The first crystal structure determination of biphosphole–transition-metal complex: crystal structure of square-planer *meso*-[Pd(3,3′,4,4′-tetramethyl-1,1′-diphenyl-2,2′-biphosphole)$_2$][BF$_4$]$_2$

Takahiko Kojima, Kaoru Saeki, Kazuhiro Ono, Masaaki Ohba and Yoshihisa Matsuda*

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-Ku, Fukuoka 812-81, Japan

The first X-ray crystal structure determination of a biphosphole–transition-metal complex is reported; the square-planar palladium(II) complex has unique intramolecular π–π interaction between phenyl groups on chiral phosphorus atoms of two biphosphole ligands.

Chelating phosphine ligands have contributed to the constuction of a fertile background for organometallic chemistry and organometallic catalysis such as hydroformylation, hydrogenation, *etc.* Among these chelating phosphine ligands, we have focused on ligands in which the phosphorus atom is involved in conjugated π systems such as phosphorins (phosphabenzenes) and phospholes (phosphapyrroles) that have been synthesized by Mathey and coworkers.[1] These ligands are expected to give the metal center some intriguing properties which are different from those of usual tertiary phosphine–metal complexes. Therefore, we started our project to develop P-containing macrocyclic π-conjugation systems including phosphorus porphyrins and to investigate the properties and reactivity of those transition-metal complexes in low valence states. This is in sharp contrast to the fact that higher valent and hard metal ions are favored in metalloporphyrins.

As for transition-metal–phosphole complexes, only monodentate phosphole complexes have been synthesized and characterized.[2] However, there are no reports on metal complexes containing chelating phosphole ligands. Here, as an initial attempt toward the goal mentioned above, we describe the synthesis and characterization of a novel Pd complex containing a chelating biphosphole ligand, 3,3′,4,4′-tetramethyl-1,1′-diphenyl-2,2′-biphosphole (bidmpp).[3]

[Pd(bidmpp)$_2$][BF$_4$]$_2$ **1** was synthesized in moderate yield *via* ligand substitution between [Pd(MeCN)$_4$][BF$_4$]$_2$ and bidmpp in CH$_2$Cl$_2$.†

X-Ray crystallography of **1** showed a structure with an inversion center at palladium (Fig. 1);‡ the square-planar Pd^{II} ion being surrounded by four phosphorus atoms [Fig. 1(*b*)]. The Pd–P bond lengths were all 2.343(3) Å and the bite angle of bidmpp [P(1)–Pd–P(2)] was 84.5(1)°, both of which were comparable to those found in homoleptic [Pd(dppe)$_2$]$^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane].[4] The geometry around the phosphorus atoms of bidmpp was distorted tetrahedral [C(1)–P(1)–C(4) 92.4(6)°, Pd–P(1)–C(1) 133.1(4)°, C(13)–P(2)–C(16) 92.3(6)° and Pd–P(2)–C(16) 129.5(4)°]. The configuration of the chiral phosphorus atoms of bidmpp in **1** was (*S*),(*S*),(*R*),(*R*), for P(1), P(2), P(1*), P(2*), respectively; the structure determined by X-ray analysis was a *meso* form. The chirality of conformation of both chelate rings were λ for the (*S*,*S*)-bidmpp and δ for the counterpart. Owing to the steric hindrance of the methyl groups on the phosphole rings, bidmpp is compelled to be chiral and the conformation is rigid. As observed in the crystal structure, the interatomic distance between the two nearest methyl groups [C(6) and C(17)] was 3.87 Å and the dihedral angle between two phosphole rings was 126.6° so as to avoid repulsion. In this configuration, phenyl rings on the same side of the Pd coordination plane were cofacial as shown in Fig. 1(*b*) and exhibited an intramolecular π–π interaction [C(12)··C(20*) 3.41 Å, C(11)··C(21*) 3.65 Å]. This type of π–π interaction has not been reported previously even in similar complexes such as [Pd(dppe)$_2$]$^{2+}$ or [Ni(3,3′,4,4′-tetramethyl-1,1′-diphenyl-2,2′,5,5′-tetrahydro-2,2′-biphosphole)$_2$]$^{2+}$.[4,5]

