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A Two-Coordinate Palladium Complex with Two Dialkylphosphinyl Ligands**

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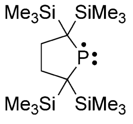
Transition-metal complexes with ligands having an unpaired electron have received much attention because of their unique electronic structures and importance in bioinorganic chemistry and catalytic chemistry.[1] Although phosphinyl radicals ($R_2P\cdot$) are one of the fascinating bifunctional ligands having an unpaired electron in addition to lone-pair electrons on the two-coordinate phosphorus center,[2] transition-metal complexes with a phosphinyl radical ligand are still quite rare compared to the complexes with pertinent aminyl radicals ($R_2N\cdot$),[3] and the structures and properties of the phosphinyl radical complexes have been discussed mainly based on EPR spectroscopy. Cowley et al. have synthesized iron and cobalt complexes of a persistent dialkylphosphinyl radical $[(Me_3Si)_2CH]_2P\cdot$[4,5] with the unpaired electron localized mainly on the metal moiety. Geoffroy et al. have generated photochemically pentacarbonyl Group 6 metal complexes of diphenylphosphinyl radical in the single crystals and found that the unpaired electron is slightly delocalized onto the metal.[6] Very recently, Streubel et al. have observed pentacarbonyl tungsten complexes of $RClP\cdot$ ($R = CH(SiMe_3)_2$, C_5Me_5) in solution and found that the planarity of the geometry around the phosphorus atom and the distribution of unpaired electron depends on the nature of the substituents at phosphorus.[7] Although complexes with two or more phosphinyl radical ligands are expected to show unique structure, properties, and reactivity owing to multiple interactions between phosphinyl ligands and the metal center, such complexes are still unknown.

Recently, we have reported the synthesis of the isolable neutral dialkylphosphinyl radical **1** ($R^H_2P\cdot$, $R^H_2 = 1,1,4,4$-tetrakis(trimethylsilyl)butane-1,4-diyl), which is monomeric both in solution and in the solid state.[8] The EPR spectra and theoretical studies indicate that an unpaired electron of **1** is highly localized on the phosphorus center because of no aromatic and heteroatom substituents that can delocalize the unpaired electron in **1**. Successful isolation of **1** prompted us to investigate the application of **1** as a bifunctional ligand for transition-metal complexes. We report herein the synthesis, X-ray analysis, and properties of neutral homoleptic bis(dialkylphosphinyl)palladium complex **2** $[(R^H_2P)_2Pd]$ as the first transition-metal complex with two or more phosphinyl ligands, which shows remarkable π-type interactions between two phosphinyl ligands and palladium center.



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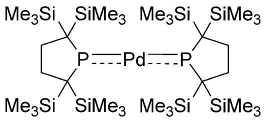

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Complex **2** was synthesized simply by a ligand-exchange reaction. Treatment of tetrakis(trimethylphosphine)palladium with two equivalents of dialkylphosphinyl radical **1** in hexane gave a dark blue solution. After removal of the volatiles, the residue was washed with hexane and acetone to give bis(dialkylphosphinyl)palladium **2** as air-sensitive navy blue crystals in 74% yield [Eq. (1)].[9] Complex **2** shows no EPR signal in 3-methylpentane solution at 107–333 K and in the solid state at ambient temperature, while ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra show signals that are due to **2** (see below), which indicates that complex **2** is diamagnetic. The molecular structure of **2** was determined by NMR spectra and X-ray single-crystal analysis.

$$\mathbf{1}\ (2\ \text{equiv}) + [Pd(PMe_3)_4] \xrightarrow[\text{RT, 5 min}]{\text{hexane}} \mathbf{2}\ (74\%) \qquad (1)$$

The molecular structure of **2** determined by X-ray analysis at 100 K is shown in Figure 1.[10] To the best of our knowledge, this is the first X-ray analysis of a transition-metal complex with a phosphinyl ligand. In the solid state, **2** has a highly symmetric structure. The P-Pd-P skeleton is almost linear, with the angle of 179.84(4)°. Two phosphorus centers adopt planar three-coordinate geometries, with the sums of angles of 360.0(2)° for P1 and P2 atoms, and two phosphacyclopentane rings are almost in the same plane, with the dihedral angle of planes C1-P1-C4 and C5-P2-C8 of 7.0°. Notably, the P1-Pd and P2-Pd distances of 2.1855(10) and 2.1869(10) Å, respectively, are considerably shorter than those reported for

