III-*d*, 106733-94-2; IV, 106733-95-3; V, 106733-96-4; VI, 106733-97-5; VII, 106733-93-1; VIII, 106733-98-6; IX, 106733-99-7; X, 106734-00-3; XI, 106734-01-4; $Fe(CO)_4CHO^-$, 48055-09-0; $Fe(CO)_5$, 13463-40-6; Co, 7440-48-4.

**Supplementary Material Available:** Numbering scheme for VIII and X (1 page); listings of structure factor amplitudes for VIII and X (20 pages). Ordering information is given on any current masthead page.

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# Hydrosilylation with Platinum Complexes. Preparation, Low-Temperature NMR Spectra, and X-ray Crystal Structure of the Novel Bis-Olefin Catalyst *cis*-$PtCl_2(PhCH{=}CH_2)_2$

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The bis-olefin complex *cis*-$PtCl_2(PhCH{=}CH_2)_2$ (1) has been prepared and shown to exist in several isomeric forms by $^1H$ and $^{195}Pt$ NMR spectroscopy. Complex 1 is a synthetically useful form of soluble $PtCl_2$ and also catalyzes the hydrosilylation of styrene with $Et_3SiH$. This latter reaction has been carried out with a variety of known complexes of platinum(II), and the results have been compared with those found for some trichlorostannate complexes of platinum. One isomer of 1 has been crystallized and its structure determined by X-ray diffraction. Crystal data for this isomer: space group $P2_1/c$, $a = 13.805$ (7) Å, $b = 10.235$ (2) Å, $c = 10.985$ (7) Å, $\beta = 106.51$ (4)°; $Z = 4$; $V = 1489.1$ Å$^3$.

## Introduction

The hydrosilylation of olefins, followed by further transformations of the alkylsilanes that form, provides a useful route to a variety of organic substrates.[1] In the realm of platinum chemistry the most commonly utilized catalyst precusor is $H_2PtCl_6$,[1,2] although this Pt(IV) complex is certainly reduced to Pt(II) during the reaction.[2] Our previous studies on trichlorostannate complexes of Pt(II) revealed these to be more labile than the corresponding chloro complexes,[3,4] so that we considered it useful to compare several of our trichlorostannate compounds with known hydrosilylation catalysts. We report here the results of these tests as well as the preparation, molecular structure, and extensive NMR spectroscopic studies of *cis*-$PtCl_2(PhCH{=}CH_2)_2$, a possible intermediate in the hydrosilylation of styrene with triethylsilane and the first characterized bis monodentate olefin complex of Pt(II).

## Results and Discussion

***cis*-$PtCl_2(PhCH{=}CH_2)_2$ Chemistry.** During our hydrosilylation catalysis we observed that styrene, $PhCH{=}CH_2$, readily dissolved $PtCl_2$. In view of the normal sparing solubility of $PtCl_2$ in noncoordinating solvents we assumed that a styrene complex was formed and have isolated this material that precipitates slowly from styrene. The compound so obtained was *cis*-$PtCl_2(PhCH{=}CH_2)_2$ (1) that is readily distinguishable from the dimer *sym-trans*-$[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ by $^1H$ and $^{195}Pt$ NMR as well as by IR and microanalytical data. Moreover, the analogous para Cl styrene analogue is also synthetically accessible (see Experimental Section).

Complex 1 reacts in a predictable fashion with a variety of reagents, e.g., 1,5-cyclooctadiene (COD), 2 equiv of $AsTol_3$ (Tol = ($C_6H_4$-*p*-$CH_3$ or 2 equiv of $PTol_3$ (or $PPh_3$), or by dissociation of 1 equiv of $PhCH{=}CH_2$ to give the known complexes shown in eq 1–4, and consequently 1 can serve as a source of "soluble" $PtCl_2$ for synthetic purposes.

$$1 \xrightarrow{\text{COD}} PtCl_2(COD) \tag{1}$$

$$1 \xrightarrow{2AsTol_3} cis\text{-}PtCl_2(AsTol_3)_2 \tag{2}$$

$$1 \xrightarrow{2PTol_3} cis\text{-}PtCl_2(PTol_3)_2 \tag{3}$$

$$1 \xrightarrow[\text{CHCl}_3,\ 60\ °C]{-PhCH{=}CH_2} sym\text{-}trans\text{-}[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2 \tag{4}$$

In solution 1 reveals several isomers whose identification is made easier by the following NMR observations.

(1) The compounds have similar $^{195}Pt$ and $^{13}C$ chemical shifts[6] (see Tables I and II), and this is consistent with isomers and not ligand dissociation or cis–trans isomerization.

(2) The $^1H$ vinyl proton chemical shifts are determined, in part, by the proximity of a styrene phenyl group to a vinyl proton on a *second* coordinated styrene.

Point 2 is important, but not obvious. Consider **1a**; the molecular structure of this isomer (discussed in the next section) clearly shows that both olefins are roughly per-

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**Table I. NMR Data[a] for *cis*-$PtCl_2(PhCH{=}CH_2)_2$ Isomers**

| isomer | δ($H_A$) | δ($H_B$) | δ($H_C$) | δ($^{195}Pt$) |
|---|---|---|---|---|
| **1a** | 4.77 (14.5, 7.7), 7.33 | 4.50 (7.7), 4.84 (8.1) | 5.70, 4.48 (14.9) | -3290 |
| **1b** | 5.49 (15.0, 8.3), 6.85 (15.0, 8.3) | 2.54 (8.3), 5.23 (8.3) | 5.08 (15.0), 5.11 (15.0) | -3310 |
| **1c** | 7.36 (14.7, 7.9) | 4.21 (7.9) | 2.82 (14.7) | -3169 |
| $(Bu_4N)[PtCl_3(PhCH{=}CH_2)]$ | 6.37 (13.6, 8.0) | 4.42 (8.0) | 4.99 (13.5) | -2572[b] |
| $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ | | | | -2317 |
| | several isomers: $H_A$, 6.4; $H_B$ and $H_C$, 4.41-5.15 | | | -2331, -2344, -2427 |
| $PhCH{=}CH_2$ | 6.71 (17.7, 10.9) | 5.27 (10.9) | 5.82 (17.7) | |

