

# Transition Metal Silyl Complexes. 62.<sup>1</sup> Platinum Dimethyl Complexes with Hemilabile P,N-Chelating Ligands: Synthesis, Structure, and Reactions with Iodotrimethylsilane and 1,2-Bis(dimethylsilyl)benzene

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Reaction of ( $\eta^4$ -2,5-norbornadiene)dimethylplatinum(II) with (2-diphenylphosphinoethyl)-dimethylamine, (3-diphenylphosphinopropyl)dimethylamine, 2-diphenylphosphino-*N,N*-dimethylaniline, or (*o*-diphenylphosphinobenzyl)dimethylamine resulted in the formation of the corresponding dimethyl platinum complexes containing the P,N-chelating ligands, while reaction with (diphenylphosphinomethyl)dimethylamine gave only the bis(phosphine) complex. Reaction of the P,N-chelated dimethyl complexes with iodotrimethylsilane stereoselectively gave the corresponding methyl iodo complexes in which only the methyl group trans to the phosphorus atom was exchanged. Reaction with 1,2-bis(dimethylsilyl)benzene yielded cyclic bis(silyl) complexes. Analogous experiments with (dppe)PtMe<sub>2</sub> revealed that the P,N-chelated complexes exhibit a considerably higher reactivity than the bis(phosphine) complex. The most interesting feature in the solid-state structures of [ $(\kappa^2$ -P,N)-Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>-NMe<sub>2</sub>]PtMe<sub>2</sub>, *trans*-[ $(\kappa^2$ -P,N)-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>NMe<sub>2</sub>]Pt(I)Me, and [ $(\kappa^2$ -P,N)-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-NMe<sub>2</sub>]Pt[*o*-(Me<sub>2</sub>Si)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] is the very long Pt–N distances (221.0(7), 223.3(6), and 236.8(5) pm, respectively), showing that the nitrogen atom of the P,N-chelating ligand is only weakly bonded. The Pt–C and Pt–Si distances trans to nitrogen are much shorter (203.7(9), 230.4(2) pm) than those trans to phosphorus (206.9(8), 237.2(2) pm).

## Introduction

Square planar complexes of late transition metals bearing P,N-chelating ligands (P(N)MX<sub>2</sub> (M = Pd, Pt; X: e.g., halide, alkyl) are known to allow highly stereoselective substitution reactions of the ligands X. The stereochemical outcome of the ligand substitution reaction can be explained by the different electronic properties of the nitrogen and phosphorus donor atoms.<sup>2</sup> For example, (P(N)Pd(Br)Me (P(N) = 2-(diphenylphosphino)benzylidene-*S*(-)- $\alpha$ -methylbenzylamine) was obtained by reaction of (P(N)PdBr<sub>2</sub> with Me<sub>4</sub>Sn with complete trans stereoselectivity.<sup>3,4</sup> In an analogous reaction, *trans*-(P(N)Pd(I)Me (P(N) = *o*-diphenylphosphinobenzyl)dimethylamine) was obtained from (P(N)-PdMe<sub>2</sub> by reaction with MeI.<sup>5</sup> Only recently, the selectivity of this reaction was used to synthesize chiral cationic phosphino-oxazoline platinum complexes by a methyl dichloromethane exchange reaction; these complexes were tested in the enantioselective epoxidation of terminal alkenes.<sup>6</sup> P,N-chelating ligands are known

to be hemilabile, with the nitrogen donor being rapidly (de)coordinated, thus providing a free coordination site.<sup>7</sup>

With respect to the chemistry of metal silyl complexes,<sup>8</sup> the introduction of P,N-chelating ligands is of special interest because of the potential to obtain hitherto unknown bis(silyl) complexes bearing two electronically different silyl ligands. This could have interesting consequences for the reactivity of these compounds. The most promising precursors for the synthesis of P,N-chelated (bis)silyl complexes are the corresponding dimethyl complexes, because of the known ease of methyl/silyl exchange reactions.<sup>9</sup>

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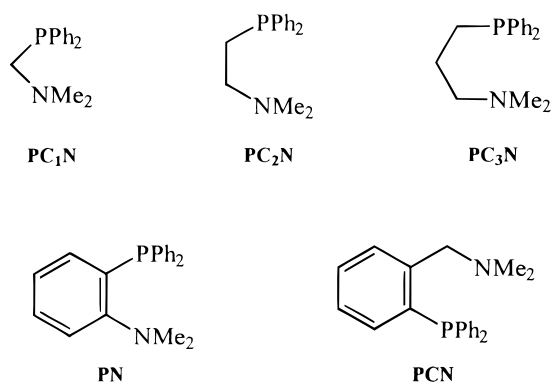
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**Figure 1.** Employed P,N-chelating ligands.

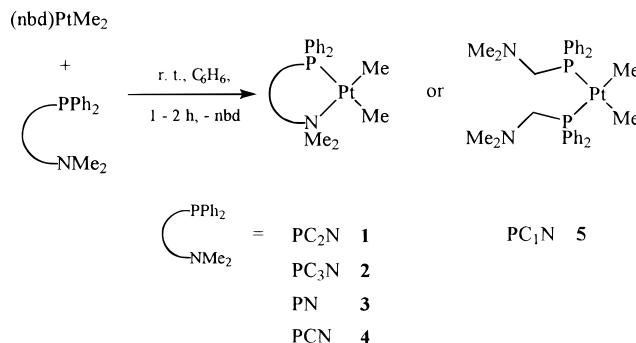
Recently, we reported that the platinum dimethyl complex  $[(\kappa^2\text{-P,N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2]\text{PtMe}_2$  (**1**), containing a hemilabile P,N-chelating ligand, readily reacts with trimethoxysilane, while the corresponding bis(phosphine) complex  $(\text{dppe})\text{PtMe}_2$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) is unreactive.<sup>10</sup> The higher reactivity was attributed to the reversible decoordination of the weakly bonded nitrogen atom that reversibly opens a coordination site at the metal. The *cis* methyl trimethoxysilyl complex *cis*- $[(\kappa^2\text{-P,N})\text{-Me}_2\text{NCH}_2\text{CH}_2\text{PPh}_2]\text{-Pt}[\text{Si}(\text{OMe})_3]\text{-Me}$ ,<sup>11</sup> the bis(trimethoxysilyl) complex  $[(\kappa^2\text{-P,N})\text{-Me}_2\text{NCH}_2\text{CH}_2\text{PPh}_2]\text{-Pt}[\text{Si}(\text{OMe})_3]_2$ , and methyltrimethoxysilane were identified among the products, but also large portions of tetramethoxysilane. The formation of the latter compounds suggests that the hemilabile ligand promotes not only the oxidative addition of the silane but also scrambling reactions of the silicon substituents, possibly via silylene intermediates.

To have a broader range of starting compounds available to exploit the potential emerging from this observation and to investigate the influence of the ring size and ring rigidity of the P,N-chelating ligand on the reactivity of the complexes, we prepared other P,N-chelated platinum dimethyl complexes. We report here on their synthesis and structure and on their reactions with iodotrimethylsilane and 1,2-bis(dimethylsilyl)benzene. The following P,N-ligands were employed (Figure 1): (diphenylphosphinomethyl)dimethylamine ( $\text{PC}_1\text{N}$ ), (2-diphenylphosphinoethyl)dimethylamine ( $\text{PC}_2\text{N}$ ), (3-diphenylphosphinopropyl)dimethylamine ( $\text{PC}_3\text{N}$ ), 2-diphenylphosphino-*N,N*-dimethylaniline ( $\text{PN}$ ), and (*o*-diphenylphosphinobenzyl)dimethylamine ( $\text{PCN}$ ).

## Results and Discussion

**Synthesis of P,N-Chelated Platinum Dimethyl Complexes.** Reaction of  $(\eta^4\text{-2,5-norbornadiene})\text{dimethylplatinum(II)}$ ,  $(\text{nbd})\text{PtMe}_2$ ,<sup>12</sup> with  $\text{PC}_2\text{N}$ ,  $\text{PC}_3\text{N}$ ,  $\text{PN}$ , or  $\text{PCN}$  in benzene at room temperature led to almost quantitative formation of the chelated complexes **1–4**. They were isolated as crystalline compounds in 77–84% yield.<sup>13</sup> In contrast, when  $(\text{nbd})\text{PtMe}_2$  was reacted with

## Scheme 1. Synthesis of the Dimethyl Complexes 1–5



(diphenylphosphinomethyl)dimethylamine ( $\text{PC}_1\text{N}$ ) under various reaction conditions and different  $(\text{nbd})\text{-PtMe}_2/\text{PC}_1\text{N}$  ratios, only the bis(phosphine) complex **5** was isolated (Scheme 1) and no P,N-chelated complex was observed. The latter result is in contrast to reactions of  $\text{dppm}$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with complexes of the type  $(\eta^4\text{-bisolefin})\text{PtCl}_2$  by which  $(\text{dppm})\text{PtCl}_2$  is obtained.<sup>14</sup> The corresponding complex  $(\text{PC}_1\text{N})\text{PtMe}_2$  is possibly too unstable because of the weak coordination of the nitrogen; the weak Pt–N bond cannot compensate the strain of a four-membered ring, and a second phosphorus donor is coordinated.

The  $^1\text{H}$  NMR spectra (Table 1) of the complexes **1–4** showed two doublets with platinum satellites resulting from the Pt–Me ligands and a singlet with platinum satellites for the methyl substituents at nitrogen. The  $^3J_{\text{PtNCH}}$  coupling of the latter resonances unambiguously proved the coordination of the nitrogen atom to the metal. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1–4** showed the resonances of the Pt–Me groups at about 14 ppm ( $\text{CH}_3$  trans to phosphorus) and about –20 ppm (*cis* to phosphorus) as doublets with platinum satellites. Their stereochemical assignment was made on the basis of the different  $^2J_{\text{PPtC}}$  coupling constants ( $^2J_{\text{PPtC}}^{\text{cis}} \approx 4\text{--}6\text{ Hz}$ ,  $^2J_{\text{PPtC}}^{\text{trans}} \approx 110\text{ Hz}$ ).<sup>15</sup> In contrast, the resonances of the chemically equivalent methyl ligands in the bis(phosphine) complex **5** appeared as a doublet of doublets with platinum satellites both in the  $^1\text{H}$  and in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum due to the *cis* and *trans* couplings to the two phosphorus atoms. The  $^1J_{\text{PTP}}$  coupling constants extracted from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **1–5** were found to be in the typical range for platinum complexes with phosphine ligands *trans* to a ligand with a strong *trans*-influence.<sup>15</sup>

**Reactions of the Complexes 1–4 with Iodotrimethylsilane.** Reactions of diimine platinum dimethyl complexes with various group IV trimethyl halides have been reported to lead to the formation of octahedral coordinated platinum(IV) complexes by *trans* addition of the M–X bond.<sup>16,17</sup> Contrary to that, when the compounds **1–4** were reacted with iodotrimethylsilane, no reaction occurred at room temperature. Only heating to 60 °C resulted in the formation of new complexes

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(13)  $(\text{nbd})\text{PtMe}_2$  was found to give better yields in the ligand substitution reaction than the analogous 1,5-cyclooctadiene (COD) complex. This is attributed to the smaller bite angle of nbd compared to COD, enhancing the ease of the ligand displacement: Appleton, T. G.; Hall, J. R.; Williams, M. A. *J. Organomet. Chem.* **1986**, *303*, 139, and references cited therein.

