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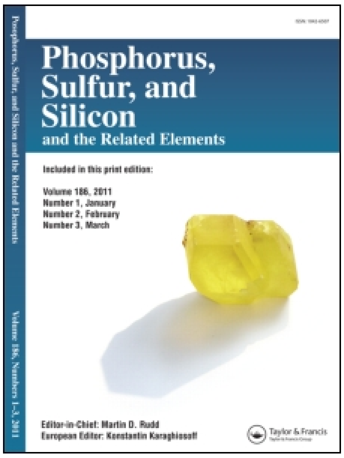

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First Isolations and Structures of cis -Bis(phosphoranido) Complexes

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FIRST ISOLATIONS AND STRUCTURES OF *cis*-BIS(PHOSPHORANIDO) COMPLEXES

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The first cis-*bis(phosphoranido) palladium(II) and platinum(II) complexes were prepared by the reaction of a lithium phosphoranide, bearing two 8-oxy-1-naphthyl groups with (dmpe)MCl$_2$ (M; Pd, Pt). The crystal structures of the racemic isomers of the complexes are determined by the X-ray structural analyses.*

Keywords: cis-Bis(phosphoranido) palladium(II) complex; *cis*-bis-(phosphoranido) platinum(II) complex; 1-naphthol; P—H phosphorane; trigonal bipyramid; X-ray structural analysis

INTRODUCTION

Although several monophosphoranido complexes have been synthesized by some methods, a bis(phosphoranido) complex has never been obtained, probably due to the steric repulsion between the ligands on the metal and the bulky phosphoranide ligand.[1] Even in the reactions of metal dichlorides with lithium phosphoranide,[1b,d] the steric demand suppresses the formation of bis(phosphoranido) complexes.

We have succeeded in the first isolation and structural characterization of the *cis*-bis(phosphoranido) complexes **4b** and **4c** by utilizing a novel compact P—H spirophosphorane **1** and MCl$_2$(dmpe) (M = Pd and Pt).[2] The crystal structure of methylphosphorane **3** was also determined.

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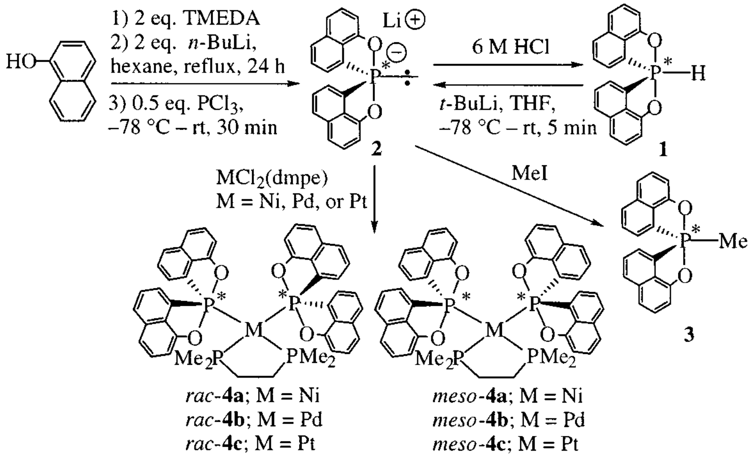
PREPARATION OF *CIS*-BIS(PHOSPHORANIDO) COMPLEXES

As shown in Scheme 1, the P—H spirophosphorane **1** [δ_P ($CDCl_3$) = -49.9 ($^1J_{P\text{—}H} = 737$ Hz)] could be obtained in 21% yield. The treatment of the phosphorane **1** with *t*-BuLi in THF could generate a lithium phosphoranide **2** [δ_P (THF) = 60.2] followed by the reaction with MeI to afford methylphosphorane **3**, quantitatively. This result indicated that the complete generation of the phosphoranide **2** would be achieved. Additionally, it was found that the crystal structure of the phosphorane **3** assumed almost ideal trigonal bipyramid (TBP) geometry with two apical oxygens (Figure 1, Table I).*



SCHEME 1

The reactions of two equivalents of the phosphoranide **2** with MCl_2(dmpe) afforded the diastereomeric mixtures of *cis*-bis(phosphoranido) complexes **4** as major products (**4b**: y. 47%, d.e. 10%: **4c**; y. 77%, d.e. 64%).** The isolation of the nickel complex **4a** was not successful by any method. The ^{31}P NMR spectra of them showed AA′XX′ systems, implying the slow rotations of the phosphoranides about M—P bonds in NMR time-scale.

