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Intermolecular Transfer of Triarylsilane from $RhCl(H)(SiAr_3)[P(i\text{-}Pr)_3]_2$ to a Platinum(0) Complex, Giving *cis*-$PtH(SiAr_3)(PEt_3)_2$ (Ar = C_6H_5, C_6H_4F-*p*, C_6H_4Cl-*p*)

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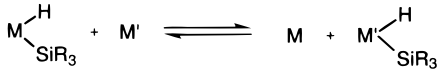
Summary: Chlorohydrido(triarylsilyl)rhodium(III) complexes $RhCl(H)(SiAr_3)[P(i\text{-}Pr)_3]_2$ (**1a**, *Ar* = C_6H_5; **1b**, *Ar* = C_6H_4F-*p*; **1c**, *Ar* = C_6H_4Cl-*p*) *react with* $Pt(PEt_3)_4$ *to give mixtures of cis*-$PtH(SiAr_3)(PEt_3)_2$ (**2a**, *Ar* = C_6H_5; **2b**, *Ar* = C_6H_4F-*p*; **2c**, C_6H_4Cl-*p*) *and* $RhCl(PEt_3)_3$. *Complexes* **2a−c** *have been characterized by X-ray crystallography and/or NMR spectroscopy.*

Introduction

Oxidative addition of an Si−H bond to low-valent transition-metal complexes, including Pt(0) complexes, provides a general synthetic route to silyl complexes of these metals and is involved in transition-metal-complex-catalyzed hydrosilation of alkenes and dehydrocoupling of organosilanes as a crucial step.[1,2] The oxidative addition of organosilanes and their reductive elimination from silyl(hydrido)metal complexes are generally accepted to be reversible and to involve silane-coordinated metal complexes as the common intermediate.[3−5] However, direct observation of reversible oxidative addition and reductive elimination of the Si−H bond is rare, probably due to the high stability of M−Si bond. Recently we observed the reaction of $Rh(SPh)(PMe_3)_3$ with $HSiAr_3$ to give an equilibrated mixture of $Rh(SPh)(PMe_3)_3$ and $Rh(H)(SiAr_3)(SPh)(PMe_3)_3$.[6] Deuterium labeling experiments of the reaction of $RhCl(H)(SiHAr_2)(PMe_3)_3$ with diarylsilane have revealed exchange of the organosilane and silyl and hydrido ligands through rapid and reversible reductive elimination and oxidative addition, shown in Scheme 1.[7]

Scheme 1

Scheme 2



Another conceptually possible *productive* reductive-elimination and oxidative-addition process of the Si−H bond could be achieved by a reaction of a hydridosilylmetal complex with a complex having a different metal center to cause transfer of both hydrido and silyl groups from one metal center to the other, as depicted in Scheme 2.

In this paper, we report the reaction of hydrido(triarylsilyl)rhodium(III) complexes with $Pt(PEt_3)_4$ to lead to formation of a $PtH(SiAr_3)(PEt_3)_2$ type complex through intermolecular exchange of the ligands.

Results and Discussion

Equimolar reactions of $RhCl(H)(SiAr_3)[P(i\text{-}Pr)_3]_2$ (**1a**, Ar = C_6H_5; **1b**, Ar = C_6H_4F-*p*; **1c**, Ar = C_6H_4Cl-*p*) with $Pt(PEt_3)_4$ in pentane for 1 h at room temperature gives $PtH(SiAr_3)(PEt_3)_2$ (**2a**, Ar = C_6H_5; **2b**, Ar = C_6H_4F-*p*; **2c**, Ar = C_6H_4Cl-*p*), which is separated as a colorless solid from the resulting solution and further purified by recrystallization from a toluene−pentane mixture.

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1997.