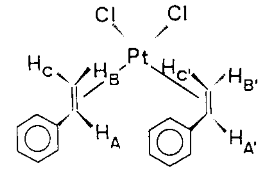
[a] $^1H$ chemical shifts in ppm; coupling constants in Hz; $CD_2Cl_2$; 183 K; $^{195}Pt$ δ values relative to external $Na_2PtCl_6$ at 198 K. [b] $H_A'$, $H_B'$, and $H_C'$ below $H_A$, $H_B$, and $H_C$; $^3J(H,H)$ coupling constant adjacent to chemical shifts in parentheses. [b] $CDCl_3$; room temperature.

**Table II. $^{13}C$ NMR Data[a] (198 K) for the *cis*-$PtCl_2(PhCH{=}CH_2)_2$ Isomers**

| isomer | $=CH_2$ | $=CH$ |
|---|---|---|
| **1b** | 73.10, 77.07 | 102.48, 103.53 |
| **1c** | 71.19 | 106.30 |

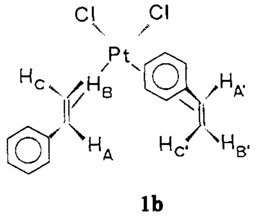
[a] Chemical shifts are given in ppm.

pendicular to the coordination plane with the phenyl groups on the same side. At low temperature in solution,

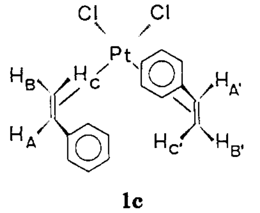


**1a**

this structure has nonequivalent styrene units as one phenyl is directed toward its cis chloride whereas the other faces away from its cis chloride. Structure **1a** brings the anisotropic aromatic ring of the styrene denoted with the "prime" notation close to $H_A$, thereby inducing an upfield shift in its $^1H$ position. We therefore anticipate, and observe, six vinyl proton resonances. Proton $H_A$, δ 4.77, is distinguishable from $H_B$ and $H_C$ by $^3J(H,H)$ values and $^1H\{^1H\}$ experiments. Proton $H_A$ resonates at much higher field than its corresponding analogues in the other isomers, δ 5.49-7.36 or, for that matter in uncoordinated styrene, δ 6.71. Similarly, isomer **1b**, in which the other face of the primed styrene is coordinated and then rotated relative to the other, should also reveal six vinyl resonances with the difference that $H_B$ should now appear at higher field, and this is indeed confirmed: δ ($H_B$) 2.54.



**1b**



**1c**

The yellow powder that we collect on precipitation from styrene dissolves in $CD_2Cl_2$ and shows structure **1b** at -90 °C. This isomer slowly isomerizes to give a mixture containing the three isomers **1a**-**c** as shown by low-temperature $^{195}Pt$ NMR, δ -3290, -3310, and -3169, respectively; see Figure 1. We note that the dimer $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ shows four signals in its $^{195}Pt$ NMR spectrum at 198 K, δ -2317, -2331, -2344, and -2427, 800 or more parts per million away from **1a**-**c**, and assume these to be isomers as well. After ca. 1 h in solution a new, and as yet unidentified, complex, **2**, appears, which then converts slowly to the dimer $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$. Addition of between 1 and 100 equiv of styrene accelerates the isomerization of **1b** to **1a** and **1c** and markedly slows the appearance of **2** (see Experimental Section) such that if its $^{195}Pt$ resonance were not known, it would be difficult to recognize its presence. The low-field platinum chemical shift of **2**, δ -2609, is reminiscent of a monolefin complex[7] (see Table I), and this fact combined with its reduced quantity in the presence of excess $PhCH{=}CH_2$ suggests that it may arise from an olefin dissociation reaction (see eq 4). The faster isomerization of **1b** might arise from olefin exchange via an association reaction. We note that dissolving $PtCl_2$ in styrene as solvent gives a solution that, after addition of a small amount of $C_6D_6$, reveals **2** as the main component by $^{195}Pt$ spectroscopy. The same signal is observed when Zeise's salt is reacted with neat styrene followed by filtration and measurement. Consequently, *in styrene solution*, **1** and its isomers are, at best, catalyst precursors. In any case **1** is definitely labile, a useful characteristic for a soluble catalyst.

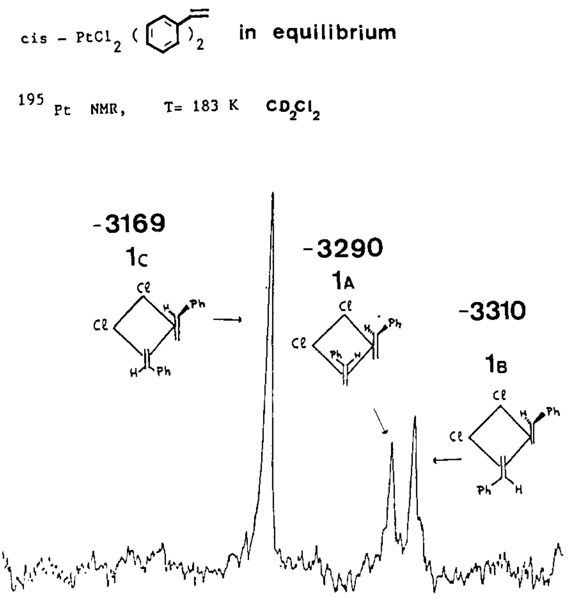


**Figure 1.** $^{195}Pt$ NMR spectrum showing the three isomers of *cis*-$PtCl_2(PhCH{=}CH_2)_2$.

**Hydrosilylation.** Results for the hydrosilylation of styrene with $Et_3SiH$ are shown in Table III. Despite the varying nature of the platinum catalyst, the product distribution shown in eq 5 is essentially unchanged. The last

$$PhCH{=}CH_2 + Et_3SiH \xrightarrow[\text{cat.}]{\text{room temp}} \underset{73\text{-}75\%}{PhCH_2CH_2SiEt_3} + \underset{1\text{-}2\%}{PhCH(CH_3)SiEt_3} + \underset{11\text{-}13\%}{PhCH_2CH_3} + \underset{11\text{-}13\%}{trans\text{-}PhCH{=}CHSiEt_3} \quad (5)$$

