

Available online at www.sciencedirect.com



Inorganica Chimica Acta 350 (2003) 201-208

www.elsevier.com/locate/ica

Chimica /

Inorganica

Rh-Pt heterobimetallic and diplatinum complexes with bridging silyl and silylene ligands

Makoto Tanabe, Kohtaro Osakada*

Chemical Resources Laboratory, Research Laboratory Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received 20 June 2002; accepted 2 October 2002

Dedicated in honor of Professor Pierre Braunstein

Abstract

Platinum complexes Pt(SiHAr₂)₂(PMe₃)₂ (Ar = C₆H₅, C₆H₄F-4) react with RhCl(PMe₃)₃ to afford Rh–Pt heterobimetallic complexes with bridging diarylsilyl and hydrido ligands, (Me₃P)(Ar₂ClSi)Pt(μ -H)(μ - η^2 -HSiAr₂)Rh(PMe₃)₃ (**1a**: Ar = C₆H₅, **1b**: Ar = C₆H₄F-4). The reaction is accompanied by the formation of small amounts of *fac*-RhH₂(SiClAr₂)(PMe₃)₃ (**2a**: Ar = C₆H₅, **2b**: Ar = C₆H₄F-4). X-ray crystallography of **1a** shows a square-planar coordination around Pt and an octahedral coordination around Rh. The diarylsilyl ligand is bridged unsymmetrically to the two metal centers via a Si–Pt σ -bond and a Rh–H–Si three-centers two-electrons bond (3c-2e bond). The ¹H and ³¹P{¹H} NMR spectra indicate exchange, on the NMR time scale, between the hydrido and Si–H hydrogen and PMe₃ ligands bonded to Rh. Crystallographic result of (Me₃P)₂Pt(μ -SiAr₂)RhH₂(SiClAr₂)(PMe₃)₂ (**3b**: Ar = C₆H₄F-4), which was obtained in a trace amount in a solution of **1b**, shows bridging diarylsilylene and hydrido ligands as well as a nonbridging hydrido ligand bonded to Rh. Heating of a mixture of Pt(SiH(C₆H₄F-4)₂)₂(PMe₃)₂ and PdMe₂(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) produces [Pt(μ -Si(C₆H₄F-4)₂)(dmpe)]₂ (**4b**) as an isolated product. The complex has a symmetrical structure with two bridging diarylsilylene ligands.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Bridging silyl ligands; Rhodium; Platinum; Heterobimetallic complexes; Dynamic behavior

1. Introduction

The bond of organosilyl ligands, such as SiH₂R and SiHR₂ groups, to transition metals has two possible coordination modes which involve M–Si σ -bonds and/ or M–H–Si three-centers two-electrons (3c-2e) bonds [1]. The organosilyl ligands stabilize bimetallic or multimetallic complexes by bridging two or more transition metal centers. A number of diplatinum [2–8] and dipalladium [9–11] complexes with bridging silyl and silylene ligands have been investigated by X-ray crystallography, NMR spectroscopy, and theoretical calculation [12]. Core structures of the reported complexes are classified into A–C shown in Scheme 1. Structure A with

0020-1693/03/\$ - see front matter 0 2003 Elsevier Science B.V. All rights reserved. doi:10.1016/S0020-1693(02)01572-4

two μ -silylene ligands is shaped as a rhombus with acute Si-Pt-Si angles (64.4–68.9°), no metal-metal bond (3.96–4.05 Å), and considerably short Si \cdots Si distances (2.55–2.72 Å) [3,7]. Structure **B** is composed of a Pt₂Si₂ four-membered ring with a short metal-metal distance (2.68–2.72 Å) and obtuse Si-Pt-Si angles (109.5–112.2°), which is due to the presence of the metal-metal bond [2,8]. The bridging coordination of Si atoms in **B**



Scheme 1.

^{*} Corresponding author. Tel.: +81-45-924 5224; fax: +81-45-924 5276.

E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

has two different M–Si distances. Structure C, which is similar to **B**, is formed by a dipalladium complex with two Pd–H–Si bonds and unsymmetrical coordination of the phosphine ligand to Pd [9]. Tessier reported crystal structures of the Pt₂Si₂ ring systems with two different bonding modes of bridging organosilyl ligands, $[(R_3P)_2Pt{\mu-SiH(Hex)}]_2$ and $\{(R_3P)Pt[\mu-\eta^2-HSi [Pt(PR_3)_2H](Hex)]\}_2$ (R = Et, Pr), formed from the reaction of $(R_3P)_3Pt$ with (Hex)SiH₃ [13]. Braddock-Wiliking found the conversion of $[(Ph_3P)Pt{\mu-\eta^2-HSi-}$ $H(IMP)\}]_2$ (IMP = 2-isopropyl-6-methylphenyl) with structure **B** to $[(PhMe_2P)_2Pt{\mu-SiH(IMP)}]_2$ with structure **A**, by replacement of PPh₃ with PhMe₂P [8a].