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**Table 1. Characteristic  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data of Complexes 1–5<sup>a</sup>**

complex	$\delta$ (PtCH <sub>3</sub> ) <sup>b</sup>	$\delta$ (N(CH <sub>3</sub> ) <sub>2</sub> ) <sup>c</sup>	$\delta$ (PtCH <sub>3</sub> ) <sup>d</sup>	$\delta$ (N(CH <sub>3</sub> ) <sub>2</sub> )	$\delta$ ( $^{31}\text{P}$ ) <sup>e</sup>
<b>1</b>	1.21 (66.68, 7.73) <sup>f</sup> 1.48 (89.73, 7.33) <sup>g</sup>	2.24 (18.01)	−24.69 (748.7, 4.2) 14.45 (709.8, 113.5)	49.19	35.93 (2071.5)
<b>2</b>	0.14 (87.04, 8.63) 0.35 (64.29, 7.58)	2.60 (18.78)	−20.93 (745.5, 5.5) 14.83 (719.6, 113.5)	51.26	15.29 (2113.0)
<b>3</b>	1.27 (65.20, 7.52) <sup>f</sup> 1.53 (91.11, 7.41) <sup>g</sup>	2.87 (17.44)	−24.04 (755.3, 4.3) 17.66 (718.4, 112.3)	52.14	34.79 (2128.9)
<b>4</b>	0.21 (86.11, 8.18) <sup>g</sup> 0.37 (65.76, 7.45) <sup>f</sup>	2.37 (18.90) 2.80 (19.26)	−20.06 (748.3, 4.4) 13.49 (723.2, 112.3)	47.52, 52.85	25.24 (2061.8)
<b>5</b>	1.18 (69.01, 6.23, 7.79) <sup>h</sup>	2.16	6.95 (617.3, 98.0, 8.2) <sup>h</sup>	48.10	9.59 (1837.2)

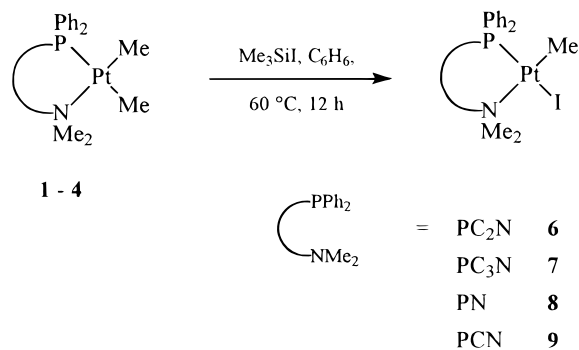
<sup>a</sup> C<sub>6</sub>D<sub>6</sub> (**1**, **3**, **5**) or acetone-*d*<sub>6</sub> (**2**); the spectra of **4** were recorded in acetone-*d*<sub>6</sub> at 233 K. <sup>b</sup>  $^2J_{\text{PtCH}}$  and  $^3J_{\text{PPtCH}}$  (Hz) in parentheses. <sup>c</sup>  $^3J_{\text{PtNCH}}$  (Hz) in parentheses. <sup>d</sup>  $^1J_{\text{PtC}}$  and  $^2J_{\text{PPtC}}$  (Hz) in parentheses. <sup>e</sup>  $^1J_{\text{PtP}}$  (Hz) in parentheses. <sup>f</sup> *trans*-CH<sub>3</sub> as determined by a gs-CH-HMQC experiment. <sup>g</sup> *cis*-CH<sub>3</sub> as determined by a gs-CH-HMQC experiment. <sup>h</sup> *Cis*- and *trans*-coupling constants to phosphorus.

**Table 2. Characteristic  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data of the Complexes 6–9 (CDCl<sub>3</sub>)<sup>a</sup>**

complex	$\delta$ (PtCH <sub>3</sub> ) <sup>b</sup>	$\delta$ (N(CH <sub>3</sub> ) <sub>2</sub> ) <sup>c</sup>	$\delta$ (PtCH <sub>3</sub> ) <sup>d</sup>	$\delta$ (N(CH <sub>3</sub> ) <sub>2</sub> )	$\delta$ ( $^{31}\text{P}$ ) <sup>e</sup>
<b>6</b>	0.89 (75.69, 3.66)	3.02 (n.o.)	−26.44 (602.7, 5.5)	51.95	29.24 (4642.3)
<b>7</b>	0.58 (71.98, 5.30)	2.98 (13.41)	−21.52 (572.2, 6.0)	54.38	9.99 (4685.0)
<b>8</b>	1.08 (75.57, 3.74)	3.52 (11.21)	−25.74 (609.3, 5.0)	54.95	19.90 (4616.7)
<b>9</b>	0.79 (72.02, 4.88)	2.66, 3.20	−21.02 (579.8, 4.5)	49.23, 56.12	16.30 (4688.7)

<sup>a</sup> 298 K (**6**–**8**) and 253 K (**9**). <sup>b</sup>  $^2J_{\text{PtCH}}$  and  $^3J_{\text{PPtCH}}$  (Hz) in parentheses. <sup>c</sup>  $^3J_{\text{PtNCH}}$  (Hz) in parentheses. <sup>d</sup>  $^1J_{\text{PtC}}$  and  $^2J_{\text{PPtC}}$  (Hz) in parentheses. <sup>e</sup>  $^1J_{\text{PtP}}$  (Hz) in parentheses.

### Scheme 2. Reaction of the P,N-Chelated Complexes 1–4 with Iodotrimethylsilane



along with tetramethylsilane within 12 h as monitored by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (3 h in the reaction of **2**). Platinum(IV) complexes were not observed by NMR spectroscopy during the reaction, and the *trans* iodo methyl complexes **6**–**9** were obtained in very good yields as the only metal-containing products after crystallization from petroleum ether (30/50)/benzene (10:1) (Scheme 2).<sup>4</sup> Puddephatt et al.<sup>18</sup> have described the formation of (bpy)Pt(I)Me (bpy = 2,2'-bipyridine) by heating (bpy)Pt(I)(SiMe<sub>3</sub>)Me<sub>2</sub> (obtained from (bpy)PtMe<sub>2</sub> and Me<sub>3</sub>SiI<sup>19</sup>) to 177–192 °C. Accordingly, the formation of the complexes **6**–**9** can be rationalized by an oxidative addition of Me<sub>3</sub>Si–I followed by a reductive elimination of tetramethylsilane.

The stereochemistry of the complexes **6**–**9** (iodide *trans* to phosphorus) was confirmed by the low chemical shift values of the Pt–Me ligands *trans* to nitrogen in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra ( $\approx -23$  ppm) and by the small

$^2J_{\text{PPtC}^{\text{cis}}}$  coupling constants ( $\approx 5$  Hz) typical for a *trans* N–Pt–C arrangement (Table 2). In addition, an X-ray structure analysis of **9** unambiguously proved the stereochemical arrangement of the ligands (*vide infra*). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were characterized by significantly larger  $^1J_{\text{PtP}}$  coupling constants ( $\approx 4600$  Hz) than in the starting compounds **1**–**4**. Such large values of  $^1J_{\text{PtP}}$  are typical for platinum phosphine complexes bearing ligands with a weak *trans* influence (e.g., halide, alkoxide).<sup>15,20</sup> The stereoselectivity of the methyl/iodide exchange reaction which has already been observed in the reaction of P,N-chelated palladium dimethyl complexes with organic halides<sup>5</sup> can be explained by the different  $\pi$ -acceptor properties of the ligands, leading to the *trans* arrangement of the strongest  $\pi$ -acceptor ligand (phosphorus) with the  $\pi$ -donor ligand (iodide).

**Reaction of the Complexes 1–4 with 1,2-Bis(dimethylsilyl)benzene.** 1,2-bis(silyl)benzenes are known for their pronounced tendency to form chelated bis(silyl) complexes when reacted, for example, with  $\eta^2$ -alkene or dialkylmetal complexes, due to the ease of an intramolecular oxidative addition reactions.<sup>9c,21</sup> Reaction of the dialkyl platinum(II) complexes **1**, **3**, and **4** with 1,2-bis(dimethylsilyl)benzene at 60 °C led to the bis(silyl)platinum(II) complexes **10**–**12** and methane (identified by GC) within 60 h. The complexes were isolated by crystallization from 1:10 benzene/petroleum ether (30/50) in very good yields (Scheme 3). They were quite stable in the solid state under an atmosphere of argon, but slowly decomposed in air. Surprisingly, complete consumption of the dimethyl complexes could only be achieved when 2 equiv of 1,2-bis(dimethylsilyl)benzene

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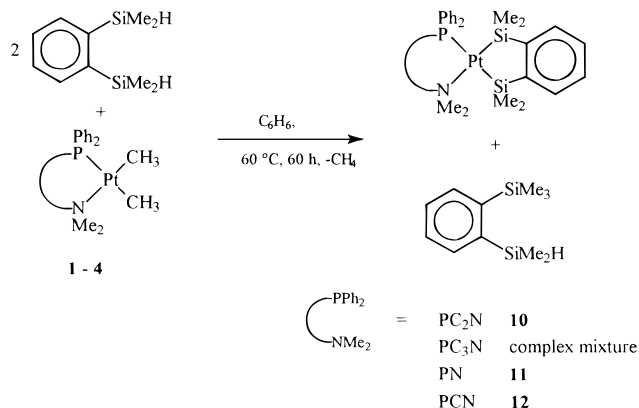


**Table 3.** Characteristic  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{29}\text{Si}$ –INEPT, and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data of the Complexes 10–12 (acetone- $d_6$ )

complex	$\delta(\text{SiCH}_3)^a$	$\delta(\text{NCH}_3)^b$	$\delta(\text{SiCH}_3)^c$	$\delta(\text{NCH}_3)$	$\delta(^{29}\text{Si})^d$	$\delta(^{31}\text{P})^e$
<b>10</b>	–0.08 (31.62) 0.42 (24.09, 2.81)	2.98 (17.57)	4.77 (3.7) 5.15 (7.4)	50.06	–0.81 (1424.3, 5.6) 29.49 (1501.8, 167.7)	57.07 (1392.8, 167.2)
<b>11</b>	–0.04 (32.51) 0.46 (22.54, 2.85)	3.41 (15.36)	4.30 (3.6) 4.99 (8.3)	54.12	–1.38 (1510.3, 3.6) 30.04 (1490.4, 164.0)	51.37 (1481.9, 161.1)
<b>12<sup>f</sup></b>	–0.46, 0.10, 0.21, 0.53	2.64 (18.43) 3.03 (20.07)	4.87 (4.9) 5.78 (n.o.) 6.33 (8.7) 8.00 (4.9)	50.09 55.41	–2.39 (1452.4, 6.2) 28.09 (1507.5, 167.3)	38.52 (1439.8, 154.9)

<sup>a</sup>  $^3J_{\text{PtSiCH}}$  and  $^4J_{\text{PPtSiCH}}$  (Hz) in parentheses. <sup>b</sup>  $^3J_{\text{PtNCH}}$  (Hz) in parentheses. <sup>c</sup>  $^3J_{\text{PPtSiCH}}$  (Hz) in parentheses. <sup>d</sup>  $^1J_{\text{PtSi}}$  and  $^2J_{\text{PPtSi}}$  (Hz) in parentheses. <sup>e</sup>  $^1J_{\text{PtP}}$  and  $^2J_{\text{SiPtP}}$  (Hz) in parentheses. <sup>f</sup> 240 K.

**Scheme 3. Reaction of Complexes 1–4 with 1,2-Bis(dimethylsilyl)benzene**



was employed, and 1-dimethylsilyl-2-trimethylsilylbenzene ( $\delta^{29}\text{Si}$ : –3.78,  $\text{SiMe}_3$ ; –20.43,  $\text{SiHMe}_2$ ) was formed along with the bis(silyl) complexes in a 1:1 ratio. In addition, traces of 4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene **13** was found (<5%,  $\delta^{29}\text{Si}$ : 14.93).

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the bis(silyl) complexes showed the phosphorus signal accompanied by platinum and trans silicon satellites (Table 3). Compared to the iodide methyl complexes **6–9**, the  $^1J_{\text{PtP}}$  coupling constants are much smaller, due to the strong trans influence of the silyl ligand.<sup>15</sup> The signals of the  $\text{Si–CH}_3$  groups in the  $^1\text{H}$  NMR spectra of **10–12** showed the coupling to phosphorus and were accompanied by platinum satellites. The chemically different silicon atoms gave resonances at significantly different chemical shifts in the  $^{29}\text{Si}$  NMR spectra (INEPT): Whereas the resonance of the silicon atom trans to phosphorus, assigned by the typically large  $^2J_{\text{PPtSi}}^{\text{trans}}$  coupling constant ( $\approx 165$  Hz), was found at about 30 ppm, the silicon atom trans to nitrogen showed a chemical shift of about –1 ppm ( $^2J_{\text{PPtSi}}^{\text{cis}} \approx 5$  Hz). This lower chemical shift of the silicon atom trans to nitrogen may be the result of the stronger electron back-donation from platinum to silicon due to the missing  $\pi$ -acceptor properties of nitrogen and the weak Pt–N bond.