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[7] A trans geometric isomer cannot be excluded, as the difference $\Delta\delta(^{195}Pt)$, due to geometric isomerism, is likely to be several hundred parts per million, with the trans isomer at the lower field.[6]

**Table III. Data[a] for the Hydrosilylation of Styrene with Triethylsilane**

| | | % reagent remaining[d] | | |
|---|---|---|---|---|
| cat.[b] | time[c] | $PhCH=CH_2$ | $Et_3Si-H$ | solubility[e] |
| $PtCl_2$ | 40 min | 53.1 | 59.4 | + |
| | 70 min | 8.3 | 13.8 | |
| | 4 h | ... | 11.5 | |
| $PtBr_2$ | 75 min | 77.6 | 78.2 | – |
| | 16 h | ... | 7.7 | |
| $PtI_2$ | 60 min | 100.0 | 98.3 | – |
| | 21 h | 4.7 | 13.3 | |
| *cis*-$PtCl_2(PhCH=CH_2)_2$ | 40 min | 51.4 | 56.7 | + |
| | 70 min | 9.7 | 12.2 | |
| | 4 h | ... | 8.4 | |
| *cis*-$PtCl_2$(*p*-chlorostyrene)$_2$ | 2.5 h | ... | 13.6 | + |
| $PtCl_2$(1,5-COD) | 40 min | 69.5 | 72.9 | + |
| | 70 min | 41.5 | 44.2 | |
| | 4 h | ... | 8.6 | |
| $K[PtCl_3(PhCH=CH_2]$[f] | 2.5 h | 5.4 | 11.2 | –[f] |
| | 4 h | ... | 9.3 | |
| (*n*-$Bu_4N)[PtCl_3(PhCH=CH_2)]$[f] | 3.5 h | 76.8 | 73.9 | + |
| $PtCl_2(CH_3CN)_2$ | 75 min | 100.0 | 100.0 | + |
| | 16 h | ... | 8.0 | |
| *trans*-$PtCl_2(NH_3)_2$ | 16 h | 100.0 | 100.0 | – |
| *cis*-$PtCl_2(PEt_3)_2$ | 5 days | 100.0 | 100.0 | + |
| *cis*-$PtCl_2(PEt_3)_2 + SnCl_2$ (1:2) | 5 days | 100.0 | 100.0 | |
| *cis*-$PtCl_2$(P-*n*-$Bu_3)_2$ | 22 h | 100.0 | 100.0 | + |
| *sym-trans*-$[Pt(\mu\text{-}Cl)Cl(PTol_3)]_2$ | 22 h | 90 | 90 | – |
| | 3.5 days | 52.4 | 52.5 | |
| | 10 days | 6.5 | 13.6 | |
| | 28 days | ... | 12.4 | |
| | | 100.0 | 100.0 | |
| *sym-trans*-$[Pt(\mu\text{-}Cl)Cl(PTol_3)]_2 + SnCl_2$ (1:4) | 10 days | 97.5 | 98.8 | |
| $K_2[PtCl_4]$ | 3 days | ... | 10.8 | – |
| $(Ph_4P)_2[PtCl_4]$ | 8.5 days | 100.0 | 100.0 | – |
| $(Ph_4P)_2[PtCl_4] + Ag(CF_3SO_3)$ | 40 min | 77.4 | 81.1 | |
| | 70 min | 52.0 | 59.9 | |
| | 3 h | 4.3 | 13.1 | |
| $Ag(CF_3SO_3)$ | 3 h | 100.0 | 100.0 | |
| (*n*-$Bu_4N)[PtCl_3(PhCH=CH_2)] + Ag(CF_3SO_3)$ | 70 min | 20.0 | 26.0 | |
| | 3 h | ... | 12.1 | |
| (*n*-$Bu_4N)_2Pt_2Cl_6$ | 2.5 days | 9.6 | 14.0 | + |
| (*n*-$Bu_4N)_2Pt_2Cl_6 + SnCl_2$ (1:4) | 18 h | 68.3 | 71.1 | – |
| | 9 days | 62.2 | 65.8 | |
| *n*-$Bu_4N[PtI_3(CO)]$ | 3 days | 100.0 | 100.0 | + |
| (*n*-$Bu_4N)_2[Pt_2I_6]$ | 3 days | 100.0 | 100.0 | – |
| (*n*-$Bu_4N)_2$*cis*-$[PtCl_2(SnCl_3)_2]$ | 2.5 days | 93.5 | 93.6 | – |
| | 5.5 days | 91.3 | 89.5 | |
| $(Me_4N)_3[Pt(SnCl_3)_5]$ | 2.5 days | 28.4 | 37.4 | – |
| | 5.5 days | ... | 12.3 | |
| $(PPN)[Pt(SnCl_3)_3(PEt_3)_2]$ | 13 days | 100.0 | 100.0 | – |
| $(PPN)[Pt(SnCl_3)_3(AsEt_3)_2$ | 13 days | 100.0 | 100.0 | – |
| $(Et_4N)[Pt(SnCl_3)_3$(1,5-COD)] | 22 h | 94.7 | 91.2 | – |
| | 3.5 days | 46.5 | 48.4 | |
| | 10 days | 38.1 | 38.9 | |

