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Preliminary communication

Double oxidative addition of the Si–Si and Si–Ge bonds onto isonitrile–platinum(0) complexes leading to the formation of tetrakis(organosilyl)- and bis(organogermyl)bis(organosilyl)platinum(IV) complexes [1]

Michinori Suginome, Hideaki Oike, Philippa H. Shuff, Yoshihiko Ito *

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

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Abstract

Tetrakis(organosilyl)bis(t-butyl isocyanide)platinum(IV) complex was prepared by reaction of 2,2-bis(disilanyl)dithiane with $Pt_3(CN^tBu)_6$ through double oxidative addition of the two Si–Si bonds to the platinum atom. In contrast, the reaction of hexamethyldisilane with the platinum(0) complex gave only the corresponding bis(trimethylsilyl)bis(t-alkyl isocyanide)platinum(II), which did not undergo further oxidative addition with hexamethyldisilane. Reactions of 2,2-bis(silylgermyl)dithiane with $Pd(CN^tBu)_2$ and $Pt_3(CN^tBu)_6$ similarly afforded bis(organogermyl)palladium(II) and bis(organogermyl)bis(organosilyl)platinum(IV) complexes respectively.

Keywords: Silicon; Germanium; Palladium; Platinum; Isocyanide

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1. Introduction

We recently reported that bis(t-alkyl isocyanide)palladium(0) complexes facilitated an intramolecular metathesis of two Si–Si bonds oriented appropriately within a molecule to give cyclic bis(organosilyl)palladium(II) complexes [1]. We assumed that the reaction involved a five-centered intermediate or transition state, in which the four silicon atoms are equally coordinated to the palladium atom. Herein, we describe the isolation of a tetrakis(organosilyl)bis(t-butyl isocyanide) platinum(IV) complex, which may be relevant to the intermediate proposed for the palladium-mediated metathesis, from the reaction of 2,2-bis(disilanyl)dithiane with $Pt_3(CN^tBu)_6$. We also found that two Si–Ge bonds of 2,2-bis(silylgermyl)dithiane reacted similarly with the isonitrile–palladium(0) and –platinum(0) complexes to give bis(organogermyl)bis(t-butyl isocyanide)palladium(II) and bis(organogermyl)bis(organosilyl)bis(t-butyl isocyanide)platinum(IV) complexes respectively, formation of the latter being accompanied by that of a tetrakis(organogermyl)platinum(IV) complex.

2. Results and discussion

2,2-Bis(disilanyl)dithiane **1**, which gave the four-membered ring bis(organosilyl)palladium(II) complex **2** in the reaction with $Pd(CN^tBu)_2$, was stirred for 24 h in refluxing benzene in the presence of a stoichiometric amount of $Pt_3(CN^tBu)_6$ (Scheme 1). The reaction was monitored by ^1H NMR, revealing that substrate **1** was gradually consumed and new signals similar to those for **2** appeared. The product mixture was chromatographed on silica gel to afford tetrakis(organosilyl)bis(t-butyl isocyanide)platinum(IV) complex **3** in 27% yield. The formation of **3** arises from double oxidative addition of the two Si–Si bonds of **1** to the platinum(0) complex. No complex corresponding to **3** was formed when **1** was treated with the complex $Pt(PPh_3)_2(CH_2{=}CH_2)$ at 50 to 80°C. (Experimental details for **3**: m.p. 166.0–167.0°C (dec.); ^1H NMR ($CDCl_3$) δ 0.46 (s, $^3J_{Pt-H} = 12.1$ Hz, 12 H), 0.53 (s, $^3J_{Pt-H} = 12.0$ Hz, 12 H), 1.46 (s, 18 H),

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* Corresponding author.

[1] Dedicated to Professor R.J.P. Corriu in recognition of his outstanding contributions to organosilicon chemistry.

