Extremely Facile Oxidative Addition of Silyl, Germyl, and Stannyl Tellurides and Other Chalcogenides to Platinum(0) Complexes. X-ray Structure of *trans*-Pt(4-PhC$_6$H$_4$Te)(SiMe$_3$)(PEt$_3$)$_2$

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Silyl chalcogenides and heavier congeners (RZ−MR′$_3$, Z = chalcogen element, M = Si, Ge, Sn), having a large share in organochalcogen chemistry, are of great synthetic utility[1] and provide important starting materials for transition metal−chalcogen clusters and nanoparticles of intriguing optical and electronic properties.[2] However, the reactivity of these Z−M bonds toward transition metal species remains totally unexplored. Herein we disclose extremely facile oxidative addition of RZ−MMe$_3$ to Pt(PEt$_3$)$_n$ (n = 3, 4) to afford *trans*-Pt(RZ)-(MMe$_3$)(PEt$_3$)$_2$.[3]

When PhTeSiMe$_3$ (0.247 mmol) was slowly added to Pt-(PEt$_3$)$_3$ (0.183 mmol) in C$_6$D$_6$ (0.5 mL) at room temperature, the color of the solution changed instantly from brown to red. As confirmed by ^{31}P NMR, starting Pt(PEt$_3$)$_3$ was completely consumed within 5 min while two new singlets ascribable to free PEt$_3$ and *trans*-Pt(TePh)(SiMe$_3$)(PEt$_3$)$_2$ (**1a**; δ 10.9 ppm, J_{PPt} = 2837.2 Hz), formed *via* selective oxidative addition of the Si−Te bond to platinum, were emerging. No other product was found by NMR.[4,5] The structure of **1a** was further confirmed by NMR spectroscopy. Thus, a singlet of Me$_3$Si bearing a satellite due to the coupling with platinum ($^3J_{HPt}$ = 20.1 Hz) was observed at δ 0.515 ppm in ^{1}H NMR. ^{29}Si NMR was more informative; Me$_3$Si displayed a triplet at δ −7.1 ($^2J_{PSi}$ = 8.5 Hz) due to the coupling with the two *cis*-PEt$_3$ ligands, and the signal was accompanied by a satellite arising from the coupling with the directly bound platinum ($^1J_{SiPt}$ = 1081.7 Hz). In a separate experiment run in hexane, analytically pure **1a** was readily isolated in 85% yield as a red solid by simply cooling the reaction mixture to −80 °C (eq 1). Although further purification of this and other similar complexes was not easy

Figure 1. Molecular structure of *trans*-Pt(4-PhC$_6$H$_4$Te)(SiMe$_3$)(PEt$_3$)$_2$ (**1b**). Selected bond lengths (Å) and angles (deg): Si−Pt = 2.351(6), Te−Pt = 2.764(2), P(1)−Pt = 2.282(5); Si−Pt−Te = 156.9(2), P(1)−Pt−P(2) = 156.4(2), P(1)−Pt−Si = 92.7(2), P(2)−Pt−Si = 95.0(2), P(1)−Pt−Te = 92.6(2), P(2)−Pt−Te = 88.9(2).

1a, R = Ph, M = Si, 85%   **1e**, R = Ph, M = Ge, 90%
1b, R = 4-biphenyl, M = Si, 91%   **1f**, R = Ph, M = Sn, 76%
1c, R = Bu, M = Si, quant. (NMR)   **1g**, R = Me$_3$Sn, M = Sn, 88%
1d, R = Me$_3$Si, M = Si, 77%

because of their instability,[6] the detailed study on their decomposition (*vide infra*) allowed us to safely recrystallize **1b**, a biphenyl analogue of **1a**, in the presence of PEt$_3$ to isolate crystals suitable for X-ray analysis.

Complex **1b** has a distorted *trans* square-planar structure (Figure 1). The Si−Pt−Te angle is 156.9°, which is much smaller than 174.9° for C−Pt−Te in analogous *trans*-PtPh-(TePh)(PEt$_3$)$_2$ (**3a**)[5] and close to 157.4° for Si−Pt−Br in *trans*-PtBr(SiMe$_3$)(PEt$_3$)$_2$,[3a] indicating a serious steric repulsion between the bulky Me$_3$Si group and PEt$_3$.

BuTeSiMe$_3$ reacted with Pt(PEt$_3$)$_3$ as selectively, affording **1c** quantitatively. Furthermore, the reactions with germyl and stannyl tellurides also resulted in the selective cleavage of Ge−Te and Sn−Te bonds.[7] Thus, the procedure offers a general and high yield access to a series of (silyl)-, (germyl)-, and (stannyl)(telluro)platinum complexes (**1a−g**), which can be readily isolated as red solids though they are extremely air- and moisture-sensitive (eq 1).

