Insertion of Acetylenes into the Si–Pt Bond Affording (β-Silylvinyl)platinum Complexes

Hiroshi Yamashita, Masato Tanaka,* and Midori Goto

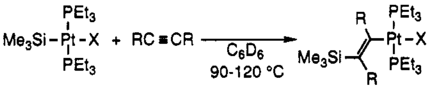
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

Received November 9, 1992

Summary: Acetylenes RC≡CR (R = Ph, Pr) inserted into the Si–Pt bond of trans-$Me_3SiPtX(PEt_3)_2$ *(X = Br, I) to give trans-(E)-*$Me_3Si(R)C{=}C(R)PtX(PEt_3)_2$ *and its stereoisomers. The structure of trans-(E)-*$Me_3Si(Ph)C{=}C(Ph)PtBr(PEt_3)_2$ *was determined by X-ray crystallography. The reactivity of trans-*$Me_3SiPtBr(PEt_3)_2$ *toward PhC≡CPh was remarkably higher than that of trans-*$HPtBr(PEt_3)_2$.

Organosilicon compounds have attracted increasing attention for their synthetic utility and unique physicochemical properties.[1] In order to develop new catalysis for organosilicon compounds, a basic understanding of the reactivities of silicon–metal bonds[2,3] is indispensable. Among various processes that silicon–metal bonds undergo, addition to acetylenes is one of the key elemental steps behind the catalysis, although direct evidences have been still rare.[4,5] Herein are reported the first examples of the (β-silylvinyl)platinum complexes obtained by the insertion of acetylenes into the Si–Pt bond and the remarkably large difference in reactivity between the Si–Pt species and a H–Pt analogue.

When a mixture of *trans*-$Me_3SiPtBr(PEt_3)_2$ (**1a**;[5b,6] 0.02 mmol, 0.1 M), diphenylacetylene (**2a**; 0.04 mmol), and benzene-d_6 (0.2 mL) was heated under nitrogen in a sealed NMR tube at 90 °C for 3.5 h, the Me_3Si–Pt proton signal at 0.48 ppm ($^3J_{HPt}$ = 25.5 Hz) declined (75% conversion) with concomitant appearance of new singlet MeSi signals at 0.03 (species A), 0.12 (B), 0.56 (C), and 0.68 ppm (D) (32:2:45:21). After heating for 12.5 h, 98% of **1a** was consumed, and the integral ratio of the MeSi signals for A–D changed to 45:1:53:1.[7] Further heating at 120 °C for 15.5 h caused the conversion of C into A (A:B:C:D = 94:0:6:0, 86% NMR yield for A). The reaction mixture was concentrated, and pentane (0.3 mL) was added to the residue. Slow cooling of the solution down to −30 °C gave pale yellow needles of *trans*-(*E*)-$Me_3Si(Ph)C{=}C(Ph)PtBr(PEt_3)_2$ (*trans*-(*E*)-**3a**, 59% yield), which was considerably stable to air and moisture in the solid state and even in solutions for short periods. The spectral and analytical data[8] were very consistent with the proposed formula. The structure was finally confirmed by X-ray diffraction analysis (vide infra).[9] Thus, the insertion of **2a** into the Si–Pt bond of **1a** was unequivocally verified (eq 1).[10,11]



(1)

1a: X = Br
1b: X = I
2a: R = Ph
2b: R = Pr
trans-(E)-**3a**: X = Br, R = Ph
trans-(E)-**3b**: X = I, R = Ph
trans-(E)-**3c**: X = I, R = Pr

Complex *trans*-(*E*)-**3a** (Figure 1) has a slightly distorted square-planar geometry, with the dihedral angle between the planes P(1)–Pt–Br and P(2)–Pt–C(1) being 5.7°. The

---

(1) (a) *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989. (c) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990.

(2) For reviews, see: (a) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1. (b) Tilley, T. D. Reference 1b, p 1415. (c) Schubert, U. *Transition Met. Chem.* **1991**, *16*, 136.

