Dinuclear Pt(II) and Pd(I) Complexes with Bridging PPh₂ Ligands from the Reaction of PPh₂H with Zero-Valent Complexes of These Metals

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Reactions of PPh₂H with $[M(PCy_3)_2]$ (M = Pt, Pd) produce the dinuclear complexes with bridging PPh₂ ligands of these metals, $[{Pt(H)(PCy_3)}_2(\mu-PPh_2)_2]$ and $[{Pd (PCy_3)}_2(\mu-PPh_2)_2]$, respectively.

Phosphides (PR₂) have been employed commonly as the useful bridging ligands¹ in forming the diplatinum²⁻⁵ and dipalladium⁶⁻⁹ complexes, as well as heterobimetallic¹⁰⁻¹³ complexes having group 10 metals. Flexible coordination of the bridging phosphido ligands enables one to bind the two metals with and without metal-metal bonds. Leoni and co-workers obtained the phosphido-bridged dinuclear Pt(II) and Pd(I) complexes from the reaction of $[M(\eta^3-C_3H_5)(\eta^5-C_5H_5)]$ (M = Pt, Pd) with secondary bulky phosphine ligands.^{14,15} Recently, we prepared dinuclear and trinuclear complexes with bridging phosphido ligands from the reaction of PPh₂H with [Pt(PEt₃)₃].¹⁶ An initial product of the reaction is the dinuclear Pt complex with bridging PPh₂ ligands, $[{Pt(H)(PEt_3)}_2(\mu -$ PPh₂)₂], although it is readily converted into cyclic or linear trinuclear Pt complexes under the reaction conditions. Similar dinuclear complexes having bulky ligands would be kinetically stabilized due to steric protection of the metal center. In this paper, we report the reaction of PPh_2H with Pt(0) and Pd(0)complexes having PCy₃ ligands to afford stable dinuclear complexes of these metals.

[Pt(PCy₃)₂] is prepared in situ by heating a toluene solution of *cis*-[Pt(Ph)₂(PCy₃)₂] at 60 °C and is reacted directly with PPh₂H in solution at room temperature. *anti*-[{Pt(H)(PCy₃)}₂-(μ -PPh₂)₂] (1) is formed as the product, as shown in Eq. 1. Figure 1 displays the molecular structure of 1, which has two Pt centers bridged by two PPh₂ ligands. Table 1 summarizes the crystallographic data of the obtained dinuclear Pt(II) and Pd(I) complexes. Each Pt center is bonded to a hydrido and a PCy₃ ligand in a distorted square planar coordination. Two hydrido ligands in the molecule are situated at the opposite sides of the Pt…Pt alignment, similarly to *anti*-[{Pt(H)(PEt₃)}₂(μ -P'Bu₂)₂].¹⁶ The length of Pt–P bond trans



Fig. 1. ORTEP drawing of 1 at 30% ellipsoidal level. The molecule has a C₂ symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (°): Pt–P1 2.282(1), Pt–P2 2.322(1), Pt–P2* 2.369(1), Pt…Pt* 3.6499(2), P2…P2* 2.945(2), Pt–H1 1.89(5), P1–Pt–P2 168.18(4), P1–Pt–P2* 107.49(4), P2–Pt–P2* 77.79(4), P1–Pt–H1 75(1), P2–Pt–H1 99(1), Pt–P2–Pt* 102.21(4).

to the hydrido ligand (2.369(1) Å) is longer than that trans to PCy₃ ligand (2.322(1) Å) due to a larger trans influence of H atom than of PCy₃.

$$2 Cy_{3}P \xrightarrow{Ph}_{PCy_{3}} \underbrace{60 \ ^{0}C}_{toluene, 1 h} 2 Pt(PCy_{3})_{2}$$

$$\underbrace{+ 2 PPh_{2}H}_{r. t., 20 h} \underbrace{Cy_{3}P}_{Cy_{3}} \underbrace{Pt}_{P} \underbrace{Pt}_{P} \underbrace{Pt}_{P} \underbrace{Pt}_{H} \underbrace{Ph_{2}}_{Ph_{2}} \underbrace{Pt}_{H} \underbrace{Pt}_{Ph_{2}} \underbrace{Pt}_{Ph_{2}} \underbrace{Pt}_{H} \underbrace{Pt}_{Ph_{2}} \underbrace{Pt}_{Ph_$$

