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Silanol-Based Pincer Pt(II) Complexes: Synthesis, Structure, and Unusual Reactivity

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Aiming at the generation of a silanone intramolecularly bound to platinum, we prepared pincer-type PSiP silanol Pt(II) complexes. While a stable silanone complex was not isolated, unusual reactivity modes, involving its possible intermediacy, were observed. Treatment of the new $PSiH_2P$-type ligand $(o\text{-}i\text{Pr}_2PC_6H_4)_2SiH_2$ (**7**) with $(Me_2S)_2Pt(Me)Cl$ yields the pincer-type hydrosilane complex $[\{(o\text{-}i\text{Pr}_2PC_6H_4)_2SiH\}PtCl]$ (**8**), which upon Ir(I)-catalyzed hydrolytic oxidation gives the structurally characterized silanol complex $[\{(o\text{-}i\text{Pr}_2PC_6H_4)_2SiOH\}PtCl]$ (**3**). Complex **3**, comprising in its structure the nucleophilic silanol fragment and electrophilic Pt(II)−Cl moiety, exhibits dual reactivity. Its reaction with the non-nucleophilic $KB(C_6F_5)_4$ in fluorobenzene leads to the ionic complex $[\{(o\text{-}i\text{Pr}_2PC_6H_4)_2SiOH\}Pt]^+ [(C_6F_5)_4B]^-$ (**9**), which reacts with CO to yield the structurally characterized $[\{(o\text{-}i\text{Pr}_2PC_6H_4)_2SiOH\}PtCO]^+ [(C_6F_5)_4B]^-$ (**10**). Treatment of **3** with non-nucleophilic bases leads to unprecedented rearrangement and coupling, resulting in the structurally characterized, unusual binuclear complex **11**. The structure of **11** comprises two different fragments: the original O−Si−Pt(II)−Cl pattern, and the newly formed silanolate Pt(II)−H pattern, which are connected via a disiloxane bridge. Complex **9** undergoes a similar hydrolytic rearrangement in the presence of $i\text{Pr}_2NEt$ to give the mononuclear silanolate Pt(II)−H complex **17**. Both these rearrangement-coupling reactions probably involve the inner-sphere generation of an intermediate silanone **14**, which undergoes nucleophilic attack by the starting silanol **3** to yield complex **11**, or adds a water molecule to yield complex **17**. X-ray diffraction studies of **3**, **10**, and **11** exhibit a very short Si−Pt bond length (2.27−2.28 Å) in the neutral complexes **3** and **11** that elongates to 2.365 Å in the carbonyl complex **10**. A significantly compressed geometry of the silanolate platinum(II)-hydride fragment **B** of the binuclear complex **11** features a Pt(2)−O(2)−Si(2) angle of 100.4 (3)° and a remarkably short Pt(2)···Si(2) [2.884 (3) Å] distance.

Introduction

Organosilanols, silicon compounds of the general formula $R_nSi(OH)_{4-n}$ have been extensively studied.[1] These compounds have found various applications, especially as building blocks for practically important siloxane-type polymers.[2] Metallosiloxanes, complexes of the type Si−O−M derived from silanols, have also attracted considerable interest as precursors for silicone polymers containing metal centers in the polymer backbone, as well as catalysts which structurally mimic metal-modified silica surfaces.[1,3] In contrast, metallosilanols, M−Si−OH, represent a relatively new and considerably less studied family of compounds.[1a,4–7] In most

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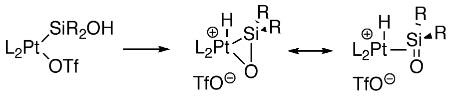
cases the preparations and structural characterizations of these compounds were reported while very little is known about their reactivity.

We reported the efficient and mild dehydrogenation of i-$\mathrm{Pr_2SiHOH}$ into transient i-$\mathrm{Pr_2Si{=}O}$ catalyzed by $\mathrm{[(dmpe)PtH]_2(OTf)_2}$, giving the cyclic trimer (i-$\mathrm{Pr_2SiO)_3}$.[7] In this catalytic cycle release of free silanone from a key intermediate, a platinum silanone complex (**2′**↔ **2″**) was suggested, resulting from β-hydrogen elimination of a Pt(II)−silanol precursor **1** (eq 1).[7,8]



(1)

1 **2'** **2''**

Such mild Pt-catalyzed generation of highly unstable silanones ($\mathrm{R_2Si{=}O}$)[9,10] raised the question whether a silanone-Pt complex, such as **2**, can be stabilized. So far, silanones with unambiguous sp^2-hybridized silicon have not been isolated except by low temperature matrix techniques.[10] The major reason for the instability of silanones is the extremely high polarization of the $\mathrm{R_2Si^{\delta+}{=}O^{\delta-} \leftrightarrow R_2Si^{+}{-}O^{-}}$ bond, which results in extraordinary reactivity, especially toward oligomerization leading to cyclosiloxanes $\mathrm{(R_2Si{=}O)}_n$ and toward addition of external nucleophiles; both processes are highly exothermic and, in the case of R = H, proceed with no barrier.[11] Considerable progress in the chemistry of silanone derivatives was reported in 2007 by Driess et al., who described the synthesis and characterization of silaurethane[12a] and silaformamide-borane complex,[12b] intramolecularly supported by a N→Si donor interaction.

As predicted by calculations, binding of silanones to transition metal centers could stabilize these short-living species.[13] Pincer-type complexes[14] have been demonstrated to be useful in the intramolecular stabilization of unusual types of structures.[15,16] It was reasonable to assume that upon generation of silanone in the inner sphere of a pincer-type complex, intramolecular binding would result in its kinetic and thermodynamic stabilization.

Herein we describe the design and synthesis of the first pincer-type silanol-Pt(II) framework, our attempts to convert the latter into the corresponding silanone-platinum complex, and an unexpected and unprecedented rearrangement and coupling of silanol-Pt(II) complexes into silanolate-Pt(II) hydrides. A number of rigid Ir(III) and Rh(III) pincer complexes, derived from NSi(Me)N-type tridentate bis(8-quinolyl)methylsilyl ligand, were recently reported by Tilley et al.[17] A single PSi(Me)P-type Pt(II)−Cl complex based on the tridentate bis(*ortho*-diphenylphosphinobenzyl)methylsilyl ligand,[18a] and some PSi(Me)P-complexes of Pt(II), Ru(II), and Ir(III) derived from the aliphatic tridentate $\mathrm{MeSiH[(CH_2)_nPR_2]_2}$ ligands (R = Ph or c-Hex, $n = 2$ or 3), were described by Stobart et al.[18b–d] While the manuscript was in preparation, rigid PSi(Me)P-type Ru(II), Rh(I), Pd(II), and Pt(II) complexes supported by bis(*ortho*-diphenylphosphinophenyl)methylsilyl ligand were also reported.[19]

Results and Discussion

1. Synthesis of the Tridentate $\mathrm{PSiH_2P}$ Ligand and Pincer-Type Pt(II) Silanols. We previously reported the synthesis of several Pt(II)-,[7] Ir(III)-,[6] and Rh(III)[6b] metallasilanols by the direct oxidative addition[20] of nonfunctional-

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[8] In contrast to the efficient catalytic dehydrogenation of i-$\mathrm{Pr_2SiHOH}$, a related reaction of the bulkier t-$\mathrm{Bu_2SiHOH}$ with (dmpe)PtMe(OTf) resulted in platinum-silanol **1** formation. See ref 7 for more details.

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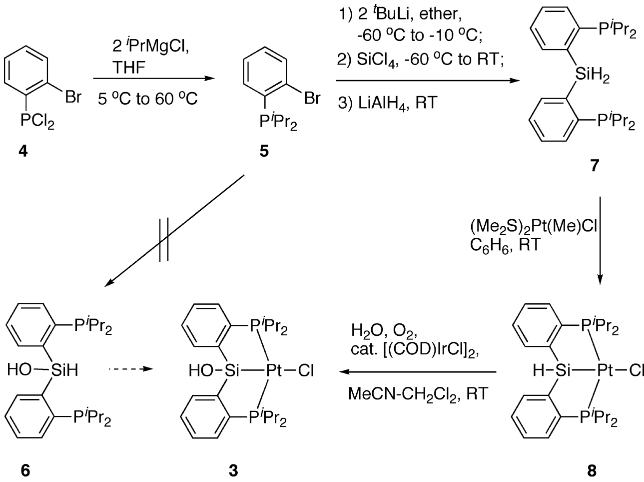
Scheme 1



ized secondary silanols (R_2SiHOH, where R = *i*-Pr or *t*-Bu) to the corresponding low valent transition metal complexes. This prompted us to construct the tridentate diphosphino-silanol ligand **6**, which, upon treatment with an appropriate $L_2Pt(Me)Cl$ precursor, was expected to provide straightforward access to **3** (Scheme 1).

The synthetic route starts with the preparation of di-*iso*-propyl(*ortho*-bromophenyl)phosphine (**5**)[21] in 61.5% yield from the known dichlorophosphine **1**,[22] as shown in Scheme 1. Our persistent attempts to prepare the diphosphino-silanol **6**, through a bromide-to-lithium exchange in **5** followed by a coupling with $HSiCl_3$ [or with $Et_2NSi(H)Cl_2$] and subsequent hydrolysis, were unsuccessful.[23] On the other hand, one pot, well-controlled lithiation of **5** with *tert*-butyl lithium, followed by coupling with silicon tetrachloride, and subsequent reduction of the intermediate silicon chlorides using $LiAlH_4$, afforded the diphosphino-dihydrosilane $PSiH_2P$ ligand **7** in reasonable yield (63% isolated yield in 3 steps).

The dihydrosilane **7**, which was isolated as a colorless oil, indefinitely stable under inert atmosphere, was characterized by multinuclear NMR-spectra, IR-spectrum, and electron spray ionization (ESI) mass-spectra. The $^{31}P\{^1H\}$ NMR spectrum of **7** exhibits a singlet at $\delta = 3.0$ ppm, whereas the silicon nuclei exhibits in the ^{29}Si-DEPT spectrum a triplet at $\delta = -39.95$ ppm because of significant coupling with the two phosphorus atoms ($^3J_{SiP} = 22.5$ Hz). In the ^{29}Si-INEPT spectrum a large coupling constant with protons, $^1J_{SiH} = 205$ Hz, was additionally detected. In the ^{1}H NMR spectra of **7** the H_2Si-fragment is observed as a triplet with ^{29}Si-satellites at $\delta = 5.45$ ppm ($^4J_{HP} = 8.7$ Hz, $^1J_{HSi} = 205$ Hz). The hydrosilane fragment in **7** is directly observed in the IR-spectrum as a strong broad band at 2139 cm^{-1}.

The tridentate $PSiH_2P$-ligand **7** readily reacts[20] with $(Me_2S)_2Pt(Me)Cl$ to give the corresponding bicyclic hydrosilane-Pt(II) chloride complex **8** in 85% yield according to the $^{31}P\{^1H\}$ NMR spectra, and in 62% isolated yield after flash chromatography (FC) (Scheme 1).[24–27] For oxygenation of metallo-hydrosilanes to metallo-silanols only a couple of peroxidic reagents, namely, dimethyldioxirane[5a,b,28] and urea-hydroperoxide adduct in the presence of catalytic amounts of $MeReO_3$,[29] have proved to be capable of chemoselective transformations. We found that the hydrosilane complex **8** underwent slow (over one month) autoxidation upon stirring its benzene solution without protection from air, yielding the silanol-Pt(II) chloride complex **3** (65%). More efficient and fast conversion of **8** to **3** in high yield (89% isolated) was accomplished using the recently developed iridium-catalyzed hydrolytic oxo-functionalization of silanes (Scheme 1).[30]

Both complexes **8** and **3**, being stable colorless solids after purification by chromatography, were fully characterized using multinuclear NMR spectroscopy, IR, and ESI-MS spectra as well as combustion analysis. A combination of ^{31}P, ^{195}Pt and ^{29}Si NMR spectroscopy clearly evidenced the connectivity of the heteroatoms and the highly symmetrical structure of these complexes with trans arrangement of the equivalent phosphine fragments. Indeed, a C_6D_6 solution of complex **8** exhibits a singlet with ^{195}Pt-satellites in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 68.89$ ppm (s, ^{195}Pt satellites $^1J_{PPt} = 2885$ Hz), which is slightly shifted downfield to $\delta = 71.08$ ppm (s, ^{195}Pt satellites $^1J_{PPt} = 3025$ Hz) in the spectrum of silanol **3**. In the $^{195}Pt\{^1H\}$ NMR spectrum of complex **8**, a triplet at $\delta = -5022$ ppm ($^1J_{PtP} = 2885$ Hz) was observed, whereas the corresponding triplet in the spectrum of **3** is slightly shifted to $\delta = -4992$ ppm ($^1J_{PtP} = 3025$ Hz, with ^{29}Si satellites $^1J_{SiPt} = 1334$ Hz). The very negative values of ^{195}Pt chemical shifts for both complexes, which are near the high field limit of the region of Pt(II) derivatives, are typical

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[21] It was mentioned that di-*iso*-propyl(*ortho*-bromophenyl)phosphine (**5**) was prepared in good yield by monolithiation of *ortho*-dibromobenzene followed by coupling with *i*-Pr_2PCl. The suggested method gave only poor results in our hands. Neither experimental details nor any characterization of **5** was reported in this article. See Tamm, M.; Drebel, B.; Baum, K.; Lügger, T.; Pape, T. *J. Organomet. Chem.* **2003**, *677*, 1.

