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Transition Metal Silyl Complexes. 60.[†,1] Enhanced Reactivity of a Platinum Dimethyl Complex toward Trimethoxysilane Due to a P,N-Chelating Co Ligand

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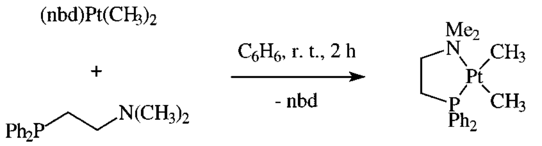
Summary: [(κ^2-P,N)-$Me_2NCH_2CH_2PPh_2$]$PtMe_2$ reacts with trimethoxysilane to yield the methyl trimethoxysilyl complex [(κ^2-P,N)-$Me_2NCH_2CH_2PPh_2$]Pt[$Si(OMe)_3$]Me, the bis(trimethoxysilyl) complex [(κ^2-P,N)-$Me_2NCH_2CH_2PPh_2$]Pt[$Si(OMe)_3$]$_2$, methyltrimethoxysilane, tetramethoxysilane, and small amounts of pentamethoxydisiloxane and hexamethoxydisiloxane. The formation of these compounds can be explained by Si−H oxidative addition/reductive elimination as well as Si−O activation and scrambling reactions of the silicon substituents.

Compared to oxidative addition reactions of hydrogenosilanes, examples for the synthesis of silyl complexes by ligand exchange reactions are rare, especially for the late transition metals.[2] The most promising preparative pathways are reactions of alkyl complexes with hydrogenosilanes, due to the high stability of the new C−H bond and the volatility of the formed alkane. Most of the complexes investigated in this type of reaction only bear phosphine ligands.[3]

Introduction of a P,N-chelating ligand into the metal complex should enhance the reactivity for alkyl/silyl exchange. (i) Nitrogen donor ligands are known to stabilize octahedral platinum(IV) complexes.[4] As a consequence, incorporation of a P,N-chelating ligand might enhance the propensity for oxidative addition reactions of platinum(II) complexes compared to corresponding bisphosphine complexes. In addition, the different electronic properties of the two ligand donor atoms (i.e. phosphorus and nitrogen) give rise to different bond strengths *trans* to the donor atoms, which might facilitate reductive elimination reactions. (ii) P,N-ligands are known to be hemilabile. They could, therefore, provide empty coordination sites by reversible (de)coordination of the nitrogen donor.[5] Oxidative addition reactions could thus be accelerated.

A C_6D_6 solution of [(κ^2-P,N)-$Me_2NCH_2CH_2PPh_2$]$PtMe_2$ (**1**), synthesized from (nbd)Pt$(CH_3)_2$[6] (nbd = 2,5-norbornadiene) and 2-(diphenylphosphino)ethyldimethylamine[7] (eq 1), was reacted with 3.5 equiv of trimethoxysilane at room temperature in an NMR tube. The tube was equipped with a poly(tetrafluoroethylene) (PTFE) liner to exclude the possibility of metal-catalyzed reactions of the silane with adsorbed water or Si−OH groups of the glass surface.[8]



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(1)

Methane evolution was observed (identified by GC), and the course of the reaction was monitored by $^{31}P\{^1H\}$, ^{29}Si, $^{13}C\{^1H\}$, CH−COSY, SiH−COLOC, and ^1H NMR spectroscopy (Figure 1). Two new platinum complexes were formed in the reaction which were unambiguously identified as the *cis* methyl trimethoxysilyl complex **2** and the corresponding bis(trimethoxysilyl) complex **3**. The ^1H NMR spectrum of the reaction mixture was characterized by three singlets (with platinum satellites) originating from the *N*-methyl protons (**1**, $\delta = 2.24$, $^3J_{PtNCH} = 18.01$ Hz; **2**, $\delta = 2.13$, $^3J_{PtNCH} = 12.30$ Hz; **3**, $\delta = 2.79$, $^3J_{PtNCH} = 18.39$ Hz). The signals of **2** and **3** in the $^{31}P\{^1H\}$ NMR spectrum showed silicon and platinum satellites (**2**, $^2J_{SiPtP} = 12.2$ Hz; **3**, $^2J_{SiPtP}{}^{cis} = 7.32$ Hz, $^2J_{SiPtP}{}^{trans} = 268.6$ Hz) (Figure 1a); the $^2J_{SiPtP}$ coupling constants were also observed in the ^{29}Si NMR spectrum (INEPT). The assignment of the signals was made on the basis of a SiH−COLOC experiment shown in Figure 1b, which also confirmed the Pt−Si connectivity and allowed us to determine the $^1J_{PtSi}$ coupling

