Transition Metal Silyl Complexes. 59.[1] Oxidative Addition of Nonactivated Si−C Bonds to Platinum(0) Centers

Hilmar Gilges and Ulrich Schubert*

Institut für Anorganische Chemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria

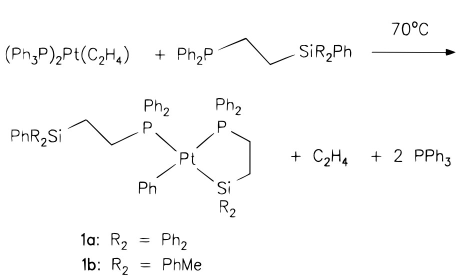
Received June 24, 1998

Summary: Reaction of $Ph_2PCH_2CH_2SiPh_{3-n}Me_n$ *(n = 0, 1) with* $(Ph_3P)_2Pt(\pi\text{-}C_2H_4)$ *at elevated temperatures results in the formation of* $(Me_nPh_{3-n}SiCH_2CH_2Ph_2P)Pt(PPh_2CH_2CH_2SiPh_{2-n}Me_n)Ph$ *by oxidative addition of the* $Si{-}C_{phenyl}$ *group. Oxidative addition of Si−Me groups is not observed. Therefore, no chelate complex is obtained with* $Ph_2PCH_2CH_2SiMe_3$*. The complex* $(Et_3P)Pt(PPh_2CH_2CH_2SiPhMe)Ph$ *is formed when a mixture of* PEt_3 *and* $Ph_2PCH_2CH_2SiPh_2Me$ *is reacted with* $(Ph_3P)_2Pt(\pi\text{-}C_2H_4)$*.*

There is a growing interest in Si−C or Si−Si activation processes, partially due to the interest in the catalytic formation of new organosilicon polymers.[2] Several examples for the oxidative addition of Si−Si bonds to transition-metal centers are now known, compared to only a few for that of Si−C bonds. Two strategies were mainly used to promote the oxidative addition of Si−C bonds (the case of intramolecular addition of the Si−C bond of a silyl ligand in binuclear complexes is not considered here). The first is to enhance of the reactivity of the transition-metal fragment, for example by geometric distortions as in $(Bu^t{}_2PCH_2Bu^t{}_2P)Pt$.[3] The second strategy is to use compounds with activated Si−C bonds[4] or to increase the reactivity of the Si−C bond by ring strain as in silacyclobutanes.[5]

In recent publications we utilized the promoting and stabilizing effect of chelation to obtain stable complexes by intramolecular oxidative addition of the Sn−C, Si−Sn, or Si−Si (E−E′) bonds in (phosphinoalkyl)silane and -stannane complexes of the type $L_nM\text{-}PR_2(CH_2)_n\text{-}ER'_2E'R''_3$.[6−8] When $(Ph_3P)_2Pt(\pi\text{-}C_2H_4)$ was reacted with $Ph_2P(CH_2)_nSiMe_2SiPh_3$ ($n = 1, 2$) at room temperature, only the Si−Si bond was oxidatively added to the metal, and the chelate complexes $(Ph_3P)Pt[PPh_2(CH_2)_nSiMe_2]SiPh_3$ were exclusively formed.[7] The alternative oxidative addition of a Si−Ph group was not observed, although this would lead to a less strained five-membered ring for $n = 1$. This is experimental proof that oxidative addition of a Si−Si bond is distinctly more favorable than a Si−C bond when both compete with each other. In the present communication we show, however, that the chelate-assisted oxidative addition of Si−C bonds is observed in the absence of competing Si−Si bonds.

The compounds $Ph_2PCH_2CH_2SiR_2R'$ (R = R′ = Ph, Me; R = Ph, R′= Me) were synthesized by irradiation of Ph_2PH and the corresponding vinyltriorganosilane in the absence of a solvent in a quartz vessel. The reaction of $(Ph_3P)_2Pt(\pi\text{-}C_2H_4)$ with any of the three (phosphinoethyl)silanes at ambient temperature under identical conditions led to the immediate formation of highly dynamic phosphine complexes $Pt(\mathbf{P})_x$ (x = 3, 4; **P** = PPh_3, $Ph_2PCH_2CH_2SiR_2R'$). This was indicated by the spontaneous evolution of ethylene, a color change to orange-red, and a very broad resonance in the ^{31}P NMR spectrum. The NMR spectrum of the reaction mixture did not change over 2 days at room temperature. However, if the reaction mixture containing the $SiPh_3$ derivative was heated to 70 °C after the ethylene evolution had stopped, a subsequent reaction was observed by ^{31}P NMR spectroscopy. Prolonged heating resulted in the almost quantitative formation of $(Ph_3SiCH_2CH_2Ph_2P)Pt(PPh_2CH_2CH_2SiPh_2)Ph$ (**1a**) (eq 1).