(3) For our recent studies on the reactivities of silylplatinum complexes toward unsaturated compounds and the related catalytic reactions, see: (a) Kobayashi, T.-a.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (b) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (c) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (d) Hayashi, T.; Kobayashi, T.-a.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (e) Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.-a.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563. (f) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (g) Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992**, 45. (h) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1. (i) Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639.

(4) To our knowledge, unambiguous examples of the isolation of the addition products seem to have been limited to those for the insertion of activated acetylenes ($F_3C{-}C{\equiv}C{-}X$; X = H, CF_3) into Si—Mn and Si—Fe bonds, and the yields of the products seem to be low (<20%). (a) Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *J. Organomet. Chem.* **1970**, *24*, 145. (b) Clark, H. C.; Hauw, T. L. *J. Organomet. Chem.* **1972**, *42*, 429.

(5) For the reactivities of silylplatinum or silylnickel complexes toward acetylenes, see the following. Si—Pt: (a) Reference 3a–c,f. (b) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1967**, 1066. (c) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107. (d) Eaborn, C.; Tune, D. J.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2255. (e) Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181. (f) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1977**, *131*, 377. Si—Ni: (g) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 105.

(6) Yamashita, H.; Hayashi, T.; Kobayashi, T.-a.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417.

(7) Small amounts of Me_3SiBr (~3%) and $(Me_3Si)_2O$ (~4%) were also formed. When the reaction temperature was higher (120 °C, 1 h, ~100% conversion) or the concentration of **1a** was lower (0.03 M, 5 h, 96% conversion), these amounts decreased to ~1% and ~3% or ~0% and ~2%, respectively.

(8) *trans*-(*E*)-**3a**: mp 181–183 °C (under N_2); ^1H NMR (C_6D_6) δ 0.04 (s, 9H, $SiCH_3$), 0.84 (tt, $^3J_{HH} \approx {}^3J_{HP} \approx 7.8$ Hz, 18H, $PCCH_3$), 1.91 (qt, $^1/_2(^3J_{HH}) \approx {}^2J_{HP} \approx 3.9$ Hz, $^3J_{HPt} \approx 22$ Hz, 12H, PCH_2), 7.02–7.33 and 7.58–7.82 (each m, 10H, C_6H_5); ^{31}P NMR (C_6D_6) δ 2.6 ($^1J_{PPt}$ = 2903 Hz); IR (KBr) 1595 (m), 1504 (m), 1489 (m), 1481 (m), 1460 (m), 1439 (m), 1417 (m), 1261 (m), 1247 (s), 1052 (m), 1033 (s), 1013 (m), 946 (s), 857 (s), 841 (s), 783 (m), 762 (s), 748 (m), 733 (s), 702 (s), 687 (m), 609 (m) cm^{-1}. Anal. Calcd for $C_{29}H_{49}BrP_2PtSi$: C, 46.57; H, 6.48. Found: C, 46.12; H, 6.11.

(9) Crystal data for *trans*-(*E*)-**3a**: $PtBrP_2SiC_{29}H_{49}$, monoclinic, space group $P2_1/c$, a = 13.571 (2) Å, b = 10.881 (1) Å, c = 22.324 (5) Å, β = 92.83 (1)°, V = 3292.3 (9) Å^3, Z = 4, D_{calcd} = 1.539 g cm^{-3}, μ(Cu Kα) = 110.74 cm^{-1}. Data collection was performed by a CAD4 (Enraf-Nonius) diffractometer with graphite-monochromated Cu Kα radiation. A crystal was sealed in a glass capillary tube, and an empirical absorption correction (ψ scan) was applied to the data. The structure was solved by MULTAN 78, and the program system UNICS III was used for calculations. A total of 5846 reflections ($|F_o| \geq 3\sigma|F_o|$) were used. Ten hydrogen atoms were taken from a difference Fourier map; the remainder were located with calculated positions. Refinement was by full-matrix least squares, R = 0.067 (R_w = 0.081); the positional and temperature factors of hydrogen atoms were fixed. Further details of the structure determination (atom coordinates and thermal parameters, complete bond lengths and angles, and structure factors) have been deposited.