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[23] As far as we are aware, there are no publications on synthesis of any functionalized secondary silanols until now.

[24] Even better (up to 95%) NMR yield of complex **8** was observed in the reactions of ligand **7** with *freshly prepared and purified by FC* (NBD)Pt(Me)Cl. However, this reaction is hardly reproducible. Therefore, for preparative purposes the use of $(Me_2S)_2Pt(Me)Cl$ is preferable.

[25] To the best of our knowledge, this is the first reported application of any dihydrosilane pincer ligands of type $ESiH_2E$ (E = P, N, S, etc.) for preparation of organometallic compounds. For additions of NSiH(Me)N and PSiH(Me)P monohydrosilane tridentate ligands to late transition metal complexes, see refs 17−19.

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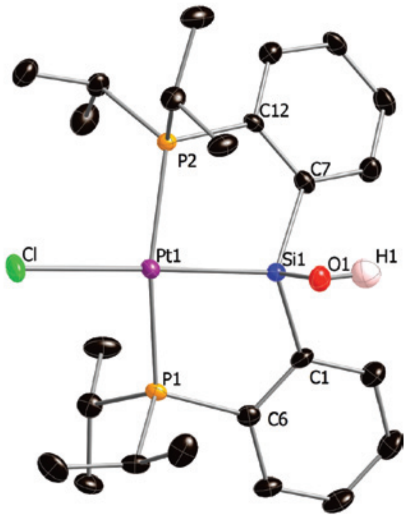


Figure 1. Crystal structure of complex **3**. Ellipsoids are at 50% probability level. Hydrogen atoms except hydroxyl were omitted for clarity.

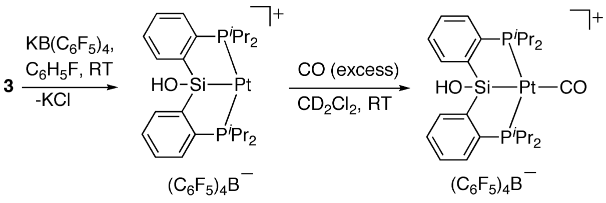
Table 1. Selected Bond Lengths (Å) and Bond Angles (Degrees) of Complex **3**

Pt(1)−Si(1)	2.2773 (10)	Si(1)−O(1)	1.652 (3)
Pt(1)-Cl	2.4694 (9)	Si(1)−C(1)	1.883 (4)
Pt(1)−P(1)	2.2892 (9)	Si(1)−C(7)	1.880 (4)
Pt(1)−P(2)	2.2957 (9)		
Si(1)−Pt(1)−Cl	175.08 (4)	O(1)−Si(1)−Pt(1)	112.70 (11)
Si(1)−Pt(1)−P(1)	84.35 (3)	O(1)−Si(1)−C(1)	105.99 (16)
Si(1)−Pt(1)−P(2)	84.12 (3)	O(1)−Si(1)−C(7)	108.08 (16)
P(1)−Pt(1)−P(2)	161.70 (3)	C(1)−Si(1)−C(7)	114.53 (17)
P(1)−Pt(1)−Cl	95.50 (3)	Pt(1)−Si(1)−C(1)	108.76 (12)
P(2)−Pt(1)−Cl	97.18 (3)	Pt(1)−Si(1)−C(7)	106.92 (13)

for Pt(II)-silyl complexes[31] and indicate high electron density at the metal center.[32] In the ^{29}Si NMR spectra (obtained using ^{29}Si−^{1}H HMBC sequence) both complexes **8** and **3** give rise to broadened singlets accompanied by one-bond coupling ^{195}Pt satellites at $\delta = 12.27$ ppm (^{195}Pt satellites $^{1}J_{\mathrm{SiPt}} = 1190$ Hz) and $\delta = 38.53$ ppm (^{195}Pt satellites $^{1}J_{\mathrm{SiPt}} = 1335$ Hz), respectively. In the ^{29}Si-DEPT NMR (which is more sensitive to small coupling constants) of the hydrosilane complex **8**, the mentioned above broadened singlet is resolved into a triplet with $^{2}J_{\mathrm{SiP}} = 5.2$ Hz and the same as before ^{195}Pt satellites, while a ^{29}Si-INEPT experiment revealed additionally the direct Si−H coupling constant, $^{1}J_{\mathrm{SiH}} = 183$ Hz. The diagnostic pattern of the Si−H proton of **8** was observed in both ^{1}H and ^{1}H{^{31}P} NMR spectra as a broadened singlet at 5.75 ppm with ^{195}Pt and ^{29}Si satellites $^{2}J_{\mathrm{HPt}} = 38.8$ Hz, $^{1}J_{\mathrm{HSi}} = 183$ Hz.

The molecular structure of the first pincer-type metallosilanol complex **3** was defined by a single crystal X-ray analysis (Figure 1, Table 1). The platinum center exhibits a significantly distorted square planar geometry, while the silicon center adopts a distorted tetrahedral structure, considerably compressed toward planarity. Because of the rigid and constrained molecular structure, the Pt−Si distance in **3** [2.2773(10) Å] is about 0.02 Å shorter than the conventional range of Pt−Si single bonds (2.30−2.40 Å)[24,33,34] and very similar to the value of the Pt═Si bond in cationic Fischer-type platinum silylene [2.270(2) Å].[35] The strong trans effect of the silyl ligand[36] causes considerable elongation (0.04 Å) of the Pt(1)−Cl bond to 2.4694(9) Å in **3** as compared with the corresponding bond length in the pincer-type PCP−Pt(II) chlorides.[37]

In agreement with the X-ray data, the strong trans effect of the silyl ligand labilizes the Pt(II)−Cl bond in complex **3**. Indeed, exchange of the chloride ligand by less nucleophilic anions in pincer-type PCP complexes requires application of the appropriate silver salts.[37b–d] In contrast to that, treatment of the PSiP-type Pt(II) chloride complex **3** with the salt $KB(C_6F_5)_4$ resulted in chloride abstraction by the K^+ cation and quantitative formation of the corresponding cationic Pt(II)−silanol **9** (in 95% purity) bearing the non nucleophilic $(C_6F_5)_4B^-$ anion (eq 2).



9 **10** (2)

Although formally a 14-electron complex with a noncoordinating counteranion and solvent (C_6H_5F), compounds **9** is relatively stable in the solid state, as well as in CD_2Cl_2, C_6D_6 or C_6H_5F solutions under standard anaerobic anhydrous conditions. It may be stabilized by agostic interaction with the *i*-Pr groups, although we have no evidence for that. The ^{31}P{^{1}H} NMR spectrum of **9** exhibits singlets with ^{195}Pt satellites at $\delta = 73.12$ ppm ($^{1}J_{\mathrm{PPt}} = 3097$ Hz) in CD_2Cl_2 and 72.84 ppm ($^{1}J_{\mathrm{PPt}} = 3105$ Hz) in C_6H_5F, which are surprisingly little shifted downfield in comparison to the parent Pt(II)−Cl complex **3** ($\delta_P = 71.08$ ppm in CD_2Cl_2).[38] It should be mentioned that in the more studied pincer-type PCP Pt(II) complexes the common differences $\Delta\delta_P$ between cationic and neutral Pt(II)−Cl complexes are as large as 10

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(37) See, for example, (a) Poverenov, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2005**, *24*, 5937. (b) Schwartsburd, L.; Poverenov, E.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2007**, *26*, 2931. (c) Vuzman, D.; Poverenov, E.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Dalton Trans.* **2007**, 5692. (d) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.

(38) For a few examples of CH_2Cl_2 coordination to cationic late transition metal complexes, see (a) Taw, F. L.; White, R. C.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2002**, *124*, 4192. (b) Gandelman, M.; Konstantinovski, L.; Rosenberg, H.; Milstein, D. *Chem.−Eur. J.* **2003**, *9*, 2595.

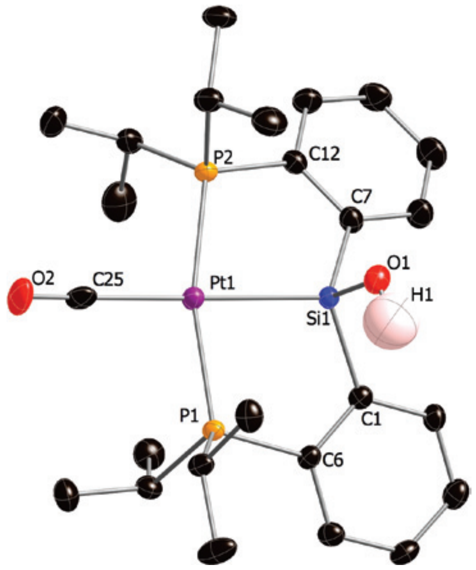

Figure 2. Crystal structure of complex **10**. The (C_6F_5)$_4$B-anion and all the hydrogen atoms except hydroxyl were omitted for clarity. The thermal ellipsoids are at 50% probability level.

ppm.[37a–c] Such a small $\Delta\delta_P$ value in complexes **9** versus **3** might be a result of an efficient compensation of positive charge by an increase of bonding from the silicon atom to the positively charged platinum atom in cationic complex **9**, although this is not supported by the observed NMR shielding of the Si and Pt nuclei. Actually, the platinum nucleus in **9** is observed as a triplet at −5075 ppm ($^1J_{PtP}$ = 3100 Hz) in the ^{195}Pt{^{1}H} NMR spectrum, and the silicon nucleus is detected in the ^{29}Si−^{1}H HMBC spectrum as a broadened singlet with characteristic ^{195}Pt satellites at 25.24 ppm ($^1J_{SiPt}$ = 1478 Hz).

Complex **9** reacts rapidly with carbon monoxide to give the Pt(II)−carbonyl complex **10** (eq 2). Because of the trans influence of the silyl group, in addition to the cationic nature of the complex, binding of CO is weak, and vacuum treatment of the carbonyl complex **10** led to the recovered precursor **9** (70% decarbonylation after 3 days at 1 mmHg).