(1)

The identity and structure of **1a** were unequivocally established by elemental analysis and NMR spectra.[9]

In contrast to this, the $SiMe_3$ derivative showed no subsequent reaction after the formation of the $Pt(\mathbf{P})_x$ species, according to the ^{31}P NMR spectra, even if the reaction mixture was heated to 70 °C for 72 h or refluxed

---

[1] Part 58: Schubert, U.; Kalt, D.; Gilges, H. *Monatsh. Chem.*, in press.

[2] Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403.

[3] Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem.* **1990**, *102*, 935; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880.

[4] Huang, D.; Heyn, R. H.; Bollinger, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 292. Osakada, K.; Koizumi, T.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 189.

[5] Cundy, C. S.; Lappert, M. F.; Dubac, J.; Mazerolles, P. *J. Chem. Soc., Dalton Trans.* **1976**, 910. Cundy, C. S.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 665. Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873. Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246.

[6] Müller, C.; Schubert, U. *Chem. Ber.* **1991**, *124*, 2181.

[7] Gilges, H.; Kickelbick, G.; Schubert, U. *J. Organomet. Chem.* **1997**, *548*, 57.

[8] Gilges, H.; Schubert, U. *Eur. J. Inorg. Chem.* **1998**, 897.

10.1021/om9805335 CCC: $15.00

in toluene. It is assumed that this different behavior was due to the lower activity of Si−Me bonds toward oxidative addition compared with Si−Ph bonds, because the same order of reactivity was already observed for the corresponding tin compounds.[8] To test this notion, $\mathrm{Ph_2PCH_2CH_2SiPh_2Me}$ was analogously reacted. The ^{31}P NMR spectra showed that the complex $\mathrm{(MePh_2SiCH_2CH_2Ph_2P)\overline{Pt(PPh_2CH_2CH_2Si}PhMe)Ph}$ (**1b**) was almost quantitatively formed after heating for 40 h.[10] Si−Ph addition could only be spectroscopically observed, because solutions of the complex showed a marked tendency to eliminate the Si−C bond again and reform Pt(**P**)$_x$ with nonchelated $\mathrm{PPh_2CH_2CH_2SiPh_2Me}$ ligand(s). To suppress this reductive elimination by increasing the electron density at the metal center, a 1:1:1 mixture of $\mathrm{(Ph_3P)_2Pt(C_2H_4)}$, $\mathrm{PEt_3}$, and $\mathrm{Ph_2PCH_2CH_2SiPh_2Me}$ was reacted, which resulted in the formation of $\mathrm{(Et_3P)\overline{Pt(PPh_2CH_2CH_2Si}PhMe)(Ph)}$ (**2**).[11] According to the ^{31}P NMR spectra, the solution of **2** was stable toward reductive elimination, due to the more electron-donating properties of the $\mathrm{PEt_3}$ ligand. There was also no indication for a byproduct originating from the oxidative addition of the Si−Me group in this modification of the reaction.

The stereochemisty of the complexes **1** and **2** is the same as previously observed for the corresponding complexes $\mathrm{(R''_3P)\overline{Pt(PPh_2CH_2CH_2Si}R_2)ER'_3}$ (E = Si, Sn; $\mathrm{R''_3P = R'_3ESiR_2CH_2CH_2Ph_2P, Ph_3P}$). There are two doublets in the ^{31}P NMR spectra for the nonequivalent phosphorus nuclei, accompanied by Pt satellites. The doublet at about 50 ppm can be assigned to the phosphorus atom of the five-membered ring because of the significant low-field shift. This is also clear proof that chelation has occurred. The value $^2J_{\mathrm{PPtP}} \approx 15$ Hz is typical for a cis arrangement of the phosphane ligands.