Bimetallic complexes with bridging organosilyl ligands are prepared by the intermolecular oxidative addition of the Si-H group-containing silyl ligand bonded to a transition metal to another low-valence transition metal (Scheme 2). Although much attention has been paid to the complexes containing the same two metal centers (M = M'), analogous heterobimetallic complexes bridged by organosilyl ligands $(M \neq M')$ have been reported only in limited numbers [14-18]. Powell reported that silvl-manganese complexes, $(OC)_5MnSiR_2H$ (R = Me, Ph, Cl), reacted with zerovalence platinum complexes, $Pt(H_2C=CH_2)(PPh_3)_2$ or Pt(PPh₃)₄, to give the Pt-Mn heterobimetallic complexes $(OC)_4Mn(\mu-SiR_2)(\mu-H)Pt(PPh_3)_2$ [15]. Sakaba studied a silylene- and hydrido-bridged Re-W heterobimetallic complex Cp*(CO)₂W(µ-SiMe₂)(µ-H)Re- $(CO)_2Cp^*$, which was prepared from the reaction of $Cp^{*}(CO)_{2}Re(H)SiMe_{2}H$ with $Cp^{*}W(CO)_{2}(NCMe)Me$ [16]. Photolysis of the complex produced a silenylbridged heterobimetallic complex Cp*(CO)₂HW(µ- η^1, η^2 -SiMeCH₂)ReH(CO)₂Cp*. Braunstein found that the amine-stabilized silvlene-iron complex, (OC)₄Fe= $Si(NMe_2)_2$ -NHMe₂, reacted with $Pt(H_2C=CH_2)(PR_3)_2$ (R = Ph, p-Tolyl) to form Fe–Pt heterobimetallic silylene complexes, $(OC)_4Fe\{\mu-Si(NMe_2)_2\}Pt(PR_3)_2$ [17]. They prepared a variety of heterodinuclear Fe-M (M = Pt, Pd, Ni) complexes with bridging trialkoxysilyl ligands which form four-membered Fe-Si-O-M rings via dative SiO-M bonds [18].

In this paper we report the preparation of Rh-Pt heterobimetallic complexes and a dinuclear Pt_2Si_2 complex from bis(silyl)platinum complexes with Si-H bonds. A part of this work was reported previously [19].



Scheme 2.

2. Results and discussion

2.1. Rh-Pt heterobimetallic complexes

Pt(SiHAr₂)₂(PMe₃)₂ reacts with RhCl(PMe₃)₃ at 50 °C for 24 h in toluene to give a mixture of Rh-Pt heterobimetallic complexes $(Me_3P)(Ar_2ClSi)Pt(\mu-H)(\mu-H)$ η^2 -HSiAr₂)Rh(PMe₃)₃ (1a: Ar = C₆H₅, 1b: Ar = C₆H₄F-4), and mononuclear rhodium complexes fac- $RhH_2(SiClAr_2)(PMe_3)_3$ [20] (2a: Ar = C₆H₅, 2b: Ar = C_6H_4F-4) (eq.1). Complexes **1a** and **1b** are isolated as crystals in 48 and 58% yields, respectively. The reaction mixture contains 2a and 2b that were identified by comparison of the NMR spectra with those reported for the complexes. Fig. 1 shows the molecular structure of 1a determined by X-ray crystallography. Compound 1a has a Rh-Pt heterobimetallic structure containing a diphenylsilyl ligand which forms a σ -bond with Pt and a 3c-2e bond with Rh. The structure is essentially the same as that of **1b** reported previously [19]. The Pt center is bonded to SiClPh₂ and PMe₃ ligands to form a squareplanar coordination. The Rh center contains distorted octahedral coordination with three PMe₃ ligands at facial coordination sites. Table 1 summarizes bond distances and angles of 1a and 1b. The Rh-Si2 bond distance (2.382(3) Å) of **1a**, which is longer than the Pt-Si2 bond (2.313(2) Å) and the Rh-Si bond distance of **2a** (2.314(2) Å) [20], is ascribed to a 3c-2e bond between the diarylsilyl ligand and Rh. The long Rh-Pt bond (2.949(2) Å) and T-shaped arrangement of two Si and P atoms around the Pt center indicate the presence of a bridging hydrido ligand, although the position of the hydrido was not determined by the crystallography. The NMR data, shown below, provided clear information on the coordination bonds of these hydrogen atoms.



Fig. 1. ORTEP drawing of **1a** with 50% thermal ellipsoids. Although hydrogen atoms of Pt–H–Rh and Si–H–Rh bonds were not located in the final Δ F-map, their existence was confirmed by the NMR spectra unequivocally. Hydrogen atoms and solvated hexane molecule are omitted for simplicity.