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*Crystal data for **3**: $C_{21}H_{15}O_2P$; $FW = 330.30$; monoclinic, $P2_1/c$, $Z = 4$; $a = 8.6480(14)$ Å, $b = 22.082(2)$ Å, $c = 8.6726(12)$ Å, $\beta = 109.079(12)°$; $V = 1565.2(4)$ Å^3, $Dc = 1.402$ g cm^{-3}; 3596 unique reflections used, 277 parameters to $R = 0.048$, $Rw = 0.138$.

**The racemic isomers were major diastereomers.

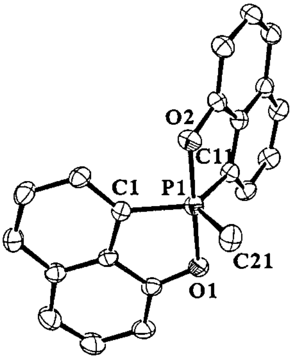

FIGURE 1 The ORTEP drawing of **3** showing the thermal ellipsoids at the 30% probability level. All hydrogens are omitted for clarity. Selected bond distances (Å): P1–O1, 1.792(2); P1–O2, 1.804(2); P1–C1, 1.817(3); P1–C11, 1.809(3); P1–C21, 1.806(4).

THE CRYSTAL STRUCTURES OF THE RACEMIC ISOMERS

We could obtain single crystals only of racemic isomers *rac*-**4b** and **4c** with a CH_2Cl_2 molecule as needles and prisms by the recrystallizations of each diastereomeric mixture **4b** and **4c** from MeOH—CH_2Cl_2 and hexane—CH_2Cl_2, respectively. Only the ORTEP structure of *rac*-**4b** is shown in Figure 2, because the structures of the two complexes are almost identical.

The relative stereochemistry at the two pentacoordinate phosphorus atoms was found to be *SS*(*RR*). In each complex, two phosphoranes assume large distorted TBP structures with apical oxygen atoms, in which the equatorial C—P—C angles are much smaller than the ideal value, although the sum of the equatorial angles and the apical O—P—O angles are nearly ideal values (Table I). Additionally, the difference of the dihedral angles reveal that *d* orbitals on the metal cannot overlap with σ^* orbitals of both apical bonds, which O4—P2—M1—P3 and

TABLE I Selected Bond Angles (deg) for **3**, *rac*-**4b** (M = Pd), and *rac*-**4c** (M = Pt)

Bond angle	**3** (M1 = C21)	*rac*-**4b**	*rac*-**4c**
O1—P1—O2 [O3—P2—O4]	179.15(11)	176.9(2) [178.9(2)]	176.4(2) [178.9(2)]
C1—P1—C11 [C21—P2—C31]	121.56(14)	104.1(3) [100.4(3)]	103.9(3) [101.0(3)]
C11—P1—M1 [C31—P2—M1]	120.50(18)	131.6(2) [129.5(2)]	131.7(2) [128.7(2)]
M1—P1—C1 [M1—P2—C21]	117.93(17)	124.3(2) [130.0(2)]	124.4(2) [130.2(2)]

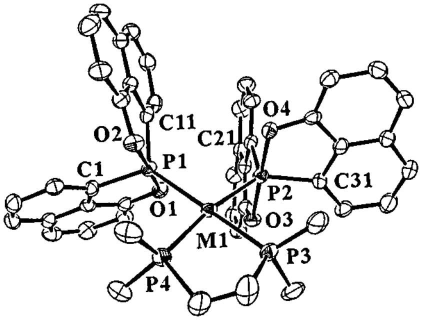

FIGURE 2 The ORTEP drawing of *rac*-**4b**·CH_2Cl_2 showing the thermal ellipsoids at the 30% probability level. A CH_2Cl_2 molecule and all hydrogens are omitted for clarity.

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. These results may caused by the *cis* disposition of the two bulky phosphoranide ligands.

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