First Isolations and Structures of the *cis*-Bis(phosphoranido) Palladium(II) and Platinum(II) Complexes

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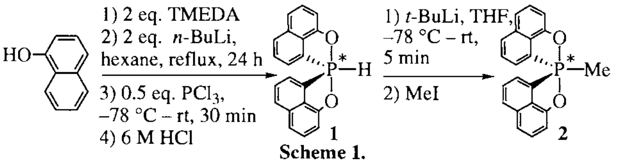
The reaction of a phosphoranide generated from a P–H spirophosphorane bearing two 8-oxy-1-naphthyl groups with (dmpe)MCl_2 (M; Pd, Pt) [dmpe; bis(dimethylphosphino)ethane] gives the first *cis*-bis(phosphoranido) palladium(II) and platinum(II) complexes. The crystal structures of the racemic isomers of the complexes are determined by the X-ray structural analyses.

The chemistry of pentacoordinate phosphorus compounds bearing a metal–phosphorus bond, phosphoranido complexes, has interest for us since they have a hypervalent bond and a phosphoranide ligand is bulky. Although several phosphoranido complexes which involved one phosphoranide ligand have been prepared by some methods, bis(phosphoranido) complex has never been obtained.[1] In the reactions of $PtCl_2(PPh_3)_2$, $NiCl_2(PMe_3)_2$ or $PdCl_2$(dmpe) with cyclenP–H,[1e] $LiP(OCMe_2COO)_2$[1g] or $LiPRf_2$[1i] (Rf = Martin ligand), respectively, the nonbonded interaction between the bulky phosphoranide and the ligands on the metal will suppress the formation of bis(phosphoranido) complexes due to steric hindrance of the ligands. If more compact P–H phosphorane is used in such reaction, it will be possible to prepare a bis(phosphoranido) complex. By utilizing a novel compact P–H spirophosphorane **1** and MCl_2(dmpe) (**3a**; M = Pd, **3b**; M = Pt) we have succeeded in the first isolation of the *cis*-bis(phosphoranido) complexes **4a** (M = Pd) and **4b** (M = Pt), and we now report their syntheses, characterization and unique crystal structures of the racemic isomers.

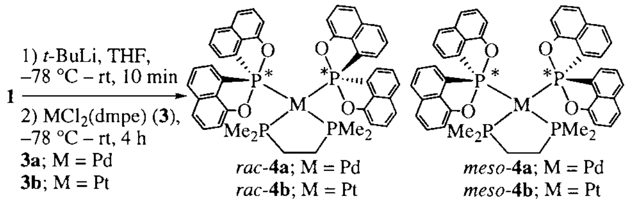
The P–H spirophosphorane **1** could be obtained in 14% yield by the reaction of PCl_3 with 8-lithio-1-naphthoxy lithium generated by the treatment of 1-naphthol with TMEDA and *n*-BuLi[2] followed by the quench with 6 M HCl (Scheme 1).[3] The structure of **1** could be supported by the crystal structure of P–Me phosphorane **2** [δ_P ($CDCl_3$) = –28.1] which assumed ideal trigonal bipyramid (TBP) geometry with two apical oxygens.[4]



1 **2**

Scheme 1.

The reactions of MCl_2(dmpe) (**3a**, **b**) with either one or two equivalents of the phosphoranide [δ_P (THF) = 60.2] generated from **1** by the treatment with *t*-BuLi in THF gave the diastereomeric mixtures of *cis*-bis(phosphoranido) complexes **4a**, **b** as major products (Scheme 2, Table 1).[5,6] In the ^1H NMR analyses of *rac*- and *meso*-**4a**, **b**,[7] two signals of methyl groups were observed, respectively, which could be expected that their structures had C_2 symmmetry. Interestingly, the ^{31}P NMR spectra of them showed AA'XX' systems probably due to the slow rotations of the phosphoranides about M–P bonds in NMR timescale.[8] In platinum complex **4b**, the $^1J_{P-Pt}$ coupling constants (3884–3903 Hz) for phosphoranes were much larger than those (2205–2235 Hz) for phosphanes. In general, such couplings are dependent on the *s* character of the phosphorus donor orbital. Therefore, the phosphoranes should involve an equatorial platinum attached to an essentially sp^2 hybrid phosphorus orbital in TBP geometry in solution.[1e,9]



3a; M = Pd
3b; M = Pt

rac-**4a**; M = Pd
rac-**4b**; M = Pt

meso-**4a**; M = Pd
meso-**4b**; M = Pt

Scheme 2.