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[†] Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

(1) Part 59: Gilges, H.; Schubert, U. *Organometallics* **1998**, *17*, 4760.

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(7) Malet, R.; Morena-Mañas, M.; Parella, T.; Pleixats, R. *J. Org. Chem.* **1996**, *61*, 758.

(8) For example: (a) Van der Boom, M. E.; Ott, J.; Milstein, D. *Organometallics* **1998**, *17*, 4263. (b) Schubert, U.; Lorenz, C. *Inorg. Chem.* **1997**, *36*, 1258.

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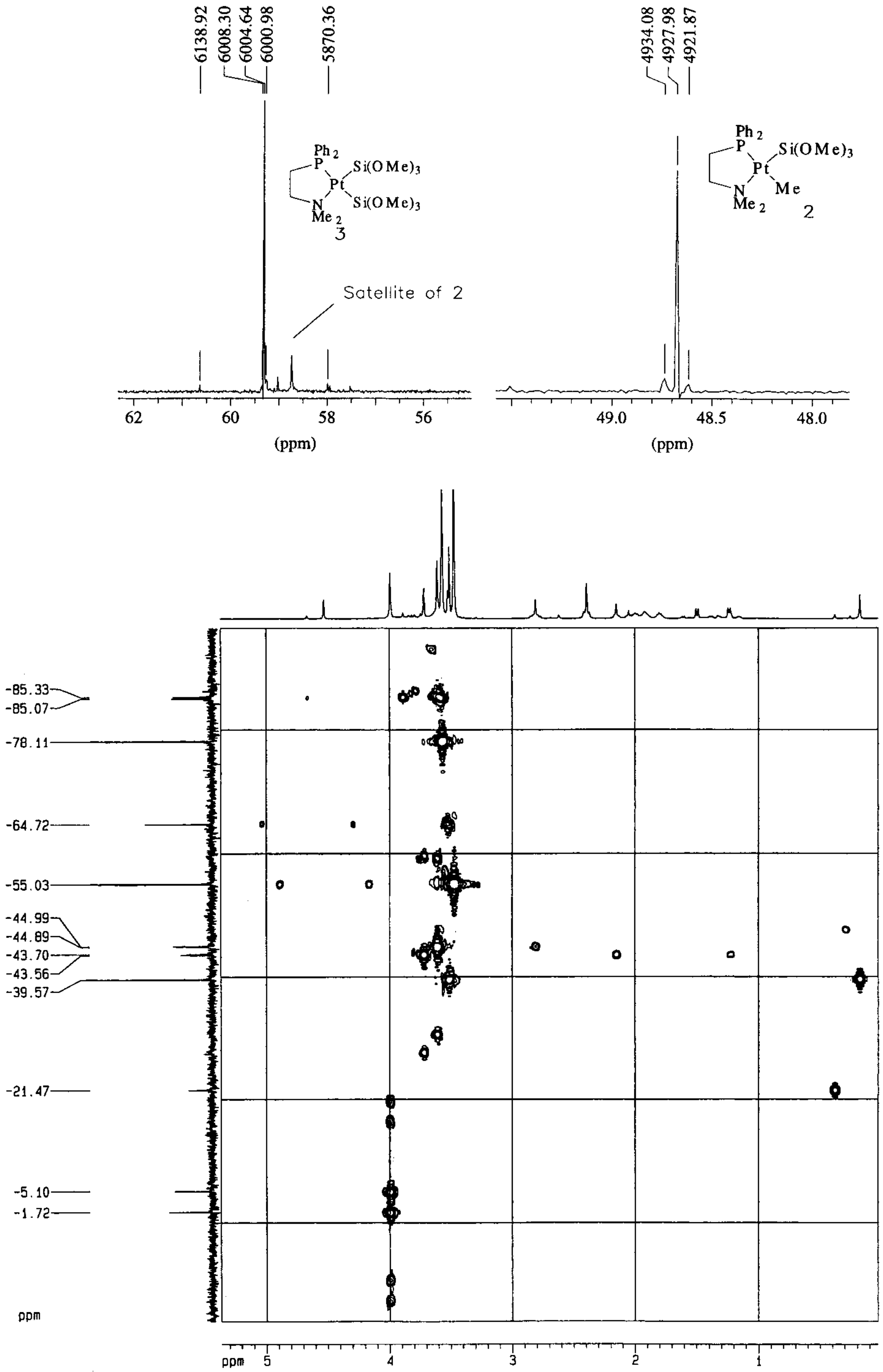

