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Dinuclear Pt(II) and Pd(I) Complexes with Bridging PPh_2 Ligands from the Reaction of PPh_2H with Zero-Valent Complexes of These Metals

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Reactions of PPh_2H with $[M(PCy_3)_2]$ (M = Pt, Pd) produce the dinuclear complexes with bridging PPh_2 ligands of these metals, $[\{Pt(H)(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$ and $[\{Pd(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$, respectively.

Phosphides (PR_2) have been employed commonly as the useful bridging ligands[1] in forming the diplatinum[2–5] and dipalladium[6–9] complexes, as well as heterobimetallic[10–13] 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 $[M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ (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 PPh_2H with $[Pt(PEt_3)_3]$.[16] An initial product of the reaction is the dinuclear Pt complex with bridging PPh_2 ligands, $[\{Pt(H)(PEt_3)\}_2(\mu\text{-}PPh_2)_2]$, 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 PCy_3 ligands to afford stable dinuclear complexes of these metals.

$[Pt(PCy_3)_2]$ is prepared in situ by heating a toluene solution of *cis*-$[Pt(Ph)_2(PCy_3)_2]$ at 60 °C and is reacted directly with PPh_2H in solution at room temperature. *anti*-$[\{Pt(H)(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$ (**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 PPh_2 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 PCy_3 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*-$[\{Pt(H)(PEt_3)\}_2(\mu\text{-}P^tBu_2)_2]$.[16] The length of Pt–P bond trans to the hydrido ligand (2.369(1) Å) is longer than that trans to PCy_3 ligand (2.322(1) Å) due to a larger trans influence of H atom than of PCy_3.

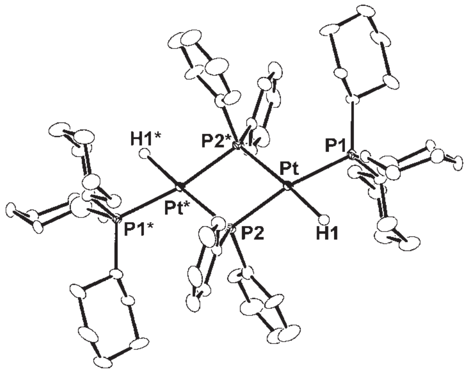
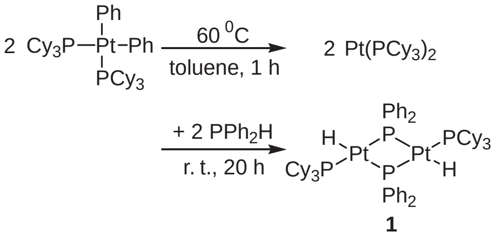


Fig. 1. ORTEP drawing of **1** at 30% ellipsoidal level. The molecule has a C_2 symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (°): Pt–P1 2.282(1), Pt–P2 2.322(1), 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).



1

(1)

The hydrido signal of **1** in the ^1H NMR 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 $^{31}P\{^1H\}$ 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 PCy_3 and bridging PPh_2 ligands, respectively. Appearance of a single signal due to the bridging PPh_2 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 ^{195}Pt satellite signals ($J(PPt) = 1330$, 1730 Hz) are observed for the signals of bridging PPh_2 ligands. These $J(PPt)$ values are attributed to the Pt nucleus involved in the linear PPh_2–Pt–H group and that in the linear PPh_2–Pt–PCy_3 group. The $^{31}P\{^1H\}$ NMR signal of PCy_3 ligand shows a large $J(PPt)$ coupling constant (2340 Hz).