Table 1. Syntheses of *cis*-bis(phosphoranido) complexes **4**

Run	M	**1** /mol : **3** /mol	Yield /%[a]	D.e. /%[b]
1	Pd	1 : 1	45[c]	18
2	Pd	2 : 1	47	10
3	Pt	1 : 1	50[c]	54
4	Pt	2 : 1	77	64

[a]Yield based on the phosphorane **1**. [b]The d.e. values estimated from ^1H NMR analyses. [c]Recovery of MCl_2(dmpe) **3** was *ca.* 49%.

Recrystallizations of the diastereomeric mixtures **4a**, **b** from MeOH–CH_2Cl_2 and hexane–CH_2Cl_2 gave single crystals of only racemic isomers *rac*-**4a**, **b** with a CH_2Cl_2 molecule as needles and prisms, respectively, and X-ray structural analyses of them were carried out.[10] Since the structures of the two complexes are essentially same except for the bond lengths around the metal, only the ORTEP structure of *rac*-**4b** is shown in Figure 1. It appears that they are *cis* disposed bis(phosphoranido) complexes with square-planar geometry. In each complex two phosphoranes assume distorted TBP structures with the two apical oxygen atoms and the relative stereochemistry at the two pentacoordinate phosphorus atoms was found to be *SS*(*RR*).[11]

While the bond lengths of *rac*-**4a**, **b** are not peculiar to bis(phosphoranido) complexes, the equatorial bond angles of the phosphoranes deviate from an ideal equatorial angle, 120° (Table 2). The equatorial C–P–C angles (100.1–104.1°) are smaller and the other two equatorial angles (124.3–131.7°) are larger than 120° although the sum of the equatorial angles and the apical O–P–O angles are nearly ideal values (360° and 180°, respectively). According to the report by Holmes,[12] the distortion from TBP of nonmetalated phosphoranes would be toward square pyramid (SP) geometry following the Berry coordinate.[13] However, Montgomery has noted that such rule could not be necessarily applied to the metalated phosphoranes.[14] The distortion from TBP of the phosphorane moieties in *rac*-**4a**, **b** does not

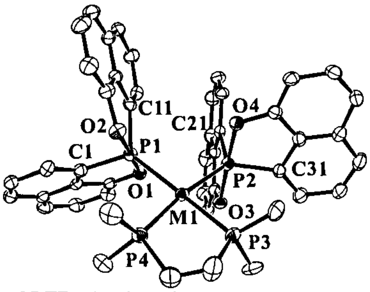


Figure 1. The ORTEP drawing of *rac*-**4b**·CH_2Cl_2 (M = Pt) showing the thermal ellipsoids at the 30% probability level. A CH_2Cl_2 molecule and all hydrogens are omitted for clarity. Selected bond distances (Å): *rac*-**4a**·CH_2Cl_2 (M = Pd) P1–O1, 1.810(5); P1–O2, 1.869(5); P1–C1, 1.836(7); P1–C11, 1.832(7); P1–Pd1, 2.383(2); P2–O3, 1.828(5); P2–O4, 1.826(5); P2–C21, 1.837(7); P2–C31, 1.852(7); P2–Pd1, 2.371(2); P3–Pd1, 2.308(2); P4–Pd1, 2.324(2); *rac*-**4b**·CH_2Cl_2 (M = Pt) P1–O1, 1.812(5); P1–O2, 1.858(5); P1–C1, 1.829(8); P1–C11, 1.838(7); P1–Pt1, 2.382(2); P2–O3, 1.835(5); P2–O4, 1.822(5); P2–C21, 1.836(7); P2–C31, 1.841(7); P2–Pt1, 2.371(2); P3–Pt1, 2.294(2); P4–Pt1, 2.302(2).