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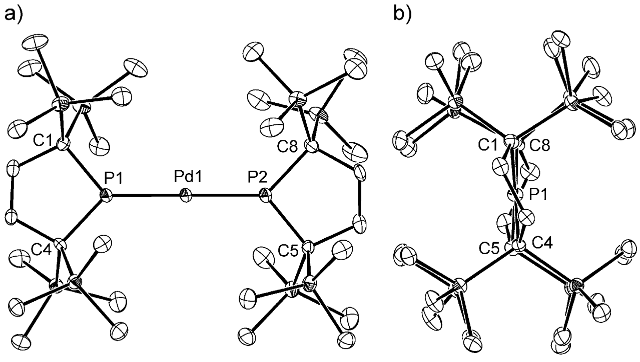


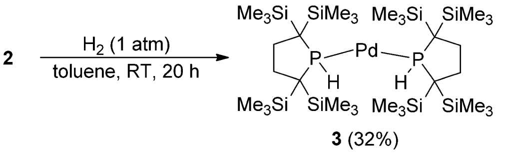
Figure 1. Molecular structure of **2** at 100 K. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. a) A perspective view. b) A view along the P1-Pd1-P2 axis.

two-coordinate bis(phosphine)palladium complexes (2.28–2.29 Å).[11]

The NMR spectra of complex **2** in [D$_6$]benzene indicate that **2** adopts a highly symmetric structure similar to that observed in the solid state. The ^{1}H NMR spectrum of **2** shows singlet signals at 0.44 and 1.98 ppm due to proton nuclei of eight SiMe$_3$ and four CH$_2$ groups on the two phosphacyclopentane ring, respectively. The ^{31}P resonance, which is due to three-coordinate phosphorus nuclei, at 244.7 ppm as a broad singlet[12] is highly deshielded compared with those for bis(phosphine)palladium complexes (40–80 ppm),[13] which is consistent with the planar geometry around three-coordinate phosphorus center.[2]

Complex **2** shows a broad and intense absorption band at 576 nm ($\varepsilon = 33400$),[14] which is remarkably different from those of colorless bis(phosphine)palladium complexes.[11]

Complex **2** reacts with molecular hydrogen (1 atm) for 20 h in toluene to give bis(dialkylhydrophosphine)palladium **3** [Eq. (2)], while dialkylhydrophosphine R$^{\mathrm{H}}{}_2$PH is not



(2)

formed by the reaction of phosphinyl radical **1** with molecular hydrogen. The structure of **3** was determined by NMR spectra, X-ray analysis,[10] and elemental analysis.

X-ray analysis shows that complex **3** has a slightly bent structure with the P1-Pd-P2 angle of 159.72(2)° (Figure 2), which is narrower than those of complex **2** (179.81(2)°) and related two-coordinate bis(phosphine)palladium complexes (176–180°); this is probably due to the crystal packing. Two phosphacyclopentane rings are almost perpendicular to each other: the dihedral angle of the plane (C1-P1-C4) and the plane (C5-P2-C8) is 82.0°. The P1–Pd and P2–Pd distances of 2.2621(7) and 2.2644(7) Å, respectively, are much longer than those of **2** but comparable to those of bis(phosphine)palladium species (2.27–2.28 Å).

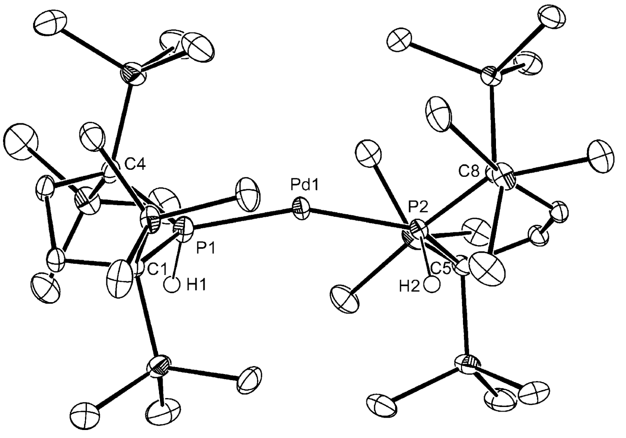


Figure 2. Molecular structure of complex **3**. Ellipsoids are set at 50% probability; hydrogen atoms except for P–H groups are omitted for clarity.