Figure 1. (a) Central signals of **2** ($\delta = 48.66$) and **3** ($\delta = 59.35$) showing the silicon satellites after 20 h ($^{31}P\{^{1}H\}$ NMR); (b) SiH−COLOC experiment of the reaction mixture after 20 h ($\delta_{Si} = -55.03$, HSi(OMe)$_3$).

constants of **2** and **3** (**2**, $\delta_{Si} = -43.63$, $^{1}J_{PtSi} = 2478.9$ Hz; **3**, $\delta_{Si} = -3.41$, $^{1}J_{PtSi}{}^{cis} = 2225.7$ Hz, $\delta_{Si} = -44.94$, $^{1}J_{SiPt}{}^{trans} = 2308.0$ Hz).

In addition to the platinum complexes **2** and **3**, methyltrimethoxysilane ($\delta_{Si} = -39.57$) and Si(OMe)$_4$ ($\delta_{Si} = -78.11$) were formed, as well as small amounts of hexamethoxydisiloxane ($\delta_{Si} = -85.33$) and pentamethoxydisiloxane ($\delta_{Si} = -85.07, -64.72$; the signal at $\delta_{Si} = -21.47$ results from an impurity in trimethoxysilane which remained unchanged during the reaction). The identity of the silanes was confirmed by comparison with authentic samples.[9]

The ratio of **1**/**2**/**3** changed from 1/0.33/0.5 (after 20 h) to 1/0.5/1.0 (after 40 h) to 1/3.4/2.2 (after 60 h) during the reaction. The amounts of MeSi(OMe)$_3$ and Si(OMe)$_4$ after 60 h were 0.8 and 2.9 equiv, respectively, relative to **2**. (MeO)$_3$Si−O−SiH(OMe)$_2$, observable after 20 h,

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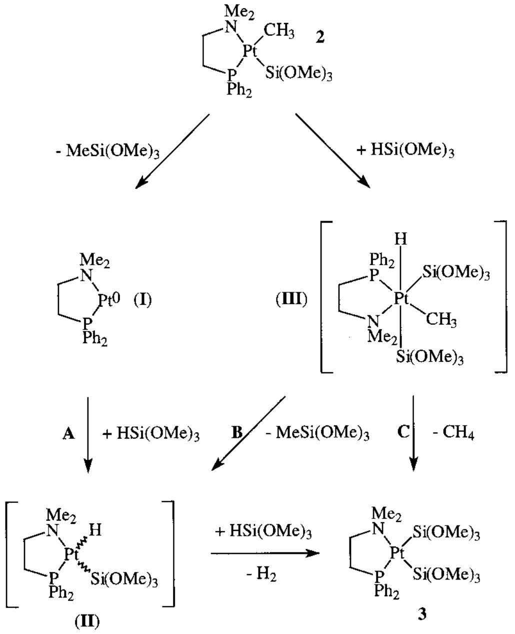
[9] Preparation of HSi(OMe)$_2$OSi(OMe)$_3$: Okinoshima, H.; Kashiwagi, T. (Shi-Etsu Chemical Industry Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 04 36,286 [92 36,286] (Cl. C07F7/04), Appl. 90/140.852; *Chem. Abstr.* **1992**, *117*, 825; 192059e.