The necessity of 2 equiv 1,2-bis(dimethylsilyl)benzene for complete consumption of the dimethyl complexes as well as the formation of 1-dimethylsilyl-2-trimethylsilylbenzene is in accordance with the reaction mechanism depicted in Scheme 4, which has already been postulated for the reaction of **1** with  $\text{HSi(OMe)}_3$ .<sup>10</sup> Oxidative addition of 1,2-bis(dimethylsilyl)benzene followed by reductive elimination of methane is presumed to lead to the formation of the methyl(silyl) complex **I**, the analogue of which was observed in the reaction of **1**

with  $\text{HSi(OMe)}_3$ . In the reaction described here, intermediate **I** was not detected. Unexpectedly, no intramolecular addition seems to occur in the next step of the reaction, but instead intermolecular oxidative addition of a second molecule of 1,2-bis(dimethylsilyl)benzene, followed by reductive C–Si elimination of 1-dimethylsilyl-2-trimethylsilylbenzene to give the hydrido(silyl) complex **II**. This is in accordance with the formation of complexes **10–12** and 1-dimethylsilyl-2-trimethylsilylbenzene in a 1:1 ratio. Subsequent intramolecular reaction via intermediate **III** followed by elimination of  $\text{H}_2$  yields the bis(silyl) complexes **10–12**. Interestingly, there is no scrambling of the substituents at the silicon atoms as we have observed in the reaction of **1** with  $\text{HSi(OMe)}_3$ .<sup>10</sup> This is probably due to the incorporation of both silicon atoms in a chelate ring.

Formation of **13** is probably due to traces of oxygen in the reacting system. However, another experiment showed that **13** is probably not formed from the bis(silyl) complexes: By heating in air, **11** was quantitatively converted to the bis(silanolate) analogue ( $\kappa^2\text{-P,N}$ )-(PN)Pt[ $\sigma\text{-(OMe}_2\text{Si)C}_6\text{H}_4$ ], but no **13** was formed.<sup>1</sup>

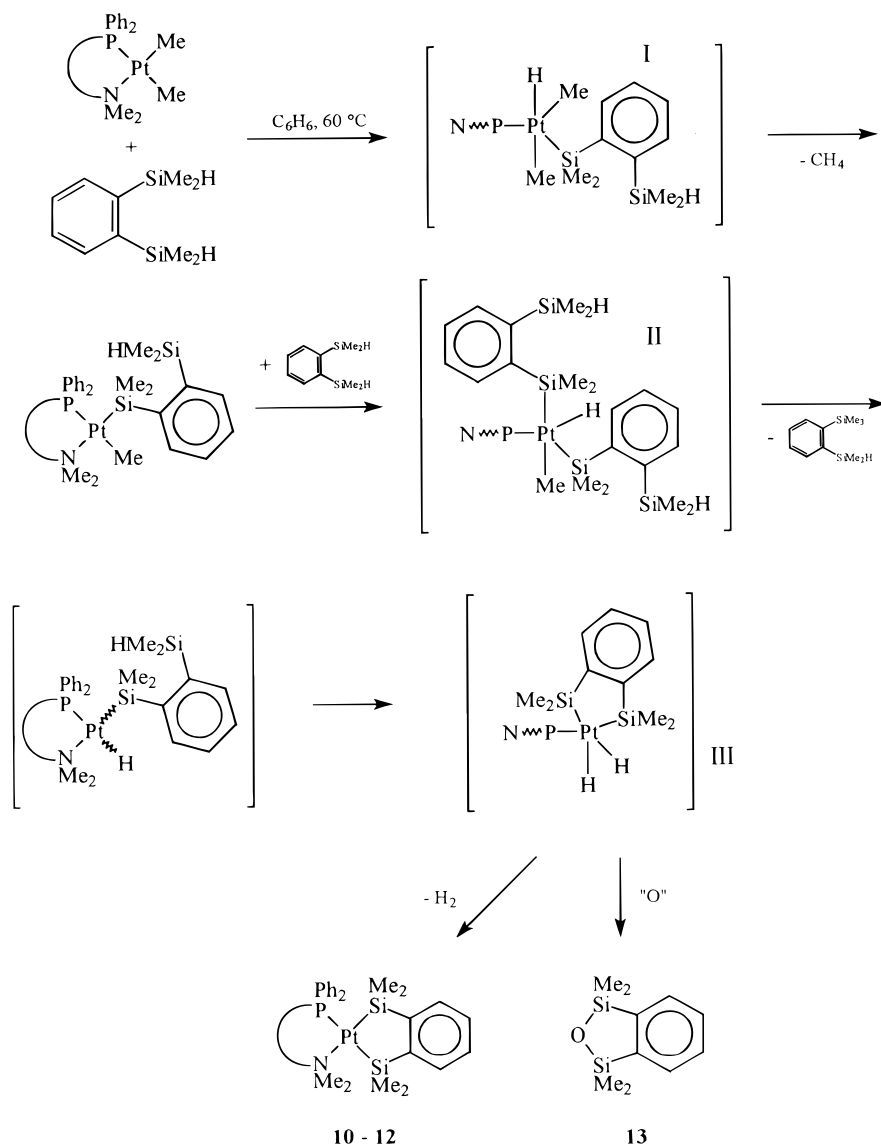
Possible explanations for the formation of **13** are the insertion of oxygen into a platinum silicon bond in a platinum(IV) intermediate and subsequent reductive elimination of **13** or the catalytic oxidation of the hydridosilane, followed by oxidative addition of the OH and the SiH group, and elimination of **13**.

Compared to the complexes **1**, **3**, and **4**,  $(\text{PC}_3\text{N})\text{PtMe}_2$  (**2**) exhibited a higher reactivity in the reaction with 1,2-bis(dimethylsilyl)benzene: A vigorous reaction accompanied by a color change of the solution from pale yellow to dark red readily occurred at room temperature. Within 6 h, **2** was completely consumed (monitored by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR). Along with 1-dimethylsilyl-2-trimethylsilylbenzene, four new platinum complexes were formed ( $\delta^{31}\text{P}$ : 7.22,  $^1J_{\text{PtP}} = 3147.23$  Hz; 19.39,  $^1J_{\text{PtP}} = 2799.87$  Hz; 23.08,  $^1J_{\text{PtP}} = 1649.50$  Hz; 25.87,  $^1J_{\text{PtP}} = 1462.07$  Hz), but the identity of these compounds remains unclear, because separation could not be achieved.

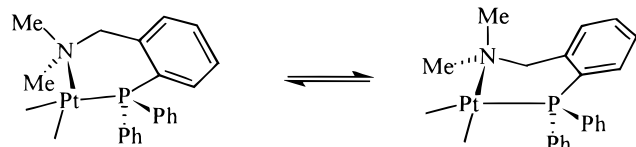
**Dynamic Behavior of the Complexes 4, 9, and 12 in Solution.** As already reported for  $(\text{PCN})\text{Pd}(\text{Me})\text{[OCH(CF}_3)_2]$ ,  $(\text{PCN})\text{Pd}(\text{Me})(\text{OC}_6\text{H}_5)$ ,<sup>22</sup> and  $(\text{PCN})\text{RhCl}(\text{CO})$ ,<sup>23</sup> the complexes **4**, **9**, and **12** containing the PCN ligand showed only broad resonances in the  $^1\text{H}$  NMR spectra for the methylene protons as well as for the protons of *N*-methyl groups at room temperature,

(22) Kapteijn, G. M.; Spec, M. R. P.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 1405.

(23) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652.

**Scheme 4. Suggested Mechanism for the Formation of the Bis(silyl) Complexes 10–12<sup>a</sup>**

<sup>a</sup> It remains unclear whether the dimethyl amino group is coordinated to the metal in the platinum(IV) intermediates; stereochemical drawing has been done arbitrarily.



**Figure 2.** Conformational interconversion of the PCN ligand in complexes **4**, **9**, and **12** in solution.

resulting from the flexibility of the PCN ligand (Figure 2). Above 323 K, these resonances formed two sharp averaged signals, whereas below the coalescence temperatures (**4**, 276 K; **9**, 289 K; **12**, 266 K) the diastereotopic protons gave rise to separate resonances. From these spectroscopic results, the activation enthalpies  $\Delta G^\ddagger$  for the conformational interconversion have been calculated to be 55 kJ/mol (**4**), 57 kJ/mol (**9**), and 51 kJ/mol (**12**), respectively.<sup>24</sup>

**Comparative Experiments with (dppe)PtMe<sub>2</sub>.** We recently reported the enhanced reactivity of (PC<sub>2</sub>N)-

PtMe<sub>2</sub> compared to (dppe)PtMe<sub>2</sub> in the reaction with HSi(OMe)<sub>3</sub>.<sup>10</sup> To confirm this observation for the reactions described in this article, (dppe)PtMe<sub>2</sub> was reacted with iodotrimethylsilane and 1,2-bis(dimethylsilyl)benzene, respectively, under the same conditions as the P,N-substituted complexes. In the reaction with Me<sub>3</sub>SiI, (dppe)Pt(Me)I and tetramethylsilane were formed, but the reaction was much slower. After 12 h (when **1–4** had completely reacted), only 30% conversion was observed by <sup>1</sup>H NMR, while complete reaction required 48 h. By crystallization from 10:1 petroleum ether (30/50)/benzene, (dppe)Pt(Me)I was isolated in 88% yield.<sup>25</sup> When (dppe)PtMe<sub>2</sub> was treated with 1,2-bis(dimethylsilyl)benzene at 60 °C for 60 h, no reaction was observed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. These experiments clearly show the enhanced reactivity of the P,N-chelated platinum dimethyl complexes compared to (dppe)PtMe<sub>2</sub> due to the weakly bonded nitrogen ligand.

**X-ray Structure Analyses of **1**, **9**, and **11**** (Figures 3–5, Tables 3 and 4). As expected, all complexes showed an almost square planar coordination of the platinum

(24) Braun, S.; Kalinowski, H.-O.; Berger, S. *150 and More Basic NMR Experiments*; Wiley-VCH: Weinheim, 1998; p 136.

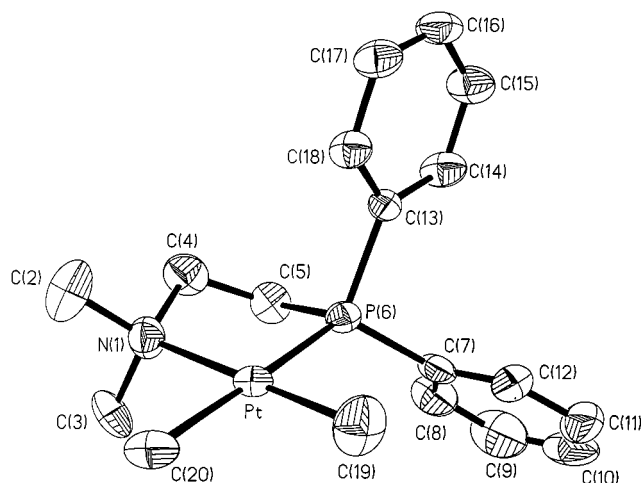


Figure 3. Molecular structure of **1**.