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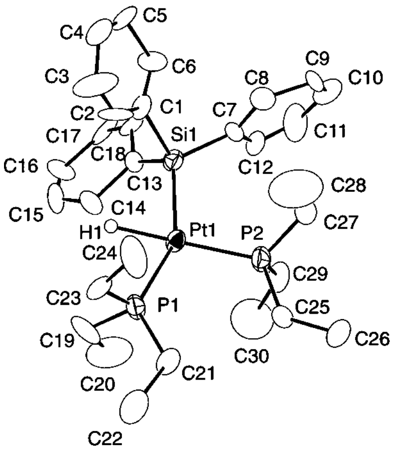
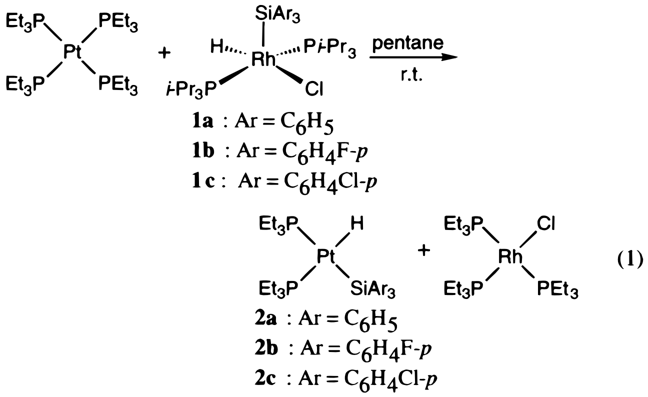


Figure 1. ORTEP drawing of $PtH(SiPh_3)(PEt_3)_2$ (**2a**) at the 50% ellipsoid level. Hydrogen atoms, except for the PtH hydrogen, are omitted for simplicity. Selected bond distances (Å) and angles (deg): Pt1−P1, 2.335(3); Pt1−P2, 2.304(3); Pt1−Si1, 2.357(3); Pt−H1, 1.75; P1−Pt1−P2, 107.2(1); P1−Pt1−Si1, 150.7(1); P2−Pt1−Si1, 102.0(1); P1−Pt1−H1, 73.1; P2−Pt1−H1, 179; Si1−Pt1−H1, 78.



1a : Ar = C_6H_5
1b : Ar = C_6H_4F-*p*
1c : Ar = C_6H_4Cl-*p*

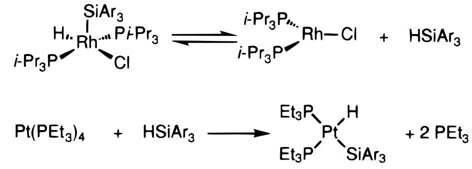
(1)

2a : Ar = C_6H_5
2b : Ar = C_6H_4F-*p*
2c : Ar = C_6H_4Cl-*p*

The NMR spectra of the reaction mixtures show the presence of $RhCl(PEt_3)_3$ as the major Rh-containing product, whereas other several Rh complexes possibly with $P(i\text{-}Pr)_3$ ligands were not characterized.

Figure 1 shows structures of **2a** determined by X-ray crystallography. The coordination geometry around the Pt center of the complexes can be rationalized as a distorted square plane containing two PEt_3 ligands at mutually cis positions and a triarylsilyl ligand and a hydrido ligand coordinated to the Pt(II) center. The Pt-Si bond distances (2.357(3) Å) are in the range of already reported silylplatinum complexes (2.335(11)−2.401(5) Å).[2,8] The Pt−P(1) bond (2.335(3) Å) is longer than the Pt−P(2) bond (2.304(3) Å), indicating that the trans influence of the triarylsilyl ligand is more significant than that of the hydride. An analogous PPh_3-coordinated complex, *cis*-$PtH(SiPh_3)(PPh_3)_2$, also has dissimilar Pt−P bonds (2.332(2) and 2.298(3) Å) resulting from the trans influence of the $SiPh_3$ ligand being greater than that of the hydride.[9] Serious deviation of the bond angles around the metal center from the ideal 90 or 180° can be attributed to steric repulsion between the silyl and phosphine ligands being more severe than that between the hydride and the other ligands.