The comparison of the results reported in this communication with our previous work on the reactions of $\mathrm{(Ph_3P)_2Pt(\pi\text{-}C_2H_4)}$ with $\mathrm{Ph_2PCH_2CH_2ER_2\text{-}E'R'_3}$ (E−E′ = Si−Si, Si−Sn,[7] and Sn−C[8]) allows conclusions about the order of reactivity of E−E′ bonds toward the same metal complex fragment in the same electronic and steric environment. Oxidative addition of the Si−Si, Si−Sn, Sn−C$_{\mathrm{phenyl}}$, or Sn−C$_{\mathrm{methyl}}$ bond of $\mathrm{Ph_2PCH_2CH_2SiR_2{-}EPh_3}$ (E = Si, Sn; R = Me, Ph) and $\mathrm{Ph_2PCH_2CH_2SnR_3}$ (R = Me, Ph) proceed even at room temperature, but the reaction rates are different. Oxidative addition of Si−C bonds in $\mathrm{Ph_2PCH_2CH_2SiR_3}$ is only observed for Si−phenyl groups at higher temperatures. Thus, the order of reactivity is $\mathrm{Sn{-}Si > Sn{-}C_{phenyl} > Sn{-}C_{methyl} \approx Si{-}Si \gg Si{-}C_{phenyl}}$. No oxidative addition reaction was observed for $\mathrm{Ph_2PCH_2CH_2SiMe_3}$; therefore, even chelate assistance is not sufficient to add the least reactive Si−C$_{\mathrm{methyl}}$ bonds to Pt(0). It is known that Si−aryl groups are more easily cleaved by electrophiles than Si−alkyl groups. Si−alkyl bonds are less polarized because of the hydrogen substituents at the carbon atom. This may be the explanation for the selectivity of Si−Ph over Si−Me in the reaction reported in this paper.

Acknowledgment. We thank the Fonds zur Förderung der wissenschaftlichen Forschung (FWF) for supporting this work.

Supporting Information Available: ^{31}P NMR spectra of **1b** and **2** (2 pages). Ordering information is given on any current masthead page.

OM9805335

---

(9) An amount of 134 mg (282 mmol) of $\mathrm{Ph_2PCH_2CH_2SiPh_3}$ was added to a solution of 106 mg (142 mmol) of $\mathrm{(Ph_3P)_2Pt(C_2H_4)}$ in 8 mL of benzene under an atmosphere of dry argon. An immediate color change to orange occurred, and gas was evolved. The solution was stirred for 15 min and then slowly heated to 70 °C and held at this temperature for 12 h. After the solution was cooled to room temperature, all volatiles were then removed in vacuo, leaving a yellow oil. The residue was extracted three times with 8 mL portions of pentane. When the combined pentane solutions were concentrated to 4 mL, a yellow precipitate was formed. Precipitation was completed by cooling to −20 °C. The yellow powder was separated at −20 °C and dried in vacuo. Yield: 84 mg (52%). Anal. Calcd for $\mathrm{C_{64}H_{58}P_2PtSi_2}$: C, 67.40; H, 5.13. Found: C, 67.15; H, 5.27. ^{31}P{^{1}H} NMR (101.25 MHz, $\mathrm{C_6D_6}$): δ 49.1 (d, $^2J_{\mathrm{PPtP}} = 14.6$ Hz, $^1J_{\mathrm{PtP}} = 2023.8$ Hz), 25.2 (d, $^1J_{\mathrm{PtP}} = 1354.9$ Hz). ^{29}Si NMR (49.69 MHz, $\mathrm{C_6D_6}$): δ 28.7 (dd, $^2J_{\mathrm{PPtSi}} = 160.0$ Hz, $J_{\mathrm{PSi}} = 10.2$ Hz), −9.2 (d, $^3J_{\mathrm{PCCSi}} = 24.0$ Hz). ^{1}H NMR (250.13 MHz, $\mathrm{C_6D_6}$): δ 1.05−1.35 (m, 2 H, $\mathrm{SiCH_2}$), 1.58−1.69 (m, 2 H, $\mathrm{SiCH_2}$), 2.09−2.39 (m, 2 H, $\mathrm{PCH_2}$), 2.47−2.58 (m, 2 H, $\mathrm{PCH_2}$), 6.77−7.73 (m, 20 H, Ph).^{13}C NMR (62.90 MHz, $\mathrm{C_6D_6}$): δ 19.7 (d, $\mathrm{SiCH_2}$, $^2J_{\mathrm{PCC}} = 18.5$), 21.6 (dd, $\mathrm{SiCH_2}$ [chel.], $J_{\mathrm{PC}} = 19.9$ Hz, $J_{\mathrm{PC}} = 3.8$ Hz), 29.3 (d, $\mathrm{PCH_2}$, $^1J_{\mathrm{PC}} = 27.2$ Hz), 32.1 (dd, $\mathrm{PCH_2}$ [chel.], $^1J_{\mathrm{PC}} = 36.8$ Hz, $^1J_{\mathrm{PC}} = 9.5$ Hz), 127.3−144.4 (Ph).

