Organometallics **2008,** *27,* 5566–5570

Reactivity of Bis(silyl)platinum(II) Complexes toward Organic Isothiocyanates: Preparation and Structures of (Dithiocarbonimidato)- and (Diphenylsilanedithiolato)platinum(II) Complexes, *cis*-[Pt($S_2C{=}NPh$)L_2] and *cis*-[Pt(S_2SiPh_2)L_2] (L = PMe_2Ph, PEt_3; L-L = dppp)

Kyung-Eun Lee,[†,‡] Xiaohong Chang,[†,§] Yong-Joo Kim,*[,†] Hyun Sue Huh,[‡] and Soon W. Lee[‡]

Departments of Chemistry, Kangnung National University, Kangnung 210-702, Korea, Liaoning University, Shenyang 110036, People's Republic of China, and Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea

Received March 19, 2008

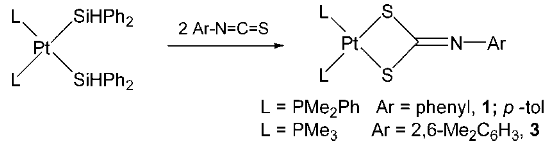
Reactions of the bis(silyl)platinum(II) complexes [Pt($SiHPh_2$)$_2L_2$] (L = PMe_3, PMe_2Ph, PEt_3; L-L = dppp (1,3-bis(diphenylphosphino)propane)) with organic isothiocyanates (RNCS) produced the dithiocarbonimidato complexes [Pt($S_2C{=}NR$)L_2] (R = Ph, *p*-tolyl, 2,6-*Me*$_2C_6H_3$, *i*-Pr) or the diphenylsilanedithiolato complexes [Pt(S_2SiPh_2)L_2], depending on the reaction temperature, the stoichiometry, and the nature of the phosphine ligand.

Introduction

Bis(silyl)platinum(II) complexes are considered important intermediates in the Pt-catalyzed mono- or bis(silylation) of unsaturated organic compounds, and they have been utilized as stoichiometric reactants for the preparation of unique silyl complexes.[1,2] Alkenes, alkynes, and 1,3-dienes typically react with these complexes via Pt−Si bond cleavage or migration. However, the insertion of other unsaturated organic compounds such as organic isonitriles (RNC), nitriles (RCN), and isothiocyanates (RNCS) into the Pt−Si bond in this type of complex is rare.[3,4] Recently, we reported the novel reactivity of the Pt(II) bis(silyl) complexes toward isocyanides to afford the Pt(II) isocyanide complexes [Pt($SiHPh_2$)$_2$(CNR)(PR'_3)] (R′ = Me, Et), whose reactivity depended on the reactants or spectator ligands.[4] In this work we report the selective formation of the Pt(II) dithiocarbonimidato and diphenylsilanedithiolato complexes [Pt($S_2C{=}NR$)L_2] (R = Ph, *p*-tolyl, 2,6-$Me_2C_6H_3$, *i*-Pr) and [Pt(S_2SiPh_2)L_2] from the reactions of the Pt(II) bis(silyl) complexes and organic isothiocyanates.

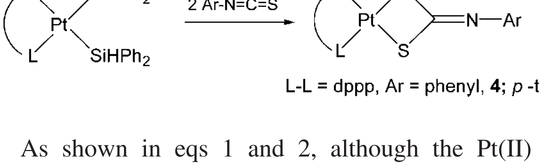
Results and Discussion

Reactions of [Pt($SiHPh_2$)$_2L_2$] (L = PMe_2Ph, PMe_3; L-L = dppp (1,3-bis(diphenylphosphino)propane)) with 2 equiv of ArNCS (Ar = phenyl, *p*-tolyl) at either room temperature (**1**, **4**, and **5**) or 50 °C (**2** and **3**) in THF gave the Pt(II) dithiocarbonimidato complexes with a 30−41% yield (eqs 1 and 2). As the reaction progressed, the IR spectra of a reaction mixture clearly showed the disappearance of the Si−H bands at 2026−2081 cm^{-1}, which are characteristic of the starting materials, and the appearance of new N=C bands at 1547−1578 cm^{-1}, which are characteristic of the products. Structural characterization of **1** and **4** by X-ray diffraction definitely confirmed the identity of these complexes.



(1)

L = PMe_2Ph Ar = phenyl, **1;** *p* -tolyl, **2**
L = PMe_3 Ar = 2,6-$Me_2C_6H_3$, **3**



(2)

L-L = dppp, Ar = phenyl, **4;** *p* -tolyl, **5**

As shown in eqs 1 and 2, although the Pt(II) bis(silyl) complexes containing phosphines such as PMe_2Ph, PMe_3, and

---

[*] To whom correspondence should be addressed. E-mail: yjkim@kangnung.ac.kr. Tel: Int + 82 + 33-640-2308. Fax: Int + 82 + 33-647-1183.

[†] Kangnung National University.

[‡] Sungkyunkwan University.

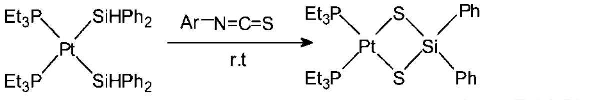
[§] Liaoning University.