Scheme 3



The ^1H NMR spectrum of **2a** shows a signal due to the hydride ligand at δ −2.43 as a doublet of doublets flanked with satellites caused by the ^{195}Pt metal center ($J(PtH) = 873$ Hz). A large difference in two $J(PtH)$ values (151 and 21 Hz) indicates that the phosphine ligands occupy mutually cis positions. The $^{31}P\{^1H\}$ NMR shows two signals at δ 17.8 and 22.0 with $J(PtP)$ values of 2414 and 1616 Hz, respectively. The latter is assigned to the phosphine ligand at the trans position of the triphenylsilyl ligand on the basis of a comparison of the J values with those of already reported silylplatinum complexes.[9] This assignment is consistent with the relative magnitude of the trans influence of $SiPh_3$ and H ligands observed in the crystallographic results. Complexes **2b**,**c** also give rise to similar NMR spectra. Although several *cis*-$PtH(SiAr_3)(PPh_3)_2$ type complexes have already been prepared from reaction of $HSiAr_3$ with $Pt(PPh_3)_4$ and with $Pt(CH_2{=}CH_2)(PPh_3)_2$,[9,10] there have been only a few reports on similar PEt_3-coordinated complexes. Bard reported the isolation of *cis*-$PtH(SiPh_3)(PEt_3)_2$ in low yield from the reaction of $PtCl_2(PEt_3)_2$ and Ph_3SiLi but did not characterize it fully.[11] The preferential cis configuration of **2a**−**c** can be attributed to the fact that the trans influence of both triarylsilyl and hydride ligands is much greater than that of PEt_3, rendering the trans structure unstable. Heating a benzene-d_6 solution of **2a** at 70 °C for 6 h results in its isomerization into *trans*-$PtH(SiPh_3)(PEt_3)_2$ to a slight degree (<3%, hydride signal at δ −0.69 in ^1H NMR), suggesting a greater thermodynamic stability of the cis isomer.

Conversion of $Pt(PEt_3)_4$ into **2a** in reaction 1 proceeds almost quantitatively, although the isolated yield of the complex is lower due to difficulty in complete separation of **2a** from the other products. On the other hand, reaction of **2a** with $RhCl(PEt_3)_3$ at room temperature does not cause transfer of $SiPh_3$ and H ligands from Pt to Rh at all.[12] A plausible reaction pathway of reaction 1 is shown in Scheme 3, involving reductive elimination of $HSiAr_3$ from **1a**−**c** and ensuing oxidative addition of $HSiAr_3$ to $Pt(PEt_3)_4$ to give the hydridosilylplatinum complexes **2a**−**c**.[13] Actually, $HSiPh_3$ reacts readily with $Pt(PEt_3)_4$ to give **2a** in almost quantitative yield. The phosphine exchange reaction of the Rh(I) complex seems to occur during the reaction to give $RhCl(PEt_3)_3$.

Since $^{31}P\{^1H\}$ NMR signals and the ^1H NMR signal of the hydride of $RhCl(H)(SiAr_3)[P(i\text{-}Pr)_3]_2$ show clear

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(12) Prolonged heating of the reaction mixture causes formation of *trans*-$PtCl(H)(PEt_3)_2$. The mechanism of the irreversible chloro ligand transfer is not clear at present.

splitting due to Rh−H and Rh−P coupling, the equilibrium of the first step in Scheme 3 is favored to the left. All these observations suggest that reaction 1 involves reductive elimination of $HSiAr_3$ from the Rh(III) complex as the rate-determining step and is motivated by the thermodynamic stability of the H−Pt−Si bond being greater than that of the corresponding coordination bonds in the Rh(III) complexes.

The ligand transfer shown in the present paper suggests the potential utility of the hydridosilylmetal complexes in the synthesis of transition-metal silyl complexes and will provide a useful tool to compare the relative stabilities of H−M−Si coordination among different transition metals.

Experimental Section

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere. $RhCl(H)(SiAr_3)[P(i\text{-}Pr)_3]_2$,[14] $RhCl(PEt_3)_3$,[15] and $Pt(PEt_3)_4$[16] were prepared according to the literature method. All the solvents were distilled from drying reagents and stored under nitrogen. NMR spectra (^1H, 400 MHz; ^{31}P, 160 MHz) were recorded in benzene-d_6 on a JEOL EX-400 spectrometer. Peak positions of the ^{31}P NMR were referenced to external 85% H_3PO_4. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder and with a Yanaco YS-10 autocorder.