The IR spectrum of complex **10** displays a distinctive band at 2087 cm^{-1}, corresponding to the CO ligand, and a very broad band centered at 3470 cm^{-1} (ν O−H). The ^{31}P{^{1}H} NMR spectrum of **10** exhibits a low-field shifted singlet at 82.24 ppm with a decreased value of the coupling constant ($^1J_{PPt}$ = 2736 Hz). The same tendency was also observed in PCP-type Pt(II) complexes.[37a–c] Rather unexpectedly, the Pt nucleus is significantly shifted upfield to δ = −5295 ppm (t with ^{29}Si satellites, $^1J_{PtP}$ = 2736 Hz, $^1J_{PtSi}$ = 980 Hz) in the ^{195}Pt{^{1}H} NMR spectra of **10**, while the silicon nucleus is deshielded and appears at 57.36 ppm (br s singlet with ^{195}Pt satellites, $^1J_{SiPt}$ = 977 Hz). The decreased value of the $^1J_{SiPt}$ coupling constant reflects considerable weakening of the Pt−Si bond in **10**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (Degrees) of Complex **10**

Pt(1)−Si(1)	2.3650 (6)	Si(1)−O(1)	1.652 (2)
Pt(1)−P(1)	2.3281 (6)	Si(1)−C(1)	1.870 (3)
Pt(1)−P(2)	2.3225 (7)	Si(1)−C(7)	1.871 (3)
Pt(1)−C(25)	1.994 (3)	C(25)−O(2)	1.111 (3)
Si(1)−Pt(1)−C(25)	173.43 (8)	O(1)−Si(1)−Pt(1)	113.73 (7)
Si(1)−Pt(1)−P(1)	82.32 (2)	O(1)−Si(1)−C(1)	102.93 (11)
Si(1)−Pt(1)−P(2)	82.07 (2)	O(1)−Si(1)−C(7)	108.20 (11)
P(1)−Pt(1)−P(2)	161.23 (2)	C(1)−Si(1)−C(7)	116.86 (12)
P(1)−Pt(1)−C(25)	97.41 (8)	Pt(1)−Si(1)−C(1)	108.43 (8)
P(2)−Pt(1)−C(25)	99.29 (8)	Pt(1)−Si(1)−C(7)	106.91 (8)
Pt(1)−C(25)−O(2)	174.5 (3)		

The molecular structure of complex **10** was confirmed by an X-ray diffraction study (Figure 2, Table 2). Colorless single crystals suitable for X-ray analysis were obtained upon partial concentration of a C_6D_6 solution of **10** at RT. The strong trans effects of both silicon and carbonyl ligands are well reflected in the molecular structure of **10**. Indeed, the Pt−Si bond in the Pt(II)−carbonyl complex **10** is elongated as compared to the Pt−Si bond in the platinum chloride complex **3** [2.3650 (9) Å in **10** vs. 2.2773 (10) Å in **3**]. This elongation enlarges the distortion of the Pt(II) center from a square planar arrangement. The Pt−CO bond length in the silanol complex **10** is considerably longer than the corresponding distances in the reported PCP-type Pt(II) carbonyls (1.99 Å vs 1.89−1.93 Å).[37b,c] The C−O bond distance in the Pt(II)-bound CO ligand in **10** is 1.111 (3) Å. This distance is even shorter than the reported experimental bond length of the free molecule of carbon monoxide (1.128 Å),[39] indicating weak bonding of the carbonyl ligand to the Pt(II) center.

2. Base-Induced Rearrangements of Neutral and Cationic Pt(II)−Silanols. According to the structure comprising nucleophilic silanol and electrophilic Pt(II) chloride centers, complex **3** was expected to exhibit dual reactivity. While it did not react with of Et_3N (in C_6D_6 and CD_2Cl_2) at ambient temperature, upon treatment with strong non-nucleophilic bases, complex **3** readily underwent unexpected rearrangement and head-to-head dimerization to afford the binuclear complex **11** as a major product rather than to give the common head-to-tail type oligomerization products (eq 3). Thus, upon addition of 1 equiv of KN($SiMe_3$)$_2$ to a solution containing complex **3** and a catalytic amount of 18-crown-6 (0.07 equiv) in ether-THF (conditions a), ^{31}P NMR monitoring of the reaction progress revealed that only about 10% of the starting **3** still remained after 12 h at −30 °C, while the novel complex **11** formed in about 65% NMR yield. Stirring the reaction mixture for an additional hour at ambient temperature resulted in complete consumption of complex **3** and simultaneous increase of the complex **11** content to about 75% yield. Running the reaction in the absence of 18-crown-6 gave the product **11** in lower yield (ca. 55%) after 12 h at −30 °C followed by 2.5 h at RT. Practically the same yield of the binuclear complex **11** was observed upon using potassium *tert*-butoxide in THF (conditions b, eq 3). The yield values given in eq 3 are of the pure complex **11** isolated as a colorless solid after anaerobic chromatography on Florisil.

The binuclear complex **11** is stable under neutral anaerobic conditions and was fully characterized by a combination of multinuclear NMR spectroscopy, IR, ESI mass-spectroscopy, and by single-crystal X-ray crystal-

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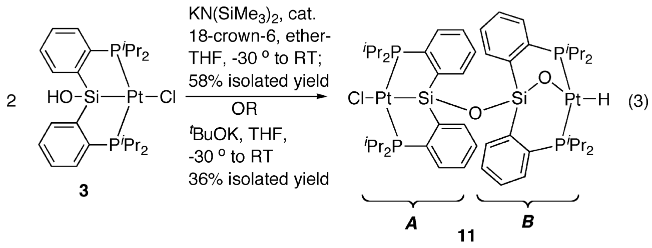

(3)

lography. Complex **11** may be viewed as consisting of two units: the original silanol-Pt(II)−chloride fragment (***A***) and rearranged silanolate-Pt(II)−hydride fragment (***B***), which are connected by a disiloxane bridge. While NMR, IR, and X-ray patterns of the fragment ***A*** in complex **11** are similar to those of the parent complex **3**, the corresponding features of the fragment ***B*** are very distinctive. Indeed, the ^{31}P{^{1}H} NMR spectrum of complex **11** in C_6D_6 shows a singlet at 69.75 ppm (^{195}Pt satellites $^1J_{PPt} = 3060$ Hz, fragment ***A***), and a broadened singlet in a higher field at 52.29 ppm (^{195}Pt satellites $^1J_{PPt} = 2844$ Hz, fragment ***B***). The broadening results from the incomplete decoupling with the hydride ligand that appears in the ^{1}H NMR spectra as a triplet at −18.31 ppm ($^2J_{HP} = 12.4$ Hz, with ^{195}Pt satellites $^1J_{HPt} = 1180$ Hz) or as the corresponding singlet with the same ^{195}Pt satellites in the ^{1}H{^{31}P} NMR spectra. In the ^{29}Si NMR spectra (^{29}Si−^{1}H HMBC) the silicon nucleus of the fragment ***A*** appears as a broadened singlet with ^{195}Pt satellites at 23.64 ppm ($^1J_{SiPt} = 1416$ Hz), whereas a broad singlet of the silicon nucleus in the fragment ***B*** appears in a higher field ($\delta = -56.83$ ppm) and without pronounced ^{195}Pt satellites ($^2J_{SiPt} \leq 100$ Hz). The ^{195}Pt{^{1}H} NMR spectrum of complex **11** exhibits a triplet at −4975 ppm ($^1J_{PtP} = 3060$ Hz), which is characteristic of the platinum nucleus of fragment ***A***. The platinum pattern in fragment ***B*** is observed using the more sensitive and selective (for platinum hydrides) ^{195}Pt−^{1}H HMQC experiment, which reveals a doublet of triplets at −4558 ppm ($^1J_{PtH} = 1180$ Hz, $^1J_{PtP} = 2845$ Hz). A broad medium intensity IR band at $\nu = 2204$ cm^{-1} is attributable to the Pt−H bond. In the high resolution ESI-MS an intensive protonated molecular ion m/z^+ 1288.3162 [M + H$^+$] is detected which corresponds to the composition $C_{48}H_{74}ClO_2P_4{}^{195}Pt^{196}PtSi_2$. The less intensive positive [M + H$^+$] ions related to the correct isotope pattern are also observed. The most intensive positive ions in the low-resolution ESI mass-spectra are of m/z^+ 1251 (65%) and 1252 (100%), both originating from [M$^+$ − Cl] (the correct isotope pattern), hence additionally confirming the composition of complex **11**.

X-ray quality colorless crystals of complex **11** were obtained upon cooling of a concentrated hexane solution at −15 °C for two weeks. The X-ray diffraction data (Figure 3, Table 3) show a binuclear complex, containing two different symmetrical fragments ***A*** and ***B***, as discussed above, linked to each other through a disiloxane bridge. The geometry of the Pt(II)−Cl fragment ***A*** in the binuclear complex **11** is very similar to the structure of the parent Pt(II)−Cl complex **3**, with a minor shortening of the Pt(1)−Si(1) bond to 2.269 (3) Å, and a slight elongation of the Pt(1)−Cl bond to 2.472 (3) Å. The parameters of the two bridging bonds Si(1)−O(1) and Si(2)−O(1), as well as the Si(1)−O(1)−Si(2) angle, are typical for disiloxanes.[40] In the newly formed Pt(II)−H fragment ***B*** the Pt(2) center has a considerably distorted square planar geometry with a P(3)−Pt(2)−P(4) angle of 162.02 (12)°, whereas the less constrained Si(2) center in this fragment adopts a geometry closer to tetrahedral than in both fragment ***A*** and in complex **3**. The Pt(2)−O(2) bond in the fragment ***B*** of complex **11** is lengthened by 0.04 Å (to 2.131 (6) Å) in comparison to the corresponding bonds in the few reported acyclic Pt(II)−silanolates (1.99−2.09 Å).[41] A remarkably short Si(2)−O(2) bond in complex **11** [1.596 (7) Å] is distinctive of

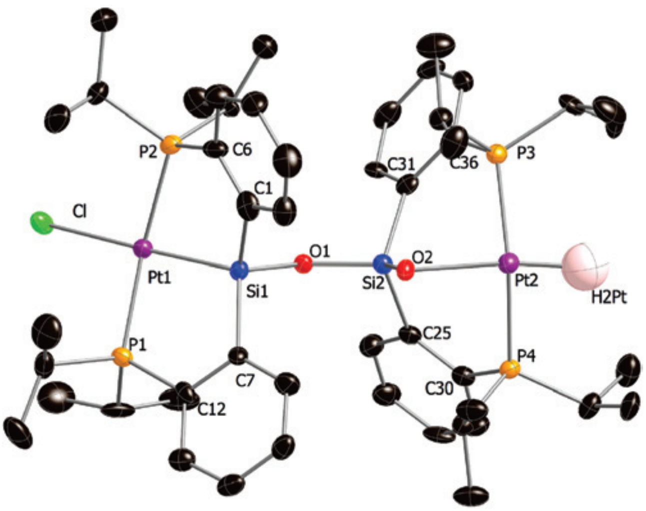

Figure 3. Crystal structure of the binuclear complex **11**. Hydrogen atoms except Pt(II)−hydride were omitted for clarity. Ellipsoids are at 50% probability level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (degrees) of the Binuclear Complex **11**

fragment **A**		fragment **B** (bonding)	
Pt(1)−Si(1)	2.269(3)	Pt(2)−O(2)	2.131(6)
Pt(1)−Cl	2.472(3)	Pt(2)−H(2Pt)	1.58(7)
Pt(1)−P(1)	2.286(2)	Pt(2)−P(3)	2.271(2)
Pt(1)−P(2)	2.294(2)	Pt(2)−P(4)	2.271(2)
Si(1)−C(1)	1.884(9)	Si(2)−O(2)	1.596(7)
Si(1)−C(7)	1.910(10)	Si(2)−C(25)	1.915(9)
		Si(2)−C(31)	1.902(9)
Si(1)−Pt(1)−Cl	176.15(9)	O(2)−Pt(2)−H(2Pt)	173(3)
Si(1)−Pt(1)−P(1)	85.52(10)	O(2)−Pt(2)−P(3)	87.97(17)
Si(1)−Pt(1)−P(2)	82.14(9)	O(2)−Pt(2)−P(4)	88.60(18)
P(1)−Pt(1)−P(2)	160.20(12)	P(3)−Pt(2)−P(4)	162.02(11)
P(1)−Pt(1)−Cl	96.33(9)	Pt(2)−O(2)−Si(2)	100.4(3)
P(2)−Pt(1)−Cl	96.96(9)	O(2)−Si(2)−C(25)	114.5(4)
Pt(1)−Si(1)−C(1)	109.4(3)	O(2)−Si(2)−C(31)	113.6(4)
Pt(1)−Si(1)−C(7)	105.3(3)	O(1)−Si(2)−O(2)	111.9(3)
C(1)−Si(1)−C(7)	113.8(4)	fragment **B** (nonbonding)	
O(1)−Si(1)−Pt(1)	114.1(2)	Pt(2)···Si(2)	2.884(3)
O(1)−Si(1)−C(1)	107.5(3)	O(2)−Pt(2)···Si(2)	32.97(18)
O(1)−Si(1)−C(7)	107.0(3)	O(2)−Si(2)···Pt(2)	46.6(2)
Disiloxane Bridge			
Si(1)−O(1)	1.655(6)	Si(1)−O(1)−Si(2)	137.8(4)
Si(2)−O(1)	1.638(6)		