[a] The conditions for the reaction are given in the Experimental Section. The ratio of reagent to catalyst is ca. 2300 unless otherwise noted. [b] The catalysts were prepared in this laboratory. [c] A sample was withdrawn after this time and subjected to $^1H$ NMR. [d] There will be a slight excess of $Et_3SiH$ due to eq 6. [e] Although not all of the catalysts are soluble in styrene, many dissolved upon addition of $Et_3Si-H$ and these are indicated with a "+". A "–" indicates those runs where some solid was still visible. [f] The solid may be KCl. This would explain the difference in rate relative to the *n*-$Bu_4N^+$ salt.

two products arise in equal amount via the reaction shown in eq 6 that has been observed previously.[8] Although the

$$2PhCH=CH_2 + Et_3SiH \xrightarrow[\text{cat.}]{} PhCH_2CH_3 + trans\text{-}PhCH=CHSiEt_3 \quad (6)$$

product distribution is not sensitive to catalyst, the reaction rate markedly depends on catalyst choice. The reaction is fastest with $PtCl_2$ and *cis*-$PtCl_2(PhCH=CH_2)_2$ whose rates are identical. Once the $PtCl_2$ is dissolved, there is little or no incubation time; i.e., the reaction starts when the silane is added. For the neutral complexes $PtCl_2L_2$, we find relative rates corresponding to $PhCH=CH_2 \simeq p\text{-}ClC_6H_4CH=CH_2 > {}^1/_2COD > CH_3CN >> NH_3, PEt_3$ (these do not react at room temperature after 16 h). We also note that $PtCl_2 > PtBr_2{}^* > PtI_2{}^*$, (*n*-$Bu_4N)_2Pt_2Cl_6 >$ (*n*-$Bu_4N)Pt_2I_6$ (inactive), (*n*-$Bu_4N)_2PtCl_6 > Pt_2(\mu\text{-}Cl)_2Cl_2(PTol_3)_2$, $K_2PtCl_4 > (Ph_4P)_2PtCl_4$, and $K[PtCl_3(PhCH=CH_2)] > (Bu_4N)_2[PtCl_3(PhCH=CH_2)]$ (the rates for the compounds with an asterisk may be a consequence of low solubility) with both $PtCl_2$ and *cis*-$PtCl_2(PhCH=CH_2)_2$ faster than any of the others.

Disappointingly, addition of $SnCl_2$, either as a preformed complex, e.g., *cis*-$PtCl_2(SnCl_3)_2{}^{2-}$, or as a mixture with one of the complexes noted above, *slows* the reaction (see entry for (*n*-$Bu_4N)_2[PtCl_2(SnCl_3)_2]$[9] among others) or brings no

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(8) Onopchencko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

(9) Alcock, N. W.; Nelson, J. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2415.

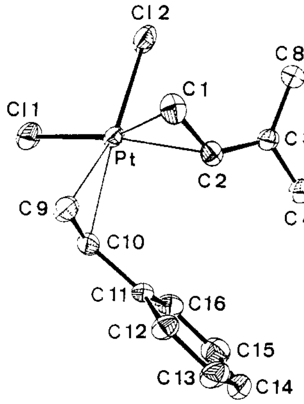

**Figure 2.** ORTEP view of isomer **1a**.

significant acceleration. Interestingly, $(Me_4N)_3Pt(SnCl_3)_5$[10] reacts faster than any of the other trichlorostannate complexes.

All of these data are consistent with a catalysis that requires facile coordination of the styrene via a labile coordination sphere. If this condition is met, the reaction proceeds with a rate-determining step that occurs later in the catalysis. The chelating olefin complex $PtCl_2(1,5\text{-COD})$ is an efficient catalyst, although somewhat slower than the bis(styrene) complex. After 70 min with the latter complex ca. 8% of the starting styrene remains whereas for the chelate olefin ca. 40% of the styrene is still present. Strongly coordinating ligands, e.g., $PEt_3$ or even $Cl^-$, slow or completely suppress the reaction at room temperature. The effect of coordinated $Cl^-$ is nicely demonstrated by a comparison of the rates for the soluble complexes $PtCl_2(PhCH{=}CH_2)_2$ (**1**), $n\text{-}Bu_4N[PtCl_3(PhCH{=}CH_2)]$ (**3**), and **3** plus 1 equiv of $Ag(CF_3SO_3)$. After 70 min of reaction time **1** has converted >90% of the styrene whereas after ~1 day, **3** has done the same for ~64% of the styrene. Introduction of 1 equiv of the silver salt, which by itself is not a catalyst, reveals 80% consumption of the olefin after 70 min. Clearly, removal of a chloride by $Ag^+$ affords **1**, in situ, which catalyzes the hydrosilylation in the usual way. Addition of 1 or more equiv of $SnCl_2$ with $PhCH{=}CH_2/Et_3Si$ as solvent results in stable complexes that do not assist in olefin coordination. We note that in aqueous solution this need not be the case, and $SnCl_2$ is recognized to accelerate ethylene coordination.[11]

