Pd−Pt Heterobimetallic and Pd−Pd or Pt−Pt Dinuclear Complexes with Bridging Diphenylsilyl Ligands

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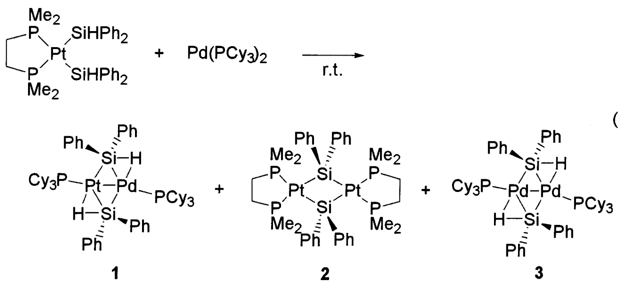
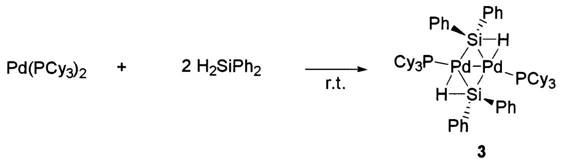
*Summary: The reaction of $Pt(SiHPh_2)_2(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with $Pd(PCy_3)_2$ forms $(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)_2Pt(PCy_3)$ (**1**), which contains two diphenylsilyl ligands bridged to Pd and Pt centers. A comparison of the crystallographic results and the NMR spectra of **1** with those of $[(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**3**) and $[(Cy_3P)Pt(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**4**) indicates that the structure of **1** contains two inequivalent Si−H hydrogens, Pd−H−Si and Pt−H−Si, with three-center two-electron bonds.*

Primary ($-SiH_2R$) and secondary ($-SiHR_2$) organosilyl ligands of di- and multinuclear transition-metal complexes were reported to coordinate to two or more metal centers as the bridging ligands with both M−Si σ-bonds and M−H−Si three-center two-electron (3c-2e) bonds.[1,2] The bridging silyl ligand, which is bonded unsymmetrically to two metal centers, often causes a change in the structure of the complex due to flexible M−H−Si bonding. Heterobimetallic complexes with such bridging organosilyl ligands are of significant interest because the coordination mode of the ligands and their dynamic behavior are influenced by the presence of two different metals.[3] Although there are a number of diplatinum complexes with bridging μ-silyl ligands,[4] only a few heterobimetallic complexes containing Pt are known. Braunstein et al. reported Fe−Pt complexes in which the two metals are bridged by $Si(OMe)_3$ ligands.[5] Recently, we have reported the synthesis of Rh−Pt heterobimetallic complexes through the reaction of $Pt(SiHPh_2)_2(PMe_3)_2$ with $RhCl(PMe_3)_3$, which involves the coordination of the Si−H group of the silyl ligand to the Rh(I) center.[6] On the other hand, dinuclear homometallic complexes of Pd and Pt, $[(R'_3P)M(\mu\text{-}\eta^2\text{-}HSiR_2)]_2$ (M = Pd, Pt), were prepared easily by the reaction of H_2SiR_2 with the zerovalent complexes of these metals.[7,8] In this paper, we report the preparation of a new Pd−Pt heterodinuclear complex with two diphenylsilyl ligands and a comparison of its spectroscopic properties with those of analogous dipalladium and diplatinum complexes.

An equimolar reaction of $Pt(SiHPh_2)_2(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with $Pd(PCy_3)_2$ in toluene at room temperature produces a mixture of the complexes $(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)_2Pt(PCy_3)$ (**1**), $[(dmpe)Pt(\mu\text{-}SiPh_2)]_2$ (**2**),[6b] and $[(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**3**) (eq 1).[9] The new Pd−Pt heterobimetallic complex **1** is the major product and is isolated as pale yellow crystals in 28% yield from the recrystallization of the product separated from the reaction mixture. The reactions of H_2SiPh_2 with $Pd(PCy_3)_2$ and with $PtMe_2(PCy_3)_2$ produce an analogous dipalladium complex, $[(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**3**), and a diplatinum complex, $[(Cy_3P)Pt(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**4**),[7] respectively (eqs 2, 3). Dinuclear complexes **1**, **3**, and **4** are air-stable in solid and CD_2Cl_2 or C_6D_6 solution.



(1)



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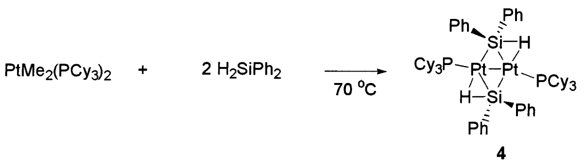

(3)

Figure 1a depicts the molecular structure of Pd−Pt heterobimetallic complex **1** as determined by X-ray

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(1) (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21. (c) Tobita, H.; Ogino, H. *Adv. Organomet. Chem.* **1998**, *42*, 223. (d) Corey, J.-Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (e) Braunstein, P.; Boag, N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2427.