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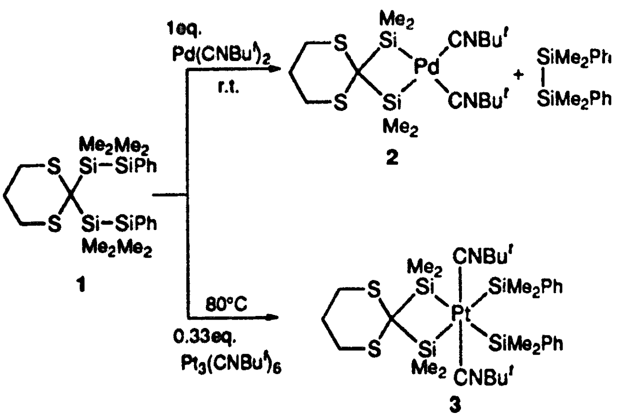


Scheme 1.

1.88–2.00 (m, 2 H), 2.52–2.58 (m, 4 H), 7.20–7.30 (m, 6 H), 7.40–7.48 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 1.4 (br), 5.1 ($^2J_{Pt-C}$ = 28.3 Hz), 26.2, 28.9, 29.9, 33.5 ($^2J_{Pt-C}$ = 103.6 Hz), 58.1 ($^3J_{Pt-C}$ = 11.0 Hz), 117.2 (br), 126.8, 127.0, 133.6, 149.0 ($^2J_{Pt-C}$ = 20.6 Hz); ^{29}Si NMR (CDCl$_3$) δ −29.6 (br $^1J_{Pt-Si}$ = 383 Hz), −30.1 ($^1J_{Pt-Si}$ = 461 Hz); IR (KBr) 2900, 2172, 1232, 800 cm^{-1}. Anal. Found: C, 47.01; H, 6.88; N, 3.21. $C_{34}H_{58}N_2PtS_2Si_4$. Calc.: C, 47.13; H, 6.75; N, 3.23%.)

The crystal structure of **3** is shown in Fig. 1, along with selected bond distances and angles. In the octahedral complex, two isocyanide ligands occupy the apical positions and the four silyl ligands lie at the vertices of a distorted square with the platinum atom at the center. Interestingly, the trans orientation of the isocyanide ligands is in contrast to the cis coordination of the phosphine ligands in a closely related tetrakis(organosilyl)platinum(IV) complex recently reported by Tanaka et al. [2].

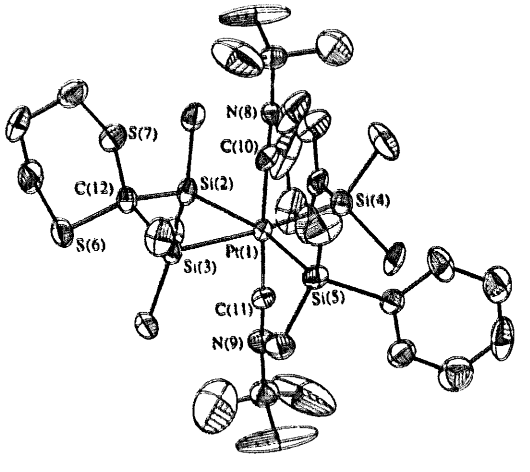
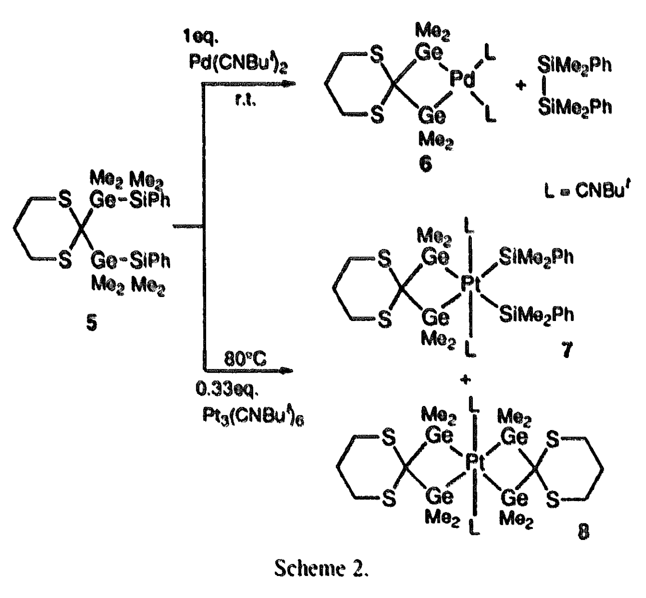