^{1}H and ^{31}P NMR studies revealed the existence of two species, *meso*- and *rac*-**1** (Fig. 2). In the ^{1}H NMR spectrum in CD$_2$Cl$_2$, peaks assigned to methyl protons were observed at δ 2.22 (d, *J* 1 Hz) and 1.94 for *meso*-**1** and δ 2.36 (d, *J* 1 Hz) and 1.78 for *rac*-**1**. Even when the crystals of **1** were dissolved into

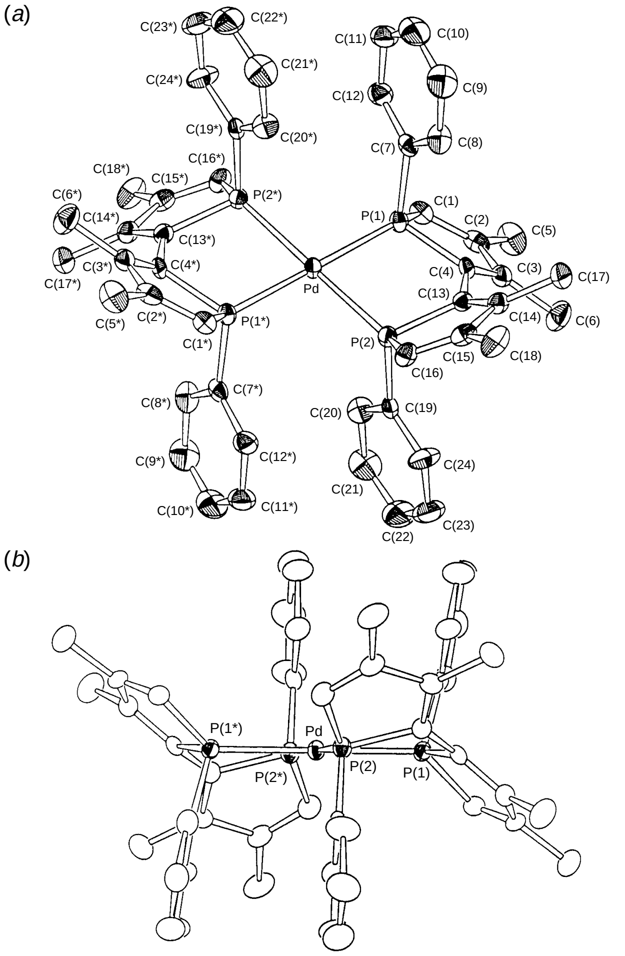

Fig. 1 An ORTEP drawing of the dication of **1** (*a*) and a side view (*b*) with thermal ellipsoids at 30% probability level. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.343(3), Pd–P(2) 2.343(3), P(1)–C(1) 1.78(1); P(1)–C(4) 1.79(1), P(1)–C(7) 1.82(1), C(1)–C(2) 1.34(2), C(2)–C(3) 1.49(2), C(3)–C(4) 1.34(2), C(2)–C(5) 1.49(2), C(3)–C(6) 1.50(2), C(4)–C(13) 1.46(2), P(1)–Pd–P(2) 84.5(2), P(1)–Pd–P(2*) 95.5(1), C(1)–P(1)–C(4) 92.4(6), C(1)–C(2)–C(3) 114(1), C(2)–C(3)–C(4) 113(1), C(3)–C(4)–C(5) 113(1), P(1)–C(4)–C(3) 109.8(9).