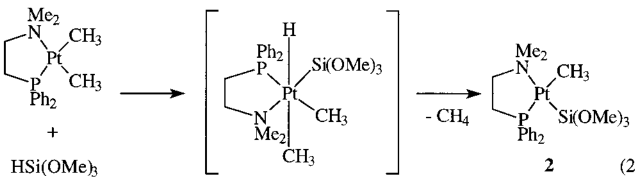
[10] In the reaction with 1 or 2 equiv of HSi(OMe)$_3$, the silane was consumed after 30 and 40 h, respectively (60 h in the reaction with 3.5 equiv). Product ratio: 1 equiv, **1**/**2**/**3**/MeSi(OMe)$_3$/Si(OMe)$_4$ = 8/1.2/1/1.1/2.8; 2equiv, **1**/**2**/**3**/MeSi(OMe)$_3$/Si(OMe)$_4$ = 3.3/1.1/1/1.1/3.4 (ratios determined from the ^{1}H NMR spectra).

Scheme 1. Suggested Mechanism for the Formation of the Bis(silyl) Complex 3 and MeSi(OMe)$_3$ from 2



was consumed in the sequel. Reaction of **1** with only 1 or 2 equivs of HSi(OMe)$_3$ led to about the same product distribution,[10] but more **1** remained unreacted after complete consumption of HSi(OMe)$_3$. The relative concentrations of the products in the reaction mixture stayed constant after all of the HSi(OMe)$_3$ had reacted.

Exchange of the first methyl group of **1**, presumably by oxidative addition of HSi(OMe)$_3$ followed by reductive elimination of methane, results in the formation of the *cis* methyl silyl platinum complex **2** (eq 2; the stereochemistry of the proposed Pt(IV) intermediate was arbitrarily drawn).[11] It is likely that this and the following reaction steps are accompanied by reversible decomplexation of the amino group of the P,N-chelating ligand. The *cis* stereochemistry of **2** is confirmed by the typically large $^2J_{\mathrm{PPtC}}$ *trans* coupling constant (89.65 Hz) and by the small $^2J_{\mathrm{PPtSi}}$ *cis* coupling constant (12.2 Hz). Its stereoselective formation can be explained by the different *trans* influence of the nitrogen and phosphorus donor centers.



(2)

There are three potential routes for the formation of the bis(silyl) complex **3** from the methyl silyl complex **2** (Scheme 1). The first (**A** in Scheme 1) involves initial reductive elimination of MeSi(OMe)$_3$ and formation of a Pt(0) intermediate (**I**), which could then add 2 equivs of HSi(OMe)$_3$ to give **3** via the intermediate hydrido(silyl) complex **II**. The first step of this mechanism (thermally driven reductive elimination of MeSi(OMe)$_3$) can be ruled out because of the high stability of **2** after consumption of all HSi(OMe)$_3$. Alternatively, the conversion of **2** to **3** could involve oxidative addition of HSi(OMe)$_3$ to give the Pt(IV) intermediate **III** followed by reductive elimination of methane to give **3** (route **C** in Scheme 1).[12] However, this possibility does not explain the formation of MeSi(OMe)$_3$. The most probable route, therefore, is that complex **III** eliminates MeSi(OMe)$_3$ (route **B** in Scheme 1). This would result in the formation of the hydrido silyl complex **II**. It is known that hydrido silyl complexes of platinum often react rapidly with HSiR$_3$ to give the corresponding bis(silyl) complexes.[13] The formation of bis(silyl) complexes by this reaction is generally favored when silicon bears electron-withdrawing substituents.[14] Accordingly, the fact that we did not observe this intermediate does not contradict the presumed mechanism. This reaction pathway is also in accordance with the formation of MeSi(OMe)$_3$ and complex **3** in an approximate 1:1 ratio[15] as well as with the observation that exchange reactions between *cis*-(R$_3$P)$_2$Pt(SiR$'_3$)$_2$ and HSiR$''_3$ proceed particularly rapidly with HSi(OMe)$_3$.[16]

