Inorg. Chem. **2006**, *45*, 502–504

Inorganic Chemistry
Communication

Novel Phosphoranido Complex of Rhodium(III) Tetraphenylporphyrin. Synthesis and Characterization

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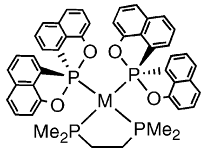
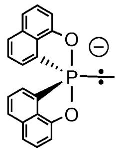
Received September 26, 2005

A novel phosphoranido complex of rhodium(III) porphyrin was prepared by the reaction of a lithium phosphoranide, generated from a P–H phosphorane bearing two 8-oxy-1-naphthyl groups, with (TPP)RhCl (TPP = dianion of 5,10,15,20-tetraphenylporphyrin). The crystal structure of the complex was determined by X-ray structural analysis.

The chemistry of phosphoranido complexes, 10-P-5[1] phosphoranes bearing a metal−phosphorus bond, has been developed with backgrounds of hypervalent,[2] coordination, and organometallic chemistries. Since the first phosphoranido complex was reported in 1981 by Riess et al.,[3] a variety of other such complexes have been prepared and characterized.[4−7] However, there have been no reports on phosphoranidoporphyrin complexes, although numerous metalloporphyrins with phosphanes as axial ligands have been well established.[8] It is noteworthy that the only previously known metalloporphyrins bearing an anionic tricoordinate phosphorus ligand are cobalt(III) porphyrin phosphoryl complexes.[9]



A; M = Pd
B; M = Pt



C

The steric demand of phosphoranide ligands often becomes a synthetic issue, as exemplified by the suppressed formation of bis(phosphoranido) complexes in some reactions involving metal dichlorides and lithium phosphoranides.[5] Furthermore, although the synthesis of an unstable bis(phosphoranido) complex had been reported, the compound could not be isolated and the formation was based only on speculation from ^{31}P NMR analysis.[6] By utilizing the compact P−H spirophosphorane **1**, however, we were able to overcome this obstacle and succeeded in the first isolation and structural characterization of cis-disposed bis(phosphoranido) complexes **A** and **B**.[7] On the basis of this precedence, we presumed that, in terms of steric bulk, it would be possible to prepare a porphyrin complex with the bis(8-oxy-1-naphthyl)phosphoranide ligand **C**, and this turned out to be true. Herein we report on the first synthesis and characterization of **2**, a phosphoranido complex of rhodium(III) tetraphenylporphyrin.

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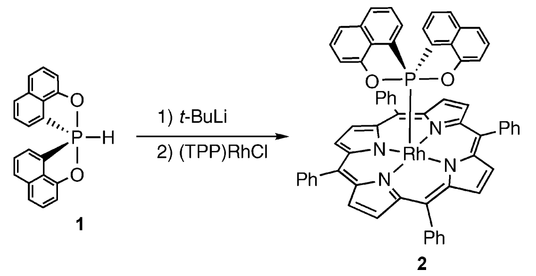
Scheme 1



The synthesis of the complex **2** could be achieved according to Scheme 1. The phosphorane **1** was deprotonated with *t*-BuLi in THF to give a lithium phosphoranide,[7] followed by reaction with (TPP)RhCl, to afford complex **2** in 96% yield.[10] The complex is soluble in common organic solvents except for aliphatic hydrocarbons and is stable in refluxing nondonor solvents (benzene, toluene, CH_2Cl_2, and $CHCl_3$), alcohols (MeOH and EtOH), and ethers (Et_2O and THF) containing a small quantity of water, while it seems to decompose slowly in CH_3CN or pyridine at room temperature.

In the ^1H NMR ($CDCl_3$) spectrum of **2** (Figure 1a), the aromatic protons of the phosphoranide ligand (δ 7.40−5.59) appeared upfield compared with those of **1** (δ 8.22−6.98),[7a] reflecting the ring-current effect of the porphyrin ring. By virtue of the same effect exerted by the naphthalene rings, the proton signals for the pyrrole moiety (δ 8.58 and 8.46) and the phenyl group (δ 7.93−7.64) of complex **2** are also at higher field than the corresponding signals (δ 8.96 and 8.12−7.95, respectively) of (TPP)RhCl.[11] The AB resonance pattern for the pyrrole protons (Figure 1b) can be rationalized to arise from the chirality of the phosphoranide ligand, which possesses C_2 symmetry. The signals did not coalesce even at 110 °C in toluene-d_8. This suggests that the barrier for permutation between the enantiomers, which could be reckoned to proceed via seven Berry pseudorotation[12] steps, is high.[4f]

