

## Rh–Pt Heterobimetallic Complexes with Unsymmetrically Bridging Organosilyl Ligands: Crystal Structure and Dynamic Behavior in Solution

Makoto Tanabe and Kohtaro Osakada\*

Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8503

(Received July 8, 2001; CL-010601)

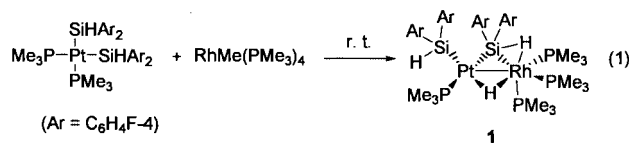
Pt{SiH(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> reacts with Rh (I) complexes to afford new Rh–Pt heterobimetallic complexes with bridging hydrido and diarylsilyl ligands. These complexes were characterized by X-ray crystallography. The NMR spectra exhibit dynamic behavior of hydrogen atoms and three PMe<sub>3</sub> ligands bonded to Rh center in solution.

There have been a number of dinuclear complexes with bridging organosilyl groups such as μ-SiHR<sub>2</sub> and μ-SiH<sub>2</sub>R ligands which form both stable M–Si σ-bond and structurally favorable M–H–Si three center two electron (3c-2e) bond.<sup>1</sup> The structure and dynamic behavior of the bridging-coordinated SiHR<sub>2</sub> group in bimetallic systems are of significant interest. Although much attention has been paid to such complexes composed of the same two metal centers (Scheme 1, M = M'), analogous heterobimetallic complexes bridged by organosilyl ligands (M ≠ M') were reported only in a limited number.<sup>2</sup> In this paper we report the synthesis of new Rh–Pt heterobimetallic complexes with bridging diarylsilyl and hydrido ligands as well as unique dynamic behavior in solution.

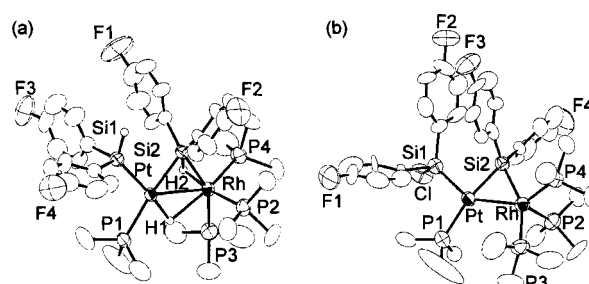
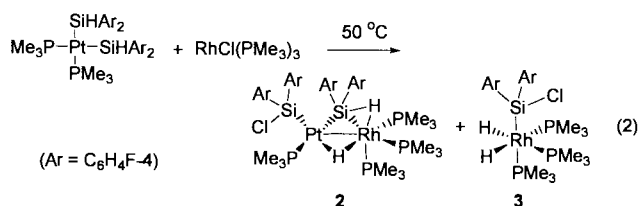


Scheme 1

Pt{SiH(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub><sup>3</sup> reacts with an equimolar amount of RhMe(PMe<sub>3</sub>)<sub>4</sub><sup>4</sup> at room temperature to produce a new Rh–Pt heterobimetallic complex {(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>HSi}(Me<sub>3</sub>P)Pt(μ-H){μ-SiH(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}Rh(PMe<sub>3</sub>)<sub>3</sub> (**1**) in 48% yield (eq 1).<sup>5</sup>