The hydrido signal of 1 in the ¹HNMR spectrum appears at δ -7.57, accompanied by coupling with three phosphorus nuclei (J(HP) = 14, -23, 161 Hz) and one Pt nucleus (J(HPt) = 1042 Hz). The IR spectrum also shows the peak due to Pt-H stretching at a characteristic position (2031 cm^{-1}). The ³¹P{¹H} NMR spectrum of **1** contains two signals at δ 42.7 and -93.4 with a large J(PP) value (265 Hz). They are assigned to PCy₃ and bridging PPh₂ ligands, respectively. Appearance of a single signal due to the bridging PPh₂ ligands indicates anti structure of the complex in solution. No formation of syn isomer is noted in the NMR spectra. The coupling pattern is consistent with the spectrum simulated by assuming an AA'MM'XX' spin system.¹⁷ Two ¹⁹⁵Pt satellite signals (J(PPt) = 1330, 1730 Hz) are observed for the signals of bridging PPh₂ ligands. These J(PPt) values are attributed to the Pt nucleus involved in the linear PPh2-Pt-H group and that in the linear PPh₂–Pt–PCy₃ group. The ³¹P{¹H} NMR signal of PCy₃ ligand shows a large J(PPt) coupling constant (2340) Hz).

The reaction of PPh₂H with [Pd(PCy₃)₂] forms the phosphido-bridged dinuclear Pd(I) complex, [{Pd(PCy₃)}₂(μ -PPh₂)₂] (**2**), as a dark red solid in 67% yield (Eq. 2). The molecule of **2** contains a Pd–Pd bond (2.5755(7) Å) and a linear alignment of two non-bridging P and two Pd atoms (Fig. 2). The Pd–P–Pd angle of the Pd₂P₂ core (67.58(5)°) is much

	1	2
Formula	$C_{60}H_{88}P_4Pt_2$ + toluene	$C_{60}H_{86}P_4Pd_2$
Formula weight	1429.60	1144.04
Color	yellow	red
Crystal size/mm ³	$0.14 \times 0.06 \times 0.04$	$0.32\times0.25\times0.20$
Crystal system	triclinic	monoclinic
Space group	<i>P</i> 1 (No. 2)	$P2_1/a$ (No. 14)
a/Å	10.258(2)	10.603(7)
b/Å	10.731(2)	17.101(12)
c/Å	14.801(3)	15.647(11)
lpha/deg	87.018(5)	
β /deg	81.025(5)	92.334(11)
γ/deg	72.603(4)	
$V/Å^3$	1535.6	2834.9
Ζ	1	2
$D_{\rm calcd}/{ m g}{ m cm}^{-3}$	1.546	1.340
F(000)	722	1196
$\mu/{ m cm}^{-1}$	46.76	7.84
No. of reflns total	11565	19964
No. of reflns obsd (>3 σ)	9067	7683
No. of variables	386	341
$R1 \ (I > 3\sigma(I))$	0.035	0.062
wR2	0.050	0.058
GOF	0.988	0.964

Table 1. Crystallographic Data for 1 and 2



Fig. 2. ORTEP drawing of 2 at 30% ellipsoidal level. The molecule has a C₂ symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (°): Pd–Pd* 2.5755(7), Pd–P1 2.291(2), Pd–P2 2.310(2), Pd–P2* 2.321(2), P1–Pd–P2 124.85(6), P2–Pd–P2* 112.42(6), Pd–P2–Pd* 67.58(5).

smaller than the Pt–P–Pt angle of diplatinum complex 1 (102.21(4)°). The ³¹P{¹H} NMR spectrum of **2** shows the bridging phosphorus signal at δ 174.6, which is in a much lower magnetic field than that of 1 (δ –93.4).