**The X-ray Structure of *cis*-$PtCl_2(PhCH{=}CH_2)_2$.** We have been successful in crystallizing one isomer of **1**, specifically, **1a**, and have determined its structure by X-ray analysis. The structure contains two styrene molecules both approximately perpendicular to the plane defined by the metal and two halogens, and Figure 2 shows an ORTEP plot of the molecule. A list of bond lengths and angles is shown in Table IV. The coordination geometry about the platinum is square-planar with *cis*-styrene ligands. The two olefins are nonequivalent in that one has a phenyl ring pseudo cis to an adjacent halogen, whereas the other has the phenyl cis to the second styrene. Both rings are on the same side of the $PtCl_2$ plane, i.e., as shown in **1a**. The four Pt-C bond distances, 2.156 (7) and 2.270 (5) Å (styrene A) and 2.173 (7) and 2.258 (6) Å (styrene B), are in good agreement with those found in *trans*-$PtCl_2(NC_5H_4\text{-}p\text{-}CH_3)(PhCH{=}CH_2)$[12] (**4**), 2.180 (12), and 2.236 (10) Å. The C-C bond separations, 1.382 (9) and 1.398 (9) Å for **1**, are shorter than either the 1.53 (5) Å separation found for for $PtCl_2(t\text{-}BuN{=}CH{-}CH{=}N\text{-}t\text{-}Bu)(PhCH{=}CH_2)$[13] or that found for the picoline complex **4**, 1.454 (17) Å,[12] but similar to that observed for $Pt(\eta^3\text{-}CH_2C(Me)CH_2)(PPh_3)(PhCH{=}CH_2)^+$, 1.341 (17) Å.[14] Interestingly, the 18-electron cationic complex $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(PhCH{=}CH_2)]PF_6$ also has a similar olefin C-C separation of 1.361 (7) Å.[15] With the assumption that a normal C=C double-bond length is ca. 1.34 Å and a C—C single bond to be ca. 1.54 Å, our data for **1** suggest only a very modest $\pi$-back-bonding contribution. The distances from the midpoints of the double bonds to the metal are 2.105 (6) and 2.106 (6) Å, respectively, for the C(1)-C(2) and C(9)-C(10) moieties. The C-C vectors of the olefins are not perpendicular to the coordination plane but are tilted by 12.7 and 15.4° for the C(9)-C(10) and C(1)-C(2) vectors, respectively. The two styrenes are also tilted with respect to one another as shown by the angle 24.1° subtended by the lines C(9)-C(10) and C(1)-C(2). The two Pt-Cl separations in **1a**, 2.304 (2) and 2.310 (2) Å, are normal for square-planar Pt(II)[16] and suggest only a weak-to-moderate trans influence for the coordinated styrene ligands.[17] The Cl-Pt-Cl angle of ca. 86° is consistent with normal square-planar geometry.

**Table IV. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 1a (Esd's on the Last Significant Figure in Parentheses)**

| | | | |
|---|---|---|---|
| Pt-Cl(1) | 2.310 (2) | Cl(1)-Pt-Cl(2) | 86.47 (7) |
| Pt-Cl(2) | 2.304 (2) | $C_{m2}$-Pt-Cl(1)[b] | 87.4 (2) |
| Pt-C(1) | 2.156 (7) | $C_{m1}$-Pt-Cl(2)[b] | 95.0 (2) |
| Pt-C(2) | 2.270 (5) | $C_{m1}$-Pt-$C_{m2}$[b] | 91.2 (6) |
| Pt-C(9) | 2.173 (6) | C(1)-C(2)-C(3) | 128.2 (6) |
| Pt-C(10) | 2.258 (6) | C(2)-C(3)-C(4) | 118.6 (5) |
| C(1)-C(2) | 1.382 (9) | C(2)-C(3)-C(8) | 123.4 (5) |
| C(2)-C(3) | 1.462 (8) | C(4)-C(3)-C(8) | 118.0 (6) |
| C(3)-C(4) | 1.396 (8) | C(9)-C(10)-C(11) | 127.0 (6) |
| C(3)-C(8) | 1.377 (8) | | |
| C(5)-C(6) | 1.361 (9) | C(10)-C(11)-C(12) | 122.4 (5) |
| C(6)-C(7) | 1.395 (10) | C(10)-C(11)-C(16) | 119.2 (6) |
| C(7)-C(8) | 1.370 (10) | C(12)-C(11)-C(16) | 118.4 (6) |
| C(9)-C(10) | 1.398 (9) | (C-C-C)Ph[a] | 120.4 (7) |
| C(10)-C(11) | 1.476 (8) | | |
| C(11)-C(12) | 1.376 (9) | C(11)-Pt-C(1)-C(2) | -173.9 |
| C(12)-C(13) | 1.393 (10) | C(12)-Pt-C(9)-C(10) | 160.5 |
| C(13)-C(14) | 1.348 (11) | C(1)-C(2)-C(3)-C(4) | 179.2 |
| C(14)-C(15) | 1.382 (11) | C(9)-C(10)-C(11)-C(12) | 22.3 |
| C(15)-C(16) | 1.346 (10) | | |

[a] Average value; the standard deviation of the mean is given in parentheses. [b] $C_{m1}$ and $C_{m2}$ represent the midpoints of C(1)-C(2) and C(9)-C(10), respectively.

## Experimental Section

NMR spectra were measured on a Bruker WM-250 MHz multinuclear spectrometer.[3,4] Infrared data were obtained from KBr pellets by using a Perkin-Elmer series 1430 spectrometer. Triethylsilane was prepared according to the literature,[18] and styrene was freshly distilled before use.

$PtCl_2$, $PtBr_2$, and $PtI_2$ were obtained from Johnson Matthey. The phosphine, arsine, and $SnCl_3^-$ complexes were prepared previously in this laboratory.[3,4]

The hydrosilylation experiments were carried out under $N_2$.

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**Synthesis of *cis*-$PtCl_2(PhCH{=}CH_2)_2$.** A suspension of $PtCl_2$ (251.4 mg, 945.1 μmol) in 6 mL of freshly distilled styrene was stirred for 55 h. The yellow suspension that resulted was filtered and the solid so obtained washed with 10 mL of benzene and 25 mL of pentane. Drying in vacuo affords 376.8 mg (84%) of product. Anal. Calcd for $C_{16}H_{16}Cl_2Pt$: C, 40.52; H, 3.40; Cl, 14.95. Found: C, 40.15; H, 3.37; Cl, 15.21.