(1) (a) Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 881. (b) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343. (c) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1977**, *131*, 377. (d) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (e) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (f) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (g) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (h) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333. (i) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (j) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (k) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (l) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373. (m) Ozawa, F.; Kamite, J. *Organometallics* **1997**, *17*, 5630. (n) Ozawa, F. *J. Organomet. Chem.* **2000**, *611*, 332. (o) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1997**, *17*, 5599. (p) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **1999**, *18*, 1818. (q) Kalt, D.; Schubert, U. *Inorg. Chim. Acta* **2000**, *301*, 211. (r) Tanabe, M.; Yamazawa, H.; Osakada, K. *Organometallics* **2001**, *20*, 4451. (s) Tanabe, M.; Osakada, K. *J. Am. Chem. Soc.* **2002**, *124*, 4550. (t) Tanabe, M.; Osakada, K. *Chem. Eur. J.* **2004**, *10*, 416.

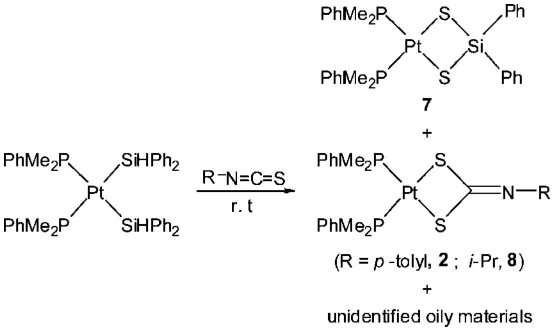
(2) Reviews: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (d) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamn Press: Oxford, U.K., 1992.

10.1021/om8006079 CCC: $40.75

dppp reacted with 2 equiv of ArNCS to give the Pt(II) dithiocarbonimidato complexes, excess ArNCS in the reaction mixture hindered the isolation of the Pt(II) products. In contrast, the corresponding 1:1 reaction of the PEt_3 complex [Pt-$(SiHPh_2)_2(PEt_3)_2$] and ArNCS (Ar = Ph, *p*-tolyl) allowed us to isolate the diphenylsilanedithiolato complex [$Pt(S_2SiPh_2)$-$(PEt_3)_2$] (**6**) as white crystals in 30−35% yield (eq 3). On the other hand, the PMe_2Ph complex [$Pt(SiHPh_2)_2(PMe_2Ph)_2$] reacted with 1 or 2 equiv of RNCS (R = *p*-tolyl, *i*-Pr) to produce a mixture of the diphenylsilanedithiolato complex [$Pt(S_2SiPh_2)$-$(PMe_2Ph)_2$] (**7**), the dithiocarbonimidato complex [$Pt(S_2C{=}NR)(PMe_2Ph)_2$] (R = *p*-tolyl (**2**), *i*-Pr (**8**)), and unidentified oily materials (eq 4). Interestingly, heating the reaction mixture converted it into the Pt(II) dithiocarbonimidato complex as a single product. The above results strongly indicate that the phosphine ligands in the starting complexes exert a critical influence on the final products in these reactions.



6 (3)



(4)

Before recrystallization, the IR spectra of the crude products in this work (eqs 1−4) displayed a common absorption band (ν(CN)) at ~2160 cm^{-1}, which is interpreted as the presence of the isonitrile group coordinated to the Pt center. We used spectroscopy (IR and NMR) and GC-mass spectrometry to identify the characteristic signals assigned to the isocyanide and H_2SiPh_2; these signals strongly support the formation of the isonitrile-coodinated intermediates. In spite of several attempts, however, we failed to isolate the isonitrile−dithiocarbonimidato−Pt complexes [$Pt(S_2C{=}NR)(CNR)L_2$] or the isonitrile−diphenylsilanedithiolato−Pt complexes [$Pt(S_2SiPh_2)(CNR)L_2$], which may be formed by the coordination of the liberated isonitrile to the final product (complexes **1**−**7**). It should be mentioned that most of the reaction products have been isolated from oily reaction mixtures in relatively low yields.

It is worth noting that the reactions of the Pt(II) bis(silyl) complex, except [$Pt(SiHPh_2)_2(PEt_3)_2$], with excess RNCS (R = Ph, *p*-tolyl, *i*-Pr) typically give the dithiocarbonimidato complex as a major product. In sharp contrast, the corresponding 1:1 reaction of the PEt_3 complex [$Pt(SiHPh_2)_2(PEt_3)_2$] and RNCS produces the diphenylsilanedithiolato complex as a major product in high yield (eq 3). The ability of [$Pt(SiHPh_2)_2(PEt_3)_2$] to exhibit higher selectivity for diphenylsilanedithiolato complex formation may result from the bulky triethylphosphine dissociation in the formation of an intermediate.