$$2 \operatorname{Pd}(\operatorname{PCy}_3)_2 + 2 \operatorname{PPh}_2 H \xrightarrow{\text{r. t., } 2 \text{ h}}_{\text{toluene}} \operatorname{Cy}_3 \operatorname{P} \xrightarrow{\operatorname{Ph}_2}_{\begin{array}{c} P \\ 2 \end{array}} (2)$$

Reactions (1) and (2) both involve initial oxidative addition of PPh_2H to the zero-valent complexes of these metals to form intermediate mononuclear complexes formulated as [M(H)-(PPh₂)(PCy₃)_n] (M = Pd, Pt; n = 1 or 2). Dimerization of [Pt(H)(PPh₂)(PCy₃)_n] yields complex **1**, while formation of **2** requires elimination of hydrogen atoms during the dimerization of the above Pd-containing intermediates. Leoni also proposed a similar pathway for formation of the dipalladium complex, [{Pd(P'Bu₂H)}₂(μ -P'Bu₂)₂] in the reaction of the secondary phosphine with the starting Pd(II) complex, [M(η^3 -C₃H₅)(η^5 -C₅H₅)].¹⁵

We report preparation of the phosphido-bridged dinuclear Pt(II) and Pd(I) complexes from the reaction of PPh_2H with the zero-valent complexes of these metals having PCy_3 ligands.

Experimental

General. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Hexane and toluene were distilled from sodium benzophenone ketyl and stored under nitrogen. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Varian Mercury 300 spectrometers. Peak position of the ³¹P{¹H} NMR spectrum was referenced to an external 85% H₃PO₄. [Pt(PCy₃)₂] was prepared by an improved version of the previous method.¹⁸ [Pt(Ph)₂(PCy₃)₂] and [Pd(PCy₃)₂] were prepared from the reaction of [Pt(Ph)₂(cod)] or [Pd(Me)₂(tmeda)] (tmeda = *N*,*N*,*N'*,*N'*tetramethylethylenediamine) with PCy₃.¹⁹ Diphenylphosphine was obtained from commercial suppliers and was distilled before using. IR absorption spectra were recorded with a Shimadzu FT/IR-8100 spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of *anti*-[{**Pt**(**H**)(**PCy**₃)}₂(μ -**PPh**_2)_2] (1). A toluene (3 cm³) solution of *cis*-[**Pt**(**Ph**)₂(**PCy**₃)₂] (211 mg, 0.23 mmol) was heated at 60 °C for 1 h to produce [**Pt**(**PCy**₃)₂] by reductive elimination of biphenyl. Diphenylphosphine (0.044 cm³, 0.26 mmol) was added to the resulting mixture, which was stirred

at room temperature for 20 h. The solvent was removed under reduced pressure. The residual material was washed with 2 cm³ of hexane twice and dried in vacuo to give 1 as yellow powder (88%). Elemental analysis. Calcd for C₆₀H₈₈P₄Pt₂: C. 54.45: H. 6.70%; Found: C, 52.31; H, 6.49%. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ -7.57 (ddd, 2H, Pt*H*, *J*(HP) = 14, -23, 161 Hz, J(HPt) = 1042 Hz, 1.06 (t, 12H, C₆ H_{11} , J(HH) = 12 Hz), 1.16 (t, 6H, C_6H_{11} , J(HH) = 12 Hz), 1.48 (t, 12H, C_6H_{11} , J(HH) =12 Hz), 1.65 (t, 24H, C_6H_{11} , J(HH) = 12 Hz), 1.79 (t, 12H, C_6H_{11} , J(HH) = 11 Hz), 7.03 (m, 12H, C_6H_5 -meta and para), 7.52 (br, 8H, C₆H₅-ortho). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C): δ 26.9 (s, PCHCH₂CH₂CH₂), 27.6 (d, PCHCH₂CH₂, J(CP) = 10.3 Hz), 30.5 (apparent triplet, PCHCH₂, J(CPt) =12.1 Hz), 36.1 (m, PCH, J(CP) = 23.5 Hz), 126.8 (m, C_6H_5 -meta, J(CP) = 8.7 Hz), 128.5 (s, C_6H_5 -para), 136.0 (m, C_6H_5 -ortho, J(CP) = 11.0 Hz), 142.7 (m, C_6H_5 -ipso, J(CP) = 28.4 Hz). $^{31}P{^{1}H} NMR$ (121 MHz, CD₂Cl₂, 25 °C): δ -93.4 (PPh₂, ${}^{2}J(PP) = -14$, -80, 265 Hz, ${}^{1}J(PPt) = 1330$, 1730 Hz), 42.7 $(PCy_3, {}^{2}J(PP) = -14, 265 \text{ Hz}, {}^{4}J(PP) = 11 \text{ Hz}, {}^{1}J(PPt) = 2340$ Hz, ${}^{3}J(\text{PPt}) = -14 \text{ Hz}$). IR(cm⁻¹, KBr): 2031 (ν (PtH)).