Table 1 Selected bond distances (Å) and angles (°) for **1a** and **1b**

	1a	1b ^a			
Bond distances (Å)					
Pt-Rh	2.949(2)	2.945(3)			
Pt-P1	2.318(3)	2.298(9)			
Pt-Si1	2.300(3)	2.289(8)			
Pt-Si2	2.313(2)	2.324(8)			
Rh-P2	2.353(4)	2.346(8)			
Rh-P3	2.372(3)	2.370(8)			
Rh-P4	2.266(3)	2.255(8)			
Rh-Si2	2.382(3)	2.378(8)			
Bond angles (°)					
Rh-Pt-P1	121.67(7)	120.8(3)			
Rh-Pt-Si1	142.02(7)	142.9(2)			
Rh-Pt-Si2	52.14(6)	52.0(2)			
P1-Pt-Si1	96.0(1)	95.7(3)			
P1-Pt-Si2	166.6(1)	169.6(3)			
Si1-Pt-Si2	91.97(9)	92.6(3)			
Pt-Rh-P2	100.92(8)	99.5(2)			
Pt-Rh-P3	107.72(9)	108.9(2)			
Pt-Rh-P4	143.40(7)	143.9(2)			
Pt-Rh-Si2	50.05(6)	50.4(2)			
P2-Rh-P3	100.3(1)	98.9(3)			
P2-Rh-P4	97.9(1)	97.7(3)			
P2-Rh-Si2	101.5(1)	100.5(3)			
P3-Rh-P4	99.4(1)	99.3(3)			
P3-Rh-Si2	151.6(1)	153.7(3)			
P4-Rh-Si2	95.57(9)	95.3(3)			
Pt-Si2-Rh	77.82(8)	77.6(2)			

^a Data of 1b were taken from ref. [19].



Fig. 2 shows ¹H and ³¹P{¹H} NMR spectra of 1a from -90 to 25 °C. The ¹H NMR spectrum of **1a** at -90 °C in CD₂Cl₂ exhibits the presence of two unequivalent hydrogens bonded to the metal centers (Fig. 2(a)). The signal at δ -7.55, showing coupling with ¹⁹⁵Pt (J(HPt) = 362 Hz) and ¹⁰³Rh nuclei (J(HRh) = 68 Hz), is ascribed to the hydrido ligand bridged to Pt and Rh. The signal at a higher magnetic field (δ -13.12) appears as a doublet due to Rh-H coupling (J(HRh) = 143 Hz)and is assigned to the hydrogen included in the Rh-H-Si 3c-2e bond. The ${}^{31}P{}^{1}H$ NMR spectrum at $-90 \degree C$ contains three signals of PMe₃ ligands bonded to the Rh center at δ -28.07, -14.23, and -10.48 and a signal of PMe₃ bonded to the Pt center (δ -17.79) (Fig. 2(b)). The last signal accompanies the ¹⁹⁵Pt satellite signals (J(PPt) = 1947 Hz). Raising the temperature of the

(a)



Fig. 2. Variable temperature (a) 1 H NMR spectra in hydrido region and (b) 31 P{ 1 H} NMR spectra of **1a** in CD₂Cl₂ between -90 and 25 °C.

solution causes changes of the ¹H and ³¹P{¹H} NMR spectra due to exchange of the ligand on the NMR time scale. The ¹H NMR signals of the two hydrido ligands are broadened at -50 °C and undergo coalescence at -10 °C or below. At 25 °C, the signal shows splitting probably due to Rh–H coupling. The ³¹P{¹H} NMR spectra between -90 and -50 °C show coalescence of the two signals that are observed at δ -14.23 and -10.48 at -90 °C. A lower coalescence temperature of the ³¹P{¹H} NMR signals than that of the ¹H NMR signals suggests that they are attributed to the same dynamic behavior of the molecule.

The change of the ¹H and ³¹P{¹H} NMR spectra between -90 and -10 °C indicates a fast exchange process of two of the three PMe₃ ligands and of the two bridging hydrido ligands and a slower exchange of the remaining PMe₃ ligand with the two PMe₃ ligands. Scheme 3 depicts a plausible mechanism of exchange of the hydrido and PMe₃ ligands bonded to Rh. The cleavage of the Si-H^A and Pt-H^B bonds of structure **A** forms the intermediate **B** with two hydrido ligands around the Rh center (i). Rotation of two PMe₃ ligands (P^X, P^Y) and of two hydrogen atoms (H^A, H^B) around



Scheme 3.

the axis of the Si-Rh-P^Z bond (ii), followed by formation of new Si-H^B and Pt-H^A bonds, leads to A' (iii). The ³¹P{¹H} NMR spectra at 25 °C show broadening of the signals at δ -31.2 and -14.4, indicating exchange of P^Z with P^X and P^Y via a pathway other than that in Scheme 3. No broadening of the ³¹P{¹H} NMR signal of the PMe₃ ligand bonded to Pt in this temperature range indicates that the activation and formation of the Si-H bond take place only at the Rh center. It contrasts with the mechanism of the dynamic behavior of {(dippe)Rh}₂(µ-H)(µ-η²-HSiR₂) (dippe = 1,2-bis(diisopropylphosphino)ethane), in which both of the Rh centers participate in Si-H bond activation and formation of the ligands [21].