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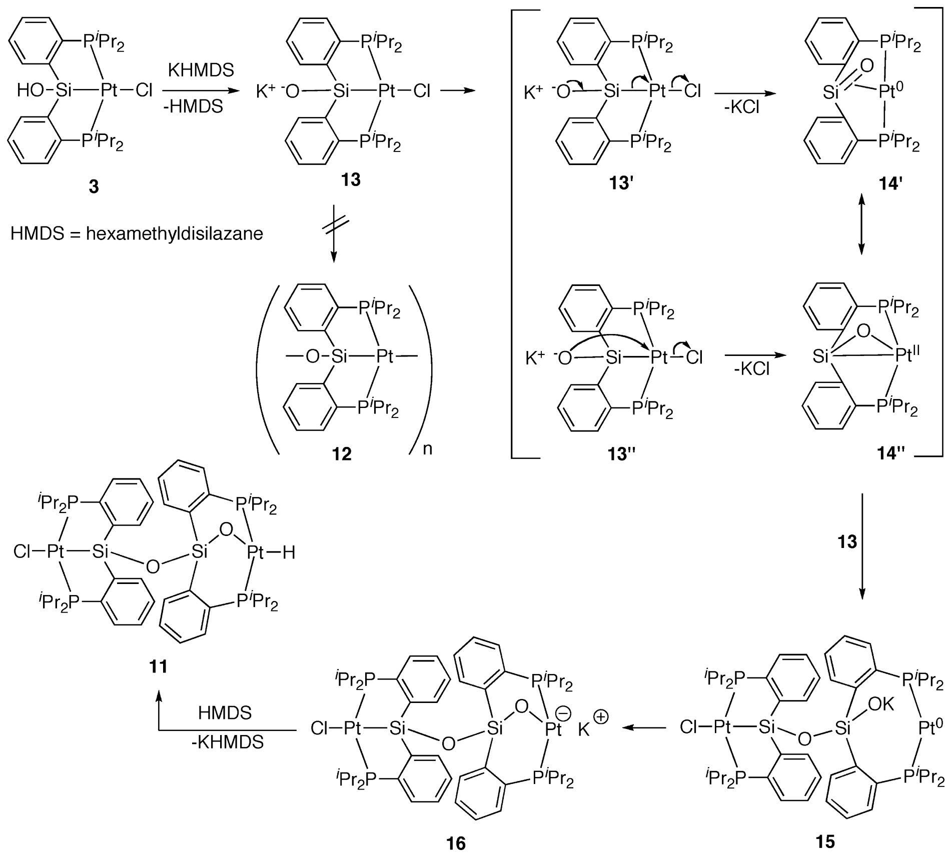
[40] Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y. , Eds.; Wiley: Chichester, 1998; Vol. 2, p 181.

[41] (a) Mintcheva, N.; Nishihara, Y.; Mori, A.; Osakada, K. *J. Organomet. Chem.* **2001**, *629*, 61. (b) Fukuoka, A.; Sato, A.; Kodama, K.; Hirano, M.; Komiya, S. *Inorg. Chim. Acta* **1999**, *294*, 266.

Scheme 2



Pt(II)−silanolate complexes (1.56−1.59 Å).[41] The unusual geometry of the middle part fragment ***B*** in complex **11**, including the angle Pt(2)−O(2)−Si(2) of 100.4 (3)° and the resulting rather short Pt(2)···Si(2) distance of 2.884 (3) Å might lead to an impression of a Pt(2)···Si(2) bonding interaction involving a Pt(2)−O(2)−Si(2) three-membered ring, related to the calculated structure for a Pt-silanone adduct.[13a] However, no spectroscopic indications for a Pt(2)···Si(2) interaction have been found.

Although the mechanism of this unusual rearrangement and head-to-head coupling has not been elucidated, the intermediate generation of an intramolecularly coordinated silanone looks like the most reasonable explanation of our experimental results (Scheme 2). Indeed, generation of the fragment ***B*** in the binuclear complex **11** ultimately requires a nucleophilic attack of the silanolate-anion (or silanol functionality itself) onto silicon atom, whereas its electrophilicity in complex **3** is expected to be negligible. On the other hand, the Pt(II) reaction center in the Pt(II)−Cl complex **3** is electrophilic in nature. In fact, the additionally labilized chloride ligand in **3** is readily abstracted by $K^+B(C_6F_5)_4^-$, as described above (eq 2). Therefore, deprotonation of **3** to **13** was expected to result in a common intermolecular nucleophilic substitution of chloride ligand at Pt(II) with the silanolate moiety, leading to the head-to-tail type oligomer **12**, unless the silicon atom is somehow activated toward nucleophiles. Moreover, the conversion of the Pt−Cl to Pt−H in the absence of an obvious hydride source is unexpected. The significant activation of silicon atom toward nucleophilic attack, as well as formation of the Pt−H fragment, can be rationalized in terms of the mechanism shown in Scheme 2.

Taking into account a formal analogy with construction of epoxides, the negatively charged oxygen atom in the silanolate Pt(II)−chloride complex **13″**could attack intramolecularly the electrophilic Pt(II) center to form a three-membered cyclic intermediate **14″**. Although the X-ray data for the neutral silanol complex **3** (Figure 1) indicated that the geometry is not very favorable for such a direct cyclization, in the silanolate complex **13** the negatively charged oxygen could move more closely to the electrophilic Pt(II) atom up to the auspicious bonding distance. Alternatively, as shown in **13′**, an electron density shift from negatively charged oxygen to silicon atom could induce cleavage of the Si−Pt σ-bond, with concomitant reduction of the metal center, to form the silanone-type Pt(0) intermediate **14′**. The conversion **13→14** can be driven by the irreversible extrusion of KCl from the ionic potassium silanolate **13**.[42–44] The intramolecular binding of the silanone moiety in the postulated intermediate **14′** (or **14″**) might

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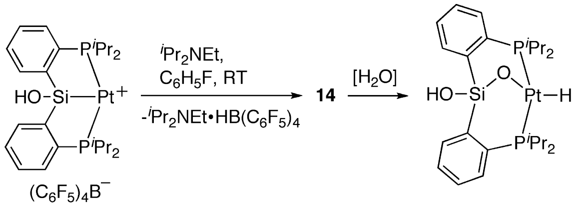
(42) It looks like the ionic nature of the potassium silanolate **13** is essential for the overall set of transformations **3→13→14→→11** (Scheme 2). For instance, our efforts to obtain the binuclear complex **11** by deprotonation of **3** by *t*-BuLi (THF, −30 °C) via the lithium analogue of **13** failed. Our attempts to induce release of di-*tert*-butylsilanone from the silanol Pt(II)−OTf complex **1** (eq 1, R = *t*-Bu) by deprotonation with organolithium reagents were also unsuccessful: Goikhman, R. ; Milstein, D. , unpublished results.

(43) A considerably covalent (vide infra) lithium silanolate, intermolecularly bound to a Ir(III)-Cl complex, was found to undergo dimerization to a Li−O−Li−O square-type dimer rather than release silanone and LiCl, even in the presence of 12-crown-4 (ref 6).

provide the required additional thermodynamic stabilization of these species. Although we are unaware of transformations related to **13′**→**14′** in silicon- or in transition metal chemistry, this process could be considered as a specific variant of a base-induced Hoffmann elimination. Reactions of this type proceed efficiently under very mild conditions, for instance, in the case of α-hydroxyalkylphosphonium salts to give the corresponding tertiary phosphines and the carbonyl compounds.[45a] Few similar degradations of α-hydroxyalkylsulfonium salts have been also reported.[45b,c]

Being reasonably stabilized toward oligomerization, the silanone intermediate **14′/14″** bearing a highly electrophilic silicon atom could undergo intermolecular nucleophilic attack by the silanolate **13** to form the binuclear siloxy-silanolate intermediate **15**. The latter can undergo an intramolecular attack on the metal to give an anionic, formally Pt(0)/Pt(II) binuclear intermediate **16**. Finally, the anionic Pt(0) complex **16** is protonated by $HN(SiMe_3)_2$ (or *t*-BuOH) to give the isolated binuclear Pt(II)−hydride product **11**.[46,47] Alternatively, albeit being significantly less basic in comparison to $HN(SiMe_3)_2$, the silanolate **15** could be reversibly protonated by $HN(SiMe_3)_2$ to the corresponding silanol, which might undergo probably irreversible oxidative addition to the neutral Pt(0) center to yield the final Pt(II)−hydride **11**.[48]

Our efforts aimed at observation of the silanone-type intermediates **14** prompted us to consider the option of retarding the bimolecular nucleophilic attack of the silanolate **13** in the process leading to the binuclear complex **11**. One possibility is applying higher dilution. Indeed, reaction of the silanol complex **3** with $KN(SiMe_3)_2$, upon 4.3 times dilution (initial concentration 0.003 M vs 0.013 M), gave a considerably lower amount of the binuclear **11** (ca. 30% ^{31}P NMR-yield), but a new Pt(II)−hydride, complex **17** (ca. 30%), was also formed. A further 3-fold dilution resulted in a slightly higher yield of complex **17** (ca. 40%) at the expense of the dimer **11** (ca. 10%). However, the insufficient content of **17** and its instability toward chromatography still prevented its isolation and characterization. Next, we employed the cationic silanol Pt(II) complex **9**, assuming that the silanolate which would be obtained upon its deprotonation would undergo intramolecular transformation to the platinum-silanone adduct **14** more effectively than the Pt−Cl silanolate **13**, but would be at the same time a considerably weaker nucleophile in the intermolecular processes. However, treatment of the cationic complex **9** with various amounts of $KN(SiMe_3)_2$ (from 0.4 to 1.1 equiv) in THF always afforded a complex mixture of Pt products. In contrast, in the presence of excess of the weaker base *i*-Pr_2NEt (3.6 equiv) in the noncoordinating solvent fluorobenzene, complex **9** was efficiently converted to complex **17** (≥60% NMR yield) over 14 days at ambient temperature (eq 4).



(4)

9 **17**

The mononuclear hydroxysilanolate Pt(II)−hydride complex **17** was isolated as a colorless waxy solid in about 35% yield (>95% ^{31}P NMR purity)[49] by extraction from the evaporated reaction mixture. The spectroscopic characteristics (multinuclear NMR and IR spectra) of complex **17** are very similar to the corresponding features of the fragment ***B*** in the binuclear complex **11** (see above). Indeed, in the ${}^{31}P\{{}^1H\}$ NMR spectrum of complex **17** in C_6D_6 a broadened singlet at 49.99 ppm with typical ^{195}Pt satellites, ${}^1J_{PPt} = 2857$ Hz, is observed. The hydride ligand appears in the ^{1}H NMR spectra as a triplet with ^{195}Pt satellites at −19.32 ppm (${}^2J_{HP} = 12.7$ Hz, ${}^1J_{HPt} = 1217$ Hz), which is transformed to a singlet with the corresponding ^{195}Pt satellites in the ${}^1H\{{}^{31}P\}$ NMR spectra. In the ^{195}Pt-^{1}H HMQC NMR spectra a doublet of triplets at −4566 ppm (${}^1J_{PtH} = 1220$ Hz, ${}^1J_{PtP} = 2858$ Hz) is detected. The ^{29}Si−^{1}H HMBC spectra exhibit the silicon nucleus resonance at −54.98 ppm as a broadened singlet. A broad, medium intensity IR band at $\nu = 2200$ cm^{-1} is attributed to Pt−H bond, whereas a very broad band centered at $\nu = 3420$ cm^{-1} corresponds to the O−H bond. In the ESI mass-spectra of complex **17**, the ions of m/z^+ 1287 (74%) and 1288 (100%) are detected, both related to [2 M + H$^+$] species (the correct isotope pattern).

Complex **17** was probably formed by nucleophilic attack of adventitious water on the electrophilic silicon center in the silanone-type intermediate **14** (eq 4), followed by a sequence of steps as discussed above for formation of the dimer **11**. The mononuclear silanol complex **17** exhibits considerable chemical lability in comparison to the structurally related dimer **11**. For example, the dimer **11** does not reveal any changes upon chromatography on Florisil, whereas its mononuclear counterpart **17** completely decomposed under these conditions. Moreover, while the purified dimer **11** is stable at ambient temperature under anaerobic condi-

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(44) A lithium silanolate complex of Os(II) −Cl was recently isolated: Albrecht, M.; Kwok, W.-H.; Lu, G.-L.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Inorg. Chim. Acta* **2005**, *358*, 1407.

(45) (a) Cristau, H. J., Plénat, F. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, 1994; Vol. *3*, p 45. (b) Knipe, A. C. In *The Chemistry of Sulphonium Group*; Stirling, C. J. M., Ed.; Wiley: Chichester, 1981; Vol. *1*, p 313. (c) Nenaidenko, V. G.; Balenkova, E. S. *Russ. J. Org. Chem.* **2003**, *39*, 291.

(46) An unstable Pt(0) anionic complex was reported. It reacts with electrophiles to form Pt(II) complexes. See Reger, D. L.; Ding, Y. *Organometallics* **1994**, *13*, 1047.