Fig. 1. ORTEP drawing of 3 (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are follows: Pt(1)–Si(2) = 2.49(1), Pt(1)–Si(3) = 2.456(8), Pt(1)–Si(4) = 2.481(9), Pt(1)–Si(5) = 2.472(8), Pt(1)–C(10) = 1.92(3), Pt(1)–C(11) = 1.902(1); Si(2)–Pt(1)–Si(3) = 68.6(3), Si(2)–Pt(1)–Si(4) = 99.6(3), Si(3)–Pt(1)–Si(5) = 93.1(3), Si(4)–Pt(1)–Si(5) = 98.8(3), Si(2)–Pt(1)–C(10) = 89.1(8), Si(2)–Pt(1)–C(11) = 93.2(2).

$$\mathrm{Pt_3(CNAd)_6}\ \xrightarrow[\text{benzene, }80^\circ\mathrm{C}]{30\text{ eq, }\mathrm{Me_3Si{-}SiMe_3}}\ \underset{\textbf{4}\ (93\%)}{\mathrm{(Me_3Si)_2Pt(CNAd)_2}} \quad (1)$$

We found that a reaction of Pt$_3$(CNAd)$_6$ (Ad = 1-adamantyl) with an excess (30 equivalents) of hexamethyldisilane in benzene at 80°C gave the complex bis(trimethylsilyl)bis(adamantyl isocyanide)platinum(II) **4** in high yield (Eq. (1)); (Pt$_3$(CN^{t}Bu)$_6$ similarly gave a complex corresponding to **4**, but high solubility in most organic solvents made its isolation difficult). This indicates that the formation of the platinum(IV) complex in the reaction of bis(disilanyl)dithiane **1** may be facilitated by the appropriate orientation of the two Si–Si bonds in **1** for simultaneous interaction with the platinum atom. (Experimental details for **4**: m.p. 155–158°C (dec.); ^{1}H NMR (C$_6$D$_6$) δ 0.95 (s, $^3J_{Pt-H}$ = 16.3 Hz, 18 H), 1.22 (br, 12 H), 1.62 (br, 6 H), 1.84 (br, 12 H); ^{13}C NMR (C$_6$D$_6$) δ 7.7 ($^2J_{Pt-C}$ = 45.9 Hz), 28.9, 35.2, 43.0, 57.9 ($^3J_{Pt-C}$ = 15.6 Hz), 146.4 (br); IR (KBr) 2940, 2144, 822 cm^{-1}. Anal. Found: C, 50.65; H, 7.34; N, 4.25. $C_{28}H_{48}N_2PtSi_2$. Calc.: C, 50.65; H, 7.29; N, 4.22%.)

The reactions of bis(silylgermyl)dithiane with palladium- and platinum–isonitrile complexes were subsequently scanned, since activation of Si–Ge bonds by transition metal complexes has been little studied. Reaction of 2,2-bis[(dimethylphenylsilyl)dimethylgermyl]dithiane (**5**) with Pd(CN^{t}Bu)$_2$ gave the four-membered ring bis(organogermyl)palladium(II) complex **6** quantitatively (Scheme 2). Though formation of a similar four-membered bis(organogermyl)(phosphine)palladium(II) complex was reported in the reaction of a highly strained digermirane with Pd(PPh$_3$)$_4$, an X-ray



Scheme 2.