Several papers have previously proposed sulfur abstraction for the formation of dithiocarbonimidato complexes, which is believed to occur in our reactions. For example, Haszeldine and co-workers[5] reported that the Pt(0) complexes [Pt(allene)L_2], [PtL_4], and [Pt(PhNCS)L_2] (L = PPh_3) reacted with excess organic isothiocyanates (RNCS; R = Ph, Me) to give the Pt(II) dithiocarbonimidato complex [$Pt(S_2C{=}NR)L_2$] as a major product as well as the isonitrile−dithiocarbonimidato−Pt(II) complex [$Pt(CNPh)(S_2C{=}NPh)L_2$] as a minor product. In addition, the Pd(0) complexes [$Pd_2(dba)_3$]·$CHCl_3$[6] (in the presence of PPh_3) and $Pd(PR_3)_n$[7b] (n = 2, 4; PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, P-*i*-Pr_3) were shown to react with RNCS (R = Me, Ph, C(O)OEt) to give the Pd dithiocarbonimidato complexes [$Pd(S_2C{=}NR)(PR_3)_2$]. Furthermore, the Powell[8] and Thewissen[9] groups reported that Ru(0) and Rh(I) complexes reacted with RNCS (R = Ph, alkyl) to produce the corresponding dithiocarbonimidato or isonitrile−dithiocarbonimidato complexes, depending on the amounts of the added isothiocyanates. Finally, $CpCo(PMe_3)_2$,[7a] [$Fe_3(CO)_{12}$],[10] and [$Mo(CO)_6$][10] reacted with PhNCS to give the isonitrile complexes $CpCo(PMe_3)$(CN-Ph), [$Fe(CO)_4$(CNPh)], and [$Mo(CO)_5$(CNPh)], respectively.

Reactions in this report seem to proceed by the initial coordination of RNCS to [$Pt(SiHPh_2)L_2$] or the elimination of H_2SiPh_2 from [$Pt(SiHPh_2)L_2$] to produce the Pt silylene intermediate followed by the liberation of isocyanides. Unfortunately, we could not detect $Ph_2HSi{-}SiHPh_2$ in the NMR or mass spectra of the reaction mixture. The disilane ($Ph_2HSi{-}SiHPh_2$) is expected to be formed by the reductive elimination from [$Pt(SiHPh_2)L_2$] to produce a Pt(0) intermediate, which would subsequently react with excess organic isothiocyanate to give the Pt(II) dithiocarbonimidato complex [$Pt(S_2C{=}NR)L_2$] by the dimerization of RNCS as described in previous reports.[9] With limited experimental evidence, however, there is no point in speculation on the mechanism at this time. Further studies to elucidate the mechanism are required.

The crystal and refinement data of complexes **1**, **4**, **6**, and **7** are summarized in Table 1. Figures 1 and 2 are ORTEP drawings of the complexes **1** and **4**, respectively, both of which show a slightly distorted square planar geometry consisting of two phosphine ligands and two bridging sulfide (μ-S) ligands attached to the carbonimidato group (ArN=C). The two doublets in $^{31}P\{^1H\}$ NMR spectra of these complexes are flanked with Pt satellites, supporting the presence of nonequivalent phosphine ligands of the dithiolato moiety coordinated to the Pt center. The N1−C17 (1.268(7) Å) and N1−C18 (1.411(8) Å) bond lengths in Figure 1 and N1−C28 (1.270(1) Å) and the N1−C29 (1.450(2) Å) bond lengths in Figure 2 indicate a C=NR moiety in both complexes. The molecular structures of complexes **6** (Figure 3) and **7** (Figure 4) also demonstrate a square-planar geometry consisting of two cis PR_3 ligands and two bridging sulfide (μ-S) groups bonded to the diphenylsilyl group ($SiPh_2$). The Pt−S bond lengths (2.337−2.340 Å) in the Pt(II) dithiocarbonimidato complexes (**1** and **4**) are similar to those (2.341(5)

---

(3) (a) Tanabe, M.; Osakada, K. *Organometallics* **2001**, *20*, 2118. (b) Yamada, T.; Tanabe, M.; Osakada, K.; Kim, Y.-J. *Organometallics* **2004**, *20*, 4771.

(4) Kim, Y.-J.; Choi, E.-H.; Lee, S. W. *Organometallics* **2003**, *22*, 3316.

(5) Bowden, F. L.; Giles, R.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* **1974**, 578.

(6) Ahmed, J.; Itoh, K.; Matsuda, I.; Ueda, F.; Ishii, Y.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 620.

(7) (a) Werner, H.; Lotz, S.; Heiser, B. *J. Organomet. Chem.* **1981**, *209*, 197. (b) Bertleff, W.; Werner, H. *Chem. Ber.* **1982**, *115*, 1012.

(8) Harris, R. O.; Powell, J.; Walker, A.; Yaneff, P. V. *J. Organomet. Chem.* **1977**, *141*, 217.

(9) Thewissen, D. H. M. W.; Van Gaal, H. L. M. *J. Organomet. Chem.* **1979**, *172*, 69.

(10) Manuel, T. A. *Inorg. Chem.* **1964**, *3*, 1703.

(11) (a) Schierl, R.; Nagel, U.; Beck, W. *Z. Naturforsch.* **1984**, *39b*, 649. (b) Schierl, R.; Nagel, U.; Beck, W. *Chem. Ber.* **1982**, *115*, 1665.