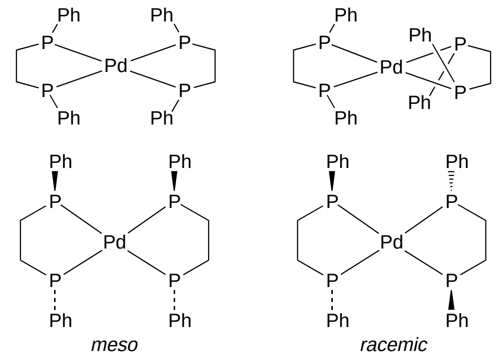

Fig. 2 Possible isomers for $[Pd(bidmpp)_2]^{2+}$

CD_2Cl_2, two sets of peaks were observed, suggesting interconversion between the *meso* and *rac* forms. We distinguished them by their different solubility in $CHCl_3$ or CH_2Cl_2; the solubility of *meso*-**1** was much lower than that of *rac*-**1**. The ring proton signal of free bidmpp was observed at δ 6.41 as a multiplet in CD_2Cl_2 whereas those of the Pd-bound bidmpp showed downfield shifts from that of free bidmpp to overlap with phenyl proton resonances at δ *ca.* 7.3 and 7.7 for *meso*- and *rac*-**1**, respectively. We could detect the ring proton resonances by ^1H–^1H COSY to observe cross peaks due to long-range coupling with methyl protons, however we were unable to determine the exact chemical shifts and the coupling constants because of overlap.

The ^{31}P NMR spectrum of **1** in CD_2Cl_2 showed two singlets at δ 34.5 for *rac*-**1** and at δ 37.3 for *meso*-**1**. The assignments were made by comparing the integration of peaks in the ^{31}P NMR spectrum with that in the ^1H NMR spectrum. Both of the resonances were downfield shifted from free bidmpp (δ 17.6). Combined with the observation in ^1H NMR spectroscopy, the bidmpp binds to the Pd center predominantly through σ-donation as observed in other tertiary phosphine complexes. The coordination shift of **1** in the ^{31}P NMR spectrum is 17–20 ppm, which is much smaller than that of homoleptic $[Pd(dppe)_2]Cl_2$ in $CDCl_3$ ($\Delta\delta$ = 68.1 ppm).[6] Therefore, it is suggested that π-back bonding from the Pd center contributes to some extent to stabilize **1**, concomitant with σ-donation to the metal center.[2b]

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Footnotes and References

* E-mail: matsuscc@mbox.nc.kyushu-u.ac.jp

† $[Pd(bidmpp)_2][BF_4]_2$ **1** was synthesized as follows: To a suspension of $[Pd(MeCN)_4][BF_4]_2$ (0.25 mmol) in CH_2Cl_2 (12 ml), was added a solution of bidmpp (200 mg, 0.53 mmol) in CH_2Cl_2 (3 ml) to give a reddish orange solution within 5 min. The solution was stirred for 30 min at room temp. and filtered through a Celite column. After removing the solvent, the residue was dissovled into a small volume of CH_2Cl_2 and then poured into hexane with stirring to obtain a reddish orange powder of **1** in 71% yield. Calc. for $C_{48}H_{48}B_2F_8P_4Pd$: C, 56.04; H, 4.70. Found: C, 55.67; H, 4.74%. FABMS: 941.2 ($[M - BF_4]^+$).

‡ A single crystal of **1** was obtained by recrystalization from CH_2Cl_2. *Crystal data*: $C_{48}H_{48}B_2F_8P_4Pd$, M = 1028.81, orange prismatic (0.20 × 0.20 × 0.20 mm), trigonal, space group $R\bar{3}$, $a = b = 31.21(3)$, $c = 14.41(2)$ Å, U = 12154(13) Å^3, $Z = 9$, D_c = 1.265 g cm^{-3}, μ(Mo-Kα) = 5.19 cm^{-1}, R = 0.055, wR_2 = 0.086 for 2492 refrections with $I > 3\sigma(I)$. Structural refinements and calculations were performed using the teXsan crystallographic software package. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located at calculated positions but not refined. We could not determine the solvent molecules (CH_2Cl_2) of crystallization due to their partial dissipation and severe disorder; a differential Fourier map showed the CH_2Cl_2 molecules located at a special position on a threefold axis. CCDC 182/543.

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