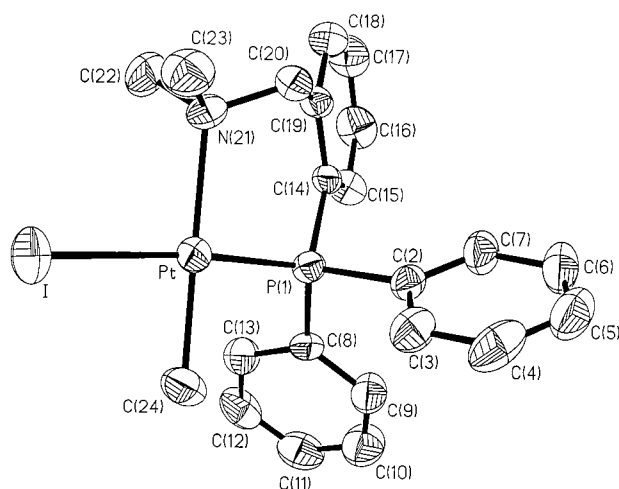


Figure 4. Molecular structure of **9**.

atom (sum of angles at Pt close to 360°). Deviations from an orthogonal arrangement of cis ligands are mainly due to the different "bite angles" of the employed P,N ligands, which is the smallest for PN (in **11**) and the largest for PCN (in **9**) and due to the steric strain imposed by the phenyl substituents bound to phosphorus. The five-membered ring in **1** adopts a distorted envelope conformation, with P, Pt, N, and C(4) being almost coplanar. In **11**, the dihedral angle between the coordination plane of the platinum atom and the plane Si(30), C(31), C(36), Si(37) is 166°, and 148.7° with the plane formed by N(1), C(2), C(7), P(8), respectively. The six-membered ring in **9** adopts a slightly distorted boat conformation with Pt, N, C(14), and C(19) being almost in one plane.

The most interesting structural feature is the distances between the platinum atom and the ligand atoms, particularly the Pt–P and Pt–N distances (Table 5). Despite the different radii of the P and N atoms, the Pt–N and Pt–P distances are of the same magnitude, as already reported for other dimethyl transition metal complexes containing phosphorus and nitrogen donor atoms in a cis arrangement ((Ph<sub>3</sub>P)(py)PtMe<sub>2</sub> Pt–P

224.3(1), Pt–N 221.0(7) pm;<sup>26</sup> (P∩N)AuMe<sub>2</sub> [P∩N = 3,7-dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane] Au–P 218.1(9), Au–N 222(1) pm<sup>27</sup>). This indicates that the Pt–N bond is much weaker than the Pt–P bond. The complexes **1** and **11** are of particular interest, because they bear the same ligands trans to phosphorus and nitrogen. The first interesting observation is that the Pt–P bond in **11** is about 6 pm longer than in **1**, whereas the Pt–N bond in **11** is lengthened by 15 pm (!) compared to **1**. This lengthening causes the Pt–N distance in **11** (similar in **9**) to become longer than the Pt–P distance. The Pt–N distance in **11** is, to the best of our knowledge, the longest Pt–N bond distance in a square planar platinum complex reported so far.<sup>28</sup> The bis(silyl) complex **11** may thus be considered a T-shaped (three-coordinate) complex weakly stabilized by a nitrogen donor atom. This is in line with the previously reported high tendency for redistribution reactions of substituents at silicon, which are favored by an empty coordination site at the metal.<sup>10,29</sup>

In general, bond lengths trans to silyl ligands are longer than trans to alkyl ligands owing to the  $\pi$ -acceptor property of the silyl ligands. On the other hand, the  $\pi$ -donation of the iodide ligand in **9** results in a shortening of the Pt–P bond (2.204(2) Å). With 2.6697(6) Å, the length of the Pt–I bond lies within the range of known complexes with a trans P–Pt–I arrangement.<sup>30</sup> In both **1** and **11**, the Pt–C or Pt–Si distance trans to the weakly bonded nitrogen atom is significantly longer than trans to the phosphorus atom. The relative increase in length is 1.6% in the dimethyl complex **1**, but 3.0% in the bis(silyl) complex **11**. This clearly shows that the Pt–C(Si) bonds are increasingly strengthened as the Pt–N interaction becomes weaker. The weaker Pt–N interaction in **11** is possibly due to the lower basicity of the aryl-bonded amino group. The combination of the trans influence of the silyl ligand and the lower basicity of the nitrogen atom results in the large lengthening of the Pt–N distance in **11** compared to **1**.

## Conclusions

We have described the synthesis of some new platinum dimethyl complexes bearing P,N-chelating ligands which show a much higher reactivity toward both iodotrimethylsilane and 1,2-bis(dimethylsilyl)benzene than (dppe)PtMe<sub>2</sub>. This is attributed to the hemilabile P,N ligands which enable reversible opening of a coordination site by decoordination of the amino group.<sup>31</sup>

(26) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1988**, 342, 269.

(27) Assmann, B.; Angermann, K.; Paul, M.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1995**, 125, 891.

(28) Ling, E. C. H.; Allen, G. W.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1993**, 3705. In some cases, longer Pt–N bond lengths have been observed in pentacoordinated platinum(II) compounds, e.g.: (a) Wernberg, O.; Hazell, A. *J. Chem. Soc., Dalton Trans.* **1980**, 973. (b) De Renzi, A.; Di Blasio, B.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Chem.* **1980**, 19, 960.

(29) (a) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed. Engl.* **1998**, 39, 2524. (b) McIndoe, J. S.; Nicholson, B. K. *J. Organomet. Chem.* **1999**, 577, 181.

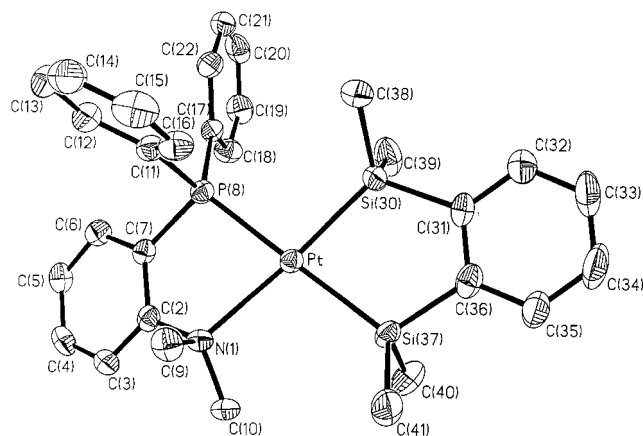
(30) See, e.g.: (a) Lin, I. J. B.; Kao, L. T. C.; Wu, F. J.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1986**, 309, 225. (b) Engelter, C.; Moss, J. R.; Nissimbeni, L. R.; Niven, M. L.; Reid, G.; Spiers, J. C. *J. Organomet. Chem.* **1986**, 315, 255. (c) Argazzi, R.; Bergamini, P.; Costa, E.; Gee, V.; Hogg, J. K.; Martin, A.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1996**, 15, 5591.

(25) Spectroscopic data: <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 45.29 (<sup>1</sup>J<sub>PP</sub> = 1706.5 Hz, *cis*-P), 45.85 (<sup>1</sup>J<sub>PP</sub> = 3978.3 Hz, *trans*-P).<sup>4</sup> <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 0.78 (dd with Pt satellites, 3 H, <sup>2</sup>J<sub>PPCH</sub> = 59.20 Hz, <sup>3</sup>J<sub>PPCH</sub> = 4.88, 7.36 Hz, CH<sub>3</sub>), 2.10–2.45 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 7.10–7.80 (m, 10 H, Ar-H).



**Table 4. Summary of Crystal Data, Data Collection, and Structure Analysis of the Complexes 1, 9, and 11**

	1	9	11
empirical formula	C <sub>18</sub> H <sub>26</sub> NPt	C <sub>22</sub> H <sub>25</sub> INPPT·2C <sub>6</sub> H <sub>6</sub>	C <sub>33</sub> H <sub>36</sub> NPtSi <sub>2</sub> ·C <sub>3</sub> H <sub>6</sub> O
fw	482.46	728.45	644.80
temp [K]	213(2)	293(2)	193(2)
cryst syst, space group	monoclinic, <i>P</i> 2(1)/ <i>n</i>	triclinic, <i>P</i> $\bar{1}$	monoclinic, <i>C</i> 2/ <i>c</i>
<i>a</i> [pm]	808.13(2)	1000.40(2)	2897.92(4)
<i>b</i> [pm]	1798.67(4)	1035.56(1)	1117.26(1)
<i>c</i> [pm]	1243.97(3)	1465.47(3)	2233.75(3)
$\alpha$ [deg]	90	100.655(1)	90
$\beta$ [deg]	91.50	107.717(1)	114.201(1)
$\gamma$ [deg]	90	103.745(1)	90
volume 10 <sup>6</sup> [pm <sup>3</sup> ]	1807.57(7)	1349.41(4)	6596.6(1)
<i>Z</i>	4	2	8
calcd density [g/cm <sup>3</sup> ]	1.773	1.793	1.512
abs coeff [mm <sup>-1</sup> ]	7.845	6.417	4.401
<i>F</i> (000)	936	692	3008
cryst size [mm]	0.24 × 0.22 × 0.015	0.24 × 0.08 × 0.06	0.56 × 0.40 × 0.30
$\theta$ range for data collection [deg]	1.99–23.26	1.52–20.81	1.96–20.86
no. of unique reflns/ <i>R</i> (int)	2576/0.0573	2752/0.0190	3456/0.0662
completeness to $\theta$ [%]	99.8	97.5	99.9
no. of data/restraints/params	2576/0/191	2752/0/290	3456/0/353
goodness-of-fit on <i>F</i> <sup>2</sup>	1.036	1.147	1.151
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0341, <i>wR</i> 2 = 0.0859	<i>R</i> 1 = 0.0274, <i>wR</i> 2 = 0.0670	<i>R</i> 1 = 0.0291, <i>wR</i> 2 = 0.0778
largest diff peak and hole [Å <sup>-3</sup> ]	1.307, −1.570	0.746, −0.890	0.961, −1.080
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0510P)^2]$ , $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 6.30P]$ , $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 53.94P]$ , $P = (F_o^2 + 2F_c^2)/3$

**Figure 5.** Molecular structure of **11**.**Table 5. Important Bond Lengths (in pm) and Angles (deg) in 1, 9, and 11**

	1	9	11
Pt–C/Si (trans P)	206.9(8)		237.2(2)
Pt–C/Si (trans N)	203.7(9)	205.6(8)	230.4(2)
Pt–N	221.0(7)	223.3(6)	236.8(5)
Pt–P	224.3(2)	220.4(2)	230.3(2)
Pt–I		266.97(6)	
N–Pt–P	84.6(1)	93.1(2)	79.1(1)
P–Pt–C/Si (cis)	96.5(2)	88.9(2)	97.18(6)
N–Pt–X (cis)	92.0(2)	92.8(2)	101.2(1)
C/Si–Pt–C/Si/I	87.0(3)	85.7(2)	82.51(6)

In both types of reactions, (PC<sub>2</sub>N)PtMe<sub>2</sub> (**1**), (PN)PtMe<sub>2</sub> (**3**), and (PCN)PtMe<sub>2</sub> (**4**) showed about the same reactivity, whereas (PC<sub>3</sub>N)PtMe<sub>2</sub> (**2**) turned out to be much more reactive. This may have two reasons: Six-membered chelate rings are known to be less stable than five-membered ones. In addition, the PC<sub>3</sub>N ligand contains a highly flexible propylene spacer. Compared to the PCN ligand with the more rigid aryl group (as indicated by the slow conformational interconversion shown by the variable-temperature NMR studies presented) this may result in a lower probability for the

recoordination of the nitrogen donor of the PC<sub>3</sub>N ligand, thus enhancing the reactivity of **3** compared to **12**. In **11**, the weaker Pt–N interaction (due to the aromatic amino group) compared to **1** may also be compensated by the rigidity of the ligand.

By reaction of the dimethyl complexes **1**, **3**, and **4** with 1,2-bis(dimethylsilyl)benzene, the complexes **10–12** were obtained, which represent the first examples of group 10 metal bis(silyl) complexes, bearing two different supporting ligands (phosphorus and nitrogen) trans to silicon. Further experiments with these unsymmetrical substituted bis(silyl) complexes bearing two electronically different Pt–Si bonds will provide further insight into the factors governing the reactivity of metal–silicon bonds.

## Experimental Section

All operations were performed under argon in flame-dried glassware. Solvents were dried (diethyl ether and tetrahydrofuran over sodium, petroleum ether over sodium hydride, chloroform and benzene over CaH<sub>2</sub>) and saturated with argon before use.