One explanation for the formation of the rather large amounts of Si(OMe)$_4$ would be the insertion of oxygen into a Pt−Si (or less likely the Pt−C) bond of intermediate **III**, followed by reductive elimination of the alkoxysilane.[17] The first indication that contaminations by air or surface OH groups of the glassware are not the oxygen source came from the observation that the product distribution and the reaction rate were independent of the reaction conditions (oven-dried glassware or PTFE liner; performance of the reaction under an argon atmosphere or in air). For unambiguous proof, the CD$_3$-substituted analogue of **1** (*d*-**1**) was prepared from (nbd)Pt(CD$_3$)$_2$ and Me$_2$NCH$_2$CH$_2$PPh$_2$. When *d*-**1** was reacted with HSi(OMe)$_3$, the ^{2}H NMR spectrum of the reaction mixture showed no Si(OMe)$_3$OCD$_3$. The signals of D$_3$CSi(OMe)$_3$ (δ = 0.09) as well as of the deuterated complexes *d*-**1** and *d*-**2** (δ = 1.01, 1.36) were observed, as expected from the mechanism depicted in Scheme 1. This experiment clearly shows that *all* methyl groups of Si(OMe)$_4$ originate from HSi(OMe)$_3$. Scrambling reactions of silicon substituents in metal silyl complexes are not uncommon and are usually explained by the intermediate formation of silylene complexes.[18] Tilley and coworkers have recently pointed out that the transfer of a silyl substituent from silicon to platinum is easier in three- than in four-coordinated Pt complexes.[19] Thus, the rather easy formation of

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[11] In general, substitution reactions at Pt(II) centers with nonpolar reagents such as H$_2$ or HSiR$_3$ are assumed to proceed by *cis*-oxidative addition followed by a *cis*-reductive elimination step from an octahedral coordinated platinum(IV) species: (a) Bentham, J. E.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587. (b) Anderson, D. W. W.; Ebsworth, E. A. V.; MacDoughall, J. K.; Rankin, D. W. H. *J. Inorg. Nucl. Chem.* **1973**, 2259. (c) Levy, C. J.; Puddephatt, R. J.; Vittal, J. J. *Organometallics* **1994**, *13*, 1559.

[12] Examples for competing CH and CSi reductive elimination reactions are known, e.g.: Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317.

[13] (a) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (b) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495.

[14] Knorr, M.; Schubert, U. *Transition Met. Chem.* **1986**, *11*, 268.

[15] The use of PTFE inlet liners for the NMR tubes leads to a significant loss of resolution in the ^{1}H NMR spectra, hampering an accurate integration of the signals.

[16] Schubert, U.; Kalt, D.; Gilges, H. *Monatsh. Chem.* **1999**, *130*, 207.

[17] Molecular oxygen has recently been shown to be a possible source for oxygen incorporated into dimethyl platinum(II) complexes: Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530 and references cited therein.

$\mathrm{Si(OMe)_4}$ in the reaction of **1** with $\mathrm{HSi(OMe)_3}$ is probably a consequence of the presence of the hemilabile ligand at platinum. It should be pointed out, however, that $\mathrm{Si(OMe)_4}$ is not formed by decomposition of the bis(silyl) complex **3**, because the latter is stable after completion of the reaction. As a consequence, $\mathrm{Si(OMe)_4}$ is probably formed from one of the presumed Pt(IV) intermediates.

The routes leading to the small amounts of the two disiloxanes are still debatable. We cannot completely exclude that a portion of the Pt−Si bonds was oxidized to Pt−O−Si bonds by small amounts of oxygen which diffused into the reaction vessel. However, the observation that the composition of the reaction mixture does not change significantly in the deliberate presence of air contradicts this assumption. A more likely rationalization may therefore be the involvement of a competing $\mathrm{H_3C{-}OSi}$ oxidative addition. A few examples of oxidative addition reactions of unstrained $\mathrm{C_{alkyl}{-}O}$ bonds are known in the literature, mainly for alkyl aryl ethers (where the alkyl−O bond is added to the metal instead of the aryl−O bond) or esters.

