

Reactivity of Bis(silyl) Platinum(II) Complexes toward Isocyanides: Preparation and Structure of *cis*-[Pt(SiHPh₂)₂(CNR)(PR'₃)] (R = *t*-Bu, cyclohexyl, *i*-Pr; R' = Me, Et)

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Summary: Reactions of organic isocyanides CNR (R = *t*-Bu, cyclohexyl, *i*-Pr) with Pt(SiHPh₂)₂(PR'₃)₂ (R' = Me, Et) gave four novel bis(silyl) platinum(II) complexes Pt(SiHPh₂)₂(CNR)(PR'₃) containing both phosphine and isocyanide ligands. X-ray crystallographic studies of the two complexes revealed a *cis* orientation of the diphenylsilyl ligands. Two different Pt–Si bond distances and *J*(Pt–H) values of the Si–H hydrogen signals strongly suggest a higher *trans* influence of the silyl ligand relative to the isocyanide.

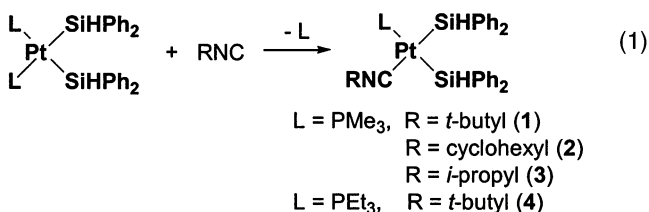
Introduction

Bis(silyl) platinum(II) complexes are important intermediates in Pt-catalyzed synthetic reactions such as the bis-silylation of alkenes or dienes and the dehydrocoupling of organosilanes, and they also act as useful starting materials for Si-containing complexes.^{1–3} Although many interesting reactivities of these complexes toward unsaturated organic compounds via the Pt–Si bond cleavage have been reported, the insertion of small molecules such as CO or isocyanide (CNR) into the Pt–Si bond in these complexes has been relatively rare. Thus, we have investigated the reactivity of bis(silyl) Pt(II) complexes toward isocyanide, which is isoelectronic with CO. We recently synthesized complexes of

the type Pt(SiHPh₂)₂(PMe₃)₂ that undergo a facile isomerization between the *trans*- and *cis*-isomers.⁴ Herein we report the reactions of isocyanides with the bis(silyl) platinum(II) complexes to afford new Pt(II) complexes containing two silyl, one phosphine, and one isocyanide ligand.

Results and Discussion

Reactions of isocyanides CNR (R = *t*-Bu, cyclohexyl, *i*-Pr) with Pt(SiHPh₂)₂(PR'₃)₂ (R' = Me, Et) in THF at room temperature gave *cis*-[(SiHPh₂)₂(CNR)(PR'₃)] (**1**–**4**) as shown in eq 1.



Molecular structures of **1** and **3** have been determined by X-ray diffraction. The crystal data and refinement data are summarized in Table 1. Figure 1 shows ORTEP drawings of both complexes, which exhibit a slightly distorted square-planar coordination, containing one PMe₃, two SiHPh₂, and one isocyanide ligand. The SiHPh₂ ligands are located at *cis* positions, which are not equivalent. Elongation of the Pt–Si bond *trans* to PMe₃ (2.378(2) and 2.373(2) Å) compared with those *trans* to the isocyanide ligand (2.360(2) and 2.362(2) Å) can be ascribed to a higher *trans* influence of the silyl

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Table 1. X-ray Data Collection and Structure Refinement for **1 and **3****

