromethane solution of the reaction mixture of **1-C_s**, **1-C₂**, and [(CO)₂RhCl]₂, and allowing diffusion to occur at RT.

2.7. Crystal data for **2**

C₅₂H₇₆N₄O₄P₄RhCl, Mw = 1083.41, triclinic, space group P-1, *a* = 12.572(2) Å, *b* = 14.298(2) Å, *c* = 16.199(2) Å, α = 98.590(2)°, β = 97.498(2)°, γ = 94.482(2)°, and volume = 2840.3(6) Å³, *Z* = 2, ρ = 1.267 g/cm³, *R*(int) = 3.64%, *R*₁ = 4.31%, *wR*₂ = 9.90% for 9846 independent reflections, *I*° > 2*s*(*I*°), with 19770 observed reflections. Data were collected at 293(2) K (Siemens SMART Platform CCD diffractometer with Mo source Kα radiation, λ = 0.71073 Å) and corrected for absorption using SADABS [7]. The structures were solved by direct methods and refined by full-matrix least-squares procedures [8].

2.8. Crystal data for **3**

C₁₀₈H₁₆₂N₈O₉P₈Rh₂Cl₂, Mw = 2240.94, monoclinic, space group *P*2(1)/*c*, *a* = 21.0259(12) Å, *b* = 26.9157(16) Å, *c* = 20.8978(12) Å, β = 103.669(3)°, volume = 11491.7(12) Å³, *Z* = 4, ρ = 1.295 g/cm³, *R*(int) = 5.36%, *R*₁ = 4.84%, *wR*₂ = 12.59% for 18975 independent reflections, *I*° > 2*s*(*I*°), with 127493 observed reflections. Data were collected at 100(2) K (APEX2 CCD diffractometer with Cu source Kα radiation, λ = 1.54178 Å) and corrected for absorption using SADABS [7]. The structures were solved by direct methods and refined by full-matrix least-squares procedures [9].



Scheme 1. Synthesis of diphosphines with hydrogen-bonding arms and their Rh complexes.

3. Results and discussion

AIBN-initiated phosphine addition to acrylamide afforded a mixture of diastereomers **1-C_s** and **1-C₂** in roughly a 2:1 ratio (Scheme 1). Ligand **1-C_s** (~95% diastereomeric excess, as estimated from ³¹P NMR) was easily isolated from the mixture with a ~45% yield by fractional crystallization from toluene. The racemic isomer **1-C₂** was not separated from the remaining **1-C_s** in the mixture. Interconversion between **1-C₂** and **1-C_s** was not observed in the solid state over months or days in solution at room temperature. When we attempted to make the Rh complex [(**1-C_s**)₂Rh(CO)Cl] by reacting equimolar amounts of **1-C_s** and [Rh(CO)₂Cl]₂, the reaction did not give the expected 1:1 ligand–Rh adduct. Instead, a complex mixture resulted as judged from the ¹H and ³¹P NMR spectra. In an attempt to make [(**1-C_s**)₂Rh(PEt₃)Cl], **2** formed unexpectedly. Indeed, the initial mixture from the reaction of **1-C_s** and [Rh(CO)₂Cl] cleanly converged to **2** after it was refluxed overnight in the presence of a substoichiometric amount of PEt₃. The yield of **2** was essentially quantitative when a 2:1 ligand: Rh molar ratio was used. Compound **2** was stable in air in the solid form indefinitely, whereas **1-C_s** had to be stored under an inert atmosphere. Compound **2** was completely characterized by standard spectroscopic methods and elemental analysis. X-ray diffraction (XRD) of a single crystal of **2** revealed a picket fence-like structure in pseudo-C_{2v} symmetry (Fig. 1). The four P atoms and the Rh atom were approximately coplanar. The Rh–Cl distance was ~5.16 Å, clearly outside the range of covalent bonding.¹ The four amide arms of the ligand surrounded the chloride ion, with the four N atoms pointing toward the chloride. Although the hydrogen atoms were not located directly on the difference map, this configuration suggests that each N atom was bonded with the chloride through a hydrogen bond. The N–Cl distances were ~3.33, 3.28, 3.42, and 3.29 Å, all of which are in the range of H···Cl hydrogen bonds.

Infrared (IR) spectroscopy indicated that the amide hydrogen bonds [10] in **2** were largely retained in the chloroform solution (Fig. 2), especially when compared with the ligand **1-C_s**. In the N–H stretching vibration region of the IR spectrum of **2**, a sizable

¹ The Cl atom was located normally on the difference map. No disorder is present in the position of the chloride.

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