The reaction of PPh_2H with $[Pd(PCy_3)_2]$ forms the phosphido-bridged dinuclear Pd(I) complex, $[\{Pd(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$ (**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 Pd_2P_2 core (67.58(5)°) is much

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Table 1. Crystallographic Data for **1** and **2**

	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 × 0.06 × 0.04	0.32 × 0.25 × 0.20
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (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)
α/deg	87.018(5)	
β/deg	81.025(5)	92.334(11)
γ/deg	72.603(4)	
V/Å^3	1535.6	2834.9
Z	1	2
D_{calcd}/g cm^{-3}	1.546	1.340
F(000)	722	1196
μ/cm^{-1}	46.76	7.84
No. of reflns total	11565	19964
No. of reflns obsd ($>3\sigma$)	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

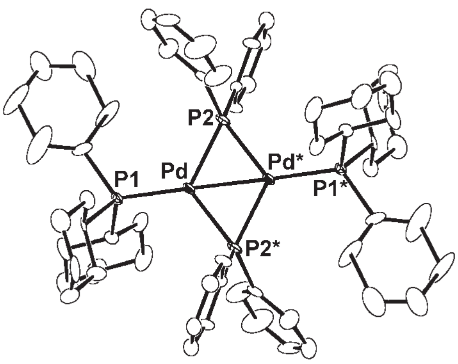
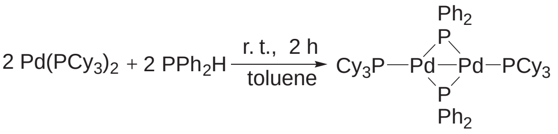


Fig. 2. ORTEP drawing of **2** at 30% ellipsoidal level. The molecule has a C_2 symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (°): Pd–Pd* 2.5755(7), Pd–P1 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 $^{31}P\{^1H\}$ 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)

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 $[M(H)(PPh_2)(PCy_3)_n]$ (M = Pd, Pt; $n = 1$ or 2). Dimerization of $[Pt(H)(PPh_2)(PCy_3)_n]$ 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, $[\{Pd(P^tBu_2H)\}_2(\mu\text{-}P^tBu_2)_2]$ in the reaction of the secondary phosphine with the starting Pd(II) complex, $[M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$.[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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 spectrometers. Peak position of the $^{31}P\{^1H\}$ NMR spectrum was referenced to an external 85% H_3PO_4. $[Pt(PCy_3)_2]$ was prepared by an improved version of the previous method.[18] $[Pt(Ph)_2(PCy_3)_2]$ and $[Pd(PCy_3)_2]$ were prepared from the reaction of $[Pt(Ph)_2(cod)]$ or $[Pd(Me)_2(tmeda)]$ (tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) with PCy_3.[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*-$[\{Pt(H)(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$ (1). A toluene (3 cm^3) 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 cm^3, 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 cm^3 of hexane twice and dried in vacuo to give **1** as yellow powder (88%). Elemental analysis. Calcd for $C_{60}H_{88}P_4Pt_2$: C, 54.45; H, 6.70%; Found: C, 52.31; H, 6.49%. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ -7.57 (ddd, 2H, Pt*H*, J(HP) $= 14$, -23, 161 Hz, J(HPt) $= 1042$ Hz), 1.06 (t, 12H, C_6H_{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, C_6H_5-*ortho*). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): δ 26.9 (s, $PCHCH_2CH_2CH_2$), 27.6 (d, $PCHCH_2CH_2$, J(CP) $= 10.3$ Hz), 30.5 (apparent triplet, $PCHCH_2$, J(CPt) $=$ 12.1 Hz), 36.1 (m, P*C*H, 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). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): δ -93.4 (*P*Ph$_2$, ^2J(PP) $= -14$, -80, 265 Hz, ^1J(PPt) $= 1330$, 1730 Hz), 42.7 (*P*Cy$_3$, ^2J(PP) $= -14$, 265 Hz, ^4J(PP) $= 11$ Hz, ^1J(PPt) $= 2340$ Hz, ^3J(PPt) $= -14$ Hz). IR(cm^{-1}, KBr): 2031 (ν(PtH)).