formula	C ₃₂ H ₄₀ NSi ₂ Ppt	C ₃₁ H ₃₈ NPSi ₂ Pt
fw	720.89	706.86
temperature, K	296(2)	296(2)
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	11.143(1)	10.874(1)
<i>b</i> , Å	16.163(3)	15.871(2)
<i>c</i> , Å	18.231(2)	18.241(2)
β , deg	98.595(6)	
<i>V</i> , Å ³	3246.6(7)	3148.2(6)
<i>Z</i>	4	4
<i>d</i> _{cal} , g cm ⁻³	1.475	1.491
μ , mm ⁻¹	.465	4.603
<i>F</i> (000)	1440	1408
<i>T</i> _{min}	0.0269	0.1574
<i>T</i> _{max}	0.0543	0.3358
2 θ range (deg)	3.5–50	3.5–50
no. of reflns measd	5801	3538
no. of reflns unique	5507	3453
no. of reflns with <i>I</i> > 2 σ (<i>I</i>)	4531	3258
no. of params refined	341	334
max., in $\Delta\rho$ (e Å ⁻³)	1.029	0.862
min., in $\Delta\rho$ (e Å ⁻³)	–1.234	–0.591
GOF on <i>F</i> ²	1.042	1.020
<i>R</i>	0.0355	0.0245
<i>wR</i> ₂ ^a	0.0865	0.0589

$$^a wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

ligand relative to the isocyanide ligand. The Pt–C bond lengths (1.998(6) for **1** and 2.014(7) Å for **3**) are slightly longer than those found in other platinum-isocyanide complexes, PtCl₂(CNC₂H₅)[P(C₂H₅)₂C₆H₅] (1.83(4) Å),⁵ PtCl₂(CNC₆H₅)₂ (1.88(2) and 1.91(2) Å),⁵ [PtH{(t-Bu)₂-PCH₂CH₂P(t-Bu)₂}(CNAr)]PF₆ (1.947(8) Å),⁶ and [Pt-(CNC₆H₂-2,4-*t*-Bu₂-6-Me)₂Cl]₂ (mean 1.95 Å) due to a high *trans* influence of the silyl ligand.⁷ Bond distances of C28–N1 (1.145(7) Å for **1**) and C1–N1 (1.128(8) Å for **3**) are similar to those in PtCl₂(CNC₆H₅)₂ (1.19(2) and 1.14(3) Å)⁵ and [(6-phenyl-2,2'-terpyridine)Pt(CN-*t*-Bu)]ClO₄ (1.13(1) Å),⁸ suggesting the triple-bond character (C≡N) of the isocyanide ligands.

All products were obtained as colorless crystals by recrystallization from diethyl ether or (diethyl ether)/hexane and characterized by IR, NMR, and elemental analyses. IR spectra display strong absorption bands at 2165–2172 cm⁻¹ due to ν (N≡C) of the C-coordinated isocyanides and also two bands at 2009–2077 cm⁻¹ due to ν (Si–H). ¹H NMR spectra of **1–4** at –60 °C display two Si–H signals coupled with a phosphine ligand. Figure 2 shows the Si–H signals of complex **1**. The doublets at 4.98 ppm flanked with Pt satellites (*J*_{Pt–H} = 28 Hz, *J*_{Pt–H} = 10 Hz) are assigned to SiH(B) *trans* to the PMe₃ ligand, whereas the other doublets at 4.67 ppm (*J*_{Pt–H} = 9.6 Hz, *J*_{Pt–H} = 120 Hz) are assigned to SiH(A) on the basis of coupling constants with the phosphorus of PMe₃. The latter signals show a much higher *J*_{Pt–H} value than the former. ¹H and ³¹P{¹H} NMR spectra of **1–4** at –60 °C indicate the existence of only the *cis*-isomer in solution. Raising the temper-