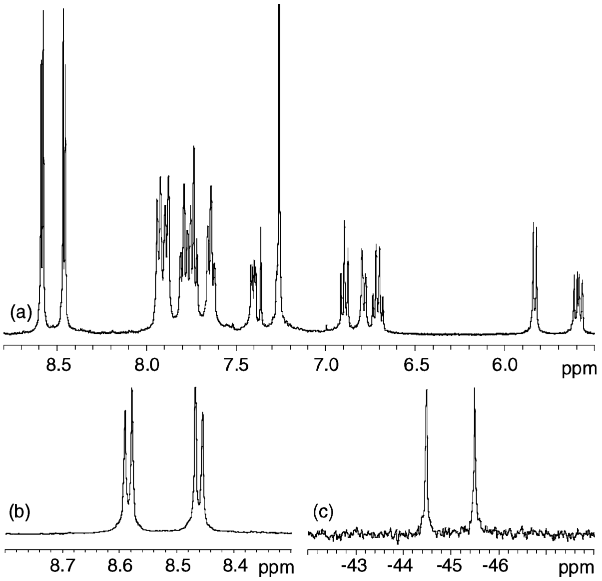
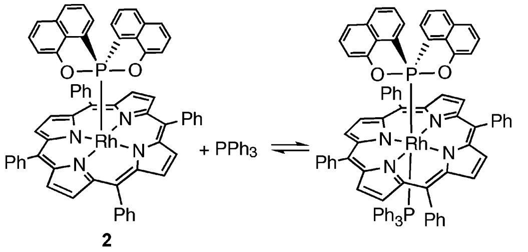


Figure 1. (a) ^1H NMR spectrum of **2**. (b) Pyrrole region of the ^1H NMR spectrum. (c) $^{31}P\{^1H\}$ NMR spectrum of **2**.

Scheme 2



In ^{31}P NMR ($CDCl_3$), the resonance appeared at −45.0 ppm as a distinct doublet (Figure 1c) and the $^1J_{P-Rh}$ coupling constant (164 Hz) was significantly larger than those (81−124 Hz) of previously reported phosphine complexes of rhodium(III) porphyrins.[8a,b] This implies that the phosphorus donor orbital of the phosphoranide has higher s character than that of phosphines. Therefore, it could be anticipated that the phosphorus orbital used for bonding to the rhodium atom in complex **2** was essentially an sp^2 hybrid orbital, and thus the phosphorane assumes trigonal-bipyramidal (TBP) geometry in solution.

The ^{31}P chemical shift (−45.2 ppm) and $^1J_{P-Rh}$ coupling constant (166 Hz) of complex **2** in C_6D_6 did not significantly vary with temperature. However, upon the addition of PPh_3 to the solution of **2** in C_6D_6 at room temperature, the ^{31}P resonance of the phosphoranide ligand was observed at lower field as a broad doublet and the $^1J_{P-Rh}$ coupling constant was slightly smaller. When a large excess of PPh_3 was added, the chemical shift of the ^{31}P signal became −38.6 ppm with a $^1J_{P-Rh}$ coupling of 146 Hz, while the resonance due to PPh_3 coordinated to rhodium could not be observed. It could be that this shift resulted from the decreased electron density on the phosphorus atom of the phosphoranide ligand by the coordination of the π-acceptor ligand at the trans position (Scheme 2).[13]

Recrystallization of complex **2** from toluene gave suitable crystals for structural analysis.[14] The ORTEP structure of

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(10) Preparation of **2**: *t*-BuLi (1.50 M hexane solution, 0.130 mL, 0.195 mmol) was added to a solution of **1** (60.0 mg, 0.190 mmol) in 20 mL of THF at −78 °C. After removal of the cooling bath, the solution was stirred at room temperature for 5 min and then added to a suspension of (TPP)RhCl (100 mg, 0.133 mmol) in 100 mL of THF at −78 °C. The reaction mixture was stirred at room temperature until the suspension turned into a clear solution, and the solvents were removed under reduced pressure. Purification of the residue was carried out by silica gel chromatography (benzene) to give **2** as a violet powder. Yield: 132 mg (96%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, 4H, J = 4.9 Hz), 8.46 (d, 4H, J = 4.9 Hz), 7.93 (d, 4H, J = 7.3 Hz), 7.88 (d, 4H, J = 7.3 Hz), 7.79 (t, 4H, J = 7.3 Hz), 7.73 (t, 4H, J = 7.3 Hz), 7.64 (t, 4H, J = 7.3 Hz), 7.40 (dd, 2H, J = 7.8 and 3.2 Hz), 6.89 (t, 2H, J = 7.8 Hz), 6.78 (dd, 2H, J = 8.1 and 2.0 Hz), 6.71 (dt, 2H, J = 7.6 and 7.3 Hz), 5.83 (d, 2H, J = 7.3 Hz), 5.59 (dd, 2H, J = 11.2 and 7.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −45.0 (d, $^1J_{P-Rh}$ = 164 Hz). UV−vis (1.15×10^{-5} M, benzene): λ_{max} (log ϵ) 413 (5.14), 528 (4.29). Anal. Calcd for $C_{64}H_{40}N_4O_2PRh$: C, 74.56; H, 3.91; N, 5.44. Found: C, 74.29; H, 4.08; N, 5.36.