**Synthesis of $PtCl_2(p\text{-}ClC_6H_4CH{=}CH_2)_2$.** To freshly distilled *p*-chlorostyrene (5.501 g, 39.7 mmol) was added $PtCl_2$ (185 mg, 0.697 mmol) and the suspension stirred for 47 h. The resulting deep red suspension was filtered and the resulting solid quickly washed with some pentane (note that prolonged washing leads to further reaction of the complex). Drying for 6 h in vacuo affords 342.6 mg (90%) of product. The complex is not stable in solution at room temperature, and even the solid begins to smell of free *p*-chlorostyrene with time. Anal. Calcd for $C_{16}H_{14}Cl_4Pt$: C, 35.38; H, 2.60; Cl, 26.11. Found: C, 34.86; H, 2.47; Cl, 26.08. The $^1H$ spectrum of this complex shows only uncoordinated ligand at room temperature, suggesting dynamic behavior.

**Preparation of $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$. Reaction 4.** *cis*-$PtCl_2(PhCH{=}CH_2)_2$ (3.121 g, 6.581 mmol) was refluxed in 30 mL of $CHCl_3$ for 1.5 h. The solution that results was cooled to room temperature and the resulting suspension treated with 30 mL of $CH_2Cl_2$ to dissolve the precipitated solids. Filtration was followed by concentration to ca. 5 mL. Addition of 50 mL of pentane causes precipitation of the product that was collected by filtration, washed with an additional 50 mL of pentane, and dried in vacuo; yield 2.261 g (93%). Anal. Calcd for $C_{16}H_{16}Cl_4Pt_2$: C, 25.96; H, 2.18; Cl, 19.16. Found: C, 25.97; H, 2.15; Cl, 19.62. $^{195}Pt$ NMR data are given in Table I. The products of reactions 1–3 were confirmed via microanalysis and the appropriate form of NMR spectroscopy.

**Preparation of $(n\text{-}Bu_4N)[PtCl_3(PhCH{=}CH_2)]$.** Styrene (0.06 mL, 0.52 mmol) was added to a solution of $(n\text{-}Bu_4N)_2[Pt_2Cl_6]$ (0.102 g, 0.137 mmol) in 0.5 mL of $CH_2Cl_2$. After 14 h the initially red-brown solution appeared yellow-orange in color. The solvent was removed and the residue treated with 0.25 mL of $CH_2Cl_2$, 1.0 mL of toluene, and then 6 mL of ether. Cooling to −78 °C for 21 h gives a yellow precipitate that was filtered, washed with 20 mL of ether, and dried in vacuo to afford 106 mg (81%) of product. Note that the toluene is present to prevent the product from precipitating from the solution as an oil: $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 6.37 ($H^A$, $^3J(H^A,H^B) = 8.0$ Hz, $^3J(H^A,H^C) = 13.6$ Hz), 4.99 ($H^C$, $^2J(H^B,H^C) = 0.5$ Hz), 4.42 ($H^B$); $^{195}Pt$ NMR (relative to $Na_2PtCl_6$) $\delta$ −2572; $^{13}C$ NMR $\delta$ 58.57 ($CH_2{=}CH$), 86.68 ($CH_2{=}CH$).

**Synthesis of $[Pt(\mu\text{-}Cl)Cl(p\text{-}ClC_6H_4CH{=}CH_2)]_2$ from $PtCl_2(p\text{-}ClC_6H_4CH{=}CH_2)_2$.** The bis $p\text{-}ClC_6H_4CH{=}CH_2$ complex (52.5 mg, 96.6 μmol) was dissolved in 10 mL of $CHCl_3$. Filtration of the solution was followed by concentration to ca. 1.5 mL. Addition of 10 mL of pentane induces precipitation of the product as an orange powder. Washing with 10 mL of pentane followed filtration. Drying in vacuo for 10 h affords 31.4 mg of product (81%). Anal. Calcd for $C_8H_7Cl_3Pt$: C, 23.75; H, 1.74. Found: C, 23.57; H, 1.62. The $^1H$ spectrum is sharp at 180 K, but is complicated. The $^{195}Pt\{^1H\}$ spectrum at 193 K shows four broadened signals at $\delta$ −2322, −2336, −2365, and −2599 (relative to external aqueous $PtCl_6^{2-}$).

**Isomerization of *cis*-$PtCl_2(PhCH{=}CH_2)_2$ in the Presence of Excess $PhCH{=}CH_2$.** Solutions a–d of $8.4 \times 10^{-3}$ M *cis*-$PtCl_2(PhCH{=}CH_2)_2$ in $CH_2Cl_2/CD_2Cl_2$ (5:1) were treated with various amounts of stryene, and the isomerization was followed by $^{195}Pt$ NMR as a function of time (Table VII).

**Reactions of $PhCH{=}CH_2$ with $Et_3SiH$ in the Presence of a Catalyst.** The catalyst (see Table III) and freshly distilled styrene (0.73 mL, 6.35 mmol) were stirred under $N_2$ for 45 min after which time triethylsilane (1.00 mL, 6.28 mmol) was added. Periodically a small quantity of the reaction mixture was withdrawn with a syringe and the course of the reaction determined by using $^1H$ NMR spectroscopy. For the catalysts that were relatively fast, the reaction proceeds with 100% conversion of the styrene. The mole ratio of silane to catalyst chosen was ca. 2300. In our experience it is important to use fresh and very pure $Et_3SiH$. An old sample of this reagent did not react *despite* having been distilled twice. We have not identified the inhibitor; however, introduction of air ($O_2$) plus exposure to light was sufficient to overcome its inhibiting effect. We have prepared our $Et_3SiH$ via a Grignard reaction.[18]