To understand the molecular structure of complex **2**, DFT calculations were carried out.[15–17] The optimized structure of **2** (**2**$_{\mathbf{opt}}$) calculated using the UB3LYP method and SDD for Pd atom and 6-31G(d) for other atoms essentially reproduced that of **2** observed experimentally.[16] The skeleton of **2**$_{\mathbf{opt}}$ adopts almost linear structure with the P-Pd-P angle of 178.6°, the P–Pd distance of 2.23 Å, and the sum of the bond angles around the three-coordinate phosphorus atoms of 360°. The calculated ^{31}P chemical shift for three-coordinate phosphorus nuclei of **2**$_{\mathbf{opt}}$ is 243.3 ppm[15] suggesting that complex **2** adopts the linear structure in solution.[17]

Kohn–Sham (KS) orbitals of **2**$_{\mathbf{opt}}$ show significant π-type interactions between the phosphinyl ligands and the palladium center, as shown in Figures 3 and 4. HOMO−5 is a π-bonding orbital between 4d$_{zx}$(Pd) orbital and a combination orbital of 3p(P) orbitals, π_A, which is antisymmetric with respect to C_2 rotation along the x axis (Figure 3), with contribution of σ(Si–C) orbitals at 2,5-positions on the phosphacyclopentane ring (Figure 4a). The lowest unoccupied KS orbital (LUMO) is the corresponding π anti-bonding

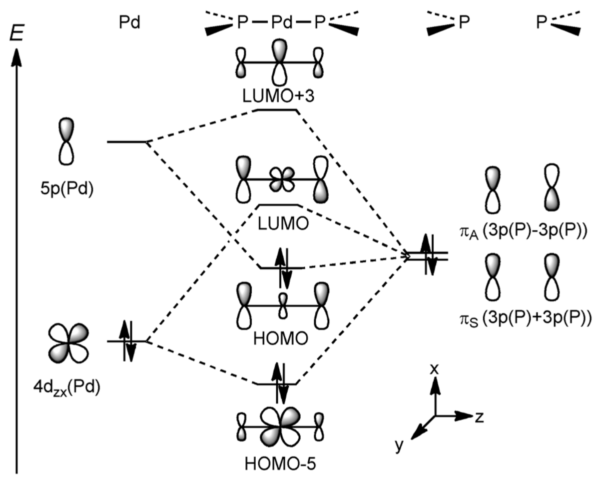


Figure 3. Orbital interactions between orbitals of palladium and SOMO orbitals of phosphinyl radicals in **2**$_{\mathbf{opt}}$.

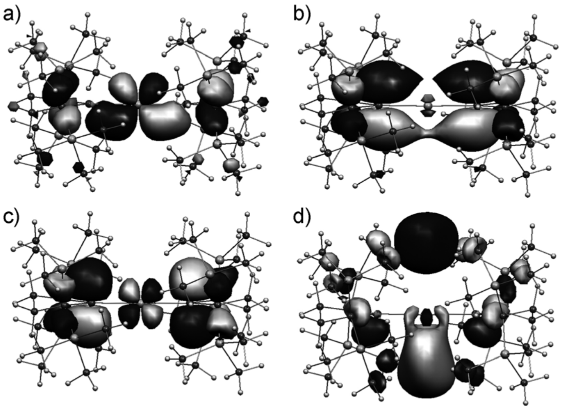


Figure 4. Selected Kohn–Sham orbitals of $\mathbf{2_{opt}}$. a) HOMO-5, b) HOMO, c) LUMO, d) LUMO + 3.

orbital (Figure 4c). Similar π-type interactions between the single SOMO of phosphinyl radical and the metal d_{zx} orbital have been suggested by Cowley[4] and Geoffroy.[7] The highest-occupied KS orbital (HOMO) of **2** is a orbital resulting from weak π-bonding interactions between 5p(Pd) orbital and a symmetric combination orbital of 3p(P) orbitals π_S (Figure 3 and Figure 4b), while LUMO + 3 is the corresponding antibonding orbital (Figure 4d). These π-type orbitals would be responsible for the remarkably short P–Pd distances of **2**.

The intense band at 576 nm is well reproduced by TD-DFT calculations of $\mathbf{2_{opt}}$ (586 nm, *f* 0.5481),[15] and is assignable to a HOMO→LUMO transition being consistent with remarkable interactions between phosphinyl radical ligands and palladium center.[20]