Leaving a toluene-hexane solution of **1b** at -20 °C for several days caused separation of yellow crystals of $(Me_3P)_2Pt{\mu-Si(C_6H_4F-4)_2}RhH_2{SiCl(C_6H_4F-4)_2} (PMe_3)_2$ (3b) which is an isomer of 1b (eq. 2). The molecular structure was determined by X-ray crystallography, as shown in Fig. 3, although an extremely low yield of the complex prevented its full characterization by spectroscopy and elemental analysis. Table 2 summarizes selected bond distances and angles. The Rh-Si2 bond distance (2.326(2) Å) of **3b** is shorter than the Pt-Si2 bond (2.359(1) Å) and Rh–Si2 bond distances of the Rh-H-Si 3c-2e bonds of 1a (2.382(3) Å) and 1b (2.378(8) Å), indicating that the Rh and Si atoms form a σ -bond. The Pt center is bonded to the bridging diarylsilylene ligand and two PMe₃ ligands to form a Tshaped coordination. The Pt-H-Rh hydrido ligand is located at the Pt-H distance of 2.19 Å and the Rh-H distance of 1.40 Å. The hydrido bound to Rh seems to coordinate weakly at the vacant site of the Pt center. The Rh center has a distorted octahedral coordination with two hydrido and two PMe₃ ligands situated at mutually



Fig. 3. ORTEP drawing of **3b** with 50% thermal ellipsoids. Positions of the hydrido were determined by final Δ F-map and were not refined further. Other hydrogen atoms and solvated hexane molecule are omitted for simplicity.

Table 2 Selected bond distances (Å) and angles (°) for 3b

Bond distances (Å)		
Pt-Rh	2.9882(4)	
Pt-P1	2.256(2)	
Pt-P2	2.343(2)	
Pt-Si2	2.359(1)	
Rh-P3	2.354(2)	
Rh–P4	2.343(2)	
Rh-Si1	2.302(1)	
Rh-Si2	2.326(2)	
Rh-H1	1.40	
Rh-H2	1.42	
Bond angles (°)		
Rh-Pt1-P1	143.47(4)	
Rh-Pt-P2	117.84(5)	
Rh-Pt-Si2	49.88(4)	
P1-Pt-P2	98.40(6)	
P1-Pt-Si2	93.81(5)	
P2-Pt-Si2	167.72(6)	
Pt-Rh-P3	112.16(4)	
Pt-Rh-P4	96.23(4)	
Pt-Rh-Si1	145.88(5)	
Pt-Rh-Si2	50.87(3)	
P3-Rh-P4	98.31(7)	
P3-Rh-Si1	96.35(6)	
P3-Rh-Si2	156.29(6)	
P4-Rh-Si1	97.81(6)	
P4-Rh-Si2	99.95(6)	
Si1-Rh-Si2	96.00(6)	
Pt-Si2-Rh	79.25(5)	
		-

cis positions and with a nonbridging SiClAr₂ ligand at the cis position of the μ -silylene ligand. The Rh-Pt bond distance of **3b** (2.9882(4) Å) is slightly longer than those of **1a** and **1b** (2.949(2), 2.945(3) Å).



The silyl ligand transfer from Pt to Rh and transfer of a PMe₃ ligand from Rh to Pt take place during the isomerization of **1b** to **3b**. Analogous intramolecular migration of the trialkoxysilyl group from iron to platinum in heterobimetallic systems, $(OC)_3(R_3Si)Fe(\mu-PPh_2)Pt(PPh_3)_2$, has been promoted by external nucleophilic substitution by CO or isonitrile [22]. The structure of **3b** determined by X-ray crystallography is similar to those of the intermediates in Scheme 3, **B** and **B'**, having dihydrido ligands on the Rh center and with a μ -silylene ligand.

2.2. Diplatinum complex

The reaction of $Pt(SiHAr_2)_2(PMe_3)_2$ (Ar = C₆H₄F-4) with $PdMe_2(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) for 5 h at 80 °C does not give a heterobimetallic complex but produces [Pt(dmpe)(µ-SiAr₂)]₂ (4b) with bridging diarylsilylene ligands (21% after recrystallization) (eq. 3). The reaction is accompanied by the deposition of metallic palladium as a black solid. Fig. 4 depicts the molecular structure determined by Xray crystallography. Complex 4b has a planar diamondshaped Pt₂Si₂ core with the phenyl substituents orientated almost perpendicularly. The selected bond distances and angles are compared with those of the complexes with a similar structure in Table 3. The Si···Si distance of **4b** (2.729(5) Å) is longer than the upper range of Si-Si single bond distances (2.33-2.70 Å) and the reported Si \cdots Si distances of similar Pt₂Si₂ four-membered rings (2.55-2.72 Å) [3,7,13]. The Pt···Pt



Fig. 4. ORTEP drawing of **4b** with 50% thermal ellipsoids. Atoms with asterisks are crystallographically equivalent to those with the same number without asterisks. Hydrogen atoms are omitted for simplicity.