When the corresponding bisphosphine complex (dppe)$\mathrm{Pt(CH_3)_2}$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) was analogously reacted under the same reaction conditions, no reaction was observed within 60 h, and the starting compounds were recovered in 95% yield. Thus, the reaction presented in this Communication shows that incorporation of a P,N-chelating ligand strongly enhances the propensity of dialkylplatinum(II) complexes for alkyl/silyl exchange by oxidative addition/reductive elimination reactions compared to the corresponding bisphosphine complexes. We attribute this to the activating effect of the hemilabile P,N-chelating ligand. There is even evidence for the addition of C−O bonds of alkoxysilyl groups to the metal center and the promotion of reactions involving silicon substituents. No products resulting from a Si−Si reductive elimination reaction were observed under the conditions applied.

Experimental Section

Synthesis of 1. An amount of 1 mmol (0.323 g) of (nbd)$\mathrm{Pt(CH_3)_2}$[6] was dissolved in 10 mL of dry, argon-saturated benzene. After addition of 1 mmol (0.257 g) of 2-(dimethylphosphino)ethyldimethylamine[11] and stirring for 2 h at room temperature, the solvent was concentrated at reduced pressure to about 2 mL. An amount of 30 mL of petroleum ether (30/50) was added, and the reaction mixture was stored at −30 °C for 24 h to complete precipitation. The product was filtered, washed with 2 × 5 mL of petroleum ether, and dried under reduced pressure. Yield 84% (0.405 g) of **1** as a colorless solid. Anal. Calcd for $\mathrm{C_{18}H_{26}NPPt}$ (482.46): C, 44.81; H, 5.43; N, 2.90. Found: C, 45.03; H, 5.35; N, 2.81. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ = 35.93 (s with Pt satellites, $^1J_{\mathrm{PtP}}$ = 2071.53 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ = −24.69 (d with Pt satellites, $^1J_{\mathrm{PtC}}$ = 748.74 Hz, $^2J_{\mathrm{PPtC}}$ = 4.21 Hz, 1 C, *cis*-$\mathrm{PtCH_3}$), 14.45 (d with Pt satellites, $^1J_{\mathrm{PtC}}$ = 709.80 Hz, $^2J_{\mathrm{PPtC}}$ = 113.48 Hz, 1 C, *trans*-$\mathrm{PtCH_3}$), 29.56 (d, $^1J_{\mathrm{PC}}$ = 25.78, 1 C, $\mathrm{PCH_2}$), 49.19 (s, 2 C, $\mathrm{N(CH_3)_2}$), 64.44 (d, $^2J_{\mathrm{PCC}}$ = 9.47 Hz, 1 C, $\mathrm{NCH_2}$), 128.62 (d, J_{PC} = 9.47 Hz, 4 C, Ph-C^{t}), 130.00 (s, 2 C, Ph-C^4), 133.41 (d, J_{PC} = 12.10 Hz, 4 C, Ph-C^{t}), Ph-C^1 not observed. ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.21 (d with Pt satellites, $^2J_{\mathrm{PtCH}}$ = 66.53 Hz, $^3J_{\mathrm{PPtCH}}$ = 7.93 Hz, 3 H, *trans*-$\mathrm{PtCH_3}$),[20] 1.48 (d with Pt satellites, $^2J_{\mathrm{PtCH}}$ = 90.34 Hz, $^3J_{\mathrm{PPtCH}}$ = 7.33 Hz, 3 H, *cis*-$\mathrm{PtCH_3}$),[20] 1.60−1.90 (m, 4 H, $\mathrm{CH_2CH_2}$), 2.24 (s with Pt satellites, $^3J_{\mathrm{PtNCH}}$ = 18.01 Hz, 6 H, $\mathrm{N(CH_3)_2}$), 6.90−7.10 (m, 6 H, Ph-H), 7.60−7.80 (m, 4 H, Ph-H). MS (70 eV): m/z = 482 ($\mathrm{M^+}$, 1), 467 ($\mathrm{M^+ - CH_3}$, 38), 452 ($\mathrm{M^+ - 2CH_3}$, 100), 422 ($\mathrm{M^+ - 4CH_3}$, 45), 405 ($\mathrm{M^+ - C_6H_5}$, 3), 345 ($\mathrm{M^+ - 4CH_3 - C_6H_5}$, 10), 328 ($\mathrm{M^+ - 2C_6H_5}$, 5).