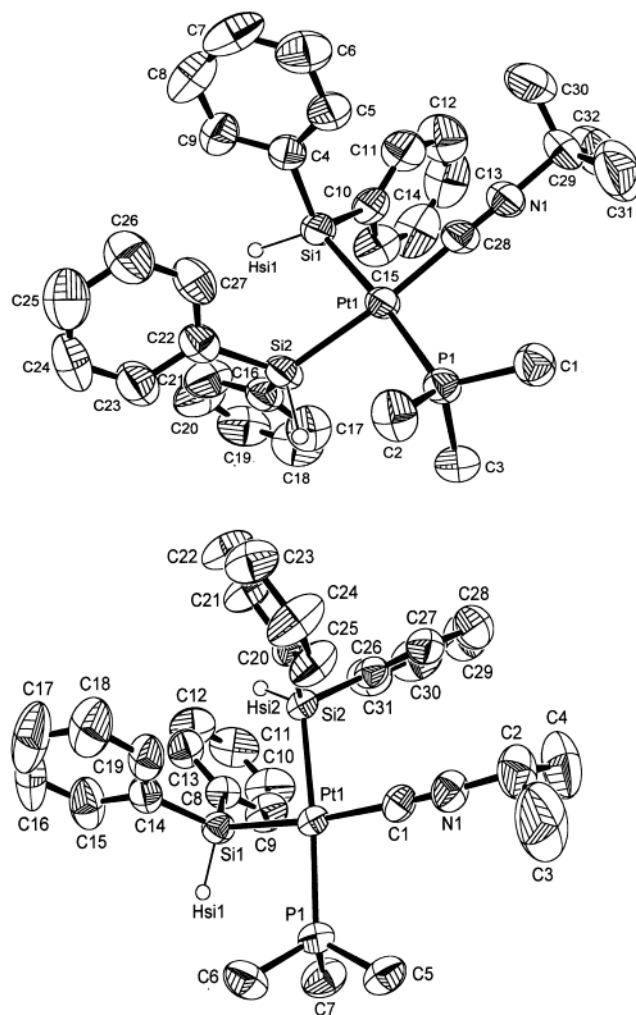


Figure 1. (a) ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Pt1–C28 1.998(6), Pt1–P1 2.332(2), Pt1–Si1 2.360(2), Pt1–Si1 2.378(2), Si1–C10 1.893(7), Si1–C4 1.895(6), Si1–Hsi1 1.46(7), Si2–C16 1.898(7), Si2–C22 1.902(7), Si2–Hsi2 1.48(7), N1–C28 1.145(7), N1–C29 1.471(8); C28–Pt1–P1 94.7(2), C28–Pt1–Si2 175.2(2), P1–Pt1–Si2 89.84(6), C28–Pt1–Si1 89.6(2), P1–Pt1–Si1 175.63(5), Si2–Pt1–Si1 85.80(6), C10–Si1–C4 108.4(3), Pt1–Si1–Hsi1 119(3), C16–Si2–C22 109.1(3), C22–Si2–Hsi2 103(3), Pt1–Si2–Hsi2 107(3), C28–N1–C29 178.1(7), N1–C28–Pt1 179.1(5). (b) ORTEP drawing of **3**. Selected bond lengths (Å) and angles (deg): Pt1–C1 2.014(7), Pt1–P1 2.329(2), Pt1–Si1 2.362(2), Pt1–Si2 2.373(2), N1–C1 1.128(8), N1–C2 1.47(1), C2–C3 1.45(1), C2–C4 1.48(1); C1–Pt1–P1 95.5(2), C1–Pt1–Si1 173.4(2), P1–Pt1–Si1 190.80(6), C1–Pt1–Si2 88.8(2), P1–Pt1–Si2 175.61(6), Si1–Pt1–Si2 84.81(6), C1–N1–C2 177.7(8), N1–C1–Pt1 176.5(6), C3–C2–N1 110.1(9), C3–C2–C4 114.4(10), N1–C2–C4 110.0(8).

ature of solutions containing **1–3** to room temperature results in NMR peak broadening due to *cis*–*trans* isomerism. However, complex **4** retains its NMR spectra even at room temperature with the negligible peaks corresponding to the *trans*-isomer, indicating the *cis*-isomer is predominant in solution at least at that temperature. This phenomenon contrasts with that previously observed for Pt(SiHPh₂)₂(PR₃) (R = Me, Et),⁴ which exhibits a facile *cis*–*trans* isomerism on the NMR time scale in solution. Differences in the *cis*–*trans*