Preparation of $[{Pd(PCy_3)}_2(\mu - PPh_2)_2]$ (2). To a solution of $[Pd(PCy_3)_2]$ (173 mg, 0.26 mmol) in 3 cm³ of toluene was added diphenylphosphine (0.045 cm³, 0.26 mmol) at -60 °C. The reaction mixture was warmed gradually to room temperature and was stirred for 2 h. The solvent was removed under reduced pressure. The residual material was washed with 1.5 cm³ of hexane twice and dried in vacuo to give 2 as a dark red solid in 67% yield. Elemental analysis. Calcd for C₆₀H₈₆P₄Pd₂: C, 62.99; H, 7.58%; Found: C, 63.42; H, 7.41%. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.99 (t, 6H, C₆ H_{11} , J(HH) = 12 Hz), 1.11 (q, 12H, C₆ H_{11} , J(HH) = 12 Hz), 1.40 (t, 12H, C₆H₁₁, J(HH) = 12 Hz), 1.56 (m, 18H, C₆H₁₁), 1.90 (m, 18H, C₆H₁₁), 7.04 (t, 4H, C₆H₅-para, J(HH) = 7.5 Hz, 7.20 (t, 8H, C₆H₅-meta, J(HH) = 7.5 Hz), 7.90 (dd, 4H, C_6H_5 -ortho, J(HH) = 7.5 Hz, J(HP) = 4.5 Hz), 7.92 (dd, 4H, C_6H_5 -ortho, J(HH) = 7.5 Hz, J(HP) = 4.5 Hz). $^{13}C{^{1}H} NMR$ (75 MHz, C_6D_6 , 25 °C): δ 26.6 (s, PCHCH₂CH₂CH₂), 27.8 (apparent triplet, PCHCH₂, J(CP) =5.1 Hz), 31.1 (s, PCHCH₂CH₂), 35.6 (apparent quintet, PCH, J(CP) = 3.9 Hz), 126.8 (s, C_6H_5 -para), 127.9 (t, C_6H_5 -meta, J(CP) = 3.5 Hz), 133.3 (t, C_6H_5 -ortho, J(CP) = 8.7 Hz), 145.1 (s, C₆H₅-ipso). ³¹P{¹H} NMR (121 MHz, C₆D₆, 25 °C): δ 52.8 (t, PCy_3 , ${}^2J(PP) = 41$ Hz), 174.6 (t, μ - PPh_2 , ${}^2J(PP) = 41$ Hz).

X-ray Crystallography. Crystals of 1 and 2 suitable for X-ray diffraction study were mounted in glass capillaries under argon. Data of 1 and 2 were collected at -160 °C on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Calculations were carried out by using the program package Crystal Structure for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms except for the PtH hydrogens of 1 were located by assuming the ideal geometry and were included in the structure calculation without further

refinement of the parameters. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 264269 and 264270 for 1 and 2, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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