Table 3 Selected bond distances (Å) and angles (°) for 4b and related

compounds

	4b	$[Pt{\mu-SiH(IMP)}-(Me_3P)_2]_2^{a}$	$\begin{array}{l} [Pt\{\mu\text{-SiH}(Hex)\}\text{-} \\ (Pr_{3}P)_{2}]_{2}^{\ b} \end{array}$	
Bond distanc	es (Å)			
Pt-P1	2.312(3)	2.3215(13), 2.3164(13)	2.313(6)-2.333(6)	
Pt-P2	2.304(3)			
Pt-Si	2.387(2)	2.4054(12), 2.4087(12)	2.374(6)-2.408(6)	
Pt-Si*	2.390(3)			
Pt···Pt*	3.921(1)	4.004	3.984(2), 4.005(2)	
Si⊷Si*	2.729(5)	2.673(2)	2.598(8), 2.612(8)	
Bond angles (°)				
P1-Pt-P2	84.9(1)	104.24(5)	105.7(2)-107.1(2)	
Si-Pt-Si	69.7(1)	67.46(5)	65.7(2)-66.6(2)	
Pt-Si-Pt	110.3(1)	112.54(5)	112.6(2)-113.7(3)	
P1-Pt-Si	106.3(1)	04.04(4) 04.67(4)		
P2-Pt-Si*	100.6(1)	94.34(4), 94.67(4)		
P1-Pt-Si*	166.4(1)	1(0,44(4), 1(0,50(5))		
P2-Pt-Si	167.4(1)	160.44(4), 160.59(5)		

^a Data taken from Ref. [7].

^b Data taken from Ref. [13].

nonbonding distance (3.921(1) Å) of **4b** is shorter than distances (3.96–4.05 Å) of the planar Pt_2Si_2 core. The acute Si–Pt–Si (69.7(1)°) and obtuse Pt–Si–Pt (110.3(1)°) angles of **4b** are not within the range of the angles (64.4–68.9° for Si–Pt–Si, 111.1–115.5° for Pt–Si–Pt) of the reported complexes.



The ${}^{31}P{}^{1}H{}$ NMR spectrum of **4b** shows an AA'XX' spin system, as depicted in Fig. 5. Recently, Braddock-Wilking reported the relationship of the ${}^{1}J(PPt)$ value of $[Pt(Ph_nMe_{3-n}P)_2{\mu-SiH(IMP)}]_2$ (n = 0-2) to the basicity and steric requirements of the phosphine ligands [7]. A higher basicity and smaller cone angle of the phosphine decreases the ${}^{1}J(PPt)$ value. The ${}^{1}J(PPt)$ value of 4b (1243 Hz) is much smaller than those of $[Pt(Ph_nMe_{3-n}P)_2{\mu-SiH(IMP)}]_2$ (1693–1793 Hz) due to the high basicity and the small P-Pt-P angle $(84.9(1)^{\circ})$ of **4b**. Simple heating of Pt(SiHPh₂)₂(PMe₃)₂ in the absence of a Pd complex provided a triplatinum complex with μ -silvlene ligands [Pt(μ -SiPh₂)(PMe₃)]₃ [23]. In reaction (3), liberation of the phosphine ligand by decomposition of the Pd complex may cause exchange of PMe₃ with a dmpe ligand to produce Pt(SiHAr₂)₂(dmpe) followed by formation of diplatinum complex 4b. Fink suggested that the Pt₂Si₂ ring complex $[Pt(\mu-SiHR)_2(dcpe)]_2$ (R = H, Me) (dcpe = 1,2-



Fig. 5. ${}^{31}P{}^{1}H$ NMR spectrum of **4b** in C₆D₆ at 25 °C.

bis(dicyclohexylphosphino)ethane) was obtained from the reaction of $PtH_2(dcpe)$ with disilane $H_2RSiSiRH_2$ via the bis(silyl)platinum as intermediates [5]. The formation of di- or tri-platinum complexes with organosilyl ligands depends on the auxiliary ligands.

3. Summary

In this study, we presented the preparation and structures of the new Rh–Pt heterobimetallic complexes and the diplatinum complex with bridging diarylsilyl or diarylsilylene groups. The unsymmetrical coordination of the diarylsilyl ligand to Rh and Pt via a 3c-2e bond shows the unique dynamic behavior of the complexes. The diplatinum complex has stable coordination bonds between the diarylsilylene ligand and Pt centers.

4. Experimental

4.1. General

All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Hexane, toluene, and THF were distilled from sodium–benzophenone and stored under nitrogen. NMR spectra (¹H, ¹³C{¹H}, and ³¹P{¹H}) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. Pt(SiHAr₂)₂(PMe₃)₂ [24], RhCl(PMe₃)₃ [25], and PdMe₂(dmpe) [26] were prepared according to the literature method. Peak position of the ³¹P{¹H} NMR spectra was referenced to an external 85% H₃PO₄. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