Mass spectra were recorded on a Finnigan Voyager mass spectrometer. NMR spectra were recorded on a Bruker AC 250 and a DRX 400 spectrometer (<sup>1</sup>H and <sup>29</sup>Si NMR, TMS as external standard; <sup>31</sup>P NMR, 85% H<sub>3</sub>PO<sub>4</sub> as external standard). Detailed assignments of the NMR signals were made based on CH-HMQC and SiH-HMBC experiments. <sup>29</sup>Si NMR spectra were recorded with an INEPT pulse sequence. The pulse programs for the 2D experiments were taken from the Bruker software library with the following parameters. 400/100 MHz

(31) One referee has suggested an alternative explanation for the enhanced reactivity of the P,N-chelated complexes compared to the bis(phosphine) complexes on the basis of the electronic ground-state properties. However, recent results indicate that reactions of late transition metal diphosphine complexes often occur via predissociation of a phosphine ligand rather than by an associative mechanism: (a) Ozawa, F.; Hikida, T. *Organometallics* **1996**, *15*, 4501. (b) Romeo, R.; Alibrandi, G. *Inorg. Chem.* **1997**, *36*, 4822. In addition, the difference in the reactivity of complex **2** compared to **1**, **3**, and **4** can hardly be explained based solely on electronic effects.

gradient selected HMQC spectra:<sup>32</sup> Relaxation delay  $D_1 = 2.0$  s; evolution delay  $D_2 = 3.45$  ms;  $90^\circ$  pulse,  $12.5 \mu\text{s}$  for  $^1\text{H}$ ,  $10.0 \mu\text{s}$  for  $^{13}\text{C}$  hard pulses; 2K points in  $t_2$ ; spectral width 12 ppm in  $F_2$  and 300 ppm in  $F_1$ ; 128 experiments in  $t_1$ . 400/79.5 MHz gradient-selected HMBC spectra:<sup>33</sup> Relaxation delay  $D_1 = 2.0$  s; evolution delay  $D_2 = 83.3$  ms; delay for evolution of long-range coupling  $D_6 = 83.3$  ms ( $J = 10$  Hz); 2K points in  $t_2$ ; spectral width 10 ppm in  $F_2$  and 300 ppm in  $F_1$ ; 128 experiments in  $t_1$ ; zero-filling up to 1K.

**X-ray Structure Analyses of Complexes 1, 9, and 11** (Table 2). Selected crystals were mounted on a Siemens SMART diffractometer with a CCD area detector by using perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo  $K\alpha$  radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 4.40 cm. A hemisphere of data was collected by a combination of three sets of exposures at the temperature mentioned in the table. Each set had a different  $\phi$  angle for the crystal, and each exposure took 20 s and covered  $0.3^\circ$  in  $\omega$ . The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structures were solved by direct methods (SHELXS86). Refinement was carried out with the full-matrix least-squares method based on  $F^2$  (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

**General Procedure for the Synthesis of the Complexes 1–5.** To a stirred solution of 1 mmol (0.317 g) of ( $\eta^4$ -2,5-norbornadiene)dimethylplatinum(II) in 3 mL of benzene was added dropwise 1 mmol of the corresponding P,N ligand, dissolved in 3 mL of benzene within 5 min. After complete consumption of the starting compound **1** (monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy), the solution was concentrated under reduced pressure to about 1 mL and diluted with 10 mL of petroleum ether (30/50). After storage of the reaction mixture at  $-30^\circ\text{C}$  for 24 h to complete precipitation, the products were filtered off, washed with two portions (5 mL each) of petroleum ether (30/50), and dried under reduced pressure to yield the complexes **1–5**.

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylamino)ethyl]diphenylphosphino]dimethylplatinum(II) (**1**):** 1 mmol (0.317 g) of (nbd)-PtMe<sub>2</sub> and 1 mmol (0.257 g) of (2-diphenylphosphinoethyl)-dimethylamine<sup>34</sup> (PC<sub>2</sub>N); reaction time 3 h. Yield: 0.4 g (0.84 mmol, 84%), pale yellow powder. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>NPPt (482.46): C, 44.81; H, 5.43; N, 2.90. Found: C, 45.03, H, 5.35, N, 2.81.  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 35.93$  (s with Pt satellites,  $^1J_{\text{PtP}} = 2071.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -24.69$  (d with Pt satellites,  $^1J_{\text{PtC}} = 748.7$  Hz,  $^2J_{\text{PPtC}} = 4.2$  Hz, *cis*-PtCH<sub>3</sub>), 14.45 (d with Pt satellites,  $^1J_{\text{PtC}} = 709.8$  Hz,  $^2J_{\text{PPtC}} = 113.5$  Hz, *trans*-PtCH<sub>3</sub>), 29.56 (d,  $^1J_{\text{PC}} = 25.8$  Hz, PCH<sub>2</sub>), 49.19 (s, N(CH<sub>3</sub>)<sub>2</sub>), 64.44 (d,  $^2J_{\text{PCC}} = 9.5$  Hz, NCH<sub>2</sub>), 128.62 (d,  $J_{\text{PC}} = 9.5$  Hz, Ar-C<sup>1</sup>), 130.00 (s, Ar-C<sup>4</sup>), 133.41 (d,  $J_{\text{PC}} = 12.1$  Hz, Ar-C<sup>1</sup>), Ar-C<sup>1</sup> not observed.<sup>35</sup>  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.21$  (d with Pt satellites,  $^2J_{\text{PtCH}} = 66.68$  Hz,  $^3J_{\text{PPtCH}} = 7.73$ , 3 H, *trans*-PtCH<sub>3</sub>), 1.48 (d with Pt satellites,  $^2J_{\text{PtCH}} = 89.73$  Hz,  $^3J_{\text{PPtCH}} = 7.33$ , 3 H, *cis*-PtCH<sub>3</sub>), 1.60–1.90 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 2.24 (s with Pt satellites,  $^3J_{\text{PtNCH}} = 18.01$  Hz, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 6.90–7.10 (m, 6 H, Ar-H), 7.60–7.80 (m, 4 H, Ar-H). MS (EI):  $m/z = 482$  ( $\text{M}^+$ , 1), 467 ( $\text{M}^+ - \text{CH}_3$ , 38), 452 ( $\text{M}^+ - 2\text{CH}_3$ , 100), 422 ( $\text{M}^+ - 4\text{CH}_3$ , 45), 405 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 3), 345 ( $\text{M}^+ - \text{C}_6\text{H}_5 - 4\text{CH}_3$ ), 10), 328 ( $\text{M}^+ - 2\text{C}_6\text{H}_5$ , 5). Crystals suitable for an X-ray structure analysis were obtained from a saturated 5:1 hexane/benzene (v/v) solution at  $0^\circ\text{C}$ .

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**[( $\kappa^2$ -P,N)-3-(*N,N*-Dimethylamino)propyl]diphenylphosphino]dimethylplatinum(II) (**2**):** 1 mmol (0.317 g) of (nbd)-PtMe<sub>2</sub> and 1 mmol (0.271 g) of (3-diphenylphosphinopropyl)-dimethylamine<sup>34</sup> (PC<sub>3</sub>N); reaction time 1 h. Yield: 0.382 g (0.77 mmol, 77%), colorless powder. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>NPPt (496.49): C, 45.96; H, 5.68; N, 2.82; Found: C, 46.13; H, 5.58; N, 2.77.  $^{31}\text{P}\{^1\text{H}\}$  NMR (acetone-*d*<sub>6</sub>):  $\delta = 15.29$  (s with Pt satellites,  $^1J_{\text{PtP}} = 2113.04$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone-*d*<sub>6</sub>):  $\delta = -20.93$  (d with Pt satellites,  $^1J_{\text{PtC}} = 745.5$  Hz,  $^2J_{\text{PPtC}} = 5.5$  Hz, *cis*-PtCH<sub>3</sub>), 14.83 (d with Pt satellites,  $^1J_{\text{PtC}} = 719.6$  Hz,  $^2J_{\text{PPtC}} = 113.53$  Hz, *trans*-PtCH<sub>3</sub>), 23.58 (d,  $^2J_{\text{PCC}} = 6.5$  Hz, CH<sub>2</sub>), 27.56 (d,  $^1J_{\text{PC}} = 24.0$  Hz, PCH<sub>2</sub>), 51.26 (s, N(CH<sub>3</sub>)<sub>2</sub>), 67.31 (d,  $^3J_{\text{PCCC}} = 6.5$  Hz, NCH<sub>2</sub>), 129.60 (d,  $J_{\text{PC}} = 8.7$  Hz, Ar-C<sup>1</sup>), 131.05 (d,  $^4J_{\text{PC}} = 1.6$  Hz, Ar-C<sup>4</sup>), 135.02 (d,  $J_{\text{PC}} = 11.4$  Hz, Ar-C<sup>1</sup>), 136.03 (d,  $^1J_{\text{PC}} = 40.9$  Hz, Ar-C<sup>1</sup>).  $^1\text{H}$  NMR (acetone-*d*<sub>6</sub>):  $\delta = 0.14$  (d with Pt satellites,  $^2J_{\text{PtCH}} = 87.04$  Hz,  $^3J_{\text{PPtCH}} = 8.63$ , 3 H, *cis*-PtCH<sub>3</sub>), 0.35 (d with Pt satellites,  $^2J_{\text{PtCH}} = 64.29$  Hz,  $^3J_{\text{PPtCH}} = 7.58$ , 3 H, *trans*-PtCH<sub>3</sub>), 1.80–2.00 (m, 2 H, CH<sub>2</sub>), 2.30–2.50 (m, 2 H, PCH<sub>2</sub>), 2.60 (s with Pt satellites,  $^3J_{\text{PtNCH}} = 18.78$  Hz, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 2.80–3.00 (m, 2 H, NCH<sub>2</sub>), 7.30–7.50 (m, 6 H, Ar-H), 7.60–7.80 (m, 4 H, Ar-H). MS (EI):  $m/z = 481$  ( $\text{M}^+ - \text{CH}_3$ , 18), 466 ( $\text{M}^+ - 2\text{CH}_3$ , 100), 421 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 7).

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylamino)phenyl]diphenylphosphino]dimethylplatinum(II) (**3**):** 1 mmol (0.317 g) of (nbd)-PtMe<sub>2</sub> and 1 mmol (0.305 g) of 2-diphenylphosphino-*N,N*-dimethylaniline<sup>36</sup> (PN); reaction time 2 h. Yield: 0.44 g (0.83 mmol, 83%), colorless powder. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>NPPt (530.51): C, 49.81; H, 4.94; N, 2.64. Found: C, 49.99; H, 4.76; N, 2.61.  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 34.79$  (s with Pt satellites,  $^1J_{\text{PtP}} = 2128.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -24.04$  (d with Pt satellites,  $^1J_{\text{PtC}} = 755.3$  Hz,  $^2J_{\text{PPtC}} = 4.3$  Hz, *cis*-PtCH<sub>3</sub>), 17.66 (d with Pt satellites,  $^1J_{\text{PtC}} = 718.4$  Hz,  $^2J_{\text{PPtC}} = 112.3$  Hz, 1 C, *trans*-PtCH<sub>3</sub>), 52.14 (s, N(CH<sub>3</sub>)<sub>2</sub>), 122.20 (d,  $J_{\text{PC}} = 9.7$  Hz, Ar-C<sup>1</sup>), 128.63 (d,  $J_{\text{PC}} = 9.7$  Hz, Ph-C<sup>1</sup>), 129.89 (d,  $J_{\text{PC}} = 2.3$  Hz, Ph-C<sup>4</sup>), 131.75 (d,  $J_{\text{PC}} = 1.9$  Hz, Ar-C<sup>1</sup>), 133.54 (d with Pt satellites,  $J_{\text{PC}} = 12.6$  Hz,  $J_{\text{PtC}} = 19.66$  Hz, Ph-C<sup>1</sup>), 134.04 (d,  $^1J_{\text{PC}} = 42.1$  Hz, Ph-C<sup>1</sup>), 134.55 (d,  $J_{\text{PC}} = 0.9$  Hz, Ar-C<sup>1</sup>), 135.07 (d,  $^1J_{\text{PC}} = 40.2$  Hz, Ar-C<sup>1</sup>), 163.19 (s, Ar-C<sup>2</sup>), one signal hidden by C<sub>6</sub>D<sub>6</sub>.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.27$  (d with Pt satellites,  $^2J_{\text{PtCH}} = 65.2$  Hz,  $^3J_{\text{PPtCH}} = 7.52$  Hz, 3 H, *trans*-PtCH<sub>3</sub>), 1.53 (d with Pt satellites,  $^2J_{\text{PtCH}} = 91.11$  Hz,  $^3J_{\text{PPtCH}} = 7.41$  Hz, 3 H, *cis*-PtCH<sub>3</sub>), 2.87 (s with Pt satellites,  $^3J_{\text{PtNCH}} = 17.44$  Hz, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 6.70–7.10 (m, 9 H, Ar-H), 7.34 (t,  $^3J_{\text{HH}} = 7.20$  Hz, 1 H, Ar-H), 7.60–7.80 (m, 4 H, Ar-H). MS (EI):  $m/z = 515$  ( $\text{M}^+ - \text{CH}_3$ , 38), 500 ( $\text{M}^+ - 2\text{CH}_3$ , 100), 453 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 5), 423 ( $\text{M}^+ - \text{C}_6\text{H}_5 - 2\text{CH}_3$ , 5), 376 ( $\text{M}^+ - 2\text{C}_6\text{H}_5$ , 12), 346 ( $\text{M}^+ - 2\text{C}_6\text{H}_5 - 2\text{CH}_3$ , 15).