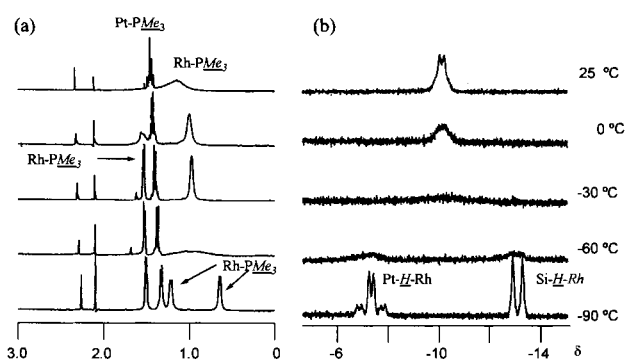
A similar reaction of Pt{SiH(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> with RhCl(PMe<sub>3</sub>)<sub>3</sub><sup>6</sup> requires heating for 24 h at 50 °C to give a mixture of complexes including {(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>ClSi}(Me<sub>3</sub>P)Pt(μ-H){μ-SiH(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}Rh(PMe<sub>3</sub>)<sub>3</sub> (**2**; 58%) and *fac*-RhH<sub>2</sub>{SiCl(C<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>}(PMe<sub>3</sub>)<sub>3</sub><sup>7</sup> (**3**; 5%) (eq 2).<sup>8</sup>



**Figure 1.** Molecular structures of a) **1** and b) **2** determined by X-ray crystallography. Selected bond distances (Å) and angles(°): **1** : Pt–Rh 2.934(2), Pt–P1 2.295(5), Pt–Si1 2.319(5), Pt–Si2 2.323(4), Pt–H1 1.66, Rh–P2 2.348(5), Rh–P3 2.368(5), Rh–P4 2.263(5), Rh–Si2 2.368(5), Rh–H1 2.24, Rh–H2 1.63, Si2–H2 2.28. P1–Pt–Si1 102.7(2), P1–Pt–Si2 174.1(2), P1–Pt–H1 73.0, Si1–Pt–Si2 83.1(2), Si–Pt–H1 169.4, Si2–Pt–H1 101.3, P2–Rh–P3 99.0(2), P2–Rh–P4 98.0(2), P2–Rh–Si2 100.8(2), P2–Rh–H1 96.1, P2–Rh–H2 166.5, P3–Rh–P4 101.0(2), P3–Rh–Si2 152.2(2), P3–Rh–H1 73.7, P3–Rh–H2 94.5, P4–Rh–Si2 95.4(2), P4–Rh–H1 165.6, P4–Rh–H2 79.1, Si2–Rh–H1 84.9, Si2–Rh–H2 66.6, H1–Rh–H2 87.9, Pt–Si2–Rh 77.4(1). **2** : Pt–Rh 2.945(3), Pt–P1 2.298(9), Pt–Si1 2.289(8), Pt–Si2 2.324(8), Rh–P2 2.346(8), Rh–P3 2.370(8), Rh–P4 2.255(8), Rh–Si2 2.378(8). P1–Pt–Si1 95.7(3), P1–Pt–Si2 169.6(3), Si1–Pt–Si2 92.6(3), P2–Rh–P3 98.9(3), P2–Rh–P4 97.7(3), P2–Pt–Si2 100.5(3), P3–Rh–P4 99.3(3), P3–Rh–Si2 153.7(3), P4–Rh–Si2 95.3(3), Pt–Si2–Rh 77.6(2). Although hydrogen atoms of Pt–H–Rh and Si–H–Rh bonds were not located in the final D-map, their existence was confirmed by the NMR spectra unequivocally.