(10) Although the reaction of *trans*-$Me_3SiPtCl(PEt_3)_2$ with phenylacetylene was previously examined,[5b] the identified silicon-containing products were Me_3SiCl, Me_3SiH, and the volatile secondary products from them ($(Me_3Si)_2O$, $PhCH{=}CHSiMe_3$, etc.).

(11) Recently a catalytic reaction which suggested insertion of acetylenes into the Si—Pd bond of the Si—Pd—I linkage was reported: Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778.

0276-7333/93/2312-0988$04.00/0

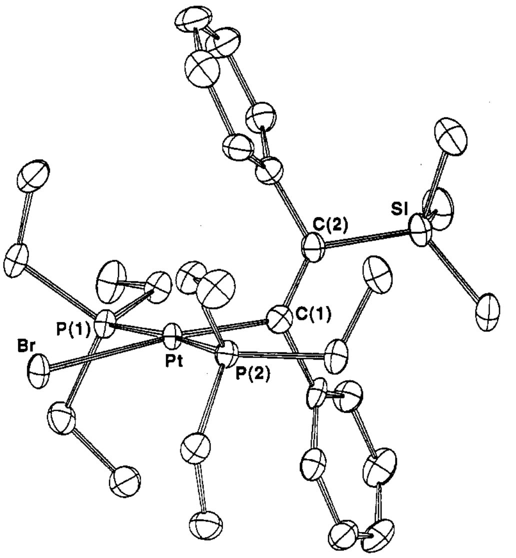


Figure 1. Perspective view of the molecular structure of *trans*-(*E*)-**3a**. Selected bond lengths (Å) and angles (deg) are as follows: Pt–P(1) = 2.289(2), Pt–P(2) = 2.334(2), Pt–Br = 2.541(1), Pt–C(1) = 2.053(9), C(1)–C(2) = 1.361(14), C(2)–Si = 1.894(9); P(1)–Pt–Br = 86.93(6), P(2)–Pt–Br = 86.09(6), P(1)–Pt–C(1) = 91.5(3), P(2)–Pt–C(1) = 95.4(3).

two PEt_3 ligands are bound to the platinum center in the positions trans to each other. The C=C double bond is projecting nearly vertically from the $BrCPtP_2$ mean plane; the dihedral angle between the plane Pt–C(1)–C(2) and the mean plane is 85.6°. The stereochemistry of the double bond is *E*, and the bulky Me_3Si group is situated in the position opposite the sterically large platinum moiety.

A separate experiment (120 °C, 1 h) gave a reaction mixture which showed the two proton signals arising from species A (=*trans*-(*E*)-**3a**) and C (65:35). ^{31}P NMR also displayed the two signals which corresponded to *trans*-(*E*)-**3a** (2.6 ppm ($^1J_{PPt}$ = 2903 Hz)) and another *trans*-bis(phosphine) complex (−0.9 ppm ($^1J_{PPt}$ = 2896 Hz)). The treatment of the mixture with Et_2Zn (1 M hexane solution, ~40 equiv) in toluene at the reflux temperature afforded (*Z*)- and (*E*)-$Me_3Si(Ph)C{=}CHPh$ ((*Z*)- and (*E*)-**4a**;[12] *Z*:*E* = 78:22). The formation of isomeric **4a**'s can be rationalized by the ethylation of (*E*)- and (*Z*)-$Me_3Si(Ph)C{=}C(Ph)PtBr(PEt_3)_2$ with Et_2Zn via transmetalation followed by *β*-hydride migration in the resulting Et–Pt species and a subsequent reductive-elimination process.[13] Accordingly, the second complex present in the original mixture could be safely assigned to *trans*-(*Z*)-$Me_3Si(Ph)C{=}C(Ph)PtBr(PEt_3)_2$ (*trans*-(*Z*)-**3a**).