To get further insight into the characteristics of phosphinyl radical **1** as a ligand, comparison of the electronic properties of $\mathbf{2_{opt}}$ and model bisphosphine complex $[(Me_3P)_2Pd]$ (**4**), which has no unpaired electron orbitals on P atoms, is worthy of discussion. The number of electrons in 5s(Pd) and 4d(Pd) orbitals obtained from NBO analysis,[21] which are related to σ donation and π back-donation,[22] are calculated to be 0.56 and 9.44 for $\mathbf{2_{opt}}$. Both for $\mathbf{2_{opt}}$ are smaller than those for **4** (0.71 and 9.64), indicating that σ donation and π back-donation in $\mathbf{2_{opt}}$ are weaker and stronger to some extent than those in **4**. These results are consistent with the natural population analysis (NPA) charges: The NPA charges for palladium and phosphorus atoms of $\mathbf{2_{opt}}$ are calculated to be −0.03 and +0.53, respectively, while the corresponding charges of **4** are −0.38 and +0.98. The weak σ donation and strong π back-donation in $\mathbf{2_{opt}}$ compared with those of **4** would be ascribed to the low-lying lone-pair orbital and SOMO of **1**.[23] The calculated Wiberg bond index,[21] which is a relative measure of bond order, for the P–Pd bond in $\mathbf{2_{opt}}$ (0.696) is about 1.6 times larger as that in **4** (0.435) confirming the presence of significant π bonds between P and Pd atom made of SOMOs of phosphinyl radicals and d orbital of palladium.

In summary, we synthesized homoleptic bis(dialkylphosphinyl)palladium complex **2** as the first transition-metal complex with two phosphinyl ligands using a simple ligand-exchange reaction. The structural characteristics of **2** involving the diamagnetic character, the short P–Pd distances, and the absorption band at long wavelength can be explained by π-type interactions between SOMO orbitals of two phosphinyl radical ligands and palladium atoms. Isolable phosphinyl radical **1** should be a fascinating ligand for metal complexes with unprecedented structures and properties.

Experimental Section

2: Phosphinyl radical **1** (1.06 g, 2.82 mmol) was added to a stirred solution of tetrakis(trimethylphosphine)palladium (579 mg, 1.41 mmol) in hexane (12 mL) at room temperature. The mixture was stirred at room temperature for 5 min. After the removal of volatiles in vacuo, the residue was washed with hexane and acetone to afford bis(dialkylphosphinyl)palladium **2** (893 mg, 1.04 mmol) as navy blue crystals in 74% yield; m.p. 170–171 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 0.44$ (s, 72H, CH$_3$), 1.98 ppm (s, 8H, CH$_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene): $\delta = 2.8$ (s, CH$_3$), 36.0 ppm (s, CH$_2$); ^{13}C NMR (201.2 MHz, CP/MAS): $\delta = 5.2$ (s, CH$_3$), 38.6 ppm (s, CH$_2$); ^{29}Si NMR (79 MHz, [D$_6$]benzene): $\delta = 2.8$ ppm (s); ^{31}P NMR (162 MHz, [D$_6$]benzene): $\delta = 244.7$ ppm ($\nu_{1/2} = 151$ Hz); MS (EI, 30 eV): *m*/*z* (%): 856 (52) [M^+], 841 (3) [$M^+{-}CH_3$], 783 (3) [$M^+{-}Si(CH_3)_3$], 481 (97) [$M^+{-}R^H{}_2P$], 375 (97) [$(R^H{}_2P)^+$]; UV/Vis (3-methypentane): λ_{max} (ε) = 576 (33 400), 408 (3090), 374 (3110), 309 nm (10 500 L mol^{-1} cm^{-1}); Elemental analysis (%) calcd for $C_{32}H_{80}P_2PdSi_8$: C 44.79, H 9.40%; found: C 44.83, H 9.28%.

Attempts to observe the ^{13}C resonance for quarternary carbon nuclei in the phosphacyclopentane rings failed both in solution and in the solid state.

3: Bis(dialkylphosphinyl)palladium **2** (320 mg, 373 μmol) was placed in a flask (50 mL) equipped with a magnetic stir bar. Dry and degassed toluene (30 mL) was then added. The blue solution of **2** was exposed to hydrogen (1 atm) at room temperature for 20 h. The color of the solution turned to pale yellow. After removal of the volatiles in vacuo, recrystallization from hexane at −30 °C afforded bis(hydrophosphine)palladium **3** (102 mg, 118 μmol) as colorless crystals in 32% yield. **3**: m.p. 213–215 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 0.32$ (s, 36H, CH$_3$), 0.52 (s, 36H, CH$_3$), 1.74–1.85 (m, 4H, CH$_2$), 1.85–1.98 (m, 4H, CH$_2$), 5.03 ppm (AA′XX′, 2H, J = 70.0, 69.4, 3.0 Hz, PH); ^{13}C NMR (100 MHz, [D$_6$]benzene): $\delta = 1.5$ (s, CH$_3$), 3.1–3.3 (m, CH$_3$), 18.0 (dd, ^1J(C-P) = 6.0 Hz, ^3J(C-P) = 6.0 Hz, C), 35.8 ppm (s, CH$_2$); ^{29}Si NMR (79 MHz, [D$_6$]benzene): $\delta = 3.2$ (dd, ^2J(Si-P) = 7.2 Hz, ^4J(Si-P) = 7.2 Hz), 6.7 ppm (s); ^{31}P NMR (162 MHz, [D$_6$]benzene): $\delta = -12.6$; MS (EI, 30 eV): *m*/*z* (%): 858 (51) [M^+], 843 (3) [$M^+{-}Me$], 467 (22) [$M^+{-}R^H{}_2PH{-}Me$], 376 (100) [$R^H{}_2PH^+$]; Elemental analysis (%) calcd for $C_{32}H_{82}P_2PdSi_8$: C 44.69, H 9.61; found: C 44.60, H 9.42.