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylaminomethyl)]phenyl]diphenylphosphino]dimethylplatinum(II) (**4**):** 1 mmol (0.317 g) of (nbd)PtMe<sub>2</sub> and 1 mmol (0.319 g) of (2-diphenylphosphinobenzyl)dimethylamine<sup>23</sup> (PCN); reaction time 2 h. Yield: 0.45 g (0.81 mmol, 81%), colorless powder. Anal. Calcd for C<sub>23</sub>H<sub>28</sub>NPPt (544.54): C, 50.73; H, 5.12; N, 2.57. Found: C, 50.92; H, 5.19; N, 2.39.  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 25.24$  (s with Pt satellites,  $^1J_{\text{PtP}} = 2061.8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -19.56$  (d with Pt satellites,  $^1J_{\text{PtC}} = 745.9$  Hz,  $^2J_{\text{PPtC}} = 4.6$  Hz, *cis*-PtCH<sub>3</sub>), 13.61 (d with Pt satellites,  $^1J_{\text{PtC}} = 728.7$  Hz,  $^2J_{\text{PPtC}} = 112.6$  Hz, *trans*-PtCH<sub>3</sub>), 49.44 (br, N(CH<sub>3</sub>)<sub>2</sub>), 68.88 (d,  $^3J_{\text{PC}} = 12.1$  Hz, CH<sub>2</sub>), 129.43 (s, Ar-C<sup>4</sup>), 129.79 (d,  $J_{\text{PC}} = 35.3$  Hz, Ph-C<sup>1</sup>), 131.44 (d,  $J_{\text{PC}} = 41.6$  Hz, Ar-C<sup>9</sup>), 132.64 (d,  $J_{\text{PC}} = 4.7$  Hz, Ph-C<sup>4</sup>), 133.87 (d,  $J_{\text{PC}} = 33.3$  Hz, Ar-C<sup>9</sup>),<sup>35</sup> 134.85 (d,  $J_{\text{PC}} = 12.1$  Hz, Ph-C<sup>1</sup>), 139.99 (d,  $J_{\text{PC}} = 17.4$  Hz, Ar-C<sup>1</sup>), two carbon signals hidden by C<sub>6</sub>D<sub>6</sub>.  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone-*d*<sub>6</sub>, 233 K):  $\delta = -20.06$  (d with Pt satellites,  $^1J_{\text{PtC}} = 748.3$  Hz,  $^2J_{\text{PPtC}} = 4.4$  Hz, *cis*-PtCH<sub>3</sub>), 13.49 (d with Pt satellites,  $^1J_{\text{PtC}} = 723.2$  Hz,  $^2J_{\text{PPtC}} = 112.3$  Hz, *trans*-PtCH<sub>3</sub>), 47.52 (s, NCH<sub>3</sub>), 52.85

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(s, NCH<sub>3</sub>), 69.22 (d, <sup>3</sup>J<sub>PC</sub> = 12.0 Hz, CH<sub>2</sub>), 129.78 (d, <sup>1</sup>J<sub>PC</sub> = 9.8 Hz, Ph-C<sup>1</sup>), 130.49 (d, <sup>n</sup>J<sub>PC</sub> = 9.3 Hz, Ph-C<sup>1</sup>), 131.21 (d, <sup>1</sup>J<sub>PC</sub> = 4.9 Hz, Ar-C<sup>1</sup>), 131.75 (s, Ar-C<sup>4</sup>), 133.67 (s, Ph-C<sup>4</sup>), 134.64 (d, <sup>1</sup>J<sub>PC</sub> = 7.6 Hz, Ar-C<sup>1</sup>), 135.59 (d, <sup>1</sup>J<sub>PC</sub> = 10.9 Hz, Ph-C<sup>1</sup>), 136.20 (d, <sup>1</sup>J<sub>PC</sub> = 12.5 Hz, Ph-C<sup>1</sup>), 141.43 (d, <sup>1</sup>J<sub>PC</sub> = 12.5 Hz, Ar-C<sup>1</sup>), 163.97 (d, <sup>1</sup>J<sub>PC</sub> = 28.9 Hz, Ar-C<sup>1</sup>), some quarternary carbon atoms could not be assigned due to overlap of the signals. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.14 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 87.49 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 8.14 Hz, 3 H, *cis*-PtCH<sub>3</sub>), 1.22 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 73.41 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 7.41 Hz, 3 H, *trans*-PtCH<sub>3</sub>), 2.35 (b, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 3.00–3.80 (b, 2 H, CH<sub>2</sub>) 6.60–6.80 (m, 1 H, Ar-H), 6.90–7.10 (m, 9 H, Ar-H), 7.50–7.90 (m, 4 H, Ar-H). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 233 K): δ = 0.21 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 86.11 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 8.18 Hz, 3 H, PtCH<sub>3</sub>), 0.37 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 65.76 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 7.45 Hz, 3 H, PtCH<sub>3</sub>), 2.37 (s with Pt satellites, <sup>3</sup>J<sub>PtNCH</sub> = 18.90 Hz, 3 H, NCH<sub>3</sub>), 2.80 (s with Pt satellites, <sup>3</sup>J<sub>PtNCH</sub> = 19.26 Hz, 3 H, NCH<sub>3</sub>), 3.69 (dd, <sup>2</sup>J<sub>HH</sub> = 11.99 Hz, <sup>n</sup>J<sub>HH</sub> = 4.36 Hz, 1 H, NCH(H)), 4.08 (dd, <sup>2</sup>J<sub>HH</sub> = 11.99 Hz, 1 H, NCH(H)), 6.70–6.80 (m, 1 H, Ar-H), 7.15–7.30 (m, 2 H, Ar-H), 7.40–7.70 (m, 11 H, Ar-H). MS (EI): *m/z* = 544 (M<sup>+</sup>, 1), 529 (M<sup>+</sup> - CH<sub>3</sub>, 12), 514 (M<sup>+</sup> - 2CH<sub>3</sub>, 100), 470 (M<sup>+</sup> - 2CH<sub>3</sub> - N(CH<sub>3</sub>)<sub>2</sub>, 10), 467 (M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>, 2), 390 (M<sup>+</sup> - 2C<sub>6</sub>H<sub>5</sub>, 20).

**Bis[(*N,N*-dimethylamino)methyldiphenylphosphino]dimethylplatinum(II) (5):** 0.642 mmol (0.204 g) of (nbd)-PtMe<sub>2</sub> and 0.642 mmol (0.214 g) of diphenylphosphinomethyldimethylamine<sup>37</sup> (PC<sub>1</sub>N); reaction time 1 h. Yield: 0.18 g (0.253 mmol, 78.9% relative to (nbd)PtMe<sub>2</sub>); pale yellow powder. Anal. Calcd for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>P<sub>2</sub>Pt (711.73): C, 54.00; H, 5.95; N, 3.94. Found: C, 53.79; H, 5.81; N, 3.76. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ = 9.59 (s with Pt satellites, <sup>1</sup>J<sub>PtP</sub> = 1837.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ = 6.95 (dd with Pt satellites, <sup>1</sup>J<sub>PtC</sub> = 617.3 Hz, <sup>2</sup>J<sub>PPtC(trans)</sub> = 98.0 Hz, <sup>2</sup>J<sub>PPtC(cis)</sub> = 8.2 Hz, Pt(CH<sub>3</sub>)<sub>2</sub>), 48.10 (s, N(CH<sub>3</sub>)<sub>2</sub>), 58.37 (d with Pt satellites, <sup>1</sup>J<sub>PC</sub> = 41.0 Hz, <sup>2</sup>J<sub>PtPC</sub> = 17.1 Hz, NCH<sub>2</sub>P), 127.8, 129.4 (Ar-C<sup>1</sup>), 134.4 (s, Ar-C<sup>4</sup>), 135.88 (d with Pt satellites, <sup>1</sup>J<sub>PC</sub> = 42.1 Hz, <sup>2</sup>J<sub>PtPC</sub> = 14.8 Hz, Ar-C<sup>1</sup>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 1.18 (dd with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 69.01 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 6.23, 7.79 Hz, 6 H, Pt(CH<sub>3</sub>)<sub>2</sub>), 2.16 (s, 12 H, N(CH<sub>3</sub>)<sub>2</sub>), 3.04 (s with Pt satellites, <sup>3</sup>J<sub>PtPCH</sub> = 12.35 Hz, 4 H, NCH<sub>2</sub>P), 7.00–7.18 (m, 12 H, Ar-H), 7.70–7.90 (m, 8 H, Ar-H). MS (EI): *m/z* = 515 (M<sup>+</sup> - CH<sub>3</sub>, 38), 500 (M<sup>+</sup> - 2CH<sub>3</sub>, 100), 453 (M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>, 5), 423 (M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub> - 2CH<sub>3</sub>, 5), 376 (M<sup>+</sup> - 2C<sub>6</sub>H<sub>5</sub>, 12), 346 (M<sup>+</sup> - 2C<sub>6</sub>H<sub>5</sub> - 2CH<sub>3</sub>, 15).

**Reactions of the Complexes 1–4 with Iodotrimethylsilane.** A 0.5 mmol sample of the corresponding platinum dimethyl complex was dissolved in 3 mL of benzene, and 0.5 mmol (0.1 g) iodotrimethylsilane was added. After stirring for 12 h at 60 °C (3 h in the case of **2**), the reaction mixture was poured into 30 mL of petroleum ether (30/50). The reaction mixture was stored for 24 h at -30 °C to complete precipitation. The product was filtered off, washed with two portions of 5 mL of petroleum ether (30/50) each, and dried under reduced pressure to give complexes **6–9** as pale yellow, air-stable powders.