(47) We have recently prepared an anionic pincer-type Pt(0) complex that undergoes facile protonation to give the corresponding Pt(II) hydride: Schwartsburd, L.; Cohen, R.; Konstantinovski, L.; Milstein, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 3603.

(48) We are unaware of reported examples of O−H oxidative addition of silanols to low-valent late transition metals. For oxidative addition of water and alcohols to Pt(0) complexes, see (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027. (b) Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (c) For recent studies on addition of water and alcohols to Ir(I) complexes, see Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **2002**, *124*, 11456. (d) Dorta, R.; Rosenberg, H.; Shimon, L. J. W.; Milstein, D. *Chem.—Eur. J.* **2003**, *9*, 5237.

(49) A small amount (2−3%) of *i*-$Pr_2NEt\cdot HB(C_6F_5)_4$ impurity, as well as residual traces of solvent, were observed in the ^{1}H NMR spectrum of complex **17**. The *i*-$Pr_2NEt\cdot HB(C_6F_5)_4$ contaminant was also detected in both positive and negative modes ESI mass-spectra.

tions for weeks in a C_6D_6 solution and for months at −30 °C, the isolated monomer **17** partially decomposed (ca. 25%) after 1 day in C_6D_6 at RT, and decomposed completely after 15 days at −30 °C (being kept as a solid or in frozen C_6D_6).[49,50]

Summary

Exploring the possibility of generation of a silanone stabilized by intramolecular coordination to platinum, pincer-type silane- and silanol-Pt(II) complexes based on the new $PSiH_2P$ tridentate ligand **7** were efficiently prepared. Treatment of the structurally characterized platinum-silanol complex **3** with a strong base resulted in an unprecedented multistep rearrangement-coupling process leading finally to the structurally characterized binuclear silanolate Pt(II)−hydride complex **11**. We believe that a likely key intermediate in the overall sequence of events is the postulated silanone **14**, being especially responsible for the coupling and rearrangement steps. An analogous weak base-induced rearrangement of the cationic Pt(II)−silanol complex **9** in the noncoordinating fluorobenzene solvent to a mononuclear silanolate Pt(II)−hydride **17** was also observed, and probably involved water attack on the intermediate silanone complex **14**. Apparently, the intramolecular stabilization possibly allowed the formation of the silanone **14** and protected it against the expected cyclooligomerization. However, the currently achieved stabilization is still unsatisfactory to exclude very fast addition of external nucleophiles to the silicon center in the silanone complex **14**, which prevented its isolation. Thus, the approach for stabilization through intramolecular binding to transition metals in pincer-type complexes could open new opportunities for the construction of more stable silanones and related transients, but requires additional protection against nucleophilic attack.

Experimental Section

General Procedures. All experiments with the phosphine ligand and the metal complexes were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with MO 40-2 inert gas purifier or using common Schlenk techniques under argon. All solvents were reagent grade or better. All nondeuterated solvents except CH_2Cl_2 were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Methylene chloride was refluxed for half a day over CaH_2 and distilled under argon. The distilled solvents were kept in the glovebox over sodium (THF, benzene) or CaH_2 (ether, CH_2Cl_2, toluene, pentane, and hexane). Triethylamine and ethyl di-*iso*-propylamine were distilled and stored over CaH_2 under inert atmosphere. Fluorobenzene and silicon tetrachloride were stored over CaH_2 in a glovebox for at least 1 week before use. Commercial $KN(SiMe_3)_2$ (95%, Fluka) was purified by dissolving in dry toluene, filtered through a short plug of Celite followed by a thorough evaporation, and used only freshly purified. Other commercially available reagents were used as received. The deuterated solvents were dried over 4 Å molecular sieves. The startings (*ortho*-bromophenyl)dihlorophosphine (**4**)[22] and the metal complexes $(Me_2S)_2Pt(Me)Cl$[51] and $[(COD)IrCl]_2$[52] were prepared according to the literature procedures. Potassium tetra-*kis*(pentafluorophenyl)borate was prepared by the essential modification (see below) of the previously reported method.[53]

Analysis. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 500, 126, and 202 MHz, respectively, using a Bruker Avance-500 NMR spectrometer, or at 400, 101, and 162 MHz, respectively, using a Bruker Avance-400 NMR spectrometer. ^{29}Si NMR spectra were recorded at 99.5 MHz (Bruker Avance-500 NMR spectrometer) or at 79.5 MHz (Bruker Avance-400 NMR spectrometer) using ^{29}Si DEPT, INEPT, and ^{29}Si-^1H HMBC experiments. ^{195}Pt NMR spectra were recorded at 107.5 MHz using a Bruker Avance-500 NMR spectrometer; $^{195}Pt\{^1H\}$- and ^{195}Pt-^1H HMQC NMR experiments were conducted. ^{11}B NMR spectra were measured on a Bruker Avance-500 NMR spectrometer at 160.5 MHz, whereas ^{19}F NMR spectra were recorded on a Bruker Avance-250 NMR spectrometer at 235.5 MHz. All measurements were done at ambient temperature. ^1H, ^{13}C, and ^{29}Si NMR chemical shifts are reported in ppm relative to tetramethylsilane (0 ppm). ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents ($\delta = 7.15$ ppm for benzene, 5.32 ppm for dichloromethane, and 7.26 ppm for chloroform). In ^{13}C NMR measurements the signals of C_6D_6 (128.00 ppm), CD_2Cl_2 (53.80 ppm), or $CDCl_3$ (77.00 ppm) were used as internal references. ^{29}Si chemical shifts were referenced to an external $CDCl_3$ solution of triphenylsilane (−17.8 ppm). ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4 and were referenced to an external 85% solution of phosphoric acid in D_2O (0 ppm). ^{195}Pt chemical shifts are reported in ppm relative to Na_2PtCl_6 (0 ppm) and referenced to an external concentrated solution of Na_2PtCl_4 in D_2O (−1620 ppm). ^{11}B chemical shifts are reported in ppm relative to neat $BF_3 \cdot Et_2O$ (0 ppm), which was used as an external standard. ^{19}F chemical shifts are reported in ppm relative $CFCl_3$ and were referenced to an external standard C_6F_6 (−163.0 ppm). Screw-cup 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: Ar, aryl; br, broad(ened); v, virtual; s, singlet; d, doublet; t, triplet; m, multiplet; sym, symmetrical.

Infrared spectra were recorded using a Nicolet Protégé 460 FT-IR spectrometer in thin films on NaCl plates. Abbreviations used in the description of IR data are as follows: br, broad; s, strong; m, medium; v, very. Low resolution electrospray ionization (ESI) mass-spectrometry was performed using Micromass Platform LCZ 4000 (Micromass, Manchester, U.K.) with sampling cone voltage of 43V, extractor voltage of 4V, and desolvation temperature of 150 °C. High resolution mass-spectra (HRMS) were recorded using SYNAPT High Definition Q-TOF mass spectrometer (Waters Micromass, Manchester, U.K.) with ESI positive mode, source temperature 125 °C, desolvation temperature 275 °C, extractor voltage of 4 V, and sampling cone voltage of 24 V. Elemental analysis was performed at H. Kolbe Mikroanalytisches Laboratorium, Germany.

Flash chromatography (FC) was commonly performed on Florisil (Fluka), which was dried in the oven at 140 °C for a week at least, and, upon introducing to the glovebox, was degassed by applying vacuum at RT followed by addition of purified nitrogen (3 times

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(50) Such instability formally contradicts the stability of **17** in the reaction mixture (prior to isolation). This could be rationalized by taking into account the buffered nature of the reaction mixture and the presence of an acidic i-$Pr_2NEt \cdot HB(C_6F_5)_4$ impurity (ca. 2−3%) which might be the cause of decomposition.

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(53) (a) Massey, A. G.; Park, A. G. *J. Organomet. Chem.* **1964**, *2*, 245. (b) Castellanos, F.; Fouassier, J. P.; Priou, C.; Cavezzan, J. *J. Appl. Polym. Sci.* **1996**, *60*, 705.

repeated cycle). TLC analysis was performed on E. Merck 0.25 mm precoated silica gel 60 F-254 plates.

X-ray Structure Determination and Refinement. General Information. The crystals were mounted in a nylon loop and flash frozen in a cold nitrogen stream (120 K) on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.71071 Å), graphite monochromator. Accurate unit cell dimensions were obtained from 20° of data. The data were processed with the Denzo-Scale pack package. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97). Idealized hydrogen atoms were placed and refined in the riding mode.

Potassium Tetrakis(pentafluorophenyl)borate. A solution of KF (294 mg, 5.078 mmol) in dry methanol (6.0 mL) was added to a clear solution of $LiB(C_6F_5)_4 \cdot 2.5Et_2O$[53a] (2.868 g, 3.244 mmol) in methanol (14 mL). The mixture that immediately became turbid was stirred for 15 min and diluted with dry ether (50 mL). After precipitation of LiF, the mixture was filtered and the solvent evaporated. Two additional re-evaporations from benzene were required for removal of methanol traces. The colorless solid residue was extracted with hot dry ether (200 mL), the extract was filtered through a glass cinter covered with Celite, and the solvent was removed under vacuum to give colorless foam. Recrystallization from dry benzene (15 mL) and CH_2Cl_2 (15 mL) afforded the major portion of potassium tetrakis(pentafluorophenyl)borate (1.96 g, 84.5%) as heavy colorless plates. Concentration of the filtrate to about 20 mL volume afforded an additional crop of the target potassium salt (0.15 g, 6.5%) as a colorless solid. The combined product was dried over P_2O_5 at 80 °C in vacuum (0.3 mmHg) for 2 days.

^{19}F NMR (acetone-d_6, 235.4 MHz): δ −128.58 (br s, 8F, *ortho-F*), −159.89 (t, $^3J_{FF}$ = 20.0 Hz, 4F, *para-F*), −163.86 (sym m, 8F, *meta-F*). ^{11}B NMR (acetone-d_6, 160.5 MHz): δ −15.98 (br s).

Anal. for $C_{24}BF_{20}K$, Calcd: C, 40.14; F, 52.91; Found: C, 40.25; F, 52.51.

Synthesis of Bis-[(2-di-iso-propylphosphanyl)phenyl]silane (7). (1) Preparation of Di-iso-propyl(2-bromophenyl)-phosphine (5). To a stirred cold (5 °C) solution of *i*-PrMgCl [prepared in situ from *i*-PrCl (8.247 g, 105 mmol) and Mg-turnings (2.45 g, 100.8 mmol)] in dry THF (50 mL) under argon was added a solution of a freshly prepared dichlorophosphine **4** (10.186 g, 39.48 mmol) in THF (30 mL) dropwise with the rate not allowing the exothermic reaction to exceed 20 °C. The reaction mixture was stirred at RT overnight, heated at 50−60 °C for 1 h, and quenched at RT with a powdered solid KH_2PO_4 (7.145 g, 52.5 mmol). The mixture was stirred for 30 min at RT and for 30 min at 40−45 °C, and diluted with a 20% solution of ethyl acetate in hexane (120 mL). Filtration, evaporation, followed by a vacuum distillation of the residue afforded the phosphine **5** (6.618 g, 61.5%) as a colorless liquid, bp 101−103 °C (0.4 mmHg).

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 9.53 (s). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.47−7.42 (m, 1H; *H* Ar), 7.11 (br d, 1H, J_{HH} = 7.7 Hz, *H* Ar), 6.92 (ddd, 1H, J_{HH} = J_{HH} = 7.7 Hz, J_{HP} = 1.3 Hz, *H* Ar), 6.72 (ddd, 1H, J_{HH} = J_{HH} = 7.7 Hz, J_{HP} = 1.4 Hz, *H* Ar), 1.94−1.84 (sym m, 2H, 2P−C*H*Me$_2$); 1.075 (dd, ca. 4H, J_{HP} = 14.6 Hz, J_{HH} = 7.0 Hz) and 1.070 (dd, ca. 2H, J_{HP} = 14.6 Hz, J_{HH} = 7.0 Hz) [two rotamers, total 6H, 2PCH-(C*H*$_3$)Me]; 0.865 (dd, ca. 4H, J_{HP} = 12.2 Hz, J_{HH} = 6.9 Hz) and 0.860 (dd, ca. 2H, J_{HP} = 12.2 Hz, J_{HH} = 6.9 Hz) [two rotamers, total 6H, 2PCH-(C*H*$_3$)Me]. ^{13}C{^{1}H}/DEPT NMR (C_6D_6, 100.6 MHz): δ 137.98 (d, J_{CP} = 22.7 Hz, *C* Ar), 134.18 (s, *C*H Ar), 133.68 (d, J_{CP} = 32.3 Hz, *C* Ar), 133.61 (d, J_{CP} = 3.1 Hz, *C*H Ar), 126.70 (s, *C*H Ar), 24.34 (d, J_{CP} = 16.0 Hz, 2P-*C*HMe$_2$), 19.95 (d, J_{CP} = 18.7 Hz, 2*C*H$_3$), 19.47 (d, J_{CP} = 11.7 Hz, 2*C*H$_3$).