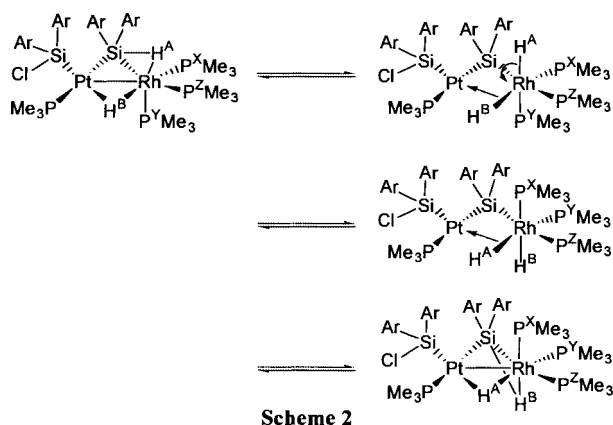
Figure 1 depicts the molecular structures of complexes **1** and **2** containing Rh and Pt centers bridged by hydrido and diarylsilyl ligands.<sup>9</sup> The Pt center is bonded also to ClSiAr<sub>2</sub> or HSiAr<sub>2</sub> ligand and a PMe<sub>3</sub> ligand, while the Rh center contains three PMe<sub>3</sub> ligands situated at facial coordination sites. The Rh–Si bonds longer (2.368(5) Å for **1**, 2.378(8) Å for **2**) than the Pt–Si bonds (2.323(4) Å for **1**, 2.324(8) Å for **2**) indicate the presence of a hydrogen atom close to Si and Rh to form a Rh–H–Si 3c-2e bond. The bond distances of Pt–Rh (2.934(2) Å for **1**, 2.945(3) Å for **2**) may suggest an elongated metal–metal bond in a Pt–H–Rh 3c-2e bond.

<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **1** and **2** are similar to each other, and provided detailed information on the structure of these complexes in solution. Figure 2 depicts the variable temperature <sup>1</sup>H NMR spectra of **2**. Two <sup>1</sup>H NMR signals of **2** are observed in the hydrido region (δ –7.47, –13.1) at –90 °C in CD<sub>2</sub>Cl<sub>2</sub>. The doublet (*J*(RhH) = 63 Hz) at δ –7.47 is flanked by the <sup>195</sup>Pt satellite signals (*J*(PtH) = 358 Hz), and the signal at a higher magnetic field (δ –13.1) appears as doublet (*J*(RhH) = 143 Hz). They are assigned to the hydrido ligand bonded to both Rh and Pt centers and to the hydrogen in the Rh–H–Si 3c-2e bond, respectively. On raising the temperature, the two hydrido signals coalesce to give a single broad doublet at δ –10.1, indicating exchange of the hydrogen atoms on the NMR time scale. The four signals of PMe<sub>3</sub> hydrogen atoms at –90 °C are also consistent with the molecular structure obtained from X-ray crystallography. At –30 °C, two of the three PMe<sub>3</sub> hydrogen signals bonded to Rh center



**Figure 2.** Variable temperature  $^1\text{H}$  NMR spectra of **2** in  $\text{CD}_2\text{Cl}_2$ . a)  $\text{PMe}_3$  and b) hydrido region.

undergo coalescence to give a sharp signal at  $\delta$  0.97. The above coalescence phenomena and those observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra indicate fast exchange of two  $\text{PMe}_3$  ligands. This exchange of hydrido and  $\text{PMe}_3$  ligands bonded to Rh is interpreted by assuming a mechanism involving rotation of two  $\text{PMe}_3$  ligands ( $\text{P}^X$ ,  $\text{P}^Y$ ) and two hydrogen atoms ( $\text{H}^A$ ,  $\text{H}^B$ ) around the axis of Si–Rh–P $^Z$  bond caused by cleavage of the Si–H interaction of the 3c–2e bond (Scheme 2). All the hydrogen signals of  $\text{PMe}_3$  bonded to Rh are observed as a very broad single peak at room temperature.



**Scheme 2**

These results indicate that the activation and formation of Si–H bond takes place at the Rh center only. It contrasts with the mechanism to account for the dynamic NMR spectra of  $[(\text{dippe})\text{Rh}]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-HSiR}_2)$  in which both Rh centers participate in Si–H bond activation and formation of the ligands.<sup>10</sup>

This study provided new Pt–Rh dinuclear complexes with bridging organosilyl ligands which formed the Si–Pt  $\sigma$ -bond and the Si–H–Rh 3c–2e bond. The unsymmetrical organosilyl ligand caused smooth and reversible dynamic motion of Si–H–Rh and Pt–H–Rh hydrogen atoms and three  $\text{PMe}_3$  ligands bonded to Rh center.