Table 1. X-ray Data Collection and Structure Refinement Details for Complexes 1, 4, 6, and 7

	1	**4**·CH_2Cl_2·H_2O	**6**	**7**
formula	$C_{23}H_{27}NP_2S_2Pt$	$C_{35}H_{35}Cl_2NOP_2S_2Pt$	$C_{24}H_{34}P_2S_2SiPt$	$C_{28}H_{32}P_2S_2SiPt$
fw	638.61	877.69	671.75	717.78
temp, K	293(2)	293(2)	293(2)	293(2)
cryst size (mm^3)	0.16 × 0.12 × 0.06	0.18 × 0.16 × 0.14	0.48 × 0.46 × 0.44	0.18 × 0.16 × 0.14
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$C2/c$	$Pnma$	$C2/c$
a, Å	9.611(1)	27.652(4)	17.707 (2)	14.898(2)
b, Å	10.071(1)	13.789(2)	13.505(2)	11.839(9)
c, Å	12.944(2)	20.128(2)	11.816(1)	16.944(4)
α, deg	94.73(1)			
β, deg	105.69(1)	112.91(1)		106.88(1)
γ, deg	92.37(1)			
V, $Å^3$	1199.4 (3)	7070(2)	2825.7(6)	2859.8(8)
Z	2	8	4	4
d_{calcd}, g cm^{-3}	1.768	1.649	1.579	1.667
μ, mm^{-1}	6.167	4.358	5.279	5.223
$F(000)$	624	3472	1328	640
T_{min}	0.3949	0.2512	0.2308	0.6523
T_{max}	0.7927	0.7080	0.3790	0.8987
no. of measd rflns	4450	6250	2580	2611
no. of unique rflns	4191	6114	2580	2510
no. of rflns with $I > 2\sigma(I)$	3677	3619	2365	2316
no. of params refined	262	369	152	156
max in $\Delta\rho$ (e $Å^{-3}$)	0.684	0.904	0.797	0.557
min in $\Delta\rho$ (e $Å^{-3}$)	−0.744	−1.315	−0.622	−0.583
GOF on F^2	1.027	1.005	1.066	1.042
R1[a]	0.0298	0.0586	0.0292	0.0223
wR2[b]	0.0666	0.1148	0.0740	0.0543

[a] $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|]$. [b] $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

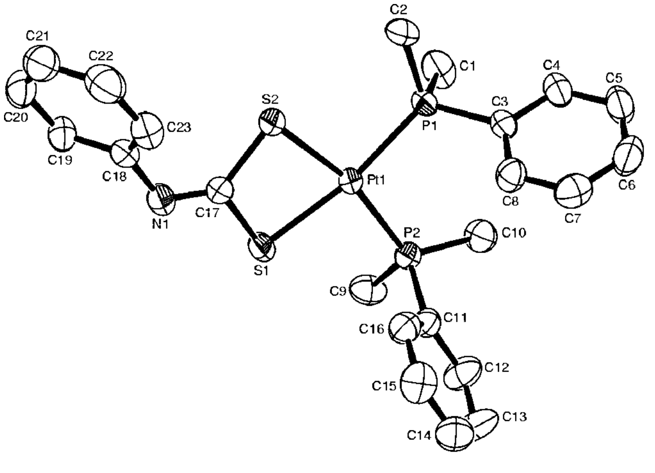


Figure 1. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.270(1), Pt1−P2 = 2.277(2), Pt1−S1 = 2.337(2), Pt1−S2 = 2.339(2), S1−C17 = 1.755(6), S2−C17 = 1.781(6), N1−C17 = 1.268(7), N1−C18 = 1.411(8); P1−Pt1−P2 = 99.26(5), P1−Pt1−S1 = 169.34, P2−Pt1−S1 = 91.35(5), P1−Pt1−S2 = 94.32(5), P2−Pt1−S2 = 165.71(5), S1−Pt1−S2 = 75.21(5), C17−S1−Pt1 = 88.83(19), C17−S2−Pt1 = 88.2(2), C17−N1−C18 = 123.2(5), N1−C17−S1 = 122.5(4), N1−C17−S2 = 129.9(5), S1−C17−S2 = 107.6(3).