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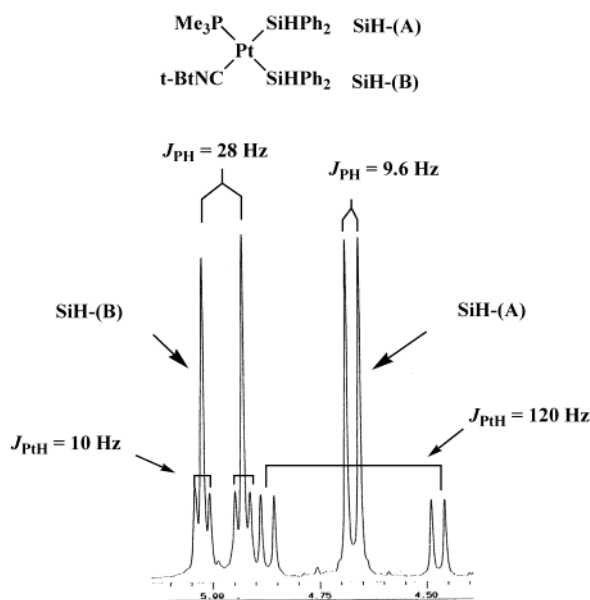


Figure 2. ^1H NMR spectrum of **1** (Si-H region) at -60°C .

isomerism behavior between complexes **1** and **4** seem to arise from the different steric requirements of the phosphine ligands (PMe_3 in **1** and PEt_3 in **4**).⁹ Previously, Ozawa and co-workers¹⁰ reported that CO, which is isoelectronic with isocyanide, selectively inserted into the Pt-C bond of alkylsilyl platinum(II) complexes and proposed the formation of an intermediate of CO-coordinated Pt(II) complexes. The corresponding isocyanide insertion into the Pt-Si bond does not occur under our reaction conditions. In fact, CO or CNR insertion into the Pt-Si bond has never been reported. Tanaka and co-workers previously reported that bis(silyl) Pt(II) complexes reductively eliminated to give a disilane in the presence of PR_3 as a two-electron donor.^{1d} By contrast, Braddock-Wilking et al. recently showed that the Pt-Si bond remained intact in the reactions of $\text{R}_3\text{P-Pt-Si}$ complexes with another PR'_3 .^{3i,1}

In summary, we synthesized four new unsymmetrical bis(silyl) platinum(II) complexes $\{\text{Pt}(\text{SiHPh}_2)_2(\text{CNR})(\text{PR}'_3)\}$, by replacing one phosphine ligand of bis(phosphine) platinum complexes with isocyanide, which might be considered as intermediates in organic substrate insertion into the Pt-Si bond to give organic silylated compounds. The relative orientation of the two silyl ligands (that is, *cis-trans* isomerization) of these platinum compounds in solution appears to be dependent on temperature and ancillary ligands.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were performed under N_2 or argon with the use of standard Schlenk line techniques. Solvents were distilled from Na-benzophenone. The Analytical Laboratory at Kangnung National University carried out elemental analyses. IR spectra were recorded on a Perkin-Elmer BX spectrophotometer. NMR

(^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$) spectra were obtained on a JEOL Lambda 300 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si (^1H and $^{13}\text{C}\{^1\text{H}\}$) and to external 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). $\text{Pt}(\text{SiHPh}_2)_2\text{L}_2$ ($\text{L} = \text{PMe}_3$, PEt_3) complexes were prepared by the literature method.⁴

Preparation of 1-4. To a Schlenk flask containing $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$ (0.181 g, 0.253 mmol) was added THF (6 mL) and *tert*-butyl isocyanide (0.021 g, 0.253 mmol) in that order. After stirring for 24 h at room temperature, the reaction mixture was completely evaporated under vacuum, and then the resulting residue was solidified with hexane at -30°C . The solids were filtered and washed with hexane (2×2 mL). Recrystallization from THF/hexane gave white crystals of $\text{Pt}(\text{SiHPh}_2)_2(\text{CN-}t\text{-Bu})(\text{PMe}_3)$, **1** (0.330 g, 67%).