**Table V. Experimental Data for the X-ray Diffraction Study[a] of Compound 1a**

| | |
|---|---|
| formula | $PtCl_2C_{16}H_{16}$ |
| mol wt | 476.32 |
| Cryst syst | monoclinic |
| space group | $P2_1/c$ |
| $a$, Å | 13.805 (7) |
| $b$, Å | 10.235 (2) |
| $c$, Å | 10.985 (7) |
| $\beta$, deg | 106.51 (4) |
| $Z$ | 4 |
| $V$, Å$^3$ | 1489.1 (4) |
| $\rho$(calcd), g cm$^{-3}$ | 2.124 |
| $\mu$, cm$^{-1}$ | 99.09 |
| radiatn | Mo $K\bar{\alpha}$ graphite monochromated; $\lambda$ = 0.71069 Å |
| measd reflctns | $\pm h,+k,+l$ |
| $2\theta$ range, deg | $2.3 \le \theta \le 25.0$ |
| scan type | $\omega/2\theta$ |
| scan width, deg | $(1.10 + 0.35 \tan \theta)$ |
| max scan speed, deg min$^{-1}$ | 10.5 |
| max counting time, s | 55 |
| bkgd time, s | 0.5 × (scan time) |
| prescan rejection limit | 0.5 ($2\sigma$) |
| prescan acceptance limit | 0.03 ($33\sigma$) |
| horiz receiving aperture, mm | $1.90 + \tan \theta$ |
| vert receiving aperture, mm | 4.0 |
| no. of independent data | 2599 |
| no. of obsd. data [$K_{net} \ge 2.5\sigma(I)$] | 1985 |
| no. of variables refined | 172 |
| $R^b$ | 0.033 |
| $R_w{}^c$ | 0.038 |
| $S^c$ | 1.47 |

[a] Collected at room temperature. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [d] $S = [\sum w(|f_o| - 1/k|F_c|)^2(n_o - n_v)]^{1/2}$.

**Table VI. Positional Parameters and Their Estimated Standard Deviations**

| atom | $x$ | $y$ | $z$ | $B_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Pt(1) | 0.29361 (2) | 0.21810 (3) | 0.11587 (2) | 2.734 (5) |
| Cl(1) | 0.4138 (2) | 0.0800 (2) | 0.0764 (2) | 4.54 (4) |
| Cl(2) | 0.1790 (2) | 0.4476 (2) | 0.5404 (2) | 4.45 (5) |
| C(1) | 0.1882 (6) | 0.2959 (9) | 0.2093 (7) | 4.2 (2) |
| C(2) | 0.1725 (5) | 0.3724 (7) | 0.1016 (7) | 3.1 (1) |
| C(3) | 0.0884 (5) | 0.3671 (7) | −0.0150 (6) | 2.9 (1) |
| C(4) | 0.0873 (5) | 0.4557 (7) | −0.1123 (7) | 3.5 (2) |
| C(5) | 0.0083 (6) | 0.4579 (8) | −0.2224 (7) | 4.2 (2) |
| C(6) | −0.0697 (6) | 0.3719 (9) | −0.2384 (8) | 4.4 (2) |
| C(7) | −0.0704 (7) | 0.2833 (8) | −0.1420 (9) | 4.6 (2) |
| C(8) | 0.0076 (6) | 0.2831 (8) | −0.0318 (8) | 3.9 (2) |
| C(9) | 0.4081 (6) | 0.3417 (9) | 0.2401 (8) | 4.6 (2) |
| C(10) | 0.4110 (5) | 0.3725 (7) | 0.1170 (7) | 3.5 (2) |
| C(11) | 0.3759 (5) | 0.4946 (7) | 0.0464 (6) | 2.9 (1) |
| C(12) | 0.3669 (6) | 0.6101 (8) | 0.1066 (7) | 3.8 (2) |
| C(13) | 0.3385 (7) | 0.7239 (8) | 0.0354 (9) | 4.7 (2) |
| C(14) | 0.3198 (6) | 0.7226 (8) | −0.0921 (9) | 4.6 (2) |
| C(15) | 0.3283 (6) | 0.6061 (9) | −0.1522 (7) | 4.6 (2) |
| C(16) | 0.3562 (6) | 0.4955 (8) | −0.0848 (7) | 3.9 (2) |

[a] Thermal parameters are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

**Crystallography.** Crystals suitable for X-ray diffraction of compound 1 were obtained by crystallization from a solution of $PtCl_2$ in styrene, have elongated prismatic habit, and are air-stable. A pale yellow crystal of approximate dimensions 0.06 × 0.1 × 0.3 mm was mounted at a random orientation on a glass fiber. A CAD4 diffractometer was used for both the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least-squares fit of the $2\theta$ values of 25 high order reflections ($10.0 \le \theta \le 15.0$) using the CAD4 centering routines. From systematic absences the space group was

**Table VII**[a]

| soln | $t$, min | **1b** | **1a** | **1c** | **2** |
|---|---|---|---|---|---|
| a | 15 | 1 | | | |
| | 83 | 1 | | 0.10 | |
| | 277 | 1 | 0.85 | 3.47 | 1.33 |
| | 345 | 1 | 0.53 | 3.14 | 1.32 |
| b | 15 | 1 | | 0.05 | |
| | 37 | 1 | 0.06 | 0.28 | |
| | 97 | 1 | 0.48 | 1.81 | 0.32 |
| | 162 | 1 | 0.69 | 2.83 | 0.48 |
| | 234 | 1 | 0.50 | 2.63 | 0.40 |
| c | 15 | 1 | 0.06 | 0.30 | |
| d | 15 | 1 | 0.07 | 0.38 | |
| | 37 | 1 | 0.24 | 1.12 | |
| | 77 | 1 | 0.56 | 2.79 | |
| | 142 | 1 | 0.81 | 3.11 | |
| | 230 | 1 | 0.65 | 2.59 | |
| | 530 | 1 | 0.55 | 3.05 | |