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

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

## References and Notes

- a) H. Tobita and H. Ogino, *Adv. Organomet. Chem.*, **42**, 223 (1998). b) J. -Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, **99**, 175 (1999).
- a) W. Malisch, H. -U. Weckel, I. Grob, and F. H. Köhler, *Z. Naturforsch.*, **37b**, 601 (1982). b) J. Powell, J. F. Sawyer, and M. Shiralian, *Organometallics*, **8**, 557 (1989). c) H. Sakaba, K. Ishida, and H. Horino, *Chem. Lett.*, **1998**, 149. See also: U. Bodensieck, P. Braunstein, W. Deck, T. Faure, M. Knorr, and C. Stern, *Angew. Chem., Int. Ed. Engl.*, **33**, 2440 (1994); P. Braunstein, T. Faure, and M. Knorr, *Organometallics*, **18**, 1791 (1999).
- Y. -J. Kim, S. -C. Lee, J. -I. Park, K. Osakada, M. Tanabe, J. -C. Choi, T. Koizumi, and T. Yamamoto, *Organometallics*, **18**, 1349 (1999).
- R. T. Price, R. A. Andersen, and E. L. Muetterties, *J. Organomet. Chem.*, **376**, 407 (1989). See: D. T. Thron and R. L. Harlow, *Inorg. Chem.*, **29**, 2017 (1990). G. P. Mitchell and T. D. Tilley, *Organometallics*, **17**, 2912 (1998).
- Data of **1**. Anal. Calcd (%) for  $\text{C}_{36}\text{H}_{55}\text{F}_4\text{P}_4\text{PtRhSi}_2 \cdot 0.5 \text{C}_7\text{H}_8$ : C, 43.61; H, 5.47; F, 6.99. Found: C 43.23, H 5.76, F 6.73.  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ ,  $-90^\circ\text{C}$ ):  $\delta$  = 7.89 (br, 2H,  $\text{C}_6\text{H}_4$ ), 7.76 (t, 2H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 7.67 (t, 2H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 7.08 (t, 2H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 7.00 (t, 2H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 6.79 (br, 2H,  $\text{C}_6\text{H}_4$ ), 6.60 (d, 4H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 4.47 (d, 1H, SiH,  $J(\text{PH})$  = 12 Hz,  $J(\text{PtH})$  = 151 Hz), 1.65 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 6 Hz), 1.51 (d, 9H, Pt– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 6 Hz), 1.39 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 7 Hz), 0.78 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 7 Hz),  $-7.69$  (d, 1H, Pt–H–Rh,  $J(\text{RhH})$  = 70 Hz,  $J(\text{PtH})$  = 356 Hz),  $-12.9$  (d, 1H, Si–H–Rh,  $J(\text{RhH})$  = 148 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{THF-d}_8$ ,  $-90^\circ\text{C}$ , referenced to 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  =  $-7.9$  (m, Rh–P,  $J(\text{RhP})$  = 115 Hz),  $-11.8$  (dt, Rh–P,  $J(\text{PP})$  = 31 Hz,  $J(\text{RhP})$  = 98 Hz),  $-15.6$  (apparent triplet, Pt–P,  $J(\text{PP})$  = 27 Hz,  $J(\text{PSi})$  = 118 Hz,  $J(\text{PtP})$  = 2220 Hz),  $-23.6$  (m, Rh–P,  $J(\text{RhP})$  = 90 Hz).
- A. J. Richard, M. R. Fernando, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, **1980**, 511.