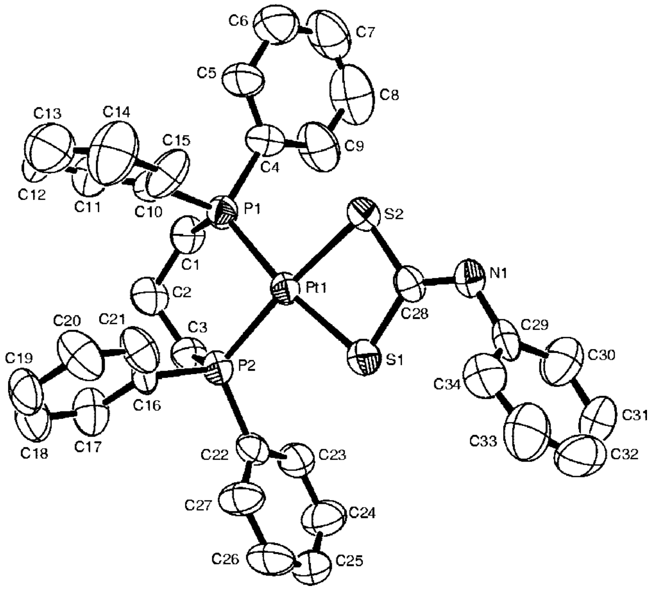


Figure 2. ORTEP drawing of **4**·CH_2Cl_2·H_2O. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.248(3), Pt1−P2 = 2.257(3), Pt1−S1 = 2.337(3), Pt1−S2 = 2.340(3), S1−C28 = 1.770(12), S2−C28 = 1.766(12), N1−C28 = 1.270(1), N1−C29 = 1.450(2); P1−Pt1−P2 = 92.0(1), P1−Pt1−S1 = 171.0(1), P2−Pt1−S1 = 97.0(1), P1−Pt1−S2 = 95.3(1), P2−Pt1−S2 = 172.3(1), S1−Pt1−S2 = 75.7(1), C28−S1−Pt1 = 87.9(4), C28−S2−Pt1 = 87.9(4), C28−N1−C29 = 119(1), N1−C28−S2 = 122.2(9), N1−C28−S1 = 129(1), S2−C28−S1 = 108.5(6).

and 2.327(5) Å) in *cis*-[Pt($S_2C{=}NCH_2Ph$)(PEt_3)$_2$].[11a] These Pt−S bond lengths are slightly shorter than those (2.392 Å for **6** and 2.376 Å for **7**) in the Pt(II) diphenysilanedithiolato complexes, probably reflecting more distorted metallacyclobutane rings in the former dithiocarbonimidato complexes as compared to those in the latter complexes. These Pt−S lengths are comparable to those (2.367(15) and 2.333(17) Å) in [Pt(S_2Si(Tbt)(Mes)(PPh_3)$_2$] (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl; Mes = 2,4,6-trimethylphenyl)[12] and are also comparable to the Pd−S bond lengths (2.362(1) and 2.392(1) Å) in [Pd(S_2SiMe_2)(PEt_3)$_2$].[13] These bonding parameters indicate that the Pt(II) dithiolato complexes in this work are more

---

(12) Tanabe, T.; Takeda, N.; Tokitoh, N. *Eur. J. Inorg. Chem.* **2007**, 1225.

(13) Komuro, T.; Matsuo, T.; Kawaguchi, H.; Tatsumi, K. *Chem. Commun.* **2002**, 988.

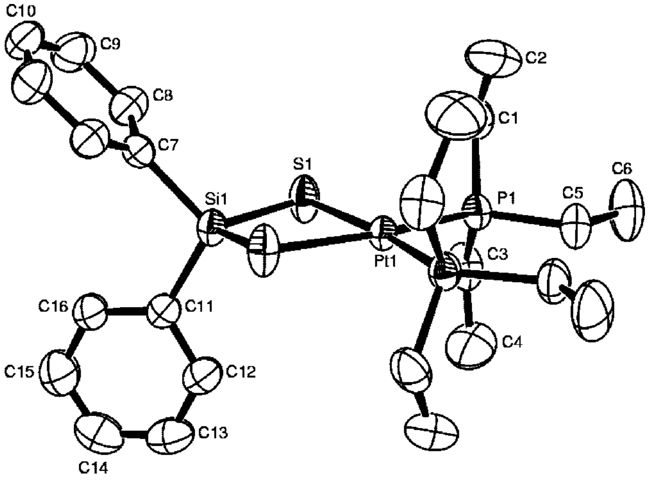


Figure 3. ORTEP drawing of **6**. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.269(1), Pt1−S1 = 2.392(1), S1−Si1 = 2.0992(16); P1−Pt1−S1 = 85.27(4), Si1−S1−Pt1 = 86.90(5).

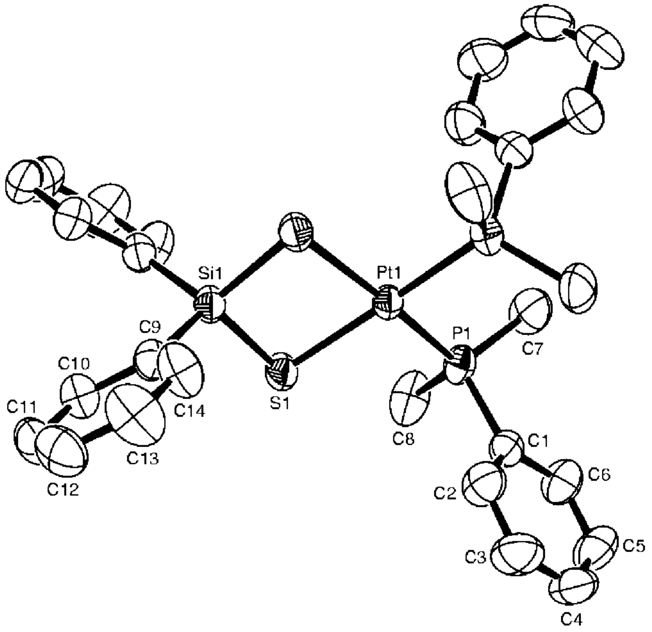


Figure 4. ORTEP drawing of **7**. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.267(1), Pt1−S1 = 2.376(1), S1−Si1 = 2.113(1); P1−Pt1−S1 = 89.57(4), Si1S1−Pt1 = 87.97(4).

symmetric (equal M−S bond lengths) than those of other Pt(II) or Pd(II) complexes having bridging silane groups.