As to species D, corresponding ^{31}P NMR signals were found, during the progress of the reaction, at −3.6 (d, $^2J_{PP} \approx 16$ Hz, $^1J_{PPt}$ = 4337 Hz, P trans to Br) and 3.5 ppm (d, $^2J_{PP} \approx 16$ Hz, $^1J_{PPt}$ = 1590 Hz, P trans to C). The strong trans influence of an alkenyl ligand as compared with bromide[14] observed in the ^{31}P NMR and the similarity in ^1H NMR chemical shifts of the MeSi signals between C (0.56 ppm) and D (0.68 ppm) seem to suggest that species D is *cis*-(*Z*)-**3a**. On the basis of the foregoing identification of A, C, and D and the comparison of the ^1H NMR chemical shifts of the MeSi signals, species B may be *cis*-(*E*)-**3a**. However, the ^{31}P NMR signals corresponding to B could not be clearly distinguished because of its small quantity.

In the place of **1a**, *trans*-$Me_3SiPtI(PEt_3)_2$ (**1b**)[6] also reacted with **2a** (90 °C, 80 min + 120 °C, 20 min) to give a *trans*-(*E*)-(*β*-silylvinyl) complex (*trans*-(*E*)-**3b**, 94% ^1H NMR and 74% isolated yields).[15] The reactivity of **1b** was much higher than that of **1a**; the conversion (90 °C, 20 min) of **1b** or **1a** was ~100% or 16%, respectively. The strong trans influence of the iodide ligand as compared with the bromide ligand[14] would make the Si–Pt bond weaker to result in facilitating the insertion of **2a**. 4-Octyne (**2b**) also inserted into the Si–Pt bond of **1b** (90 °C, 80 min + 120 °C, 100 min) to give *trans*-(*E*)-$Me_3Si(Pr)C{=}C(Pr)PtI(PEt_3)_2$ (*trans*-(*E*)-**3c**, 94% ^1H NMR and 76% isolated yields).[16] However, the rate was considerably lower than that for **2a**; the conversion of **1b** (90 °C, 20 min) was ~100% for **2a**, while it was 29% for **2b**. The *E* structures of *trans*-(*E*)-**3b** and *trans*-(*E*)-**3c** were confirmed by their transformation to the known compounds (*Z*)-**4a** and (*Z*)-$Me_3Si(Pr)C{=}CHPr$ ((*Z*)-**4b**),[17] upon Et_2Zn treatment as mentioned above.[18] The complexes *trans*-(*E*)-**3b** and *trans*-(*E*)-**3c** were also considerably stable to air and moisture. During the reactions of **2b**, other species assignable to *trans*-(*Z*), *cis*-(*E*), and/or *cis*-(*Z*) isomers could also be found by NMR.[19] However, the maximum contents of *trans*-(*Z*)-**3b** (~5%) and *trans*-(*Z*)-**3c** (~5%), which were obtained at the end of the reactions, were much smaller than that of *trans*-(*Z*)-**3a** (90 °C, 12.5 h, 48%), indicative of somewhat different reactivities between **1b** and **1a** (vide infra). Besides **2a** and **2b**, 1-phenylpropyne and 1,4-diphenylbutadiyne also reacted with **1b** to give (*β*-silylvinyl)platinum complexes (NMR monitoring), although further studies are required to confirm the structures.

In the insertion of **2a** into **1a**, addition of PEt_3 remarkably suppressed the reaction; the conversion (added PEt_3/equiv) of **1a** (0.03 M) at 90 °C for 5 h was 96% (0), 11% (0.4), ~6% (1, 2, and 4). Under these conditions, the complex **1a** did not react at all with the added phosphine to form any tris(phosphine) complexes such as

---

(12) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Org. Chem.* **1987**, *52*, 1276.

(13) For reactions involving *β*-hydride migration, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 386. In the present system, partial isomerization between some *E* and *Z* species seems to take place during the reaction with Et_2Zn.