- K. Osakada, S. Sarai, T. Koizumi, and T. Yamamoto, *Organometallics*, **16**, 3973 (1997).
- Data of **2**. Anal. Calcd. (%) for  $\text{C}_{36}\text{H}_{54}\text{ClF}_4\text{P}_4\text{PtRhSi}_2 \cdot 0.5 \text{C}_7\text{H}_8$ : C, 42.27; H, 5.21; Cl, 3.16; F, 6.77. Found: C, 43.04; H, 5.17; Cl, 3.03; F, 6.28.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-90^\circ\text{C}$ ):  $\delta$  = 7.75 (br, 2H,  $\text{C}_6\text{H}_4$ ), 6.95–6.89 (br, 6H,  $\text{C}_6\text{H}_4$ ), 6.81 (t, 2H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 6.60 (t, 6H,  $\text{C}_6\text{H}_4$ ,  $J$  = 7 Hz), 1.51 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 6 Hz), 1.33 (d, 9H, Pt– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 7 Hz), 1.21 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 6 Hz), 0.65 (d, 9H, Rh– $\text{P-CH}_3$ ,  $J(\text{PH})$  = 6 Hz),  $-7.47$  (d, 1H, Pt–H–Rh,  $J(\text{RhH})$  = 63 Hz,  $J(\text{PtH})$  = 358 Hz),  $-13.1$  (d, 1H, Si–H–Rh,  $J(\text{RhH})$  = 143 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-90^\circ\text{C}$ , referenced to 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  =  $-10.2$  (m, Rh–P,  $J(\text{RhP})$  = 137 Hz),  $-14.4$  (dt, Rh–P,  $J(\text{PP})$  = 31 Hz,  $J(\text{RhP})$  = 98 Hz),  $-17.0$  (apparent triplet, Pt–P,  $J(\text{PP})$  = 29 Hz,  $J(\text{PSi})$  = 136 Hz,  $J(\text{PtP})$  = 1995 Hz),  $-25.7$  (m, Rh–P,  $J(\text{RhP})$  = 90 Hz).
- Crystallographic data for **1**:  $\text{C}_{36}\text{H}_{55}\text{F}_4\text{P}_4\text{PtRhSi}_2$ ,  $M_r$  = 1041.89, triclinic, space group  $P\bar{1}$  (No. 2),  $a$  = 12.097(3) Å,  $b$  = 19.705(7) Å,  $c$  = 11.002(2) Å,  $\alpha$  = 98.25(2)°,  $\beta$  = 109.71(1)°,  $\gamma$  = 79.04(2)°,  $V$  = 2415(1) Å<sup>3</sup>,  $Z$  = 2,  $\mu(\text{Mo K}\alpha)$  = 3.441 mm<sup>-1</sup>,  $D_c$  = 1.433 g cm<sup>-3</sup>, 11105 unique reflections, 433 variables,  $R$  = 0.050,  $R_w$  = 0.073, for 6125 reflections with  $I > 3\sigma(I)$ . CCDC-162856. For **2**·THF:  $\text{C}_{36}\text{H}_{52}\text{ClF}_4\text{P}_4\text{PtRhSi}_2 \cdot \text{C}_4\text{H}_8\text{O}$ ,  $M_r$  = 1146.42, triclinic, space group  $P\bar{1}$  (No. 2),  $a$  = 12.189(5) Å,  $b$  = 18.547(8) Å,  $c$  = 11.536(4) Å,  $\alpha$  = 90.72(4)°,  $\beta$  = 104.31(3)°,  $\gamma$  = 94.63(4)°,  $V$  = 2517(2) Å<sup>3</sup>,  $Z$  = 2,  $\mu(\text{Mo K}\alpha)$  = 3.362 mm<sup>-1</sup>,  $D_c$  = 1.512 g cm<sup>-3</sup>, 9664 unique reflections, 487 variables,  $R$  = 0.060,  $R_w$  = 0.067, GOF = 1.67 for 2838 reflections with  $I > 3\sigma(I)$ . CCDC-162857.
- a) M. D. Fryzuk, L. Rosenberg, and S. J. Retting, *Organometallics*, **10**, 2537 (1991). b) M. D. Fryzuk, L. Rosenberg, and S. J. Retting, *Organometallics*, **15**, 2871 (1996).