In contrast to the tellurides, no reaction was observed between PhSSiMe$_3$ and Pt(PEt$_3$)$_3$ even when a mixture was heated at 50 °C over 5 h.[8] However, PhSeSiMe$_3$ did react, albeit more slowly than PhTeSiMe$_3$, with Pt(PEt$_3$)$_3$. The reaction was reversible. For instance, the reaction of PhSeSiMe$_3$ (0.140 mmol) with Pt(PEt$_3$)$_3$ (0.093 mmol) at room temperature gave a 24% NMR yield of *trans*-Pt(SePh)(SiMe$_3$)(PEt$_3$)$_2$ (**2a**) after 0.5 h, and the system gradually reached equilibrium over a day to form **2a** in 63% yield.[9] The corresponding stannyl selenide PhSeSnMe$_3$ was more reactive; the reaction of PhSeSnMe$_3$ with

(1) Reviews: (a) Armitage, D. A. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1991; pp 213−243. (b) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 2, pp 34−37, 166−174, and 293−296. (c) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, pp 167−177, 443−447, and 604−607.

(2) For example, see: (a) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41. (b) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1079. (c) Behrens, S.; Bettenhausen, M.; Deveson, A. C.; Eichhöfer, A.; Fenske, D.; Lohde, A.; Woggon, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2215. (d) Fischer, J. M.; Piers, W. E.; Batchilder, S. D. P.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 283 and references cited therein.

(3) Oxidative addition of Si−heteroatom bonds is a subject of current intense study. See: (a) Yamashita, H.; Hayashi, T.; Kobayashi, T.-a.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417. For reviews on Si−transition metal complexes, see: (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (c) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (d) Tilley, T. D. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1991; pp 245−364. (e) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, pp 1043−1114. See also: (f) Sasaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660. (g) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408. (h) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108.

(4) Pt(PEt$_3$)$_4$ was as reactive as Pt(PEt$_3$)$_3$. Starting PhTeSiMe$_3$ may be occasionally contaminated by (PhTe)$_2$, resulting in the formation of a trace of Pt(PhTe)$_2$(PEt$_3$)$_2$.

(5) Possible formation of Pt(Ph)(TeSiMe$_3$)(PEt$_3$)$_2$ *via* the C−Te bond oxidative addition of PhTeSiMe$_3$ was not found at all, indicative of the highly preferential cleavage of the Si−Te bond. For the C−Te bond oxidative addition, see: Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1997**, *119*, 1795.
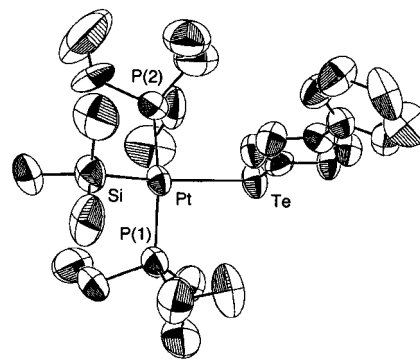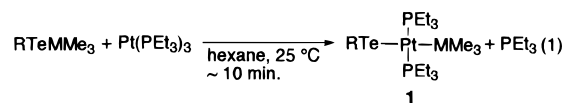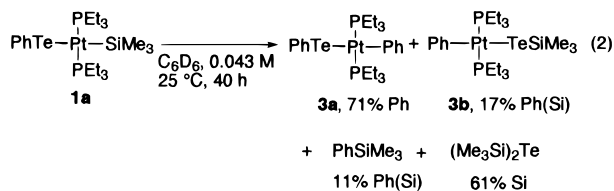
(6) This was not only because of the extreme air and moisture sensitivities of PhTeSiMe$_3$, but also because of an unexpected observation that **1a** formed quantitatively in the solution was disappearing during the evaporation of the volatiles *in vacuo*.

(7) Both PhTeGeMe$_3$ and PhTeSnMe$_3$ are as reactive as PhTeSiMe$_3$ toward Pt(PEt$_3$)$_3$. Though bond dissociation energies for Te−M ($E_{Te−M}$, M = Si, Ge, and Sn) do not appear available, they may be expected to follow an order of Si < Sn as predicted from the facile exchange reaction of PhTeSiMe$_3$ with Me$_3$SnCl ($E_{Cl−Sn}$ = 422 kJ mol^{-1}; see ref 3c, p 523), quantitatively forming PhTeSnMe$_3$ and Me$_3$SiCl ($E_{Cl−Si}$ = 380 kJ mol^{-1}; see ref 3c, p 6). Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879.
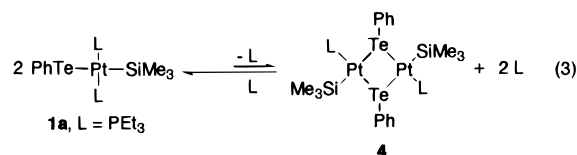
(8) An interesting activation of [(R$_2$SnS)$_3$] by a dimethyl−Pt(II) complex was communicated. Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 1749.