(2) Preparation of $PSiH_2P$ Ligand 7. A pentane solution of *t*-BuLi (5.30 mL of 1.7 M solution, 8.95 mmol) was added dropwise (over 10 min) to an intensively stirred solution of bromophenylphosphine **5** (2.32 g, 8.53 mmol) in dry Et_2O (30 mL) at −60 °C under argon. The yellowish heterogeneous reaction mixture was allowed to warm up to −10 °C over 2 h and was stirred for 1 h at that temperature. The reaction mixture was cooled to −60 °C again, and a solution of silicon tetrachloride (0.725 g, 4.265 mmol) in ether (8 mL) was added rapidly (over 2 min). The reaction mixture was allowed to warm up to ambient temperature over 3 h, stirred at RT for 3 days, and after solid $LiAlH_4$ (0.530 g, 13.25 mmol) was added to the reaction mixture in small portions. After stirring for 15 h at ambient temperature, the reaction was quenched by cautious addition of acetone (in small portions; total 2.48 g, 42.65 mmol), stirred at RT for 4 h, diluted with pentane, and filtered through a short plug of Celite. After evaporation, the residue was subjected to vacuum distillation from a short vapor path distillation flask to give the silane **7** (1.114 g, 63%) as a pale-greenish viscous oil, b.p. 180−182 °C (0.33 mmHg).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 3.01 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (br dvt, 2H, J_{HH} = 7.4 Hz, J_{HP} = 1.6 Hz, 2*H* Ar), 7.52−7.46 (m, 2H, 2*H* Ar), 7.37 (2H, ddd, J_{HH} = J_{HH} = 7.4 Hz, J_{HP} = 1.4 Hz, 2*H* Ar), 7.26 (ddvt, 2H, J_{HH} = J_{HH} = 7.4 Hz, J_{HP} = 1.3 Hz, 2*H* Ar), 5.45 (t with ^{29}Si satellites, 2H, $^4J_{HP}$ = 8.7 Hz, $^1J_{HSi}$ = 205 Hz, *H*$_2$Si), 2.14−2.03 (sym m, 4H, 4P−C*H*Me$_2$), 1.09 [dd, J_{HP} = 14.3 Hz, J_{HH} = 7.0 Hz, 12H, 4PCH-(C*H*$_3$)Me], 0.86 [dd, J_{HP} = 12.0 Hz, J_{HH} = 7.0 Hz, 12H, 4PCH-(C*H*$_3$)Me]. The assignment of the coupling constants was confirmed by ^{1}H{^{31}P} NMR. ^{13}C{^{1}H}/DEPT NMR ($CDCl_3$, 100.6 MHz): δ 143.61 (d, J_{CP} = 14.9 Hz, 2*C* Ar), 143.17 (dd, J_{CP} = 45.6 Hz, J_{CP} = 5.1 Hz, 2*C* Ar), 138.09 (dd, J_{CP} = 14.3 Hz, J_{CP} = 2.7 Hz, 2*C*H Ar), 131.53 (d, J_{CP} = 2.4 Hz, 2*C*H Ar), 128.95 (s, 2*C*H Ar), 127.86 (d, J_{CP} = 1.1 Hz, 2*C*H Ar), 24.70 (d, J_{CP} = 13.1 Hz, 4CH, 4P*C*HMe$_2$), 20.04 (d, J_{CP} = 17.4 Hz, 4*C*H$_3$), 19.70 (d, J_{CP} = 10.8 Hz, 4*C*H$_3$). ^{29}Si NMR ($CDCl_3$, 99.4 MHz, ^{29}Si-DEPT/INEPT): δ −39.95 ppm (t in DEPT or tt in INEPT, $^3J_{SiP}$ = 22.5 Hz, $^1J_{SiH}$ = 205 Hz). IR (film): ν 2139 cm^{-1} (br s, Si−H). ESI MS (in MeOH/CH_2Cl_2, addition of HCOOH/ HCOONa), found *m*/*z* (%): 439 (67) [MNa$^+$], 417 (100) [MH$^+$] (both with the correct isotopic pattern). HRMS, calcd. *m*/*z* for $C_{24}H_{39}P_2Si$ [MH$^+$]: 417.2296; found: 417.2289.

Synthesis of [ClPt{HSi(2-$C_6H_4PPr_2$-i)$_2$}] (8). A solution of ligand **7** (118.0 mg, 0.283 mmol) in dry benzene (2.5 mL) was added to a yellow solution of *trans*-$(Me_2S)_2Pt(Me)Cl$ (106.2 mg, 0.287 mmol) in benzene (2.5 mL). The reaction mixture, which turned to pale yellow after a few minutes, was stirred for 1 h, filtered through a plug of Celite, and evaporated to give a yellowish solid residue. Complex **8** was purified by sequential FC on Florisil (gradient elution, from 10% to 70% of ether in hexane). Totally 113.6 mg, (62%) of the pure complex **8** was isolated as a colorless solid, R_f = 0.52 (EtOAc /hexane 3:7).

^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 68.89 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 2885 Hz). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.04 (d, 2H, J_{HH} = 7.3 Hz, 2 *ortho-H* ArSi), 7.30 (dvt, 2H, J_{HH} = 7.4 Hz, J_{HP} = 2.4 Hz, 2 *ortho-H* ArP), 7.21 (br dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 7.10 (br dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 5.75 (br s with ^{195}Pt and ^{29}Si satellites, 1H, $^2J_{HPt}$ = 38.8 Hz, $^1J_{HSi}$ = 183 Hz, *H*Si), 3.44−3.34 (sym m, 2H, 2P−C*H*Me$_2$), 2.51−2.41 (sym m, 2H, 2P−C*H*Me$_2$), 1.43 (dvt, 6H, J_{HH} = J_{HP} = 7.3 Hz, 2C*H*$_3$), 1.39 (dvt, 6H, J_{HH} = J_{HP} = 7.5 Hz, 2C*H*$_3$), 1.10 (dvt, 6H, J_{HH} = J_{HP} = 7.2 Hz, 2C*H*$_3$), 0.92 (dvt, 6H, J_{HH} = J_{HP} = 7.4 Hz, 2C*H*$_3$). The assignment was confirmed by ^{1}H{^{31}P} and COSY NMR experiments. $^{13}C\{^1H\}$/DEPT NMR (C_6D_6, 125.8 MHz): δ 151.40 (vt, J_{CP} = 20.7 Hz, 2*C* Ar), 141.70 (vt, J_{CP} = 25.7 Hz, 2*C* Ar), 133.98 (vt, J_{CP} = 9.6 Hz, 2*CH* Ar), 131.17 (vt, J_{CP} = 2.7 Hz, 2*CH* Ar), 130.35 (br s with ^{195}Pt satellites, J_{CPt} = 9.2 Hz, 2*CH* Ar), 128.86 (vt, J_{CP} = 3.7 Hz, 2*CH* Ar), 27.69 (vt, J_{CP} = 13.9 Hz, ^{195}Pt satellites J_{CPt} = 17.6 Hz, 2*C*HMe$_2$), 25.92 (br vt, J_{CP} = 14.8 Hz, 2*C*HMe$_2$), 19.20 (vt, J_{CP} = 2.1 Hz, ^{195}Pt satellites J_{CPt} = 17.5 Hz, 2*C*H$_3$), 19.04 (br s with ^{195}Pt satellites, J_{CPt} = 20.6 Hz, 2*C*H$_3$), 18.61 (br s with ^{195}Pt satellites, J_{CPt} = 11.3 Hz, 2*C*H$_3$), 18.19 (br s with ^{195}Pt satellites, J_{CPt} = 22.2 Hz, 2*C*H$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz, ^{29}Si-DEPT/INEPT): δ 12.27 ppm (t with ^{195}Pt satellites in DEPT, $^2J_{SiP}$ = 5.2 Hz, $^1J_{SiPt}$ = 1190 Hz; dt with ^{195}Pt satellites in INEPT, $^1J_{SiH}$ = 183 Hz). $^{195}Pt\{^1H\}$ NMR (C_6D_6, 107.5 MHz): δ −5022 (t with ^{29}Si satellites, $^1J_{PtP}$ = 2885 Hz, $^1J_{PtSi}$ = 1190 Hz). IR (film): ν 2040 cm^{-1} (br m, Si−H). ESI MS (in MeCN), found *m/z* (%): 651 (57) [M$^+$ − Cl + MeCN], 652 (95), 610 (58) [M$^+$ − Cl], 611 (100) (both sets of ions with the correct isotope pattern).

Anal. for $C_{24}H_{37}ClP_2PtSi$, Calcd: C, 44.61; H, 5.77; Found: C, 44.85; H, 5.83.

Synthesis of [ClPt{HOSi(2-$C_6H_4PPr_2$-i)$_2$}] (3). To a solution of complex **8** (28.0 mg, 0.0433 mmol) in a mixture of acetonitrile (2.5 mL) and CH_2Cl_2 (0.5 mL) was added water (8.0 mg, 0.444 mmol) followed by a catalytic amount [(COD)IrCl]$_2$ (0.5 mg), and the yellow reaction mixture was stirred for 24 h under the common aerobic conditions (without protection from atmospheric oxygen and moisture). The reaction mixture was diluted with benzene and evaporated. Sequential FC on Florisil (gradient elution, from 100% pentane to 100% ether) afforded the silanol complex **3** (25.5 mg, 89%) as a colorless solid, R_f = 0.14 (EtOAc /hexane 3:7).

$^{31}P\{^1H\}$ NMR (C_6D_6, 202.5 MHz): δ 71.08 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 3025 Hz). ^1H NMR (C_6D_6, 500 MHz): δ 8.14 (d, 2H, J_{HH} = 7.3 Hz, 2 *ortho-H* ArSi), 7.34 (dvt, 2H, J_{HH} = 7.5 Hz, J_{HP} = 2.3 Hz, 2 *ortho-H* ArP), 7.23 (br dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 7.12 (br dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 3.43−3.31 (sym m, 2H, 2P−C*H*Me$_2$), 2.57−2.44 (sym m, 2H, 2P−C*H*Me$_2$), 1.42 (dvt, 6H, J_{HH} = J_{HP} = 7.5 Hz, 2C*H$_3$*), 1.36 (dvt, 6H, J_{HH} = J_{HP} = 7.5 Hz, 2C*H$_3$*), 1.08 (dvt, 6H, J_{HH} = J_{HP} = 7.2 Hz, 2C*H$_3$*), 0.93 ppm (dvt, 6H, J_{HH} = J_{HP} = 7.4 Hz, 2C*H$_3$*). $^{13}C\{^1H\}$/DEPT NMR (C_6D_6, 125.8 MHz): δ 155.47 (vt, J_{CP} = 21.9 Hz, 2*C* Ar), 141.23 (vt, J_{CP} = 25.3 Hz, 2*C* Ar), 132.99 (vt, J_{CP} = 9.8 Hz, ^{195}Pt satellites J_{CPt} = 44.0 Hz, 2*CH* Ar), 130.81 (vt, J_{CP} = 3.0 Hz, ^{195}Pt satellites J_{CPt} = 38.2 Hz, 2*CH* Ar), 130.44 (br s with ^{195}Pt satellites, J_{CPt} = 10.8 Hz, 2*CH* Ar), 129.50 (vt, J_{CP} = 3.5 Hz, ^{195}Pt satellites J_{CPt} = 16.2 Hz, 2*CH* Ar), 27.51 (br vt, J_{CP} = 13.9 Hz, ^{195}Pt satellites J_{CPt} = 13.8 Hz, 2*C*HMe$_2$), 25.86 (br vt, J_{CP} = 14.9 Hz, ^{195}Pt satellites J_{CPt} = 9.0 Hz, 2*C*HMe$_2$), 19.52 (br s with ^{195}Pt satellites, J_{CPt} = 20.2 Hz, 2*C*H$_3$), 19.34 (vt, J_{CP} = 2.0 Hz, ^{195}Pt satellites J_{CPt} = 12.1 Hz, 2*C*H$_3$), 18.69 (br s with ^{195}Pt satellites, J_{CPt} = 12.3 Hz, 2*C*H$_3$), 18.29 (br s with ^{195}Pt satellites, J_{CPt} = 23.6 Hz, 2*C*H$_3$). The assignment was confirmed by $^1H\{^{31}P\}$, COSY, and $^1H-^{13}C$ HSQC NMR experiments. ^{29}Si NMR (C_6D_6, 99.4 MHz, $^{29}Si-^1H$ HMBC): δ 38.53 (br s with ^{195}Pt satellites, $^1J_{SiPt}$ = 1335 Hz). $^{195}Pt\{^1H\}$ NMR (C_6D_6, 107.5 MHz): δ −4992 (t, $^1J_{PtP}$ = 3025 Hz, ^{29}Si satellites $^1J_{PtSi}$ = 1334 Hz). IR (film): ν 3404 cm^{-1} (v br, m, O−H).