In summary, we carried out several reactions of Pt(II) bis(silyl) complexes with organic unsaturated isothiocyanates (RNCS) under various conditions. These reactions produced novel Pt(II) dithiocarbonimidato complexes [Pt(S_2C=NR)L_2] (R = Ph, *p*-tolyl, 2,6-$Me_2C_6H_3$, *i*-Pr) or Pt(II) diphenylsilanedithiolato complexes [Pt(S_2SiPh_2)L_2], depending on the temperature, stoichiometry, and the nature of the phosphine ligand, and may proceed via either sulfur abstraction from organic isothiocyanate-coordinated complexes or the silyl migration from them.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were performed under N_2 or Ar by 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 (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra were obtained on a JEOL Lambda 300 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si (^{1}H and ^{13}C{^{1}H}) and to external 85% H_3PO_4 (^{31}P{^{1}H}). PhNCS, *p*-tolylNCS, 2,6-$Me_2C_6H_3NCS$, and *i*-PrNCS were purchased and used without further purification. [Pt($SiHPh_2$)$_2L_2$] (L = PMe_3, PEt_3, PMe_2Ph) complexes were prepared according to the literature[14] with some modified methods. [Pt($SiHPh_2$)$_2$(dppp)] was prepared by treating [Pt($SiHPh_2$)$_2$(PMe_3)$_2$] with 1 equiv of dppp. IR (KBr, cm^{-1}): ν(SiH) 2063, 2026. ^{1}H NMR ($CDCl_3$, δ): 1.90 (m, 2H, PCH_2CH_2−), 2.46 (m, 4H, PCH_2−), 4.97 (dd, 2H, J_{P-H} = 17 Hz, J_{Pt-H} = 68 Hz, SiH), 6.91−7.34 (m, 40H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 20.2 (s, PCH_2CH_2−), 28.8 (t, J_{C-P} = 14.9 Hz, PCH_2−), 126.4, 126.7, 127.9 (t, J_{C-P} = 4.9 Hz), 129.8, 132.4, 132.7, 133.0, 133.3 (t, J_{C-P} = 6.2 Hz, J_{Pt-C} = 27 Hz), 136.6 (s, J_{Pt-C} = 22 Hz), 141.8 (t, J_{C-P} = 3.8 Hz, J_{PtC} = 35 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): 5.13 (s, J_{Pt-P} = 1604 Hz, J_{P-Si} = 118 Hz).

Preparation of Complexes 1, 4, and 5. THF (7 mL) and PhNCS (0.158 g, 1.17 mmol) were added to a Schlenk flask containing [Pt($SiHPh_2$)$_2$(PMe_2Ph)$_2$] (0.490 g, 0.585 mmol). After it was stirred for 40 h at room temperature, the reaction mixture was completely evaporated under vacuum and the resulting oily residue was solidified with ether/CH_2Cl_2 (7:1). The solids were filtered and washed with hexane (2 × 2 mL). Recrystallization with ether/CH_2Cl_2 (3:1) gave white crystals of [Pt(S_2C=NPh)(PMe_2Ph)$_2$], (**1**; 0.150 g, 41%). IR (KBr, cm^{-1}): ν(CN) 1564. ^{1}H NMR ($CDCl_3$, δ): 1.57 (dd, J_{P-H} = 9.9, 51 Hz, 12H, P*Me*$_2$Ph), 7.00−7.05 (m, 1H, Ph), 7.16−7.19 (m, 2H, Ph), 7.26−7.47 (m, 12H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 14.2 (d, J_{P-C} = 27 Hz, P*Me*$_2$Ph), 14.7 (d, J_{P-C} = 25 Hz, P*Me*$_2$Ph), 122.3, 123.1, 128.4, 128.6, 128.8, 130.5, 130.7, 130.8, 130.9, 130.9, 147.1, 173.6 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −19.2 (d, *J* = 27 Hz, J_{Pt-P} = 2982), −19.9 (d, *J* = 27 Hz, J_{Pt-P} = 2956 Hz). Anal. Calcd for $C_{23}H_{27}NP_2S_2Pt$: C, 43.26; H, 4.26; N, 2.19. Found: C, 42.90; H, 4.29; N, 2.27.