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(13) The stability constant of $K = 3.4 \times 10^3$ was roughly estimated from the data obtained by a log−log analysis of the UV−vis spectral changes observed during the titration of **2** with PPh_3 in benzene. The spectral changes and log−log plots are shown in the Supporting Information.

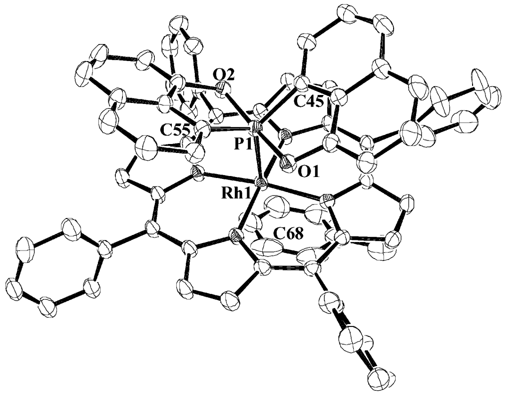

Figure 2. ORTEP drawing of **2**·toluene showing the thermal ellipsoids at the 30% probability level. All hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−O1 1.804(2), P1−O2 1.796(2), P1−Rh1 2.267(1), P1−C45 1.825(2), P1−C55 1.821(2), Rh1···C68 3.087(5); O1−P1−O2 172.79(9), Rh1−P1−C45 117.58(8), C45−P1−C55 123.2(1), C55−P1−Rh1 119.23(8), O1−P1−Rh1 93.67(6), O1−P1−C45 87.81(8), O1−P1−C55 88.54(8), O2−P1−Rh1 93.54(6), O2−P1−C45 89.02(8), O2−P1−C55 87.78(8).

complex **2** with an incorporated toluene molecule is shown in Figure 2. It is notable that a meta carbon (C68) of the incorporated toluene molecule lies at the position trans to the phosphoranide ligand and is the closest of the toluene carbons to the porphyrin plane because there have been several reports on the electrophilic aromatic metalation by rhodium(III) porphyrins.[15] The rhodium atom has a square-pyramidal geometry coordinated by four porphyrinato nitrogen atoms occupying the basal positions and the phosphorus atom of the phosphoranide ligand dwelling at the axial position. The steric demand of the phosphoranide ligand does not seem to affect the structure of the (TPP)Rh fragment. The mean Rh−N distance (2.028 Å) agrees with values observed for (TPP)RhI(MeOH) (2.027 Å) and (TPP)RhMe(DPAP) (2.029 Å).[8b] The sum of the four acute N−Rh−N angles is 359.15°, and the rhodium atom is only slightly out of the basal plane formed by the four nitrogens by 0.129 Å toward phosphorus. The P−Rh bond length of 2.266(1) Å is similar to that [2.276(1) Å] of the only other known phosphoranidorhodium(III) complex[4d] and shorter than reported values [2.306(3)−2.512(3) Å] for phosphine complexes of rhodium(III) porphyrins.[8a−c] This difference in bond length compared with phosphine ligands is primarily a consequence of the difference in the bonding scheme of the metal−phosphorus bond (sp^2 for phosphoranides and sp^3 for phosphines).

As for the structure of the phosphorane moiety, it assumes TBP structure in which the two oxygens occupy the apical positions. The distortion of the TBP geometry about the phosphorus atom is along the Berry pseudorotation coordinate, in contrast to the racemic isomers of the bis(phosphoranido) complexes **A** and **B** whose large distortions did not follow either the Berry or the turnstile mechanism.[7] Through analysis by the dihedral angle method using unit bond distances,[16] the distortion of **2** from TBP to square-pyramidal geometry was evaluated to be 14.4%. The reasons for the distortion being only modest are probably the rigid planarity of the 8-oxy-1-naphthyl group and the π back-donation by the equatorial (TPP)Rh substituent, which is more favorable when the phosphorane assumes TBP geometry.[4a]

In summary, we have succeeded in the first synthesis and structural characterization of a phosphoranido complex of rhodium(III) tetraphenylporphyrin **2**. To the best of our knowledge, complex **2** is also a rare example of a metalloporphyrin with asymmetry only at the atom bound to the metal, thus suggesting possible application as an asymmetric catalyst, although it may be necessary to modify the porphyrin ligand.

Supporting Information Available: Crystallographic data for **2**·toluene in CIF format and details of the experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal data for **2**·toluene: $C_{64}H_{40}N_4O_2PRh·C_7H_8$, M_r = 1123.07, triclinic, $P\bar{1}$, a = 11.780(2) Å, b = 23.978(3) Å, c = 9.686(1) Å, α = 95.36(1)°, β = 101.90(1)°, γ = 87.79(1)°, V = 2664.8(6) $Å^3$, Z = 2, D_c = 1.400 g cm^{-3}, μ(Mo Kα) = 4.04 cm^{-1}, GOF = 1.06, 13 253 reflections measured, 12 979 unique (R_{int} = 0.016). The final wR2 value was 0.107 (all data) and R1 = 0.035 [$I > 2\sigma(I)$].

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