4.2. Preparation of the complex

4.2.1. Preparation of 1a and 1b

To a toluene (5 ml) solution of RhCl(PMe₃)₃ (282 mg, 0.77 mmol) was added $Pt(SiHPh_2)_2(PMe_3)_2$ (494 mg, 0.69 mmol) at room temperature (r.t.). The solution was heated at 50 °C for 24 h, which caused change of the color from yellow to red accompanied by separation of a pale yellow solid. The solid product was collected by filtration and washed with hexane. Recrystallization from toluene-hexane affords 1a as pale yellow crystals (242 mg, 48% based on Pt complex). The filtrate was pumped off and the yellow residue was washed with hexane. The mononuclear Rh complex 2a was obtained by recrystallization from toluene-hexane (11 mg, 5%) based on Rh complex). The ¹H and ³¹P{¹H} NMR spectra of the crystal were accorded with those of Rh complex fac-RhH₂(SiPh₂Cl)(PMe₃)₃. Complex 1b was prepared similarly (58%). Complex 2b was found in the NMR spectra of the reaction mixture but not isolated. Data for 1a. Anal. Calc. for C₃₆H₅₈ClP₄PtRhSi₂: C, 43.05; H, 5.82; Cl, 3.53. Found: C, 43.39; H, 5.88; Cl, 3.29%. ¹H NMR (CD₂Cl₂, 400 MHz, r.t.): δ -10.27 (br, 2H, Rh-H-Si and Pt-H-Rh), 1.13 (br, 27H, RhP Me_3), 1.43 (d, 9H, PtP Me_3 , J(HP) = 8 Hz, J(HPt) = 28 Hz, 6.98 (m, 6H, C₆H₅-m and p), 7.14-7.19 (C_6H_5 -m and p, overlapped with solvent signal), 7.64 (m, 4H, C_6H_5-o), 8.02 (d, 4H, C_6H_5-o). ¹H NMR $(CD_2Cl_2, 400 \text{ MHz}, -90 \degree \text{C}): \delta -13.12 \text{ (d, 1H, Si}-H-$ Rh, J(HRh) = 143 Hz), -7.55 (d, 1H, Pt-H-Rh, J(HP) = 68 Hz, J(HPt) = 362 Hz), 0.63 (d, 9H, $RhPMe_3$, J(HP) = 7 Hz), 1.21 (d, 9H, $RhPMe_3$, J(HP) = 7 Hz), 1.33 (d, 9H, PtP Me_3 , J(HP) = 6 Hz), 1.51 (d, 9H, RhP Me_3 , J(HP) = 6 Hz), 6.9–7.1 (m, 16H, C_6H_5), 7.32 (br, 2H, C_6H_5-o), 7.78 (br, 2H, C_6H_5-o). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, r.t.): δ -31.2 (br, RhP), -19.00 (s, PtP, J(PPt) = 2017 Hz), -14.4 (br, Rh*P*). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, $-90 \degree$ C): δ -28.07 (m, RhP, J(PRh) = 90 Hz), -17.79 (apparent triplet, PtP, J(PP) = 12 Hz, J(PSi) = 109 Hz, J(PPt) =1947 Hz), -14.23 (dt, RhP, J(PP) = 31 Hz, J(PRh) =98 Hz), -10.48 (m, RhP, J(PRh) = 156 Hz). Data for **1b.** Anal. Calc. for $C_{36}H_{54}ClF_4P_4PtRhSi_2 \cdot 1/2$ toluene: 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%. ¹H NMR (CD₂Cl₂, 400 MHz, r.t.): $\delta -10.32$ (br, 2H, Rh-H-Si and Pt-H-Rh), 0.75 $(br, 27H, RhPMe_3), 1.36 (d, 9H, PtPMe_3, J(HP) = 8 Hz,$ J(HPt) = 28 Hz), 6.57 (t, 4H, C₆H₄F-m, J = 10 Hz), 6.74 (t, 4H, C_6H_4F -m, J = 10 Hz), 7.00 (m, 4H, C_6H_4F o, J = 7 Hz), 7.57 (m, 4H, C₆H₄F-o, J = 7 Hz). ¹H NMR (400 MHz, CD₂Cl₂, -90 °C): $\delta = -13.13$ (d, 1H, Si-H-Rh, J(HRh) = 143 Hz), -7.47 (d, 1H, Pt-H-Rh, J(HRh) = 63 Hz, J(HPt) = 358 Hz), 0.65 (d, 9H, $RhPMe_3$, J(HP) = 6 Hz), 1.21 (d, 9H, $RhPMe_3$, J(HP) = 6 Hz), 1.33 (d, 9H, PtPMe₃, J(HP) = 7 Hz), 1.51 (d, 9H, RhP Me_3 , J(HP) = 6 Hz), 6.60 (t, 6H,

Table 4 Crystal data and details of structure refinement of complexes 1a, 3b, and 4b