Complexes **4** and **5** were prepared analogously. Data for [Pt(S_2C=N-Ph)(dppp)] (**4**; 30%) are as follows. IR (KBr, cm^{-1}): ν(CN) 1558. ^{1}H NMR ($CDCl_3$, δ): 2.01 (m, 2H, PCH_2CH_2−), 2.56 (m, 4H, PCH_2), 6.82−6.86 (m, 3H, Ph), 7.05−7.12 (m, 2H, Ph), 7.28−7.33 (m, 7H, Ph), 7.50 (m, 13H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 19.9 (s, PCH_2CH_2−), 25.3 (br, PCH_2), 122.5, 123.0, 128.6, 128.8, 128.9, 130.0, 131.5, 133.2, 133.3, 133.5, 147.5, 173.6 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −4.74 (d, *J* = 38 Hz, J_{Pt-P} = 2801 Hz), −5.13 (d, *J* = 35 Hz, J_{Pt-P} = 2887 Hz). Anal. Calcd for $C_{34}H_{31}NP_2S_2Pt \cdot 0.5CH_2Cl_2$: C, 50.70; H, 3.95; N, 1.71. Found: C, 50.61; H, 3.95; N, 1.79. Data for [Pt(S_2C=NC_6H_4-*p*-Me)(dppp)] (**5**; 37%) are as follows. IR (KBr, cm^{-1}): ν(CN) 1547. ^{1}H NMR ($CDCl_3$, δ): 2.01−2.26 (m, 2H, PCH_2CH_2−), 2.21 (s, 3H, Me), 2.50−2.64 (m, 4H, PCH_2), 6.94−7.03 (m, 4H, Ph), 7.26−7.38 (m, 12H, Ph), 7.52−7.60 (m, 8H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 19.7 (s, PCH_2CH_2−), 20.9 (s, Me), 25.3 (br, PCH_2), 122.5 (s, J_{C-P} = 4.4 Hz), 128.5 (dd, J_{C-P} = 4.4, 10 Hz), 128.8, 131.0, 131.1, 132.0, 133.0 (dd, J_{C-P} = 4.9, 10 Hz), 144.3, 172.9 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −4.75 (d, *J* = 35 Hz, J_{Pt-P} = 2821 Hz), −5.29 (d, *J* = 38 Hz, J_{Pt-P} = 2858 Hz). Anal. Calcd for $C_{35}H_{33}NP_2S_2Pt$: C, 53.29; H, 4.22; N, 1.78. Found: C, 53.50; H, 4.32; N, 1.58.

Preparation of Complexes 2 and 3. THF (7 mL) and *p*-tolylNCS (0.158 g, 1.10 mmol) were added to a Schlenk flask containing [Pt($SiHPh_2$)$_2$(PMe_2Ph)$_2$] (0.422 g, 0.504 mmol). After it was stirred for 6 h at 50 °C, the reaction mixture was completely evaporated under vacuum, and the resulting oily residue was solidified with ether/CH_2Cl_2 (14:1). The solids were filtered and washed with hexane (2 × 2 mL). Recrystallization with ether/CH_2Cl_2 (6:1) gave white crystals of [Pt(S_2C=NC_6H_4-*p*-Me)(PMe_2Ph)$_2$] (**2**; 0.105 g, 32%). IR (KBr, cm^{-1}): ν(CN) 1578.

---

(14) Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349.

^{1}H NMR ($CDCl_3$): 1.57 (dd, J_{P-H} = 9.9, 20 Hz, 12H, P*Me*$_2$Ph), 2.30 (s, 3H, Me), 7.10 (s, 4H, Ph), 7.27−7.47 (m, 10H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 14.2 (dd, J_{C-P} = 2.5, 29 Hz, P*Me*$_2$Ph), 14.7 (dd, J_{C-P} = 2.5, 29 Hz, P*Me*$_2$Ph), 21.0 (s, Me), 122.1, 128.6, 128.7, 129.0, 130.5, 130.6, 130.7, 130.8, 130.9, 132.3, 144.4, 172.5 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −19.1 (d, *J* = 27 Hz, J_{Pt-P} = 2978), −19.9 (d, *J* = 27 Hz, J_{Pt-P} = 2955 Hz). Anal. Calcd for $C_{24}H_{29}NP_2S_2Pt$: C, 44.17; H, 4.48; N, 2.15. Found: C, 44.66; H, 4.66; N, 1.89.

Complex **3** was prepared analogously. Data for [Pt($S_2C{=}NC_6H_3$-2,6-Me_2)(PMe_3)$_2$] (**3**; 33%) are as follows. IR (KBr, cm^{-1}): ν(CN) 1564. ^{1}H NMR ($CDCl_3$): 1.63 (br, 18H, P*Me*$_3$), 2.18 (s, 6H, Me), 6.86 (dd, 1H, *J* = 6.6, 8.1 Hz, Ph). 6.98 (d, *J* = 7.3 Hz, 2H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 16.6 (d, J_{C-P} = 38 Hz, J_{Pt-C} = 38 Hz, PMe_3), 18.4 (s, CH_3), 122.5, 127.2, 128.9, 145.0, 170.9 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −29.7 (br s, J_{Pt-P} = 2923 Hz), −30.6 (br s, J_{Pt-P} = 2901 Hz). Anal. Calcd for $C_{15}H_{27}NP_2S_2Pt$: C, 33.21; H, 5.02; N, 2.58. Found: C, 33.48; H, 5.05, N, 2.44.