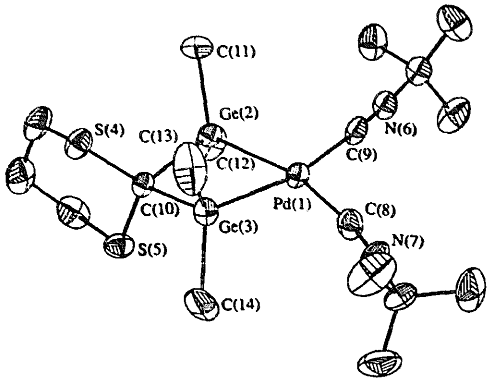


Fig. 2. ORTEP drawing of **6** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are follows: Pd(1)–Ge(2) = 2.427(2), Pd(1)–Ge(3) = 2.404(2), Pd(1)–C(8) = 2.06(2), Pd(1)–C(9) = 2.06(2), N(6)–C(9) = 1.12(2), N(7)–C(8) = 1.13(3); Ge(2)–Pd(1)–Ge(3) = 69.9(1), Ge(2)–Pd(1)–C(9) = 93.1(4), Ge(3)–Pd(1)–C(8) = 89.7(5), C(8)–Pd(1)–C(9) = 107.3(6), Pd(1)–Ge(2)–C(10) = 100.3(4), Ge(2)–C(10)–Ge(3) = 86.3(5), Pd(1)–Ge(3)–C(10) = 101.5(4).

structural determination could not be carried out owing to the instability of the complex toward the radiation [3]. In contrast, complex **6** exhibited a crystal structure similar to that of the silicon analog **2**, in which the two isocyanides coordinated at a relatively large angle (Fig. 2). (Experimental details for **6**: m.p. 158.5–160°C (dec.); ^{1}H NMR (C_6D_6) δ 0.90 (s, 18 H), 1.09 (s, 12 H), 2.00–2.14 (m, 2 H), 2.67–2.78 (m, 4 H); ^{13}C NMR (C_6D_6) δ 2.1, 28.0, 29.9, 31.0, 35.8, 56.0, 146.6 (br); IR (C_6H_6) 2146 cm^{-1}. Anal. Found: C, 36.02; H, 6.17; N, 4.49. $C_{18}H_{36}Ge_2N_2PdS_2$. Calc.: C, 36.26; H, 6.09; N, 4.70%.)

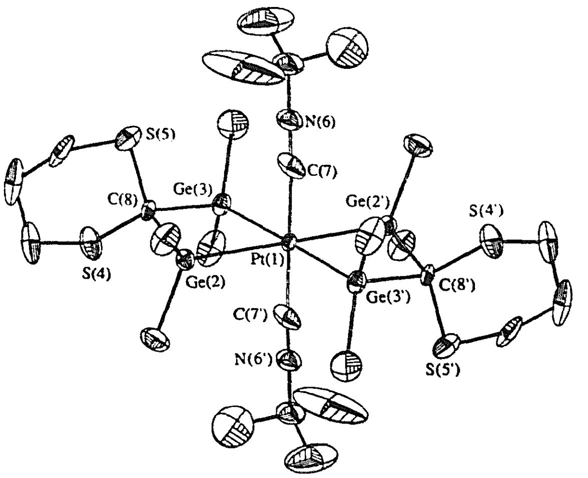


Fig. 3. ORTEP drawing of **8** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are follows: Pt(1)–Ge(2) = 2.506(2), Pt(1)–Ge(3) = 2.489(3), Pt(1)–C(7) = 1.98(3), N(6)–C(7) = 1.14(3); Ge(2)–Pt(1)–Ge(3) = 72.7(1), Ge(2)–Pt(1)–Ge(3′) = 107.3(1), Ge(2)–Pt(1)–C(7) = 90.7(7), Ge(2)–Pt(1)–C(7′) = 89.3(7), Ge(3)–Pt(1)–C(7) = 90.8(7), Ge(3)–Pt(1)–C(7′) = 89.2(7), Pt(1)–Ge(2)–C(8) = 94.9(5), Pt(1)–Ge(3)–C(8) = 95.6(6), Ge(2)–C(8)–Ge(3) = 94.5(7).