[a] PhCH=CH$_2$/**1b**: a, 0; b, 1.4; c, 10.4; d, 105. Values represent relative integrals at 193 K.

umambigously determined as $P2_1/c$. Crystallographic and other relevant data collection parameters are listed in Table V. Data were collected by using the parameters listed in Table V with variable scan speed to obtain constant statistical precision on the intensities collected. Three standard reflections ($\bar{6}\bar{1}0$; $\bar{7}\bar{1}2$; $\bar{4}4\bar{1}$) were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variations were detected. The orientation of the crystal was checked by measuring three reflections ($\bar{5}1\bar{2}$; $\bar{5}40$; $\bar{4}42$) every 300 measurements. Data have been corrected for Lorentz and polarization factors, using the data reduction programs of the CAD4-SDP package.[19] An empirical adsorption correction was applied by using azimuthal ($\psi$) scans of five "high-$\chi$" angle reflections ($\chi > 83.0°$): $\bar{3}04$; $\bar{4}06$; $\bar{6}06$; $\bar{7}08$; $\bar{7}19$. Transmission factors were in the range 0.790–0.997. Intensities were considered as observed if $I_{net} \geq 2.5\sigma(I_{tot})$, while an $I_{net}$ of 0.0 was given to those reflections having negative net intensities.

The structure was solved by a combination of Patterson and Fourier methods and refined by full-matrix least squares using the CAD4-SDP programs[19] (the function minimized was $(\sum w(|F_o| - 1/k|F_c|)^2)$ and with weight according to the expression $w^{-1} = [\sum\sigma^2(F_o^2) + 0.07(F_o^2)]$. Anisotropic temperature factors were used for all atoms, while the contribution of the hydrogen atoms in their idealized positions (C–H = 0.95 Å; $B_{iso}$ = 5.0 Å$^2$) was taken into account but not refined. Upon convergence (no parameter to shift ratio > $0.07\sigma$ ($p$)) the Fourier difference map showed no significant features. The scattering factors were taken from ref 20, and a correction for the real and imaginary part of the anomalous scattering[20] was taken into account. Final positional and equivalent thermal parameters for the refined atoms are given in Table VI. Tables of $F_o/F_c$ (Table S1), anisotropic thermal parameters (Table S2), a complete list of bond lengths and angles (Table S3) are given in the supplementary material.

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**Registry No. 1a**, 106862-48-0; **1b**, 106862-49-1; **1c**, 106862-50-4; *cis*-PtCl$_2$(*p*-ClC$_6$H$_4$CH=CH$_2$)$_2$, 106799-80-8; *sym-trans*[Pt($\mu$-Cl)Cl(PhCH=CH$_2$)]$_2$, 60018-53-3; [PtCl$_3$(PhCH=CD$_2$)](Bu$_4$N), 106799-82-0; [PtCl$_3$](Bu$_4$N)$_2$, 18129-78-7; *sym-trans*[Pt($\mu$-Cl)Cl($\pi$-ClC$_6$H$_4$CH=CH$_2$)]$_2$, 38856-92-7; PtCl$_2$, 10025-65-7; PtBr$_2$, 13455-12-4; PtI$_2$, 7790-39-8; K[PtCl$_3$(PhCH=CH$_2$)], 12080-15-8; PtCl$_2$(CH$_3$CN)$_2$, 13869-38-0; *trans*-PtCl$_2$(NH$_3$)$_2$, 14913-33-8; *cis*-PtCl$_2$(PEt$_3$)$_2$, 15692-07-6; SnCl$_2$, 7772-99-8; *cis*-PtCl$_2$(PBu$_3$)$_2$, 15390-92-8; *sym-trans*-[Pt($\mu$-Cl)Cl(Ptol$_3$)]$_2$, 86322-36-3; K$_2$[PtCl$_4$], 10025-99-7; [PtCl$_4$](Ph$_4$P)$_2$, 60219-45-6; Ag(CF$_3$SO$_3$), 2923-28-6; [PtI$_3$(CO)](Bu$_4$N), 66213-27-2; [Pt$_2$I$_6$](Bu$_4$N), 62428-79-9; *cis*-[PtCl$_2$(SnCl$_3$)$_3$](Bu$_4$N)$_2$, 106799-83-1; [Pt(SnCl$_3$)$_5$](Me$_4$N)$_3$, 41071-62-9; [Pt(SnCl$_3$)$_3$(PEt$_3$)$_2$](PPN), 83161-33-5; [Pt(SnCl$_3$)$_3$(AsEt$_3$)$_2$](PPN), 82306-26-1; [Pt(SnCl$_3$)$_3$(1,5-COD)](Et$_4$N), 85081-66-9; PtCl$_2$COD, 12080-32-9; *cis*-PtCl$_2$(Astol$_3$)$_2$, 79390-60-6; *cis*-PtCl$_2$(Ptol$_3$)$_2$, 31173-67-8; PhCH=CH$_2$, 100-42-5; *p*-ClC$_6$H$_4$CH=CH$_2$, 1073-67-2; Et$_3$SiH, 617-86-7; Ph(CH$_2$)$_2$SiEt$_3$, 14355-62-5; PhCH(CH$_3$)SiEt$_3$, 87555-71-3; PhCH$_2$CH$_3$, 100-41-4; *trans*-PhCH=CHSiEt$_3$, 21209-32-5.

**Supplementary Material Available:** Tables containing final positional and equivalent thermal parameters, anisotropic thermal parameters, and a complete list of bond lengths and angles (4 pages); a listing of $F_o/F_c$ (24 pages). Ordering information is given on any current masthead page.

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