(14) For instance, see: (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

(15) *trans*-(*E*)-**3b**: mp 186–187 °C (under N_2); ^1H NMR (C_6D_6) δ 0.04 (s, 9H, $SiCH_3$), 0.80 (tt, $^3J_{HH} \approx {}^3J_{HP} \approx 7.8$ Hz, 18H, $PCCH_3$), 2.05 (qt, $^1/_2(^3J_{HH}) \approx {}^2J_{HP} \approx 3.9$ Hz, $^3J_{HPt} \approx 22$ Hz, 12H, PCH_2), 7.03–7.30 and 7.61–7.81 (each m, 10H, C_6H_5); ^{31}P NMR (C_6D_6) δ −2.0 ($^1J_{PPt}$ = 2854 Hz); IR (KBr) 1593 (m), 1506 (m), 1489 (m), 1454 (m), 1437 (m), 1415 (m), 1379 (m), 1245 (s), 1172 (m), 1035 (s), 944 (s), 851 (s), 835 (s), 781 (m), 762 (s), 725 (s), 698 (s), 625 (m), 607 (m) cm^{-1}. Anal. Calcd for $C_{29}H_{49}IP_2PtSi$: C, 43.02; H, 6.10. Found: C, 43.23; H, 5.83.

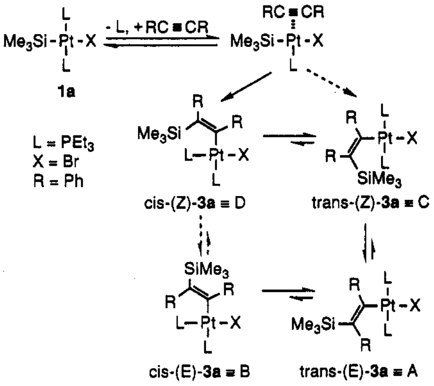
(16) *trans*-(*E*)-**3c**: mp 164–166 °C (under N_2); ^1H NMR (C_6D_6) δ 0.31 (s, 9H, $SiCH_3$), 0.98 (tt, $^3J_{HH} \approx {}^3J_{HP} \approx 7.8$ Hz, 18H, $PCCH_3$), 1.03 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $=CCCCH_3$), 1.37–1.61 and 1.78–2.02 (each m, 4H $=CCCH_2$), 2.02 (qt, $^1/_2(^3J_{HH}) \approx {}^2J_{HP} \approx 3.9$ Hz, $^3J_{HPt} \approx 22$ Hz, 12H, PCH_2), 2.31–2.76 (m, 4H, $=CCH_2$); ^{31}P NMR (C_6D_6) δ 4.0 ($^1J_{PPt}$ = 2920 Hz); IR (KBr) 1537 (s), 1458 (s), 1410 (m), 1375 (m), 1245 (s), 1151 (m), 1035 (s), 1000 (m), 847 (s), 835 (s), 760 (s), 719 (m), 677 (m), 625 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{53}IP_2PtSi$: C, 37.25; H, 7.20. Found: C, 37.50; H, 7.10.

(17) Hudrlik, P. F.; Kulkarni, A. A.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877.

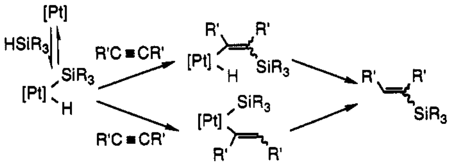
(18) From *trans*-**3b** (*E*:*Z* = ≥99:1) or *trans*-**3c** (*E*:*Z* = 97:3), **4a** (*Z*:*E* = 95:5) or **4b** (*Z*:*E* = 90:10) was obtained, respectively.

(19) ^1H NMR (δ, ppm, $SiCH_3$): *trans*-(*Z*)-**3b**, 0.53 (s); *cis*-(*E* or *Z*)-**3b**, 0.15 (s); *trans*-(*Z*)-**3c**, 0.48 (s); *cis*-(*E* or *Z*)-**3c**, 0.42 (s). ^{31}P NMR (δ, ppm): *trans*-(*Z*)-**3b**, −5.5 ($^1J_{PPt}$ = 2847 Hz); *cis*-(*E* or *Z*)-**3b**, −4.3 (d, $^2J_{PP} \approx 15$ Hz, $^1J_{PPt}$ = 4209 Hz, P trans to I), 1.5 (d, $^2J_{PP} \approx 15$ Hz, $^1J_{PPt}$ = 1646 Hz, P trans to C); *cis*-(*E* or *Z*)-**3c**, −2.6 (d, $^2J_{PP} \approx 16$ Hz, $^1J_{PPt}$ = 4280 Hz, P trans to I), 2.1 (d, $^2J_{PP} \approx 16$ Hz, $^1J_{PPt}$ = 1494 Hz, P trans to C). The ^{31}P NMR signals for *trans*-(*Z*)-**3c** were not clearly distinguished because of their weak intensity.