***trans*-(κ<sup>2</sup>-P,N)-2-(*N,N*-Dimethylamino)ethyldiphenylphosphinoiodomethylplatinum(II) (6):** Yield: 0.269 g (0.39 mmol, 78%). Anal. Calcd for C<sub>17</sub>H<sub>23</sub>INPpt (594.33): C, 34.36; H, 3.90; N, 2.36. Found: C, 34.10; H, 3.84; N, 2.24. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 29.24 (s with Pt satellites, <sup>1</sup>J<sub>PtP</sub> = 4642.33 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = -26.44 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 602.7 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 5.5 Hz, PtCH<sub>3</sub>), 31.38 (d, <sup>1</sup>J<sub>PC</sub> = 35.4 Hz, 1 C, PCH<sub>2</sub>), 51.95 (s, N(CH<sub>3</sub>)<sub>2</sub>), 61.95 (d, <sup>2</sup>J<sub>PCC</sub> = 2.2 Hz, NCH<sub>2</sub>), 129.00 (d, <sup>1</sup>J<sub>PC</sub> = 58.3, Ph-C<sup>1</sup>), 129.86 (d, <sup>1</sup>J<sub>PC</sub> = 10.9 Hz, Ph-C<sup>1</sup>), 132.44 (d, <sup>1</sup>J<sub>PC</sub> = 2.7 Hz, Ph-C<sup>4</sup>), 134.28 (d, <sup>1</sup>J<sub>PC</sub> = 11.5 Hz, Ph-C<sup>4</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.89 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 75.69 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 3.66 Hz, 3 H, PtCH<sub>3</sub>), 2.30–2.80 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 3.02 (s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 7.40–7.60 (m, 6 H, Ar-H), 7.70–7.90 (m, 4 H, Ar-H). MS

(EI): *m/z* = 594 (M<sup>+</sup>, 10), 579 (M<sup>+</sup> - CH<sub>3</sub>, 40), 467 (M<sup>+</sup> - I, 30), 58 (H<sub>2</sub>C=N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>, 100).

***trans*-(κ<sup>2</sup>-P,N)-3-(*N,N*-Dimethylamino)propyldiphenylphosphinoiodomethylplatinum(II) (7):** Yield: 0.269 g (0.39 mmol, 78%). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>INPpt (608.36): C, 35.54; H, 4.14; N, 2.30. Found: C, 35.54; H, 4.28; N, 2.18. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 9.99 (s with Pt satellites, <sup>1</sup>J<sub>PtP</sub> = 4685.1 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = -21.52 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 572.2 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 6.0 Hz, PtCH<sub>3</sub>), 22.27 (s with Pt satellites, <sup>1</sup>J<sub>PtC</sub> = 25.6 Hz, CH<sub>2</sub>), 26.39 (d, <sup>1</sup>J<sub>PC</sub> = 34.9 Hz, PCH<sub>2</sub>), 54.37 (s, N(CH<sub>3</sub>)<sub>2</sub>), 65.97 (d, <sup>2</sup>J<sub>PCC</sub> = 6.0 Hz, NCH<sub>2</sub>), 129.55 (d, <sup>1</sup>J<sub>PC</sub> = 10.9, Ph-C<sup>1</sup>), 131.02 (d, <sup>1</sup>J<sub>PC</sub> = 60.5 Hz, Ph-C<sup>1</sup>), 131.86 (s, 2 C, Ph-C<sup>4</sup>), 134.45 (d, <sup>1</sup>J<sub>PC</sub> = 10.9 Hz, Ph-C<sup>4</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.58 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 71.98 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 5.30 Hz, 3 H, PtCH<sub>3</sub>), 1.75–1.95 (m, 2 H, -CH<sub>2</sub>-), 2.20–2.50 (m, 2 H, PCH<sub>2</sub>), 2.65–2.80 (m, 2 H, NCH<sub>2</sub>), 2.98 (s with Pt satellites, <sup>3</sup>J<sub>PtNCH</sub> = 13.41 Hz, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 7.30–7.50 (m, 6 H, Ar-H), 7.60–7.80 (m, 4 H, Ar-H). MS (EI): *m/z* = 608 (M<sup>+</sup>, 4), 593 (M<sup>+</sup> - CH<sub>3</sub>, 12), 481 (M<sup>+</sup> - I, 7), 58 (H<sub>2</sub>C=N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>, 100).

***trans*-(κ<sup>2</sup>-P,N)-2-(*N,N*-Dimethylamino)phenyldiphenylphosphinoiodomethylplatinum(II) (8):** Yield: 0.272 g (0.43 mmol, 86%). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>INPpt (642.38): C, 39.27; H, 3.61; N, 2.18. Found: C, 39.26; H, 3.75; N, 2.15. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 19.90 (s with Pt satellites, <sup>1</sup>J<sub>PtP</sub> = 4616.7 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = -25.74 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 609.3 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 5.0 Hz, 1 C, PtCH<sub>3</sub>), 54.95 (s, 2 C, N(CH<sub>3</sub>)<sub>2</sub>), 123.51 (d, <sup>1</sup>J<sub>PC</sub> = 9.8 Hz, 1 C, Ar-C<sup>1</sup>), 129.55 (d, <sup>1</sup>J<sub>PC</sub> = 11.4 Hz, 4 C, Ph-C<sup>1</sup>), 129.91 (d, <sup>1</sup>J<sub>PC</sub> = 73.0 Hz, 2 C, Ph-C<sup>1</sup>), 131.99 (d, <sup>4</sup>J<sub>PC</sub> = 2.7 Hz, 2 C, Ph-C<sup>4</sup>), 134.08 (d, <sup>1</sup>J<sub>PC</sub> = 12.0 Hz, 4 C, Ph-C<sup>4</sup>), 161.16 (d, <sup>1</sup>J<sub>PC</sub> = 15.3 Hz, 1 C Ar-C<sup>2</sup>), some of the aromatic carbon atoms could not be assigned unambiguously due to overlap of the signals. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.08 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 75.57 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 3.74 Hz, 3 H, PtCH<sub>3</sub>), 3.53 (s with Pt satellites, <sup>3</sup>J<sub>PtNCH</sub> = 11.21 Hz, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 7.25–7.75 (m, 14 H, Ar-H). MS (EI): *m/z* = 642 (M<sup>+</sup>, 10), 627 (M<sup>+</sup> - CH<sub>3</sub>, 100), 515 (M<sup>+</sup> - I, 20).

***trans*-(κ<sup>2</sup>-P,N)-2-(*N,N*-Dimethylaminomethyl)phenyldiphenylphosphinoiodomethylplatinum(II) (9):** Yield: 0.269 g (0.41 mmol, 82%). Anal. Calcd C<sub>22</sub>H<sub>25</sub>INPpt (656.41): C, 40.26; H, 3.84; N, 2.38. Found: C, 40.01; H, 3.87; N, 2.12. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 16.30 (s with Pt satellites, <sup>1</sup>J<sub>PtP</sub> = 4688.7 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ = -21.23 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 582.8 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 5.3 Hz, PtCH<sub>3</sub>), 67.99 (d, <sup>3</sup>J<sub>PC</sub> = 2.1 Hz, CH<sub>2</sub>), 127.91 (d, <sup>1</sup>J<sub>PC</sub> = 61.6 Hz, Ph-C<sup>1</sup>), 129.30 (d, <sup>1</sup>J<sub>PC</sub> = 54.5 Hz, Ar-C<sup>1</sup>), 129.33 (d, <sup>1</sup>J<sub>PC</sub> = 11.4 Hz, Ph-C<sup>1</sup>), 130.25 (d, <sup>1</sup>J<sub>PC</sub> = 7.6 Hz, Ar-C<sup>1</sup>), 131.73 (d, <sup>4</sup>J<sub>PC</sub> = 2.2 Hz, Ph-C<sup>4</sup>), 131.99 (br, Ar-C<sup>1</sup>), 133.17 (d, <sup>1</sup>J<sub>PC</sub> = 3.8 Hz, Ar-C<sup>1</sup>), 133.53 (d, <sup>1</sup>J<sub>PC</sub> = 9.3 Hz, Ar-C<sup>1</sup>), 135.07 (d, <sup>1</sup>J<sub>PC</sub> = 11.4 Hz, Ph-C<sup>4</sup>), 140.12 (d, <sup>1</sup>J<sub>PC</sub> = 14.2 Hz, Ar-C<sup>2</sup>), the N(CH<sub>3</sub>)<sub>2</sub> carbon atoms were not observed at 298 K due to the conformational flexibility of the complex. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 253 K): δ = -21.02 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 579.8 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 4.5 Hz, PtCH<sub>3</sub>), 49.23 (s, NCH<sub>3</sub>), 56.12 (s, NCH<sub>3</sub>), 67.69 (d, <sup>3</sup>J<sub>PC</sub> = 9.3 Hz, CH<sub>2</sub>), 126.46 (d, <sup>1</sup>J<sub>PC</sub> = 69.8 Hz, Ph-C<sup>1</sup>), 126.72 (d, <sup>1</sup>J<sub>PC</sub> = 55.0 Hz, Ph-C<sup>1</sup>), 127.85 (d, <sup>1</sup>J<sub>PC</sub> = 55.0 Hz, Ar-C<sup>1</sup>), 128.83 (d, <sup>1</sup>J<sub>PC</sub> = 10.9 Hz, Ph-C<sup>1</sup>), 129.39 (d, <sup>1</sup>J<sub>PC</sub> = 7.6 Hz, Ar-C<sup>1</sup>), 130.74 (d, <sup>4</sup>J<sub>PC</sub> = 1.2 Hz, Ph-C<sup>4</sup>), 130.96 (d, <sup>4</sup>J<sub>PC</sub> = 1.2 Hz, Ph-C<sup>4</sup>), 131.62 (br, Ar-C<sup>4</sup>), 132.21 (d, <sup>1</sup>J<sub>PC</sub> = 4.4 Hz, Ar-C<sup>1</sup>), 132.68 (d, <sup>1</sup>J<sub>PC</sub> = 8.7 Hz, Ar-C<sup>1</sup>), 133.65 (d, <sup>1</sup>J<sub>PC</sub> = 10.9 Hz, Ph-C<sup>1</sup>), 134.41 (d, <sup>1</sup>J<sub>PC</sub> = 12.0 Hz, Ph-C<sup>4</sup>), 138.90 (d, <sup>2</sup>J<sub>PC</sub> = 13.6 Hz, Ar-C<sup>2</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ = 0.82 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 73.24 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 4.89 Hz, 3 H, PtCH<sub>3</sub>), 2.50–4.00 (br, 8 H, CH<sub>2</sub> + N(CH<sub>3</sub>)<sub>2</sub>), 6.91 (t, <sup>1</sup>J<sub>HH</sub> = 9.26 Hz, 1 H, Ar-H), 7.27 (m, 1 H, Ar-H), 7.40–7.80 (m, 12 H, Ar-H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 253 K): δ = 0.79 (d with Pt satellites, <sup>2</sup>J<sub>PtCH</sub> = 72.02 Hz, <sup>3</sup>J<sub>PPtCH</sub> = 4.88 Hz, 3 H, PtCH<sub>3</sub>), 2.66 (s, 3 H, NCH<sub>3</sub>), 3.20 (s, 3 H, NCH<sub>3</sub>), 3.43 (d, <sup>2</sup>J<sub>HH</sub> = 12.21 Hz, 1 H, CH(H)), 4.04 (d, <sup>2</sup>J<sub>HH</sub> = 12.20 Hz, 1 H, CH(H)), 6.88 (t, <sup>1</sup>J<sub>HH</sub> = 8.31 Hz, 1 H, Ar-H), 7.20–7.80 (m, 13 H, Ar-H). MS (EI): *m/z* = 656

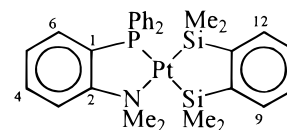
(37) (a) Bohme, H.; Hartke, K. *Chem. Ber.* **1960**, *93*, 1305. (b) Aguiar, A. M.; Hansen, K. C.; Mague, J. T. *J. Chem. Soc. (A)* **1967**, 2883.

( $M^+$ , 8), 641 ( $M^+ - CH_3$ , 60), 529 ( $M^+ - I$ , 30), 58 ( $H_2C=N(CH_3)_2^+$ , 100). Crystals suitable for an X-ray structure analysis were obtained by slow evaporation of the solvent from a concentrated benzene solution at room temperature. The crystals contained two benzene molecules in the asymmetric unit.

**Reaction of the Complexes 1–4 with 1,2-Bis(dimethylsilyl)benzene.** To a solution of 0.5 mmol of the corresponding dimethylplatinum(II) complex in 2 mL of benzene was added dropwise 1.0 mmol (0.196 g) of 1,2-bis(dimethylsilyl)benzene. After stirring the reaction mixture for 60 h at 60 °C, the solution was cooled to room temperature and transferred into 20 mL of petroleum ether (30/50) via a syringe. After storage at –30 °C for 24 h to complete precipitation, the products were filtered off, washed with three portions of 2 mL of petroleum ether each, and dried under reduced pressure, yielding pale yellow powders.