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[9] [Pd(PMe$_3$)$_4$] is important for the synthesis of complex **2**. Reaction of (η^3-allyl)(η^5-cyclopentadienyl)palladium or bis(tricyclohexylphosphine)palladium with phosphinyl radical **1** gave a complex mixture. When 1 equiv of [Pd(PMe$_3$)$_4$] was used, complex **2** and **1** were obtained.

[10] CCDC 898441 (**2** (100 K)), CCDC 898442 (**2** (298 K)), and CCDC 898443 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. No remarkable difference in structure of **2** between at 100 K and 298 K was observed (as shown in the Supporting Information, Table S2).

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[12] On going from 298 K to 243 K, the ^{31}P signal is sharpened. For details, see the Supporting Information. Dissociation of the phosphinyl radical can be ruled out as the reason for the broadening of the ^{31}P resonance at higher temperature, because no EPR signal was observed at 298 K and higher temperatures and no reaction of **2** with TEMPO radical was observed, whereas **1** reacts with TEMPO. Details of the reaction of **1** with TEMPO will be reported elsewhere. Chemical shielding anisotropy relaxation may be responsible for the broadening because the broadening occurs at higher temperature and ^{31}P nuclei in **2** should have a large chemical shift anisotropy.

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[14] This band has a shoulder peak at around 675 nm. For details, see the Supporting Information. With decreasing temperature, the band at 576 nm increases, while the shoulder peak at around 675 nm decreases with an isosbestic point at around 590 nm, suggesting the existence of equilibrium between two species in solution. Two conformers of **2**, which differ primarily in the geometry around P-Pd-P moiety and the extinction coefficients at around 576 and 675 nm, may be responsible for the temperature dependence of the UV/Vis spectra of **2**.

[15] The geometry was optimized using UB3LYP method with SDD and 6-31G(d) basis sets for Pd and other atoms (B1 basis), respectively. The NMR chemical shift was calculated using B3LYP method with SDD and 6-311+G(2d,2p) basis sets for Pd and other atoms (B2 basis). The calculated ^{31}P isotropic absolute chemical shifts of a substrate (σ(calc, S)) was converted into the chemical shift relative to 85% H$_3$PO$_4$ (δ(calc, S)) using δ(calc, S) = σ(calc, PH$_3$)$-\sigma$(calc, S)$-$266.1.[18] σ(calc, PH$_3$) is calculated to be +560.6 at the UB3LYP/B2 level. The calculated value are corrected using the following equation reported by Rezaei-Sameti: δ(experimental) = (δ(calc)$-$18.673)/1.0959.[19] TD-DFT calculations was performed at the BLYP/B1 level.

[16] Compound **2** in the triplet state (**2T**) is calculated to be 22.5 kJ mol^{-1} higher in energy than **2**$_{\mathbf{opt}}$ in the singlet state at the UB3LYP/B1 level. For details, see the Supporting Information.

[17] Model bisphosphinyl complex (Me$_2$P)$_2$Pd (**2′**$_{\mathbf{opt}}$) optimized at the B3LYP/B1[15] level has a bent P-Pd-P skeleton with the angle of 115.1° and a pyramidalized geometry around phosphorus atoms with the sums of the bond angles around the P atoms of 322.6°. Linear **2′** (**2′**$_{\mathbf{lin}}$) with having linear P-Pd-P skeleton and planar three-coordinate phosphorus atoms similar to **2** is located as a transition state for bending of the P-Pd-P skeleton and inversion of the three-coordinate phosphorous atoms, and **2′**$_{\mathbf{lin}}$ is 55.6 kJ mol^{-1} higher in energy than **2′**$_{\mathbf{opt}}$. The linear structure of **2** can be rationalized by severe steric repulsion between two phosphacyclopentane units.

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[23] For comparison of calculated energy levels of phosphinyl radical **1** and Me$_3$P (**5**), see the Supporting Information, Figure S18. The low energy level of the lone-pair orbital of **1** compared to that of **5** would be due to the absence of one alkyl group on the phosphorus atom.