Table 2. Selected bond angles (deg) for *rac*-**4a**·CH_2Cl_2 (M = Pd) and *rac*-**4b**·CH_2Cl_2 (M = Pt)[a]

Bond angle	*rac*-**4a**·CH_2Cl_2	*rac*-**4b**·CH_2Cl_2
O1–P1–O2; O3–P2–O4	176.9; 178.9	176.4; 178.9
C1–P1–C11; C21–P2–C31	104.1; 100.4	103.9; 101.0
C11–P1–M1; C31–P2–M1	131.6; 129.5	131.7; 128.7
M1–P1–C1; M1–P2–C21	124.3; 130.0	124.4; 130.2
O1–P1–C1; O3–P2–C21	88.0; 88.3	87.5; 87.6
O2–P1–C11; O4–P2–C31	86.4; 87.6	85.9; 87.9

[a]The e.s.d.'s of bond angles are within ±0.3°.

also follow the Berry coordinate and is larger than that of the similarly distorted mono(phosphoranido) complexes[1g] because of *cis* disposition of the two bulky phosphoranide ligands. Additionally, one apical bond of the phosphorane is nearly perpendicular to the plane formed by the four phosphorus atoms and metal, which would be affected by the π interaction of a d orbital on the metal with the σ^* orbital of an apical bond,[1h,9] the other is not: O4–P2–M1–P3 and O2–P1–M1–P4 angles are –93.9(2) and 66.5(2)° for Pd, and –94.4(2) and 65.8(2)° for Pt. This difference will be also due to the large steric demand mentioned above.

Attempted coupling reactions of the complexes **4a**, **b** to give P(V)–P(V) compounds[15] has not succeeded at 60 °C in $CHCl_3$ or THF, or at 110 °C in toluene for a week in the dark. Although we couldn't find rational account for the exclusive formation process of bis(phosphoranido) complexes **4**, it may be key point that they are very stable in THF even at high temperature.

In summary, we could synthesize and isolate first *cis* disposed bis(phosphoranido) palladium(II) and platinum(II) complexes and crystallize out the only racemic isomers. In their crystal structures, it was found that large distorted TBP geometry of both phosphorane moieties did not follow the Berry coordinate and the π–σ^* interaction of the metal with phosphoranide ligand would exist in only one M–P bond, because of *cis* disposition of the two bulky phosphoranide ligands. Kinetic study on their isomerization and syntheses of *trans*-bis(phosphoranido) palladium(II) and platinum(II) complexes are under investigation.

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2 Dilithiation of 1-naphthol based on the ortho lithiation of benzyl alcohol, see: N. Meyer and D. Seebach, *Chem. Ber.*, **113**, 1304 (1980).

3 **1**: m.p. 273 °C; ^{1}H NMR ($CDCl_3$) δ 9.16 (d, $^1J_{H-P}$ = 737 Hz, 1H), 8.22 (dd, $^3J_{H-P}$ = 12.7 Hz, J = 7.3 Hz, 2H), 7.98 (dd, J = 8.3, 2.9 Hz, 2H), 7.60 (dt, $^4J_{H-P}$ = 7.5 Hz, J = 8.3 Hz, 2H), 7.51 (t, J = 8.3 Hz, 2H), 7.35 (dd, J = 6.8, 2.0 Hz, 2H), 6.98 (d, J = 7.3 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ –49.9; Anal. calcd for $C_{20}H_{13}O_2P$: C, 75.95; H, 4.14%. Found: C, 75.78; H, 4.26%.

4 The details of X-ray structural analysis, NMR data of **2** will be described in future. The equatorial angles are in the range of 117.9(2)–121.6(2)°.