Anal. for $C_{24}H_{37}ClOP_2PtSi$, Calcd: C, 43.54; H, 5.63; Found: C, 43.68; H 5.61.

X-ray Structural Analysis of 3. The X-ray quality single crystals of **3** were formed upon cooling of a hexane/benzene solution (5:1) at −15 °C for 2 weeks.

Crystal Data. $C_{24}H_{37}ClOP_2PtSi$, fw = 662.21, colorless prism, 0.6 × 0.3 × 0.3 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 8.4654(1), b = 18.2462(3), c = 16.8102(3) Å, α = 90°, β = 94.9815(11)°, γ = 90°, V = 2586.8(1) Å^3, Z = 4, ρ_{calc} = 1.700 g cm^{-3}, μ = 5.712 mm^{-1}.

Data Collection and Treatment. A total of 22636 reflections were collected, $-10 \le h \le 10$, $0 \le k \le 23$, $0 \le l \le 21$, frame scan with 1°, scan speed 1° per 30 s, 6096 independent reflections (R_{int} = 0.052, $2\theta_{max}$ = 54.9°), final **R** = 0.0281 (wR = 0.0743) for 5233 reflections with $I > 2\sigma(I)$, and **R** = 0.0333 (wR = 0.0771) for all data.

Preparation of the Cationic Pt(II)−Silanol Complex [{(2-$C_6H_4PPr_2$-i)$_2$SiOH}Pt]$^+$ [(C_6F_5)$_4$B]$^-$ (9). To a solid mixture of complex **3** (6.9 mg, 0.0104 mmol) and KB(C_6F_5)$_4$ (7.9 mg, 0.0110 mmol) was added dry fluorobenzene (0.7 mL), and the reaction mixture was stirred at RT for 20 h. Complete consumption of the neutral complex **3** and practically quantitative formation of the cationic complex **9** was observed in the ^{31}P NMR spectrum. The reaction mixture was thoroughly evaporated, and the residue was extracted with dry benzene (4.0 mL). The extract was filtered through a fine Teflon filter (0.2 μm), evaporated and dried under vacuum overnight at 0.5 mmHg to give the practically pure (95% purity in ^{31}P NMR) cationic complex **9** (13.7 mg, quantitative yield) as a colorless light solid.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 73.12 (br s with ^{195}Pt satellites, $^1J_{PPt}$ = 3097 Hz). ^1H NMR (CD_2Cl_2, 500 MHz): δ 8.23 (d, 2H, J_{HH} = 7.3 Hz, 2 *ortho-H* ArSi), 7.78−7.71 (m, 2H, 2 *ortho-H* ArP), 7.65 (dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 7.59 (dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 3.38−3.21 (br sym m, 2H, 2P−C*H*Me$_2$), 2.86−2.70 (br sym m, 2H, 2P−C*H*Me$_2$), 1.38 (br dvt, 6H, J_{HH} = 7.2 Hz, J_{HP} = 8.5 Hz, 2C*H$_3$*), 1.36 (br dvt, 6H, J_{HH} = 7.4 Hz, J_{HP} = 8.3 Hz, 2C*H$_3$*), 1.29 (br dvt, 6H, J_{HH} = 6.6 Hz, J_{HP} = 7.6 Hz, 2C*H$_3$*), 1.19 (dvt, 6H, J_{HH} = J_{HP} = 7.2 Hz, 2C*H$_3$*). The assignment was confirmed by $^1H\{^{31}P\}$ and COSY NMR experiments. $^{13}C\{^1H\}$/DEPT NMR (CD_2Cl_2, 125.8 MHz): δ 149.40 (br m, 2*C* Ar + *C* ArF), 147.45 (br m, *C* ArF), 139.60 (m, 2*C* Ar), 137.61 (br m, *C* ArF), 135.68 (br m, *C* ArF), 132.96 (br vt, J_{CP} = 9.5 Hz, 2*CH* Ar), 131.75 (br s, 2*CH* Ar), 131.33 (br s, 2*CH* Ar), 130.95 (m, 2*CH* Ar), 28.10 (vt, J_{CP} = 13.5 Hz, 2*C*HMe$_2$), 26.73 (br vt, J_{CP} = 12.2 Hz, 2*C*HMe$_2$), 19.97 (br s, 2*C*H$_3$), 18.87 (br s, 2*C*H$_3$), 18.64 (br s, 4*C*H$_3$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 160.5 MHz): δ −16.03 ppm (s). ^{19}F NMR (CD_2Cl_2, 235.4 MHz): δ −133.45 (br s, 8F, *ortho-F* ArF), −163.45 (t, $^3J_{FF}$ = 20.5 Hz, 4F, *para-F* ArF), −167.44 (sym m, 8F, *meta*-F ArF). ^{29}Si NMR (CD_2Cl_2, 99.4 MHz, $^{29}Si-^1H$ HMBC): δ 25.24 (br s with ^{195}Pt satellites, $^1J_{SiPt}$ = 1478 Hz). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, 107.5 MHz): δ −5075 (t, $^1J_{PtP}$ = 3100 Hz).

Preparation of the Silanol-Pt(II)−carbonyl complex [{(2-$C_6H_4PPr_2$-i)$_2$SiOH}PtCO]$^+$[(C_6F_5)$_4$B]$^-$ (10). Through a solution of **9** (13.7 mg, 0.0104 mmol) in CD_2Cl_2 (0.7 mL) in a screw-cap NMR tube equipped with a Teflon septum CO gas was mildly bubbled for 5 min, resulting in quantitative formation of the platinum carbonyl complex **10**. After NMR and IR characterizations, the solution was evaporated followed by re-evaporation from C_6D_6 and vacuum drying for 3 h under oil pump vacuum, to give complex **10** as a colorless solid (13.7 mg, quantitative yield, ≥95% purity according to ^{31}P and ^1H NMR spectra). The analytically pure complex could not be obtained because of some CO loss under prolonged vacuum drying

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 82.24 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 2736 Hz). ^1H NMR (CD_2Cl_2, 500 MHz): δ 8.27 (d, 2H, J_{HH} = 7.3 Hz, 2 *ortho-H* ArSi), 7.82 (dvt, 2H, J_{HH} = 7.6 Hz, J_{HP} = 3.0 Hz, 2 *ortho-H* ArP), 7.77 (br dd, 2H, J_{HH} = J_{HH} = 7.3 Hz, 2*H* Ar), 7.70 (ddvt, 2H, J_{HH} = J_{HH} = 7.5 Hz, J_{HP} = 1.4 Hz, 2*H* Ar), 3.23−3.08 (sym m, 2H, 2P−C*H*Me$_2$), 2.87−2.74 (sym m, 2H, 2P−C*H*Me$_2$), 1.32 (br dvt, 6H, J_{HH} = 6.7 Hz, J_{HP} = 10.0

Hz, 2CH_3), 1.27 (br dvt, 6H, $J_{HH} = 8.4$ Hz, $J_{HP} = 10.8$ Hz, 2CH_3), 1.23 (br dvt, 6H, $J_{HH} = 6.7$ Hz, $J_{HP} = 9.0$ Hz, 2CH_3), 1.00 (dvt, 6H, $J_{H,H} = 6.7$ Hz, $J_{H,P} = 9.0$ Hz, 2CH_3). The assignment of the coupling constants was confirmed by $^1H\{^{31}P\}$ NMR. $^{13}C\{^1H\}$/DEPT NMR (CD_2Cl_2, 125.8 MHz): δ 190.81 (vt, $J_{CP} = 7.0$ Hz, Pt-*C*O), 151.86 (vt, $J_{CP} = 21.0$ Hz, 2*C* Ar), 149.40 (br m, *C* ArF), 147.49 (br m, *C* ArF), 139.55 (br vt, $J_{CP} = 17.0$ Hz, 2*C* Ar), 137.60 (br m, *C* ArF), 135.68 (br m, *C* ArF), 134.24 (vt, $J_{CP} = 9.8$ Hz, ^{195}Pt satellites $J_{CPt} = 20.0$ Hz, 2*C*H Ar), 133.32 (br s, 2*C*H Ar), 132.29 (vt, $J_{CP} = 3.7$ Hz, ^{195}Pt satellites $J_{CPt} = 15.2$ Hz, 2*C*H Ar), 131.54 (vt, $J_{CP} = 3.2$ Hz, ^{195}Pt satellites $J_{CPt} = 36.4$ Hz, 2*C*H Ar), 30.11 (br vt, $J_{CP} = 15.1$ Hz, ^{195}Pt satellites $J_{CPt} = 16.2$ Hz, 2*C*HMe$_2$), 28.18 (br vt, $J_{CP} = 16.3$ Hz, ^{195}Pt satellites $J_{CPt} = 6.0$ Hz, 2*C*HMe$_2$), 20.12 (br s with ^{195}Pt satellites, $J_{CPt} = 17.3$ Hz, 2*C*H$_3$), 19.40 (s with ^{195}Pt satellites, $J_{CPt} = 22.4$ Hz, 2*C*H$_3$), 19.00 (s with ^{195}Pt satellites, $J_{CPt} = 18.5$ Hz, 2*C*H$_3$), 18.67 (br s, 2*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 235.4 MHz): δ −134.00 (br s, 8F, *ortho-F* ArF), −164.30 (t, $^3J_{FF} = 20.3$ Hz, 4F, *para-F* ArF), −168.22 (sym m, 8F, *meta-F* ArF). ^{29}Si NMR (CD_2Cl_2, 99.4 MHz, ^{29}Si−^{1}H HMBC): δ 57.36 (br s with ^{195}Pt satellites, $^1J_{SiPt} = 977$ Hz). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, 107.5 MHz): δ −5295 (t, $^1J_{PtP} = 2736$ Hz, with ^{29}Si satellites, $^1J_{PtSi} = 980$ Hz). IR (film): ν 3470 cm^{-1} (br m, O−H), 2087 cm^{-1} (m, Pt-*CO*). ESI MS (in MeOH/CH_2Cl_2), found m/z^+ (%): 625 (72), 626 (100) [M^+ − CO], 627 (87) (the correct isotopic pattern); m/z^- (%): 678 (22), 679 (100) [Anion$^-$], 680 (24) (the correct isotope pattern). HRMS, calcd. m/z^+ for $C_{24}H_{37}OP_2{}^{195}PtSi$ [M^+ − CO]: 626.1738; found: 626.1749.

X-ray Structural Analysis of 10. The X-ray quality single crystals of **10** grew from a concentrated benzene solution at RT.

Crystal Data. $C_{25}H_{37}O_2P_2PtSi\cdot BC_{24}F_{20}$, fw = 1333.72, colorless prism, 0.4 × 0.3 × 0.1 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 13.6579(1), b = 15.0983(3), c = 15.2010(2) Å, α = 112.5430(7)°, β = 94.5989(6)°, γ = 116.8269(3)°, V = 2458.58(7) Å^3, Z = 2, ρ_{calc}= 1.802 g cm^{-3}, μ = 3.060 mm^{-1}.

Data Collection and Treatment. A total of 51413 reflections were measured, $-17 \le h \le 17$, $-19 \le k \le 18$, $0 \le l \le 19$, frame scan width 1°, scan speed 1° per 80 s, 11206 independent reflections (R_{int}= 0.040, $2\theta_{max}$ = 54.9°), final **R** = 0.0244 (wR = 0.0543) for 10076 reflections with $I > 2\sigma(I)$, and **R** = 0.0302 (wR = 0.0516) for all data.