Reaction of 1 with $\mathrm{HSi(OMe)_3}$. An amount of 0.1 mmol (0.0482 g) of **1** was dissolved in 0.5 mL of argon-saturated benzene-d_6 (dried over $\mathrm{CaH_2}$) in an NMR tube equipped with a PTFE liner at room temperature, followed by addition of 0.35 mmol (0.0427 g) of trimethoxysilane. All operations were performed under an atmosphere of dry argon. Data for **2**. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ = 48.66 (d with Pt and Si satellites, $^1J_{\mathrm{PtP}}$ = 2037.35 Hz, $^2J_{\mathrm{SiPtP}}$ = 12.2 Hz). ^{29}Si NMR (INEPT): δ = −43.66 (d with Pt satellites, $^1J_{\mathrm{PtSi}}$ = 2478.9 Hz, $^2J_{\mathrm{PPtSi}}$ = 12.2 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 4.62 (d, $^2J_{\mathrm{PPtC}}$ = 89.65 Hz, $\mathrm{PtCH_3}$), 32.10 (d, $^1J_{\mathrm{PC}}$ = 25.76 Hz, $\mathrm{PCH_2}$), 47.15 (s, $\mathrm{N(CH_3)_2}$), 50.02 (s, $\mathrm{Si(OCH_3)_3}$), 62.46 (d, $^2J_{\mathrm{PCC}}$ = 8.25 Hz, $\mathrm{NCH_2}$). ^{1}H NMR: δ = 0.87 (d with Pt satellites, $^2J_{\mathrm{PtCH}}$ = 53.21 Hz, $^3J_{\mathrm{PPtCH}}$ = 7.45 Hz, 3 H, $\mathrm{PtCH_3}$), 1.85−2.09 (m, 4 H, 2 × $-\mathrm{CH_2}-$), 2.13 (s with Pt satellites, $^3J_{\mathrm{PtNCH}}$ = 12.30 Hz, 6 H, $\mathrm{N(CH_3)_2}$), 3.71 (s, 9 H, $\mathrm{O(CH_3)_3}$). Data for **3**. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ = 59.32 (d with Pt and Si satellites, $^1J_{\mathrm{PtP}}$ = 1424.56 Hz, $^2J_{\mathrm{SiPtP}}{}^{\mathrm{cis}}$ = 7.32 Hz, $^2J_{\mathrm{SiPtP}}{}^{\mathrm{trans}}$ = 268.6 Hz). ^{29}Si NMR (INEPT): δ = −44.94 (d with Pt satellites, $^1J_{\mathrm{PtSi}}$ = 2225.7 Hz, $^2J_{\mathrm{PPtSi}}$ = 7.32 Hz, *cis*-$\mathrm{Si(OCH_3)_3}$), −3.41 (d with Pt satellites, $^1J_{\mathrm{PtSi}}$ = 2308.0 Hz, $^2J_{\mathrm{PPtSi}}$ = 268.6 Hz, *trans*-$\mathrm{Si(OCH_3)_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ = 33.29 (d, $^1J_{\mathrm{PC}}$ = 22.24 Hz, $\mathrm{PCH_2}$), 49.73 (s, $\mathrm{N(CH_3)_2}$), 49.87 (s, *trans*-$\mathrm{Si(OCH_3)_3}$), 50.16 (s, *cis*-$\mathrm{Si(OCH_3)_3}$), 63.59 (d, $^2J_{\mathrm{PCC}}$ = 9.86 Hz, $\mathrm{NCH_2}$). ^{1}H NMR: δ = 1.85−2.09 (m, 4 H, 2 × $-\mathrm{CH_2}-$), 2.79 (s with Pt satellites, $^3J_{\mathrm{PtNCH}}$ = 18.39 Hz, 6 H, $\mathrm{N(CH_3)_2}$), 3.62 (s, 9 H, *cis*-$\mathrm{Si(OCH_3)_3}$), 3.98 (s, 9 H, *trans*-$\mathrm{Si(OCH_3)_3}$). The hydrogen and carbon atoms of the phenyl groups could not be assigned due to overlapping signals.