IR (KBr, cm^{-1}): $\nu(\text{SiH})$ 2031, 2071; $\nu(\text{CN})$ 2166. ^1H NMR (-60°C , CDCl_3 , 300 MHz, δ): 1.27 (s, 9H, CH_3), 1.53 (d, $J_{\text{P-H}} = 8.8$ Hz, $J_{\text{P-H}} = 20$ Hz, 9H, PMe_3), 4.67 (d, $J_{\text{P-H}} = 9.6$ Hz, $J_{\text{P-H}} = 120$ Hz, 1H, SiH), 4.98 (d, $J_{\text{P-H}} = 28$ Hz, $J_{\text{P-H}} = 10$ Hz, 1H, SiH), 7.18–7.31 (m, 16H, Ph), 7.61–7.64 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 75 MHz, δ): 15.0 (d, $J_{\text{P-C}} = 28$ Hz, PMe_3), 29.3 (s, CH_3), 57.1 (s, $\text{C}(\text{CH}_3)_3$), 126.7, 126.9, 127.2, 135.9 (d, $J_{\text{P-C}} = 4.8$ Hz, $J_{\text{P-C}} = 19$, Ph), 136.7 (s, $J_{\text{P-C}} = 25$ Hz, Ph), 141.2 (d, $J_{\text{P-C}} = 2.5$ Hz, $J_{\text{P-C}} = 47$ Hz, Ph), 143.5 (d, $J_{\text{P-C}} = 5.0$ Hz, $J_{\text{P-C}} = 16$, Ph), 145.7, 145.8 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 120 MHz, δ): -13.8 (s, $J_{\text{P-P}} = 1594$ Hz, $J_{\text{Si-P}} = 145$ Hz). Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{NPSi}_2\text{Pt}$: C, 53.32; H, 5.59; N, 1.94. Found: C, 52.94; H, 5.60; N, 1.90.

Complexes **2-4** were prepared analogously. Data for **2** (54%). IR (KBr, cm^{-1}): $\nu(\text{SiH})$ 2047, 2075; $\nu(\text{CN})$ 2172. ^1H NMR (-60°C , CDCl_3 , 300 MHz, δ): 1.43–1.90 (br, 11H, C_6H_{11}), 1.51 (br, 9H, $J = 9$ Hz, PMe_3), 4.71 (d, 1H, $J = 9$ Hz, 1H, $J_{\text{P-C}} = 116$ Hz, SiH), 4.98 (d, 1H, $J = 27$ Hz, $J_{\text{P-C}} = 27$ Hz, SiH), 7.18–7.38 (m, 16H, Ph), 7.58–7.64 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 75 MHz, δ): 16.2 (d, $J_{\text{P-C}} = 29$ Hz, $J_{\text{P-C}} = 29$ Hz, PMe_3), 24.0, 32.2, 54.4, 66.1 (s, C_6H_{11}), 126.8, 126.9, 127.3, 135.9 (d, $J_{\text{P-C}} = 2$ Hz, $J_{\text{P-C}} = 43$ Hz), 136.7 (s, $J_{\text{P-C}} = 25$ Hz), 141.3 (d, $J_{\text{P-C}} = 3$ Hz, $J_{\text{P-C}} = 46$ Hz), 143.6 (d, $J = 4$ Hz, $J_{\text{P-C}} = 17$ Hz), 141.7 (s, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 120 MHz, δ): -14.9 (s, $J_{\text{P-C}} = 1809$ Hz). Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{NPSi}_2\text{Pt}$: C, 54.67; H, 5.67; N, 1.88. Found: C, 54.85; H, 5.73; N, 1.85.

Data for **3** (71%). IR (KBr, cm^{-1}): $\nu(\text{SiH})$ 2012, 2076; $\nu(\text{CN})$ 2168. ^1H NMR (-60°C , CDCl_3 , 300 MHz, δ): 1.19 (d, $J_{\text{H-H}} = 6.6$ Hz, CH_3), 1.50 (d, $J_{\text{P-H}} = 8.8$ Hz, $J_{\text{P-H}} = 20$ Hz, 9H, PMe_3), 4.71 (d, $J_{\text{P-H}} = 9.2$ Hz, $J_{\text{P-H}} = 118$ Hz, 1H, SiH), 4.92 (s, $J_{\text{P-H}} = 19$ Hz, 1H, SiH), 5.02 (s, $J_{\text{P-H}} = 25$ Hz, 1H, SiH), 7.19–7.63 (m, 20H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 75 MHz, δ): 16.2 (d, $J_{\text{P-C}} = 29$ Hz, $J_{\text{P-C}} = 27$ Hz, PMe_3), 25.5 (s, CH_3), 48.2 (t, $J_{\text{P-C}} = 8$ Hz, CH_2), 126.8, 126.9, 127.3, 135.9 (d, $J_{\text{P-C}} = 1.2$ Hz, $J_{\text{P-C}} = 19$ Hz), 136.7 (s, $J_{\text{P-C}} = 26$ Hz), 141.3 (d, $J_{\text{P-C}} = 2.5$ Hz, $J_{\text{P-C}} = 46$ Hz), 143.6 (d, $J_{\text{P-C}} = 4.4$ Hz, $J_{\text{P-C}} = 8.4$ Hz), 147.0 (d, $J_{\text{P-C}} = 46$ Hz), 147.2 (d, $J_{\text{P-C}} = 1.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 120 MHz, δ): -13.8 (s, $J_{\text{P-P}} = 1604$ Hz, $J_{\text{Si-P}} = 145$, 656 Hz). Anal. Calcd for $\text{C}_{31}\text{H}_{38}\text{NPSi}_2\text{Pt}$: C, 52.67; H, 5.42; N, 1.98. Found: C, 52.79; H, 5.52; N, 1.97.