(2) Choi, S.-H.; Lin, Z. *J. Organomet. Chem.* **2000**, *608*, 42.

(3) (a) Malisch, W.; Weckel, H.-U.; Grob, I.; Köhler, F. H. *Z. Naturforsch.* **1982**, *37b*, 601. (b) Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 577. (c) Bodensieck, U.; Braunstein, P.; Deck, W.; Faure, T.; Knorr M.; Stern, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2440. (d) Sakaba, H.; Ishida, K.; Horino, H. *Chem. Lett.* **1998**, 149.

(4) (a) Levchinsky, Y.; Rath N. P.; Braddock-Wilking, J. *Organometallics* **1999**, *18*, 2583. (b) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2000**, *19*, 5500. (c) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192.

(5) (a) Knorr, M.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1995**, *14*, 4910. (b) Knorr, M.; Strohmann, C.; Braunstein, P. *Organometallics* **1996**, *15*, 5653. (c) Knorr, M.; Hallauer, E.; Hush, V.; Veith, M.; Braunstein, P. *Organometallics* **1996**, *15*, 3868. (d) Braunstein, P.; Faure, T.; Knorr, M. *Organometallics* **1999**, *18*, 1791.

(6) (a) Tanabe, M.; Osakada, K. *Chem. Lett.* **2001**, 962. (b) Tanabe, M.; Osakada, K. *Inorg. Chim. Acta*, in press.

(7) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659.

(8) (a) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929. (b) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **2000**, 417.

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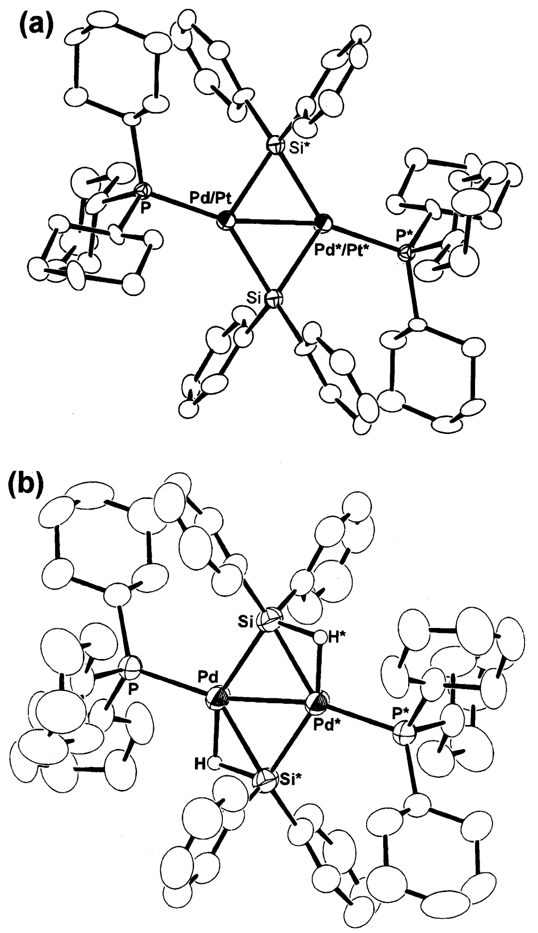

Figure 1. ORTEP drawings of complex (a) **1** and (b) **3** as determined by X-ray crystallography with 50% probability thermal ellipsoids. Hydrogens except for SiH hydrogen were omitted for simplicity. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. M = Pd and Pt with equal occupancy. Two SiH hydrogens of **1** were not found due to the disorder of two metal centers. Selected bond distances (Å) and angles (deg) for **1**: M−M* 2.691(2), M−P 2.299(3), M−Si 2.377(3), M−Si* 2.328(4), M*−M−P 160.68(8), M*−M−Si 55.97(8), M*−M−Si* 54.27(8), P−M−Si 106.72(11), P−M−Si* 141.87(11) Si−M−Si* 110.24(11), M−Si−M* 69.8(1). Selected bond distances (Å) and angles (°) for **3**: Pd−Pd* 2.691(1), Pd−P 2.316(2), Pd−Si 2.326(2), Pd−Si* 2.384(2), Pd−H 1.61, Si−H 1.63. Pd*−Pd−P 161.40(7), Pd*−Pd−Si 56.19(6), Pd*−Pd−Si* 54.14(6), P−Pd−Si 107.69(8), P−Pd−Si* 140.66(8), Si−Pd−Si* 110.32(7), Pd−Si−Pd* 69.68(7).