Preparation of Complex 6. THF (7 mL) and PhNCS (0.103 g, 0.762 mmol) were added to a Schlenk flask containing [Pt($SiHPh_2$)$_2$(PEt_3)$_2$] (0.608 g, 0.762 mmol). After it was stirred for 18 h at room temperature, the reaction mixture was completely evaporated under vacuum, and the resulting oily residue was solidified with diethyl ether. The solids were filtered and washed with hexane (2 × 2 mL). Recrystallization with ether/CH_2Cl_2 (5:1) gave white crystals of [Pt(S_2SiPh_2)(PEt_3)$_2$], (**6**; 0.160 g, 31%). ^{1}H NMR ($CDCl_3$, δ): 1.13 (qt, *J* = 7.5, 16 Hz, 18H, P(CH_2CH_3)$_3$), 2.00 (m, 12H, P(CH_2CH_3)$_3$), 7.28−7.32 (m, 6H, Ph), 7.78−7.81 (m, 4H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 8.28 (s, J_{Pt-C} = 24 Hz, P(CH_2CH_3)$_3$), 16.3 (d, J_{C-P} = 36 Hz, J_{Pt-C} = 26 Hz, P(CH_2CH_3)$_3$), 127.2, 128.5, 133.4, 144.9. ^{31}P{^{1}H} NMR ($CDCl_3$): 7.14 (s, J_{Pt-P} = 3076 Hz). Anal. Calcd for $C_{24}H_{40}P_2S_2SiPt$: C, 42.53; H, 5.95. Found: C, 42.92; H, 5.81.

Similar treatments with *p*-tolylNCS also gave complex **6**.

Preparation of Complexes 7 and 8. THF (3 mL) and *p*-tolylNCS (0.114 g, 0.764 mmol) were added to a Schlenk flask containing [Pt($SiHPh_2$)$_2$(PMe_2Ph)$_2$] (0.320 g, 0.382 mmol). After it was stirred for 40 h at room temperature, the reaction mixture was completely evaporated under vacuum, and then the resulting oily residue was solidified with ether/CH_2Cl_2 (10:1). The solids were filtered and washed with hexane (2 × 2 mL). Recrystallization with ether/CH_2Cl_2 (5:1) gave pale yellow crystals of [Pt(S_2SiPh_2)(PMe_2Ph)$_2$], (**7**; 0.061 g, 22%). ^{1}H NMR ($CDCl_3$, δ): 1.64 (d, J_{P-H} = 10 Hz, J_{Pt-H} = 34 Hz,, 12H, P*Me*$_2$Ph), 7.26−7.50 (m, 16H, Ph), 7.84−7.90 (m, 4H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 14.3 (d, J_{C-P} = 42 Hz, J_{Pt-C} = 31 Hz, P*Me*$_2$Ph), 127.4, 128.5, 129.1, 130.9, 133.5, 144.6. ^{31}P{^{1}H} NMR ($CDCl_3$): −17.3 (s, J_{Pt-P} = 3076 Hz). Anal. Calcd for $C_{28}H_{32}P_2S_2SiPt$: C, 46.85; H, 4.49. Found: C, 47.01; H, 4.64.

An analogous reaction of [Pt($SiHPh_2$)$_2$(PMe_2Ph)$_2$] with *i*-PrNCS gave a mixture of [Pt(S_2SiPh_2)(PMe_2Ph)$_2$] (**7**) and [Pt($S_2C{=}NR$)(PMe_2Ph)$_2$] (**8**; R = *i*-Pr). Data for **8** are as follows. IR (KBr, cm^{-1}): ν(CN) 1583. ^{1}H NMR ($CDCl_3$, δ): 1.23 (d, *J* = 6.2 Hz, 6H, CH(CH_3)$_2$), 1.58 (dd, *J* = 3.1, 10 Hz, J_{Pt-H} = 33 Hz, 12H, P*Me*$_2$Ph), 4.35 (sept, *J* = 6.2 Hz, 1H, C*H*(CH_3)$_2$), 7.29−7.48 (m, 10H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 14.2 (dd, J_{C-P} = 4.4, 28 Hz, P*Me*$_2$Ph), 14.7 (dd, J_{C-P} = 5.6, 27 Hz, P*Me*$_2$Ph), 23.6 (CH(CH_3)$_2$), 53.4 (*C*H(CH_3)$_2$), 128.6, 128.7, 130.6, 130.7, 130, 8, 130.9, 133.1 (dd, J_{C-P} = 6.8, 10 Hz), 133.7, 166.0 (CN). ^{31}P{^{1}H} NMR ($CDCl_3$): −19.5 (d, *J* = 26 Hz, J_{Pt-P} = 2948 Hz), −19.9 (d, *J* = 26 Hz, J_{Pt-P} = 2955 Hz). Complexes **7** and **8** could not be separated due to similarities in solubility.

Structure Determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ-scan data. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode. All calculations were carried out with the use of the SHELX-97 programs.[15]

Acknowledgment. This work was supported by the research fund (2007) of Kangnung National University and partly by a Korea Research Foundation Grant funded by the Korean Government (MOEHARD, Basic Research Promotion Fund; No. KRF-2007-521-C00148).

Supporting Information Available: CIF files giving crystallographic data for complexes **1**, **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8006079

---

[15] Sheldrick, G. M. SHELX-97; University of Göttingen, Göttingen, Germany, 1997.