5 The corresponding nickel complex could be generated but the isolation was not successful in any method.

6 General procedure for the preparation of **4**. To a solution of **1** in THF was added *t*-BuLi (1.50 M in pentane) at –78 °C. After removal of the cooling bath, the solution was stirred at room temperature (rt) for 5 min. The solution was added to a suspension of **3** in THF at –78 °C, and the reaction mixture was stirred at rt for 4 h followed by the removal of solvent under reduced pressure. Purification of the residue was carried out on silica gel column chromatography (CH_2Cl_2–MeOH = 20 : 1) to give **4** as yellow powder. *rac*-**4a**: m.p. 194 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (dd, J = 9.8, 7.3 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.32–7.22 (m, 6H), 7.09 (d, J = 7.7 Hz, 2H), 7.00–6.85 (m, 6H), 6.62–6.57 (m, 4H), 6.45–6.39 (m, 2H), 1.62 (br s, 4H), 1.51–1.45 (m, 6H), 0.42–0.39 (m, 6H); ^{31}P NMR ($CDCl_3$) δ 31.2 ($|^2J_{P-P}|$ = 569, 48, 52 Hz), –11.7 ($|^2J_{P-P}|$ = 569, 48, 34 Hz). *meso*-**4a**: ^{1}H NMR ($CDCl_3$) δ 7.85–6.20 (m, 24H), 1.70–1.40 (m, 10H), 0.53–0.49 (m, 6H); ^{31}P NMR ($CDCl_3$) δ 32.5 ($|^2J_{P-P}|$ = 569, 51, 41 Hz), –11.1 ($|^2J_{P-P}|$ = 569, 51, 35 Hz). *rac*-**4b**: m.p. 237 °C; ^{1}H NMR ($CDCl_3$) δ 7.86 (dd, J = 9.8, 6.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.30–7.23 (m, 6H), 6.96–6.70 (m, 12H), 6.37–6.32 (m, 2H), 1.90 (br s, 4H), 1.57–1.48 (m, 6H), 0.63–0.55 (m, 6H); ^{31}P NMR ($CDCl_3$) δ 22.7 ($|^2J_{P-P}|$ = 531, 45, 9 Hz, $^1J_{P-Pt}$ = 2205 Hz), –23.3 ($|^2J_{P-P}|$ = 531, 45, 47, $^1J_{P-Pt}$ = 3903 Hz). *meso*-**4b**: ^{1}H NMR ($CDCl_3$) δ 7.96–6.24 (m, 24H), 1.49–1.15 (m, 10H), 0.71–0.63 (m, 6H); ^{31}P NMR ($CDCl_3$) δ 23.3 ($|^2J_{P-P}|$ = 528, 47, 6 Hz, $^1J_{P-Pt}$ = 2235 Hz), –21.7 ($|^2J_{P-P}|$ = 528, 47, 54 Hz, $^1J_{P-Pt}$ = 3884 Hz).

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10 Crystal data for *rac*-**4a**·CH_2Cl_2: $C_{47}H_{42}Cl_2O_4P_4Pd$; *FW* = 971.99; monoclinic, *P* 2/c, *Z* = 4; *a* = 20.031(3) Å, *b* = 10.400(2) Å, *c* = 20.383(3) Å, β = 98.984(11)°; *V* = 4194.0(12) Å^3, *D*c = 1.539 g cm^{-3}; 9661 unique reflections used, 523 parameters to *R* = 0.065, *Rw* = 0.143; Goodness of fit *S* = 1.028. Crystal data for *rac*-**4b**·CH_2Cl_2: $C_{47}H_{42}Cl_2O_4P_4Pt$; *FW* = 1060.68; monoclinic, *P* 2/c, *Z* = 4; *a* = 20.061(2) Å, *b* = 10.366(2) Å, *c* = 20.3988(14) Å, β = 99.015(7)°; *V* = 4189.6(10) Å^3, *D*c = 1.682 g cm^{-3}; 9633 unique reflections used, 523 parameters to *R* = 0.046, *Rw* = 0.106; Goodness of fit *S* = 1.003.

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