	1a·1/2 Hexane	3b · 1/2 Hexane	4b
Chemical formula	C ₃₉ H ₆₅ ClP ₄ PtRhSi ₂	C ₃₉ H ₆₁ ClF ₄ P ₄ PtRhSi ₂	$C_{36}H_{48}F_4P_4Pt_2Si_2$
Formula weight	1045.44	1119.42	1127.02
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> 1 (No. 2)	$P2_1/n$ (No.14)	<i>P</i> 1 (No. 2)
a (Å)	12.106(3)	16.2204(5)	11.465(2)
b (Å)	9.830(3)	22.6095(7)	11.693(3)
c (Å)	10.246(9)	12.7902(3)	9.223(2)
α (°)	96.86(3)		112.13(2)
β (°)	109.06(4)	90.221(2)	104.24(2)
γ (°)	89.51(2)		65.49(1)
V (Å ³)	2307(2)	4690.6(2)	1036.2(4)
Ζ	2	4	1
μ (Mo K α) (mm ⁻¹)	3.647	3.605	6.971
F(000)	1054	2236	544
$D_{\rm calc} ({\rm g \ cm^{-3}})$	1.508	1.585	1.806
Crystal size (mm)	$0.10 \times 0.22 \times 0.22$	$0.50\times0.61\times0.69$	$0.16 \times 0.16 \times 0.32$
2θ Range (°)	5.0-55.0	5.0-55.0	5.0-55.0
Index ranges	$-15 \le h \le 15, -25 \le k \le 0, -13 \le l \le 13$	$0 \le h \le 21, 0 \le k \le 28, -15 \le l \le 16$	$0 \le h \le 14, -13 \le k \le 15, -11 \le l \le 11$
Unique reflections	10 589	10 104	4995
Used reflections	6357	8234	3919
$[I > 3\sigma(I)]$			
Variables	433	454	241
$R(F_{\rm o})^{\rm a}$	0.045	0.037	0.057
$R_{\rm w}(F_{\rm o})^{\rm a}$	0.039	0.054	0.078

^a $R = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|, R_{w} = [\Sigma w |F_{o} - F_{c}|^{2} / \Sigma w |F_{o}|^{2}]^{1/2}.$

C₆*H*₄F, *J* = 7 Hz), 6.81 (t, 2H, C₆*H*₄F, *J* = 7 Hz), 6.89– 6.95 (br, 6H, C₆*H*₄F), 7.75 (br, 2H, C₆*H*₄F). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, r.t.): δ -30.8 (br, Rh*P*), -19.05 (s, Pt*P*, *J*(PtP) = 2013 Hz,), -14.6 (br, Rh*P*). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, -90 °C): δ = -25.74 (m, Rh*P*, *J*(PRh) = 90 Hz), -17.07 (apparent triplet, Pt*P*, *J*(PP) = 29 Hz, *J*(PSi) = 136 Hz, *J*(PPt) = 1995 Hz), -14.45 (dt, Rh*P*, *J*(PRh) = 137 Hz).

4.2.2. Crystallization of 3b

After recrystallization of **1b** in toluene–hexane solution under argon, the filtrate was stored in freezer (ca. -20 °C) for several days to produce **3b** as a trace amount of yellow crystals. Although the crystal structure was determined by X-ray crystallography, the detail information such as spectroscopy and elemental analysis could not be collected.

4.2.3. Preparation of 4b

To a toluene (10 ml) solution of $Pt{SiH(C_6H_4F-4)_2}_2(PMe_3)_2$ (489 mg, 0.62 mmol) was added $PdMe_2(dmpe)$ (178 mg, 0.62 mmol). After stirring the solution for 5 h at 80 °C, the solvent was removed under reduced pressure. Addition of hexane to the residue caused separation of a yellow solid, which was collected by filtration, washed with hexane, and dried in vacuo. Recrystallization from toluene–hexane gives **4b** (72 mg, 21%) as pale yellow crystals. ¹H NMR (400 MHz, C₆D₆,

r.t.): δ 0.74 (d, 32H, CH₃PCH₂, J(HP) = 7 Hz. The methyl and methylene signals are overlapped), 6.95 (t, 8H, C₆H₄F-*m*, J = 8.8 Hz), 7.80 (m, 8H, C₆H₄F-*o*). ³¹P{¹H} NMR (162 MHz, C₆D₆, r.t.): δ 38.59 (⁴J(PP) = 27.3 Hz, ³J(PPt) = 211 Hz, J(PPt) = 1243 Hz).

4.3. Crystal structure determination

Crystals of 1a, 3b, and 4b suitable for X-ray diffraction study were mounted in glass capillaries under argon. Data of 1a and 4b were collected at 23 °C on Rigaku AFC-5R automated four-circle diffractometer equipped with monochromated Mo K α radiation ($\lambda =$ 0.71073 Å). Intensities were collected for Lorentz and by using diffractometer and $\omega - 2\theta$ scan methods, and an empirical absorption correction (ψ -scan) was applied. The intensities of the three standard reflections, measured every 150 reflections, were monitored throughout the data collection. Data of **3b** were collected at $-60 \degree C$ on Rigaku RAXIS IV imaging plate area detector with Mo Ka radiation. Calculations were carried out by using a program package TEXSAN or CrystalStructure[™] for Windows. The structures were solved by a Patterson method and subsequent Fourier technique. A fullmatrix least-squares refinement was used for the nonhydrogen atoms with anisotropic thermal parameters. Hydrogen atoms except for the RhH hydrogens of 3b were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Position of the RhH hydrogens were determined by difference Fourier map and were not refined further. Crystallographic data and details of refinement are summarized in Table 4.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 186891, 186892, and 186893 for **1a**, **3b**, and **4b**, 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 www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan and from Japan Society for the Promotion of Science (JSPS). We thank Professor Munetaka Akita at the Tokyo Institute of Technology for X-ray measurement using imaging plate area detector. M.T. is grateful for the fellowship from JSPS.