(10) ^{31}P{^{1}H} NMR (101.25 MHz, $\mathrm{C_6D_6}$): main product **1b**, δ 49.7 (d, $^2J_{\mathrm{PPtP}} = 13.4$ Hz, $^1J_{\mathrm{PtP}} = 2074.0$), 24.7 (d, $^1J_{\mathrm{PtP}} = 1307.4$ Hz). Byproduct (∼10%). $\mathrm{[(Ph_3P)\overline{Pt(Ph_2PCH_2CH_2Si}PhMe)Ph]}$, δ 50.1 (d, $^2J_{\mathrm{PPtP}} = 12.2$ Hz, $^1J_{\mathrm{PtP}} = 2036.2$ Hz), 26.5 (d, $^1J_{\mathrm{PtP}} = 1328.1$ Hz).

(11) A solution of 51 mg (123 mmol) of $\mathrm{Ph_2PCH_2CH_2SiPh_2Me}$ in 1.5 mL of benzene and then a solution of 21 mg (177 mmol) of $\mathrm{PEt_3}$ in 1.0 mL of benzene was added to a solution of 92 mg (123 mmol) of $\mathrm{(Ph_3P)_2\text{-}Pt(C_2H_4)}$ in 8 mL of benzene under an atmosphere of dry argon. An immediate color change to orange occurred, and gas was evolved. The solution was stirred for 30 min and then slowly heated to 75 °C and held at this temperature for 21 h. After the solution was cooled to room temperature, all volatiles were then removed in vacuo, leaving a yellow oil. ^{31}P{^{1}H} NMR (101.25 MHz, $\mathrm{C_6D_6}$): δ 50.6 (d, $^2J_{\mathrm{PPtP}} = 14.6$ Hz, $^1J_{\mathrm{PtP}} = 2054.5$ Hz), 13.4 (d, $^1J_{\mathrm{PtP}} = 1390.4$ Hz, $^2J_{\mathrm{PPtSi}} = 156.2$ Hz). ^{1}H NMR (250.13 MHz, $\mathrm{C_6D_6}$): δ 0.59 (d, 3 H, SiMe, $^4J_{\mathrm{PPtSiCH}} = 2.1$ Hz, $^3J_{\mathrm{PtSiCH}} = 24.7$ Hz), 0.69−0.75 (m, 9 H, CMe), 0.95−1.15 (m, 6 H, $\mathrm{PCH_2\text{-}Me}$), 1.31−1.54 (m, 2 H, $\mathrm{SiCH_2}$), 2.25−2.45 (m, 2 H, $\mathrm{PCH_2}$), 6.99−7.76 (m, 10 H, Ph).^{13}C NMR (62.90 MHz, $\mathrm{C_6D_6}$): δ −0.4 (d, $\mathrm{SiCH_3}$, $^3J_{\mathrm{PPtSiC}} = 3.7$ Hz, $^3J_{\mathrm{PPtSiC}} = 68.4$ Hz), 15.1, 15.2 ($\mathrm{SiCH_2}$ and $\mathrm{C{\mathit{C}}H_3}$, $^2J_{\mathrm{PCC}} = 20.3$ Hz), 20.1 (d, $\mathrm{PCH_2}$, $^1J_{\mathrm{PC}} = 65.7$ Hz), 20.1 (dd, $\mathrm{PCH_2}$, $^1J_{\mathrm{PC}} = 37.9$ Hz, $^4J_{\mathrm{PPtPC}} = 10.6$ Hz), 127.0−147.1 (Ph), 162.3 (dd, ipso-$\mathrm{C_{Ph}}$, $^2J_{\mathrm{PPtC}} = 96.2$ Hz, $^2J_{\mathrm{PPtC}} = 13.4$).