crystallography.[10] The molecule has a crystallographic center of symmetry at the midpoint of the two metal centers, which causes a disorder of the Pd and Pt centers at the two metal positions with equal occupancy. Thus each M−Si bond distance is an average of the Pd−Si and Pt−Si bonds. Different lengths between two crystallographically independent M−Si bonds, 2.377(3) and 2.328(4) Å, are ascribed to the presence of hydrogen bridged to the metals (Pd and Pt) in the former bond, forming an M−H−Si, 3c-2e bond. Dipalladium complex **3** also has a C_2-symmetrical Pd_2Si_2 core with two Pd−H−Si bonds (Figure 1b),[11] which is quite similar to that of the reported $[(Me_3P)Pd(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$.[8a]

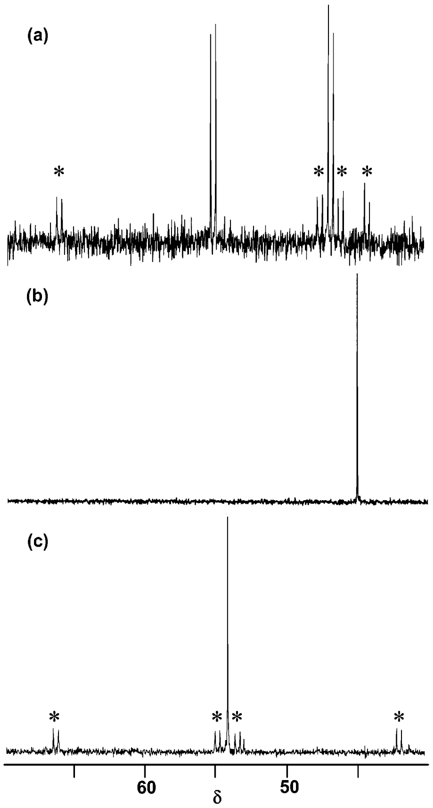

Figure 2. $^{31}P\{^1H\}$ NMR spectra of (a) **1**, (b) **3**, and (c) **4** at 25 °C in benzene-d_6. Peaks with asterisks are due to ^{195}Pt satellite signals.

Figure 2a−c depicts the $^{31}P\{^1H\}$ NMR spectra for **1**, **3**, and **4**. Two inequivalent phosphine signals for **1** are observed as two sets of doublets ($^3J(PP) = 59$ Hz) at δ 55.2 and 46.7. The former doublet with the larger $J(PPt)$ (3588 Hz) than the latter ($^2J(PPt) = 239$ Hz) is assigned to the phosphorus nucleus directly bonded to Pt. The ^{31}P NMR signal for the PCy_3 bonded to the Pt in **1** is close to that of diplatinum complex **4** (δ 54.2), and the chemical shift of the phosphorus bonded to Pd is similar to that of dipalladium analogue **3** (δ 45.1). The ^1H NMR spectrum for **1** exhibits the signals for the Si−H hydrogens at δ 2.49 and 1.70 due to the inequivalent environmets of the two SiH hydrogens (Figure 3a). The ^2H NMR spectrum of $(Cy_3P)Pd(\mu\text{-}\eta^2\text{-}DSiPh_2)_2Pt(PCy_3)$ (**1-*d*₂**), which is prepared from $Pt(SiDPh_2)_2(dmpe)$ and $Pd(PCy_3)_2$, shows two resonances of deuterium bonded to Si at δ 2.51 and 1.72. The peak positions clearly indicate that the above ^1H peaks are due to the Si−H hydrogens rather than to the hydrogens of PCy_3 ligands. The ^1H NMR peak for **1** at δ 2.49 is observed with relatively small coupling to the ^{195}Pt nucleus ($^2J(HPt) = 73$ Hz), which is assigned to the hydrogen involved in the Pd−H−Si, 3c-2e bond and is shifted to a lower

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[9] Complex **2** was characterized by NMR spectroscopy. $^{31}P\{^1H\}$ NMR of **2** (122 MHz, C_6D_6, rt): δ 39.0 ($J(PPt) = 1263$ Hz, $^2J(PPt) = 222$ Hz, $^3J(PP) = 29$ Hz).

[10] X-ray data of **1**: $C_{60}H_{88}P_2Si_2PdPt$, $M_r = 1228.96$, monoclinic, $P2_1/c$ (No. 14), $a = 10.202(5)$ Å, $b = 13.930(8)$ Å, $c = 20.010(11)$ Å, $\beta = 92.746(8)°$, $V = 2840.4(27)$ Å^3, $Z = 2$, μ(Mo Kα) = 2.902 mm^{-1}, $D_c = 1.437$ g cm^{-3}, $F(000) = 1260$, 6229 unique reflections, 341 variables, $R = 0.073$, $R_w = 0.097$, GOF = 1.00 using 3826 $I > 2\sigma(I)$.