Data for **4** (75%). IR (KBr, cm^{-1}): $\nu(\text{SiH})$ 2020, 2069; $\nu(\text{CN})$, 2166. ^1H NMR (25 $^\circ\text{C}$, CDCl_3 , 300 MHz, δ): 1.05 (q, $J_{\text{P-H}} = 1.8$ Hz, 9H, CH_2CH_3), 1.16 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.93 (q, $J_{\text{H-H}} = 7.9$ Hz, CH_2CH_3), 4.72 (d, $J_{\text{P-H}} = 9.2$ Hz, $J_{\text{P-H}} = 123$ Hz, 1H, SiH), 5.13 (d, $J_{\text{P-H}} = 24$ Hz, $J_{\text{P-H}} = 24$ Hz, 1H, SiH), 7.13–7.57 (m, 20H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (-60°C , CDCl_3 , 75 MHz, δ): 8.51 (s, $J_{\text{P-C}} = 18$ Hz, $\text{P}(\text{CH}_2(\text{CH}_3)_3)$), 16.3 (d, $J_{\text{P-C}} = 25$ Hz, $\text{P}(\text{CH}_2(\text{CH}_3)_3)$), 29.3 (s, $\text{C}(\text{CH}_3)_3$), 58.0 (s, $\text{C}(\text{CH}_3)_3$), 126.7, 126.8, 127.1, 136.0 (d, $J_{\text{P-C}} = 2$ Hz, $J_{\text{P-C}} = 20$ Hz), 136.7 (s, $J_{\text{P-C}} = 26$ Hz), 141.5 (d, $J_{\text{P-C}} = 2$ Hz, $J_{\text{P-C}} = 50$ Hz), 143.8 (d, $J_{\text{P-C}} = 4$ Hz, $J_{\text{P-C}} = 16$ Hz), 146.0. $^{31}\text{P}\{^1\text{H}\}$ NMR (25 $^\circ\text{C}$, CDCl_3 , 120 MHz, δ): 19.0 (s, $J_{\text{P-P}} = 1631$ Hz). Anal. Calcd for $\text{C}_{35}\text{H}_{46}\text{NPSi}_2\text{Pt}$: C, 55.10; H, 6.08; N, 1.84. Found: C, 55.50; H, 6.13; N, 1.73.

Structure Determination. All X-ray data were collected

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with a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. Intensity data were empirically corrected for absorption with ψ -scan data. Both structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to silicon atoms were located and refined with a fixed thermal parameter ($U = 0.08 \text{ \AA}^2$). The remaining hydrogen atoms were generated in ideal positions and refined in a riding mode. All calculations were carried out with use of the SHELX-97 programs.¹¹

A colorless crystal of **1**, shaped as a plate, of approximate dimensions $0.80 \times 0.22 \times 0.12 \text{ mm}^3$, was used for crystal- and intensity-data collection. A colorless crystal of **3**, shaped as a

plate, of approximate dimensions $0.64 \times 0.42 \times 0.09 \text{ mm}^3$, was used.

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Supporting Information Available: Crystallographic data of **1** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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