Scheme I



Scheme II



$[Me_3SiPt(PEt_3)_3]^+Br^-$ and $Me_3SiPtBr(PEt_3)_3$ as judged from ^1H NMR (taken at added PEt_3/**1a** = 0–4; 0.48 ppm ($^3J_{HPt}$ = 25.5 Hz, $SiCH_3$)) and ^{31}P NMR (taken at PEt_3/**1a** = 0–1; 18.6 ppm ($^1J_{PPt} \approx$ 2864 Hz)). Accordingly, the suppression is probably not due to the transformation of **1a** to a less reactive species such as $[Me_3SiPt(PEt_3)_3]^+Br^-$ [20] but is due to the prevention of phosphine dissociation somehow involved in the reaction sequence. On the other hand, the reaction of **1a** with **2a** was accelerated by decreasing the concentration of **1a**; the conversion of **1a** (90 °C, 2 h) was 46% for 0.1 M, while it was 72% for 0.03 M.

As far as the reaction of **1a** is concerned, the foregoing results seem to be best explained by the following sequence of events (Scheme I). The phosphine dissociation followed by cis addition of the Si–Pt bond to the acetylene affords *cis*- and *trans*-(*Z*)-**3a** (D and C, respectively), which were observed as transient intermediates.[21] The cis isomer (D) readily isomerizes to the trans isomer (C), which further isomerizes, albeit at somewhat lower rate, to the thermodynamically most stable *trans*-(*E*)-**3a** (A). The time-dependent distribution among **3a**'s is fully consistent with the reaction pathways shown in Scheme I. On the other hand, as another mechanistic possibility, one can envision direct formation of the *E* isomers via electron transfer from the platinum species to the acetylene, as was demonstrated for the insertion of acetylenes into the H–Pt bond.[22] Although we cannot provide convincing evidence at present, such an alternative mechanism may be valid for the formation of **3b**'s and **3c**'s, judging from the time course of these reactions.

Finally, it is noteworthy that **1a** showed remarkably higher reactivity than the corresponding hydride *trans*-$HPtBr(PEt_3)_2$ (**5**). Thus, **1a** smoothly reacted with **2a** at 90 °C (12.5 h, 98% conversion, vide supra), while **5** remained almost intact under the same conditions. Although additional studies are required, the results suggest that platinum-complex-catalyzed hydrosilylation of acetylenes may proceed under certain conditions via insertion of acetylenes into the Si–Pt bond rather than into the H–Pt bond (Scheme II).[23]

Further investigations on the mechanistic details and on the reactivities of other unsaturated compounds toward silicon–metal bonds are under way.

Supplementary Material Available: Tables of crystal data, atom coordinates and thermal parameters, and complete bond lengths and angles and a figure giving a perspective view for *trans*-(*E*)-**3a** (10 pages). Ordering information is given on any current masthead page.

OM920709H

---

(20) We thank the reviewer for bringing us to consider this possibility.

(21) We cannot rigorously exclude alternative possible intermediates such as the pentacoordinate species $Me_3SiPtXL_2(RC{\equiv}CR)$ and/or the ionic species $[Me_3SiPtL_2(RC{\equiv}CR)]^+X^-$, in place of the $Me_3SiPtXL(RC{\equiv}CR)$ species. An ionic intermediate has been proposed for the insertion of acetylenes into the H—Pt bond of *trans*-$HPtCl(PEt_3)_2$ in polar solvents.[22]

(22) Acetylene insertion into the H—Pt bond has been well studied by Clark et al. See: Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961 and references cited therein.

(23) For details of a recent controversy about the mechanism of hydrosilylation, see: Reference 2b, p 1458.