Pt(PEt$_3$)$_3$ took place rapidly (<10 min) at room temperature to afford *trans*-Pt(SePh)(SnMe$_3$)(PEt$_3$)$_2$ (**2b**) in 83% isolated yield. Evidently, the heavier silyl chalcogenides react more readily. Likewise PhSeSnMe$_3$ was more reactive than PhSeSiMe$_3$, which may reflect the strengths of Pt—Sn and Pt—Si bonds.[7,10]

Complex **1a** was stable in the solid state under argon atmosphere,[11] but gradually decomposed in benzene even at room temperature. The extent of the decomposition, when monitored by NMR spectroscopy (concentration 0.043 M), was 65% (after 14 h), 76% (20 h), and more than 90% (40 h). As shown in eq 2, the process formed new complexes **3a** and **3b**

and organosilanes PhSiMe$_3$ and (Me$_3$Si)$_2$Te.[12] Heating at 80 °C resulted in disappearance of **1a** (in C$_6$D$_6$) in 1.5 h. On the other hand, the presence of free PEt$_3$ strongly retarded the decomposition; even an addition of only 1 equiv of PEt$_3$ to a C$_6$D$_6$ solution completely prohibited the process to show no indication of the decomposition over a day at room temperature. Scrupulous studies on the decomposition revealed that the process was also significantly retarded by increasing the concentration; conversions of **1a** after 14 h at room temperature, as a function of its initial concentration (shown in parentheses), were 71% (0.014 M), 65% (0.043 M), and ~6% (0.152 M). Though the detailed decomposition mechanism remains to be elucidated, NMR studies strongly suggest **1a** being in equilibrium with bridged dimer **4** (eq 3).[13] The ^{1}H NMR spectrum of analytically pure **1a** in C$_6$D$_6$ displayed, in addition to the signals arising from **1a**, a weak broad singlet bearing a satellite due to

the coupling with platinum (δ 0.65, $^3J_{HPt}$ = 23.6 Hz) in a slightly low field as compared with the singlet for the Me$_3$SiPt of parent **1a**, while in ^{31}P NMR were observed a broad singlet for free PEt$_3$ (δ −20 ppm) and another broad singlet accompanied by a satellite due to the coupling with platinum (δ 16.1, J_{PPt} = 2651.8 Hz). As anticipated, these new signals completely disappeared when PEt$_3$ (1 equiv) was added. Moreover, the equilibrium composition of **4** was higher in a more diluted solution; integration of the ^{1}H NMR signals for Me$_3$Si moieties in **4** and **1a** indicated that the **4**/**1a** ratios were ~3/97, 7/93, and 17/83 for 0.15, 0.043, and 0.014 M solutions, respectively. The trends obviously agree with the observed dependence of the decomposition rate of **1a** on the concentration.[14]

Complex **1f**, a tin analogue of **1a**, did not decompose in benzene at room temperature and sustained its structural integrity over a day. As anticipated by the lack of decomposition, the ^{1}H NMR spectrum of a C$_6$D$_6$ solution of **1f** did not exhibit any indication of a similar equilibrium at room temperature.

A detailed mechanistic study and synthetic applications are underway.

Supporting Information Available: Experimental details and spectral and/or analytical data of the chalcogenide complexes and a perspective view and tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **1b** (13 pages). See any current masthead page for ordering and Internet access instructions.

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(9) Although very inefficient, palladium-catalyzed addition of PhSeSiMe$_3$ to phenylacetylene, which may involve activation of the Si—Se bond, has been very briefly disclosed in a review article. See: Ogawa, A.; Sonoda, N. *Yuki Gosei Kagaku Kyokaishi* **1993**, *51*, 815.

(10) Reference 3e, pp 1096−1097.

(11) No detectable decomposition was recognized (by ^{1}H and ^{31}P NMR spectroscopies) over one week when the complex was stored at −30 °C. Upon exposure to air, however, it decomposed within a few hours.

(12) Yields shown in the equation were based on **1a** consumed and estimated by ^{1}H and ^{31}P NMR spectroscopies of the crude reaction mixture. A trace of (Me$_3$Si)$_2$O was also occasionally observed (~10%), which was presumed to be formed through a reaction of extremely air- and moisture-sensitive (Me$_3$Si)$_2$Te with oxygen contamination in argon or the solvent. Other possible products from the decomposition such as *trans*-Pt(PhTe)$_2$-(PEt$_3$)$_2$, Pt(Me$_3$Si)$_2$(PEt$_3$)$_2$, and (Me$_3$Si)$_2$ were not detected at all.

(13) Bridged dimeric structures of organotellurium complexes, [Pd(μ-TeAr)(TeAr)PPh$_3$]$_2$, for example, are known. See: Chia, L. Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165.

(14) Events leading to the decomposition are ambiguous at the moment. However, another dimeric four-centered intermediate such as **5** can be envisioned to be involved, based on the structures of the final decomposition products.

Complex **5**