Preparation of *d*-1. Reaction of (nbd)$\mathrm{PtCl_2}$ with 2.2 molar equiv of $\mathrm{CD_3MgI}$ (1 M solution in $\mathrm{Et_2O}$) according to ref 10 led to formation of (nbd)$\mathrm{Pt(CD_3)_2}$ in 89% yield. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ = 5.71 (sept, $^1J_{\mathrm{DC}}$ = 19.35 Hz, $\mathrm{Pt(CD_3)_2}$, the Pt satellites could not be observed), 49.80 (s with Pt satellites, J_{PtC} = 39.23 Hz), 73.01 (s with Pt satellites, J_{PtC} = 44.14, 2 C), 87.81 (s with Pt satellites, J_{PtC} = 48.5 Hz, η-$\mathrm{C_{alkene}}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 0.95 (b, 2 H), 3.23 (b, 2 H), 4.54 (s with Pt satellites, J_{PtH} = 39.78 Hz, 4 H, η-$\mathrm{HC_{alkene}}$). Reaction of (nbd)$\mathrm{Pt(CD_3)_2}$ with $\mathrm{Me_2NCH_2CH_2PPh_2}$ according to ref 12 resulted in the isolation of $[(\kappa^2\text{-P, N})\text{-}\mathrm{Me_2NCH_2CH_2PPh_2}]\mathrm{Pt(CD_3)_2}$ in 85% yield. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ = 36.17 (s with Pt satellites, $^1J_{\mathrm{PtP}}$ = 2060.54 Hz). $^{13}\mathrm{C}$ $\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ = −25.66 (sept, $^1J_{\mathrm{DC}}$ = 18.47 Hz, *cis*-$\mathrm{CD_3}$, no coupling to P and Pt could be observed), 3.34 (dsept, $^1J_{\mathrm{DC}}$ = 18.47 Hz, $^2J_{\mathrm{PPtC}}$ = 112.43 Hz, *trans*-$\mathrm{CD_3}$, the Pt satellites could not be observed), 29.75 (d, $^1J_{\mathrm{PC}}$ = 26.1 Hz, $\mathrm{PCH_2}$), 49.52 (s, $\mathrm{N(CH_3)_2}$), 64.84 (d, $^2J_{\mathrm{PCC}}$ = 9.23 Hz, $\mathrm{NCH_2}$), 128−135 (Ar−C). ^{2}H NMR ($\mathrm{C_6H_6}$:$\mathrm{C_6D_6}$ = 20:1): δ = 0.41 (d, $^3J_{\mathrm{PPtCD}}$ = 0.92 Hz, 3 D, $\mathrm{CD_3}$), 0.66 (d with Pt satellites, $^2J_{\mathrm{PtCD}}$ = 14.08 Hz, $^3J_{\mathrm{PPtCD}}$ = 0.91 Hz, 3 D, $\mathrm{CD_3}$). ^{1}H NMR ($\mathrm{C_6D_6}$): 1.5−1.7 (m, 2 H, $\mathrm{CH_2}$), 1.75−2.00 (m, 2 H, $\mathrm{CH_2}$), 2.26 (s with Pt satellites, $^3J_{\mathrm{PtNCH}}$ = 18.0 Hz, $\mathrm{N(CH_3)_2}$), 6.90−7.15 (m, 6 H, Ar−H), 7.5−7.7 (m, 4 H, Ar−H).

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Supporting Information Available: NMR spectra of **1**, *d*-**1**, and taken from the reaction mixture after 20 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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