Bis(silylgermane) **5** was found to give the bis(organogermyl)bis(organosilyl)platinum(IV) complex **7** in 30% yield in the reaction with $Pt_3(CN^tBu)_6$ (Scheme 2); tetrakis(organogermyl)platinum(IV) complex **8** was also obtained as a by-product, but in low yield (11%) (Fig. 3).(Experimental details for **7**: m.p. 181.0–182.0°C (dec.); ^{1}H NMR ($CDCl_3$) δ 0.53 (s, $^3J_{Pt-H}$ = 13.5 Hz, 12 H), 0.54 (s, $^3J_{Pt-H}$ = 8.8 Hz, 12 H), 1.48 (s, 18 H), 1.88–2.00 (m, 2 H), 2.46–2.54 (m, 4

Table 1
Summary of crystallographic data for **3**, **6**, and **8** [a]

compound	**3**	**6**	**8**
Formula	$C_{34}H_{58}H_2PtS_2Si_4$	$C_{18}H_{36}Ge_2N_2PdS_2$	$C_{26}H_{54}Ge_4N_2PtS_4$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P*21/c (no. 14)	*P*1 (no. 2)	*P*21/a (no. 14)
a (Å)	19.298(8)	8.263(4)	13.061(6)
b (Å)	17.196(8)	10.936(6)	16.809(9)
c (Å)	12.552(6)	15.431(8)	9.563(4)
a (deg)		94.57(4)	
β (deg)	95.82(3)	100.06(4)	111.38(3)
γ (deg)		102.40(4)	
Cell vol (Å^3)	4144(3)	1331(1)	1955(2)
Z	4	2	2
ρ (calcd), g cm^{-3}	1.39	1.49	1.71
Crystal size, mm	0.40 × 0.40 × 0.20	0.30 × 0.55 × 0.70	0.50 × 0.40 × 0.40
μ, cm^{-3}	86.375	96.629	121.96
Reflns measured	7683	4939	3610
Independent reflns	6671	4348	3204
Reflns used	5243	3775	2860
No. of variables	425	259	196
R, *Rw*	0.101, 0.134	0.072, 0.087	0.080, 0.093

[a] Intensity data collections were carried out with a Mac Science MXC3 diffractometer using graphite-monochromatized Cu K α (λ = 1.54178 Å) radiation at 293K. Intensity data was collected using ω/2θ scans and corrected for Lorentzian polarization and for absorption by analytical function.

H), 7.20–7.30 (m, 6 H), 7.38–7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -0.4 (br), 5.3 ($^2J_{Pt-C} = 33.0$ Hz), 26.4, 29.5, 30.0, 44.6 ($^2J_{Pt-C} = 85.7$ Hz), 58.3 ($^3J_{Pt-C} = 11.3$ Hz), 117.1 (br), 127.0, 127.1, 133.5, 148.3 ($^2J_{Pt-C} = 23.5$ Hz); ^{29}Si NMR ($CDCL_3$) δ -26.3 ($^1J_{Pt-Si} = 515$ Hz); IR (KBr) 2904, 2172, 1194, 798 cm^{-1}. Anal. Found: C, 42.69; H, 6.19; N, 2.95. $C_{34}H_{58}Ge_2N_2PtS_2Si_2$. Calc.: C, 42.74; H, 6.12; N, 2.93%.) (Table 1).

The formation of the platinum(IV) complexes in the reaction of bis(disilane) **1** and bis(silylgermane) **5** with the platinum(0)–isonitrile complex provides support for the suggested involvement of the corresponding palladium complexes in the palladium-mediated intramolecular metathesis of Si–Si and Si–Ge bonds.

Acknowledgements

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