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylamino)ethyl]diphenylphosphino][1,2-bis(dimethylsilyl)benzene]platinum(II) (10).** Yield: 0.235 g (0.365 mmol, 73%). Anal. Calcd for  $C_{26}H_{36}NPPtSi_2$  (644.80): C, 48.43; H, 5.63; N, 2.17. Found: C, 48.17; H, 5.28; N, 2.09.  $^{31}P\{^1H\}$  NMR (acetone- $d_6$ ):  $\delta = 57.07$  (s with Pt satellites,  $^1J_{PtP} = 1392.8$  Hz,  $^2J_{SiPtP} = 167.2$  Hz).  $^{29}Si$  NMR (acetone- $d_6$ ): –0.81 (d with Pt satellites,  $^1J_{PtSi} = 1424.3$  Hz,  $^2J_{PPtSi} = 5.6$  Hz, *cis*-Si), 29.49 (d with Pt satellites,  $^1J_{PtSi} = 1501.8$  Hz,  $^2J_{PPtSi} = 167.7$  Hz, *trans*-Si).  $^{13}C\{^1H\}$  NMR (acetone- $d_6$ ):  $\delta = 4.77$  (d,  $^3J_{PPtSiC} = 3.7$  Hz, *cis*-Si( $CH_3$ ) $_2$ ), 5.15 (d,  $^3J_{PPtSiC} = 7.4$  Hz, *trans*-Si( $CH_3$ ) $_2$ ), 33.56 (d,  $^1J_{PC} = 21.2$  Hz,  $PCCH_2$ ), 50.06 (s,  $N(CH_3)_2$ ), 62.73 (d,  $^2J_{PCC} = 9.2$  Hz,  $NCH_2$ ), 126.91 (s,  $Ar-C^5$ ), 127.10 (s,  $Ar-C^4$ ), 128.00 (d,  $^1J_{PC} = 23.9$  Hz,  $Ph-C^1$ ), 128.88 (d,  $J_{PC} = 10.1$  Hz,  $Ph-C^4$ ), 130.24 (s,  $Ar-C^6$ ), 130.19 (d,  $^4J_{PC} = 1.8$  Hz,  $Ph-C^4$ ), 131.08 (s,  $Ar-C^3$ ), 134.15 (d,  $J_{PC} = 11.9$  Hz,  $Ph-C^1$ ), 158.13 (d,  $J_{PC} = 4.6$  Hz,  $Ar-C^9$ ), 158.30 (d,  $J_{PC} = 6.4$  Hz,  $Ar-C^9$ ).  $^1H$  NMR (acetone- $d_6$ ):  $\delta = -0.08$  (s with Pt satellites,  $^3J_{PtSiCH} = 31.62$  Hz, 6 H, *cis*-Si( $CH_3$ ) $_2$ ), 0.42 (d with Pt satellites,  $^3J_{PtSiCH} = 24.09$  Hz,  $^4J_{PPtSiCH} = 2.81$  Hz, 6 H, *trans*-Si( $CH_3$ ) $_2$ ), 2.50–2.70 (m, 4 H,  $CH_2CH_2$ ), 2.98 (s with Pt satellites,  $^3J_{PtNCH} = 17.57$  Hz, 6 H,  $N(CH_3)_2$ ), 7.08 (t,  $J_{HH} = 7.03$  Hz, 1 H,  $Ar-H^5$ ), 7.14 (t,  $J_{HH} = 7.03$  Hz, 1 H,  $Ar-H^4$ ), 7.29 (d,  $J_{HH} = 7.03$  Hz, 1 H,  $Ar-H^6$ ), 7.50–7.65 (m, 7 H,  $Ph-H + Ar-H^3$ ), 7.75–7.90 (m, 4 H,  $Ar-H$ ).

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylamino)phenyl]diphenylphosphino][1,2-bis(dimethylsilyl)benzene]platinum(II) (11).** Yield: 0.291 g (0.42 mmol, 84% with respect to **3**). Anal. Calcd for  $C_{30}H_{36}NPPtSi_2 \cdot C_6H_6O$  (750.93): C, 52.78; H, 5.64; N, 1.87. Found: C, 52.64; H, 5.66; N, 1.81.  $^{31}P\{^1H\}$  NMR (acetone- $d_6$ ):  $\delta = 51.37$  (s with Pt and Si satellites,  $^1J_{PtP} = 1481.9$  Hz,  $^2J_{SiPtP}^{trans} = 161.1$  Hz).  $^{29}Si$  NMR (acetone- $d_6$ ): –1.38 (d with Pt satellites,  $^1J_{PtSi} = 1510.3$  Hz,  $^2J_{PPtSi} = 3.6$  Hz, *cis*-Si), 30.04 (d with Pt satellites,  $^1J_{PtSi} = 1490.4$  Hz,  $^2J_{PPtSi} = 164.0$  Hz, *trans*-Si).  $^{13}C\{^1H\}$  NMR (acetone- $d_6$ ):  $\delta = 4.30$  (d,  $^3J_{PPtSiC} = 3.6$  Hz, *cis*-Si( $CH_3$ ) $_2$ ), 4.99 (d,  $^3J_{PPtSiC} = 8.3$  Hz, *trans*-Si( $CH_3$ ) $_2$ ), 54.12 (s,  $N(CH_3)_2$ ), 121.67 (d,  $J_{PC} = 8.3$  Hz,  $Ar-C^6$ ), 127.10 (s,  $Ar-C^{11}$ ), 127.30 (s,  $Ar-C^{10}$ ), 127.99 (d,  $^1J_{PC} = 23.9$  Hz,  $Ph-C^1$ ), 128.40 (d,  $J_{PC} = 10.1$  Hz,  $Ar-C^4$ ), 128.95 (d,  $J_{PC} = 9.2$  Hz,  $Ph-C^4$ ), 130.20 (s,  $Ar-C^{12}$ ), 130.81 (s,  $Ph-C^4$ ), 131.29 (d,  $J_{PC} = 24.8$  Hz,  $Ar-C^1$ ), 133.06 (d,  $J_{PC} = 9.2$  Hz,  $Ar-C^5$ ), 133.53 (d,  $J_{PC} = 11.0$  Hz,  $Ar-C^3$ ), 134.45 (d,  $J_{PC} = 14.7$  Hz,  $Ph-C^1$ ),



**Figure 6.** Atom labeling of the platinum complex **11**.

135.30 (s,  $Ar-C^9$ ), 152.80 (s,  $SiC^{Ar}$ ), 157.60 (s,  $SiC^{Ar}$ ), 160.05 (d,  $^2J_{PC} = 21.1$  Hz,  $Ar-C^2$ ).  $^1H$  NMR (acetone- $d_6$ ):  $\delta = -0.04$  (s with Pt satellites,  $^3J_{PtSiCH} = 32.51$  Hz, 6 H, *cis*-Si( $CH_3$ ) $_2$ ), 0.46 (d with Pt satellites,  $^3J_{PtSiCH} = 22.54$  Hz,  $^4J_{PPtSiCH} = 2.85$  Hz, 6 H, *trans*-Si( $CH_3$ ) $_2$ ), 3.41 (s with Pt satellites,  $^3J_{PtNCH} = 15.36$  Hz, 6 H,  $N(CH_3)_2$ ), 7.12 (t,  $J_{HH} = 7.04$  Hz, 1 H,  $Ar-H^{11}$ ), 7.17 (t,  $J_{HH} = 7.04$ , 1 H,  $Ar-H^{10}$ ), 7.32 (d,  $J_{HH} = 6.91$ , 1 H,  $Ar-H^{12}$ ), 7.36 (t,  $J_{HH} = 7.55$  Hz, 1 H,  $Ar-H^4$ ), 7.45–7.58 (m, 8 H,  $Ar-H$ ), 7.64 (t,  $J_{HH} = 7.68$ , 1 H,  $Ar-H^5$ ), 7.75–7.85 (m, 4 H,  $Ar-H$ ), 7.90 (dd,  $J = 4.35$ , 8.19 Hz, 1 H,  $Ar-H^6$ ). Crystals suitable for an X-ray structure analysis were obtained by slow cooling of saturated acetone solution to 0 °C. The crystals contained one acetone molecule in the asymmetric unit (see Figure 6).

**[( $\kappa^2$ -P,N)-2-(*N,N*-Dimethylaminomethyl)phenyl]diphenylphosphino][1,2-bis(dimethylsilyl)benzene]platinum(II) (12).** Yield: 0.272 g (0.385 mmol, 77%). Anal. Calcd for  $C_{31}H_{38}NPPtSi_2$  (706.87): C, 52.67; H, 5.42; N, 1.98. Found: C, 52.24; H, 5.35; N, 1.88.  $^{31}P\{^1H\}$  NMR (acetone- $d_6$ ):  $\delta = 38.52$  (s with Pt satellites,  $^1J_{PtP} = 1439.8$  Hz,  $^2J_{SiPtP}^{trans} = 154.9$  Hz).  $^{29}Si$  NMR (acetone- $d_6$ , 233 K): –2.39 (d with Pt satellites,  $^1J_{PtSi} = 1452.4$  Hz,  $^2J_{PPtSi} = 6.2$  Hz, *cis*-Si( $CH_3$ ) $_2$ ), 28.09 (d with Pt satellites,  $^1J_{PtSi} = 1507.5$  Hz,  $^2J_{PPtSi} = 167.3$  Hz, *trans*-Si( $CH_3$ ) $_2$ ).  $^{13}C\{^1H\}$  NMR (acetone- $d_6$ , 240 K):  $\delta = 4.87$  (d,  $^3J_{PPtSiC} = 4.9$  Hz,  $SiCH_3$ ), 5.78 (s,  $SiCH_3$ ), 6.33 (d,  $^3J_{PPtSiC} = 8.7$  Hz,  $SiCH_3$ ), 8.00 (d,  $^3J_{PPtSiC} = 4.9$  Hz,  $SiCH_3$ ), 50.09 (s,  $NCH_3$ ), 55.41 (s,  $NCH_3$ ), 68.10 (d,  $^3J_{PCCC} = 10.9$  Hz,  $NCH_2$ ), 127.50–134.00 ( $Ar-C$ ), 134.75 (d,  $J_{PC} = 8.5$  Hz,  $Ar-C$ ), 137.20 (d,  $J_{PC} = 14.7$  Hz,  $Ar-C$ ), 140.45 (d,  $J_{PC} = 17.4$  Hz,  $Ar-C$ ), 158.01 (d,  $^3J_{PPtSiC} = 4.4$  Hz,  $Si-C^{Ar}$ ), 160.82 (d,  $^3J_{PPtSiC} = 6.0$  Hz,  $Si-C^{Ar}$ ).  $^1H$  NMR (acetone- $d_6$ , 240 K):  $\delta = -0.46$  (s with Pt satellites,  $^3J_{PtSiCH} = 26.22$  Hz, 3 H,  $SiCH_3$ ), 0.10 (s with Pt satellites,  $^3J_{PtSiCH} = 30.72$  Hz, 3 H,  $SiCH_3$ ), 0.21 (s with Pt satellites,  $^3J_{PtSiCH} = 26.22$  Hz, 3 H,  $SiCH_3$ ), 0.53 (s, 3 H,  $SiCH_3$ ), 2.64 (s with Pt satellites,  $^3J_{PtNCH} = 18.43$  Hz, 3 H,  $NCH_3$ ), 3.03 (s with Pt satellites,  $^3J_{PtSiCH} = 20.07$  Hz, 3 H,  $NCH_3$ ), 3.55 (d,  $^2J_{HH} = 12.29$  Hz, 1 H,  $CH(H)$ ), 3.91 (d,  $^2J_{HH} = 12.29$  Hz, 1 H,  $CH(H)$ ), 7.00–7.90 (m, 18 H,  $Ar-H$ ).

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**Supporting Information Available:** NMR spectra of complexes **1–12** (PDF) and X-ray diffraction data for **1**, **9**, and **11** (CIF). This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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