Reactions of 1a−c with $Pt(PEt_3)_4$. Complex **1a** (151 mg, 0.21 mmol) dispersed in pentane (5 mL) was mixed with $Pt(PEt_3)_4$ (141 mg, 0.21 mmol) at room temperature. Stirring the reaction mixture turned the solid remaining undissolved from yellow to pale yellow and the solution from colorless to yellow-orange. After 12 h, the resulting solid was collected by filtration and dried in vacuo to give **2a** as a white solid (87 mg, 60%). Recrystallization from a toluene−pentane mixture afforded colorless crystals. ^1H NMR: δ −2.43 (dd, 1H, $J(P_{trans}H) = 151$ Hz, $J(P_{cis}H) = 21$ Hz, $J(PtH) = 873$ Hz, Pt−*H*), 0.77 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 0.92 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 1.24 (m, 6H, PCH_2CH_3), 1.54 (m, 6H, PCH_2CH_3), 7.20 (t, 3H, $J(HH) = 7$ Hz, Si-C_6H_5-*p*) 7.29 (t, 6H, $J(HH) = 7$ Hz, Si-C_6H_5-*m*), 8.07 (d, 6H, $J(HH) = 7$ Hz, Si-C_6H_5-*o*). $^{31}P\{^1H\}$ NMR: δ 17.8 ($J(PP) = 16$ Hz, $J(PtP) = 2414$ Hz, cis to Si), 22.0 ($J(PP) = 16$ Hz, $J(PtP) = 1616$ Hz, trans to Si). Anal. Calcd for $C_{30}H_{46}P_2PtSi$: C, 52.08; H, 6.70. Found: C, 51.94; H, 6.64.

The filtrate after separation of **2a** from the reaction mixture was reduced to *ca.* 1 mL by evaporation of the solvent. The $^{31}P\{^1H\}$ NMR spectrum of the mixture showed peaks due to **2a** and $RhCl(PEt_3)_3$ (δ 19.3 (dd) and 36.4 (dt)) in addition to several uncharacterized Rh-containing products. Leaving the mixture at 25 °C caused separation of $RhCl(PEt_3)_3$ as orange crystals.

The reaction of **1b** with $Pt(PEt_3)_4$ was carried out analogously to give **2b** (56%). ^1H NMR: δ −2.71 (dd, 1H, $J(P_{trans}H) = 151$ Hz, $J(P_{cis}H) = 21$ Hz, $J(PtH) = 867$ Hz, Pt−*H*), 0.70 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 0.87 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 1.15 (m, 6H, PCH_2CH_3), 1.50 (m, 6H, PCH_2CH_3), 6.99 (dd, 6H, $J(FH) = 9$ Hz, $J(HH) = 9$ Hz, Si-C_6H_4-*o*), 7.80 (d, 6H, $J(HH) = 6$ Hz, Si-C_6H_4-*m*). $^{31}P\{^1H\}$ NMR: δ 17.4 ($J(PP) = 16$ Hz, $J(PtP) = 2410$ Hz, cis to Si), 21.8 ($J(PP) = 16$ Hz, $J(PtP) = 1635$ Hz, trans to Si). Anal. Calcd for $C_{30}H_{43}F_3P_2PtSi$: C, 48.31; H, 5.81; F, 7.64. Found: C, 48.31; H, 5.79; F, 7.64.