[11] X-ray data of **3**: $C_{60}H_{88}P_2Si_2Pd_2$, $M_r = 1140.28$, monoclinic, $P2_1/c$ (No. 14), $a = 10.188(3)$ Å, $b = 14.141(2)$ Å, $c = 20.184(4)$ Å, $\beta = 94.46(2)°$, $V = 2899.2(9)$ Å^3, $Z = 2$, μ(Mo Kα) = 0.753 mm^{-1}, $D_c = 1.306$ g cm^{-3}, $F(000) = 1196$, 6934 unique reflections, 298 variables, $R = 0.050$, $R_w = 0.042$, GOF = 1.50 using 2806 $I > 3\sigma(I)$.

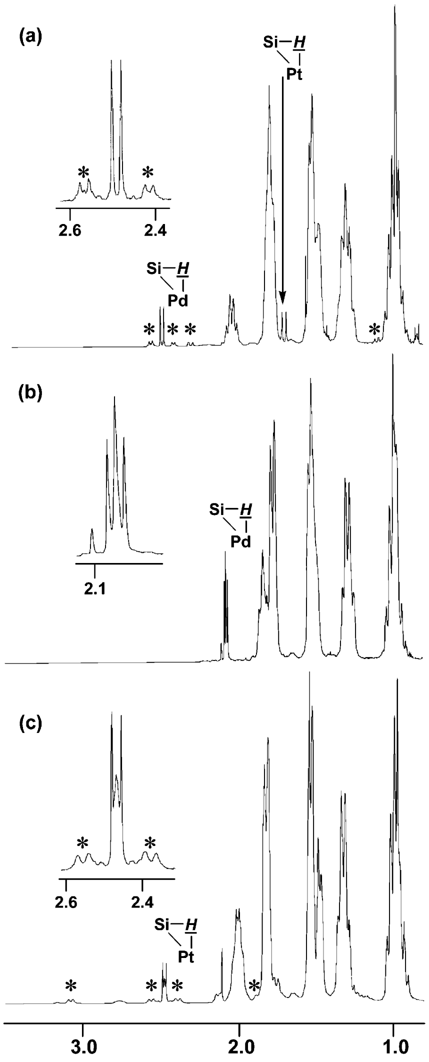

Figure 3. ^{1}H NMR spectra of (a) **1** at 40 °C, (b) **3** at 25 °C, and (c) **4** at 25 °C in benzene-d_6. The signals without assignment are due to PCy$_3$ hydrogens. Peaks with asterisks are due to ^{195}Pt satellite signals.

field than the observed chemical shift of **3** (δ 2.07) (Figure 3b). The bridging Pt–H–Si signal at a higher magnetic field (δ 1.70) shows a large J(HPt) value (601 Hz). These J(HPt) values are similar to those of diplatinum complex **4** with two sets of ^{195}Pt satellites (^2J(HPt) = 88 Hz, J(HPt) = 605 Hz) (Figure 3c). The Pt–H–Si signals for **1** are observed as doublets, whereas those of **3** and **4** appear as apparent triplets due to virtual coupling. The Pd–H–Si hydrogen signal for **1** is at a lower field than that of **3**, whereas the Pt–H–Si hydrogen signal for **1** is shifted from **4** to a higher field.

The reaction of Pd(SiHPh$_2$)$_2$(dmpe) with Pt(PCy$_3$)$_2$ forms a mixture of the diplatinum and dipalladium complexes **2** and **3**. The ^{31}P{^{1}H} NMR study of the reaction mixture showed that complex **1** was formed initially in a much smaller amount than **2** and **3** and that the heterobimetallic complex diminished soon to give a mixture of **2** and **3** in approximately 6:4 molar ratio. The low yield of **1** in the reaction, which causes exchange of the phosphine ligands between Pd and Pt, and conversion of **1** into other products in the reaction mixture are contrasted with the reaction in eq 1 to form **1** as the major product among the three complexes.

In summary, this study provided a new Pd–Pt heterobimetallic complex **1** with organosilyl ligands. The two SiH hydrogens of **1** are unsymmetrically coordinated to Pd and Pt centers via 3c-2e bonds. The complex prefers a structure having Pt–Si, Pd–Si, Pt–H–Si, and Pd–H–Si bonds rather than that with two Pt–Si and Pd–H–Si bonds (or two Pd–Si and two Pt–H–Si bonds).

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Supporting Information Available: Experimental procedures for the synthesis of the complexes of **1**–**4** and results of X-ray crystallography for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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