Base-Induced Rearrangement-Coupling of [ClPt{HOSi(2-C$_6$H$_4$PPr$_2$-i)$_2$}] (3). Synthesis of the binuclear complex 11. (a) A cold solution of KN(SiMe$_3$)$_2$ (3.8 mg, 0.0191 mmol) in dry ether (1.0 mL) and dry THF (0.5 mL) was added dropwise to a cold (−30 °C) stirred solution of complex **3** (12.8 mg, 0.0193 mmol) and a catalytic amount of 18-crown-6 (0.7 mg, 0.0014 mmol) in a mixture of ether (1.0 mL) and THF (0.5 mL). The slightly turbid reaction mixture was left at −30 °C for 12 h and was stirred for 1 h at RT. At that time, ^{31}P NMR monitoring revealed complete consumption of the starting complex **3** and formation of the dimer **11** in about 75% yield. The reaction mixture was evaporated, and the brownish solid residue was extracted with ether (4.0 mL). The ethereal extract was filtered through a plug of Celite, evaporated, and the residue subjected to chromatography on Florisil (gradient elution, from 5% ether in hexane to 100% ether) to give the dimer **11** (7.2 mg, 58% yield, eluted with 50−60% ether in hexane) as a colorless solid.

(b) To a stirred cold (−30 °C) solution of **3** (13.0 mg, 0.0196 mmol) in dry THF (0.8 mL) was added a solution of *t*-BuOK (2.8 mg, 0.0250 mmol) in THF (1.0 mL). The mixture was stirred for 4 h at ambient temperature, at which time ^{31}P NMR monitoring revealed disappearance of the starting complex **3** and formation of the dimer **11** in about 55% yield along with several byproducts. The reaction mixture was evaporated, and extracted with pentane (6.0 mL). Evaporation of the extract followed by chromatography of the residue on Florisil as described above afforded the dimer **11** (4.6 mg, 36%).

$^{31}P\{^1H\}$ NMR (C_6D_6, 202.5 MHz): δ 69.75 (s with ^{195}Pt satellites, $^1J_{PPt} = 3060$ Hz, 2*P*Pt^1), 52.29 (br s with ^{195}Pt satellites, $^1J_{PPt} = 2844$ Hz, 2*P*Pt^2). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.17 (d, 2H, $J_{HH} = 7.3$ Hz, 2*ortho-H* ArSi^1), 8.11 (d, 2H, $J_{HH} = 7.4$ Hz, *ortho-H* ArSi^2), 7.33 (dvt, 2H, $J_{HH} = 7.5$ Hz, $J_{HP} = 3.6$ Hz, 2*ortho-H* ArPPt^1), 7.13 (dd, 2H, $J_{HH} = J_{HH} = 7.1$ Hz, 2*H* Ar), 7.08−7.02 (m, 4H, 4*H* Ar), 6.97 (dd, 2H, $J_{HH} = J_{HH} = 7.7$ Hz, 2*H* Ar), 6.97−6.91 (m, 2H, 2*H* Ar), 3.42−3.28 (sym m, 2H, 2Pt^{1}P−C*H*Me$_2$), 2.76−2.64 (sym m, 2H, 2Pt^{1}P−C*H*Me$_2$), 2.22−1.99 (m, 4H, 4Pt^{2}P−C*H*Me$_2$), 1.55 (dvt, 6H, $J_{HH} = J_{HP} = 7.4$ Hz, 2C*H$_3$*), 1.39 (dvt, 6H, $J_{HH} = J_{HP} = 7.3$ Hz, 2C*H$_3$*), 1.29 (dvt, 6H, $J_{HH} = J_{HP} = 7.3$ Hz, 2C*H$_3$*), 1.27 (br dvt, 6H, $J_{HH} \approx J_{HP} = 8.0$ Hz, 2C*H$_3$*), 1.15 (dvt, 6H, $J_{HH} = J_{HP} = 7.6$ Hz, 2C*H$_3$*), 1.11 (br dvt, 6H, $J_{HH} \approx J_{HP} = 7.7$ Hz, 2C*H$_3$*), 1.01 (dvt, 6H, $J_{HH} = J_{HP} = 7.0$ Hz, 2C*H$_3$*), 0.83 (dvt, 6H, $J_{HH} = J_{HP} = 7.3$ Hz, 2CH$_3$), −18.31 (t with ^{195}Pt satellites, $^2J_{HP} = 12.4$ Hz, $^1J_{HPt} = 1180$ Hz, 1H; *H*Pt^2). $^{13}C\{^1H\}$/DEPT NMR (C_6D_6, 125.8 MHz): δ 155.77 (vt, $J_{CP} = 23.0$ Hz, 2*C* Ar), 151.77 (vt, $J_{CP} = 10.8$ Hz, 2*C* Ar), 142.31 (vt, $J_{CP} = 26.3$ Hz, 2*C* Ar), 137.92 (vt, $J_{CP} = 6.6$ Hz, 2*C*H Ar), 137.45 (vt, $J_{CP} = 22.8$ Hz, 2*C* Ar), 133.75 (br vt, $J_{CP} = 9.9$ Hz, 2*C*H Ar), 130.04 (br s, 2*C*H Ar), 129.98 (m, 2*C*H Ar), 129.43 (br s, 2*C*H Ar), 127.46 (br s, 2*C*H Ar), 28.50 (vt, $J_{CP} = 13.7$ Hz, 2P*C*HMe$_2$), 26.65 (vt, $J_{CP} = 13.6$ Hz, 2P*C*HMe$_2$), 25.70 (vt, $J_{CP} = 14.5$ Hz, 2P*C*HMe$_2$), 21.34 (br s, 2*C*H$_3$), 20.82 (br s, 2*C*H$_3$), 20.67 (vt, $J_{CP} = 16.6$ Hz, 2P*C*HMe$_2$), 19.57 (br s, 2*C*H$_3$), 19.36 (vt, $J_{CP} = 4.1$ Hz, 2*C*H$_3$), 18.77 (br s, 2*C*H$_3$), 18.71 (br s, 2*C*H$_3$), 18.69 (br s, 2*C*H$_3$), 17.14 ppm (br s, 2*C*H$_3$). The assignment was confirmed by $^1H\{^{31}P\}$, COSY, and ^{1}H−^{13}C HSQC NMR experiments. ^{29}Si NMR (C_6D_6, 99.4 MHz, ^{29}Si−^{1}H HMBC): δ 23.64 (br s with ^{195}Pt satellites, $^1J_{SiPt} = 1416$ Hz, Si^1), −56.83 ppm (br s, Si^2). ^{195}Pt NMR (C_6D_6, 107.5 MHz): δ −4558 (dt, $^1J_{PtP} = 2845$ Hz, $^1J_{PtH} = 1180$ Hz in ^{195}Pt−^{1}H HMQC, Pt^2), −4975 ppm (t, $^1J_{PtP} = 3060$ Hz in $^{195}Pt\{^1H\}$, Pt^1). IR (film): ν 2204 cm^{-1} (br m, Pt−H). ESI MS (in MeOH/CH_2Cl_2), found m/z (%): 1251 (65), 1252 (100) [M^+ − Cl] (the correct isotope pattern). HRMS, calcd. m/z for $C_{48}H_{74}ClO_2P_4{}^{195}Pt^{196}PtSi_2$ [MH$^+$]: 1288.3164; found: 1288.3162.

X-ray Structural Analysis of 11. The X-ray quality single crystals of **11** grew from a solution in hexane at −20 °C over 1 month.

Crystal Data. $C_{48}H_{73}ClO_2P_4Pt_2Si_2$, fw = 1287.75, colorless plate, 0.3 × 0.1 × 0.1 mm^3, orthorhombic, space group $Pca2_1$ (No. 29), a = 22.827(5), b = 12.115(2), c = 18.502(4) Å, V = 5116.7(18) Å^3, Z = 4, ρ_{calc} = 1.672 g cm^{-3}, μ = 5.722 mm^{-1}.

Data Collection and Treatment. A total of 38094 reflections were measured, $0 \le h \le 29$, $0 \le k \le 15$, $0 \le l \le 23$, frame scan width 1°, scan speed 1° per 240 s, 7104 independent reflections (R_{int} = 0.130, $2\theta_{max}$ = 54.9°), final **R** = 0.0378 (wR = 0.0635) for 5466 reflections with $I > 2\sigma(I)$, and **R** = 0.0458 (wR = 0.0656) for all data.

Base-Induced Hydrolytic Rearrangement of [{(2-C$_6$H$_4$PPr$_2$-i)$_2$SiOH}Pt]$^+$ [(C$_6$F$_5$)$_4$B]$^-$ (9). Isolation of the Monomeric Hydroxysilanolate Pt(II)−Hydride 17. To a mixture of complex **3** (9.0 mg, 0.0136 mmol) and KB(C$_6$F$_5$)$_4$ (10.7 mg, 0.0150 mmol) was added dry fluorobenzene (1.0 mL), and the reaction mixture was stirred for 15 h at RT. At that time ^{31}P NMR monitoring revealed complete consumption of the starting platinum chloride complex **3** and clean formation of the cationic complex **9**. Dry *i*-Pr$_2$NEt (6.3 mg, 0.0488 mmol) was added to the reaction mixture to induce slow conversion of **9** to the platinum hydride complex

17 (ca. 60% ^{31}P NMR yield after 14 d at RT). All the volatiles were evaporated; the residue was dissolved in a minimal amount of benzene (0.3 mL) and diluted with hexane (5.0 mL) upon shaking. After sedimentation of the colorless solid, the colorless solution was filtered through a fine (0.2 μm) Teflon filter. Evaporation of the filtrate followed by vacuum drying of the residue afforded the complex **17** (3.3 mg, 38%, $\geq$95% purity in ^{31}P NMR) as a colorless waxy mass. An additional amount of less pure compound **17** could be obtained by a repetition of the extraction procedure.

^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 49.99 (br s with ^{195}Pt satellites, $^{1}J_{PPt} = 2857$ Hz). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.19 (d, 2H, $J_{HH} = 7.4$ Hz, 2 *ortho-H* ArSi), 7.07 (dd, 2H, $J_{HH} = J_{HH} = 7.4$ Hz, 2*H* Ar), 6.99 (dd, 2H, $J_{HH} = J_{HH} = 7.4$ Hz, 2*H* Ar), 6.90 (dvt, 2H, $J_{HH} = 7.4$ Hz, $J_{HP} = 3.3$ Hz, 2 *ortho-H* ArP), 2.11−2.00 (sym m, 2H, 2P−C*H*Me$_2$), 2.03−1.93 (sym m, 2H, 2P−C*H*Me$_2$), 1.01−0.91 (m, 18H, 6C*H*$_3$), 0.65 (dvt, $J_{HH} = J_{HP} = 7.7$ Hz, 6H, 2C*H*$_3$), −19.32 (t with ^{195}Pt satellites, $^{2}J_{HP} = 12.7$ Hz, $^{1}J_{HPt} = 1217$ Hz, 1H, *H*Pt). The assignment was confirmed by ^{1}H{^{31}P} and COSY NMR experiments. ^{13}C{^{1}H}/DEPT NMR (C_6D_6, 125.8 MHz): δ 150.04 (m, 2*C* Ar), 138.06 (m, 2*C* Ar), 137.11 (vt, $J_{CP} = 6.8$ Hz, 2*C*H Ar), 136.16 (br s, 2*C*H Ar), 130.95 (br s, 2*C*H Ar), 127.47 (br s, 2*C*H Ar), 27.14 (vt, $J_{CP} = 13.2$ Hz, 2P*C*HMe$_2$), 22.96 (vt, $J_{CP} = 16.7$ Hz, 2P*C*HMe$_2$), 19.96 (br s, 2*C*H$_3$), 19.08 (br s, 2*C*H$_3$), 18.82 (vt, $J_{CP} = 3.8$ Hz, 2*C*H$_3$), 17.98 (br s, 2*C*H$_3$). ^{29}Si NMR (C_6D_6, 99.4 MHz, ^{29}Si−^{1}H HMBC): δ −54.98 ppm (br s). ^{195}Pt NMR (C_6D_6, 107.5 MHz, ^{195}Pt−^{1}H HMQC): $\delta = -4566$ ppm (dt, $^{1}J_{PtP} = 2858$ Hz, $^{1}J_{PtH} = 1220$ Hz). IR (film): ν 3420 (v br m, O−H), 2200 cm^{-1} (br m, Pt−H). ESI MS (in MeCN), found *m*/*z* (%): 1287 (74), 1288 (100) [2 M + H^{+}] (the correct isotope pattern).

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Supporting Information Available: CIF files containing X-ray crystallographic data for compounds **3**, **10** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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