References

- (a) U. Schubert, Adv. Organomet. Chem. 30 (1990) 151;
 (b) P. Braunstein, M. Knorr, J. Organomet. Chem. 500 (1995) 21;
 (c) H. Tobita, H. Ogino, Adv. Organomet. Chem. 42 (1998) 223;
 (d) J.-Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175;
 (e) P. Braunstein, N.M. Boag, Angew. Chem., Int. Ed. 40 (2001) 2427.
- [2] M. Auburn, M. Ciriano, J.A.K. Howard, M. Murray, N.J. Pugh, J.L. Spencer, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. (1980) 659.
- [3] (a) E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, J. Am. Chem. Soc. 110 (1988) 4068;
 (b) E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, J. Chem.
- Soc., Chem. Commun. (1989) 577.[4] R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 1917.
- [5] M.J. Michalczyk, C.A. Recatto, J.C. Calabrese, M.J. Fink, J. Am.
- Chem. Soc. 114 (1992) 7955.
 [6] S. Shimada, M. Tanaka, K. Honda, J. Am. Chem. Soc. 117 (1995) 8289
- [7] J. Braddock-Wilking, Y. Levchinsky, N.P. Rath, Organometallics 20 (2001) 474.

- [8] (a) Y. Levchinsky, N.P. Rath, J. Braddock-Wilking, Organometallics 18 (1999) 2583;
 (b) J. Braddock-Wilking, Y. Levchinsky, N.P. Rath, Organometallics 19 (2000) 5500.
- [9] (a) Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, T. Yamamoto, Organometallics 17 (1998) 4929;
 (b) Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, T. Yamamoto, J. Chem. Soc., Dalton Trans. (2000) 417.
- [10] A. Fürstner, H. Krause, C.W. Lehmann, Chem. Commun. (2001) 2372.
- [11] W. Chen, S. Shimada, M. Tanaka, Science 295 (2002) 308.
- [12] (a) A.B. Anderson, P. Shiller, E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, Organometallics 8 (1989) 2320;
 (b) G. Aullón, P. Alemany, S. Alvarez, J. Organomet. Chem. 478 (1994) 75;
 (c) S.-H. Choi, Z. Lin, J. Organomet. Chem. 608 (2000) 42;
 (d) S. Sakaki, S. Yamaguchi, Y. Musashi, M. Sugimoto, J. Organomet. Chem. 635 (2001) 173.
- [13] L.M. Sanow, M. Chai, D.B. McConnville, K.J. Galat, R.S. Simons, P.L. Rinaldi, W.J. Youngs, C.A. Tessier, Organometallics 19 (2000) 192.
- [14] W. Malisch, H.-U. Weckel, I. Grob, F.H. Köhler, Z. Naturforsch., B 37 (1982) 601.
- [15] J. Powell, J.F. Sawyer, M. Shiralian, Organometallics 8 (1989) 557.
- [16] H. Sakaba, K. Ishida, H. Horino, Chem. Lett. (1998) 149.
- [17] U. Bodensieck, P. Braunstein, W. Deck, T. Faure, M. Knorr, C. Stern, Angew. Chem., Int. Ed. Engl. 33 (1994) 2440.
- [18] (a) M. Knorr, C. Strohmann, P. Braunstein, Organometallics 15 (1996) 5653;
 - (b) P. Braunstein, X. Morise, Organometallics 17 (1998) 540;
 (c) P. Braunstein, J. Durand, X. Morise, A. Tiripicchio, F. Ugozzoli, Organometallics 19 (2000) 444;
 (d) P. Braunstein, J. Durand, M. Knorr, C. Strohmann, Chem. Commun. (2001) 211.;
 (e) P. Braunstein, G. Clerc, X. Morise, Organometallics 20 (2001) 5036.
- [19] M. Tanabe, K. Osakada, Chem. Lett. (2001) 962.
- [20] K. Osakada, S. Sarai, T. Koizumi, T. Yamamoto, Organometallics 16 (1997) 3973.
- [21] (a) M.D. Fryzuk, L. Rosenberg, S.J. Retting, Organometallics 10 (1991) 2537;
 (b) M.D. Fryzuk, L. Rosenberg, S.J. Retting, Organometallics 15 (1996) 2871.
 [22] (a) P. Braunstein, M. Knorr, B. Hirle, G. Reinhard, U. Schubert,
- Angew. Chem., Int. Ed. Engl. 31 (1992) 1583;
 (b) P. Braunstein, M. Knorr, G. Reinhard, U. Schubert, T. Stährfeldt, Chem. Eur. J. 6 (2000) 4265.
- [23] K. Osakada, M. Tanabe, T. Tanase, Angew. Chem., Ind. Ed. 39 (2000) 4053.
- [24] Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, M. Tanabe, J.-C. Choi, T. Koizumi, T. Yamamoto, Organometallics 18 (1999) 1349.
- [25] R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans. (1980) 511.
- [26] W. Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. Koten, Organometallics 8 (1989) 2907.