Preparation of $[\{Pd(PCy_3)\}_2(\mu\text{-}PPh_2)_2]$ (2). To a solution of $[Pd(PCy_3)_2]$ (173 mg, 0.26 mmol) in 3 cm^3 of toluene was added diphenylphosphine (0.045 cm^3, 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 cm^3 of hexane twice and dried in vacuo to give **2** as a dark red solid in 67% yield. Elemental analysis. Calcd for $C_{60}H_{86}P_4Pd_2$: C, 62.99; H, 7.58%; Found: C, 63.42; H, 7.41%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.99 (t, 6H, C_6H_{11}, J(HH) $= 12$ Hz), 1.11 (q, 12H, C_6H_{11}, J(HH) $= 12$ Hz), 1.40 (t, 12H, C_6H_{11}, J(HH) $= 12$ Hz), 1.56 (m, 18H, C_6H_{11}), 1.90 (m, 18H, C_6H_{11}), 7.04 (t, 4H, C_6H_5-*para*, J(HH) $= 7.5$ Hz), 7.20 (t, 8H, C_6H_5-*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). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ 26.6 (s, $PCHCH_2CH_2CH_2$), 27.8 (apparent triplet, $PCHCH_2$, J(CP) $=$ 5.1 Hz), 31.1 (s, $PCHCH_2CH_2$), 35.6 (apparent quintet, P*C*H, 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, C_6H_5-*ipso*). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C): δ 52.8 (t, *P*Cy$_3$, ^2J(PP) $= 41$ Hz), 174.6 (t, μ-*P*Ph$_2$, ^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 Kα 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).

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References

1 P. Braunstein and N. M. Boag, *Angew. Chem., Int. Ed.*, **40**, 2427 (2001).

2 E. Alonso, J. Forniés, C. Fortuño, A. Martín, and A. G. Orpen, *Organometallics*, **20**, 850 (2001).

3 P. Leoni, G. Chiaradonna, M. Pasquali, and F. Marchetti, *Inorg. Chem.*, **38**, 253 (1999).

4 E. Alonso, J. M. Casas, F. A. Cotton, X. Feng, J. Forniés, C. Fortuño, and M. Tomas, *Inorg. Chem.*, **38**, 5034 (1999).

5 P. Leoni, M. Pasquali, A. Fortunelli, G. Germano, and A. Albinati, *J. Am. Chem. Soc.*, **120**, 9564 (1998).

6 P. Leoni, F. Marchetii, S. Papucci, and M. Pasquali, *J. Organomet. Chem.*, **593–594**, 12 (2000).

7 R. Giannandrea, P. Mastrorilli, C. F. Nobile, and U. Englert, *J. Chem. Soc., Dalton Trans.*, **1997**, 1355.

8 P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albinati, F. Lianza, P. S. Pregosin, and H. Rueegger, *Organometallics*, **12**, 1702 (1993).

9 A. M. Arif, D. E. Heaton, R. A. Jones, and C. M. Nunn, *Inorg. Chem.*, **26**, 4228 (1987).

10 P. Braunstein, M. Knorr, G. Reinhard, U. Schubert, and T. Stährfeldt, *Chem.—Eur. J.*, **6**, 4265 (2000).

11 L. R. Falvello, J. Forniés, C. Fortũno, and F. Martinez, *Inorg. Chem.*, **33**, 6242 (1994).

12 J. Powell, E. Fuchs, and J. F. Sawyer, *Organometallics*, **9**, 1722 (1990).

13 R. T. Baker, W. C. Fultz, T. B. Marder, and I. D. Williams, *Organometallics*, **9**, 2357 (1990).

14 P. Leoni, S. Manetti, and M. Pasquali, *Inorg. Chem.*, **34**, 749 (1995).

15 P. Leoni, G. Chiaradonna, M. Pasquali, F. Marchetti, A. Fortunelli, and G. Germano, *Inorg. Chim. Acta*, **264**, 185 (1997).

16 M. Itazaki, Y. Nishihara, and K. Osakada, *Organometallics*, **23**, 1610 (2004).

17 P. H. M. Budzelaar, "gNMR," Adept Scientific Publishing, Amor Way, Letchworth, Herts, SG6 1ZA, U.K., Vol. 4.1.2.

18 S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1976).

19 M. Tanabe and K. Osakada, unpublished results.