The reaction of **1c** with $Pt(PEt_3)_4$ was carried out analogously to give **2c** (60%). ^1H NMR: δ −2.88 (dd, 1H, $J(P_{trans}H) = 150$ Hz, $J(P_{cis}H) = 19$ Hz, $J(PtH) = 858$ Hz, Pt−*H*), 0.67 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 0.83 (td, 9H, $J(PH) = 16$ Hz, $J(HH) = 7$ Hz, PCH_2CH_3), 1.11 (m, 6H, PCH_2CH_3), 1.49 (m, 6H, PCH_2CH_3), 7.27 (d, 6H, $J(HH) = 7$ Hz, Si-C_6H_4-*m*), 7.70 (d, 6H, $J(HH) = 9$ Hz, Si-C_6H_4-*o*). $^{31}P\{^1H\}$ NMR: δ 17.0 ($J(PP) = 16$ Hz, $J(PtP) = 2398$ Hz, cis to Si), 21.9 ($J(PP) = 16$ Hz, $J(PtP) = 1663$ Hz, trans to Si). Anal. Calcd for $C_{30}H_{43}Cl_3P_2PtSi$: C, 45.31; H, 5.45; Cl, 13.37. Found: C, 45.54; H, 5.49; Cl, 13.93.

Preparation of *cis*-$PtH(SiPh_3)(PEt_3)_2$ (2a). To a pentane (5 mL) solution of $Pt(PEt_3)_4$ (419 mg, 0.63 mmol) was added $HSiPh_3$ (196 mg, 0.75 mmol) at room temperature. The yellow solution soon changed to colorless, and white solid was generated after 1 min on stirring. After 1 h the resulting solid product was collected by filtration, washed with pentane, and dried in vacuo (284 mg, 65%).

Reaction of $RhCl(PEt_3)_3$ with 2a. $RhCl(PEt_3)_3$ and **2a** were dissolved in THF (5 mL), and the resulting solution was stirred at room temperature for 8 h. The solvent was removed in vacuo, and NMR spectra of the resulting orange viscous product were measured. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed peaks for **2a** and $RhCl(PEt_3)_3$ only.

Crystal Structure Determination. Crystals of **2a** suitable for crystallography were obtained by recrystallization from toluene−pentane and mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 20 reflections with $20° \le 2\theta < 30°$. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation ($\lambda = 0.710\ 69$ Å) and the $\omega-2\theta$ scan method, and an empirical absorption correction (ψ scan) was applied. Crystal data for **2a**: $C_{30}H_{46}P_2PtSi$; M_r, 691.82; monoclinic; space group, $P2_1$ (No. 4); *a*, 9.833(4) Å; *b*, 19.065(6) Å; *c*, 10.415(4) Å; β, 95.29(3)°; *V*, 1536(1) Å^3; *Z*, 2; μ(Mo Kα), 47.05 cm^{-1}; *F*(000), 696.00; D_{calcd}, 1.495 g cm^{-3}; crystal size, $0.5 \times 0.7 \times 0.9$ mm; number of unique reflections, 3672; number of reflections used ($I \ge 3\sigma(I)$), 2624; number of variables, 306; $R(F_o)$, 0.037; $R_w(F_o)$, 0.028; GOF, 1.33.

Calculations were carried out by using the program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature.[17] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. The position of the hydride ligand was determined by the difference Fourier technique, while the other hydrogens were located by assuming ideal positions ($d(C-H) = 0.95$ Å) and included in the structure calculation without further refinement of the parameters. Parameters of the hydride were fixed in the structural calculations.

Crystallographic results for **2c** are included in the Supporting Information.

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Supporting Information Available: Tables of positional parameters, thermal parameters, bond distances and angles, and crystallographic data and details of refinement of **2a** and **2c** and a figure giving the structure of **2c** (13 pages). Ordering information is given on any current masthead page.

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(13) Substitution of the $P(i\text{-}Pr)_3$ ligand bonded to **1** by PEt_3 liberated from $Pt(PEt_3)_4$ might occur prior to the ligand transfer. The resulting $RhCl(H)(SiAr_3)(PEt_3)_2$ or $RhCl(H)(SiAr_3)(PEt_3)[P(i\text{-}Pr)_3]$ would undergo reductive elimination of $HSiAr_3$ initiated by further PEt_3 ligation (A mechanism) in addition to the direct reductive elimination from the pentacoordinated Rh complexes.

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