# Regioselective Si–C bond activation in silicon-bridged *ansa*-cycloheptatrienyl-cyclopentadienyl complexes†

**Matthias Tamm,* Andreas Kunst and Eberhardt Herdtweck**

*Received (in Cambridge, UK) 26th November 2004, Accepted 17th January 2005*
*First published as an Advance Article on the web 3rd February 2005*
**DOI: 10.1039/b417884j**

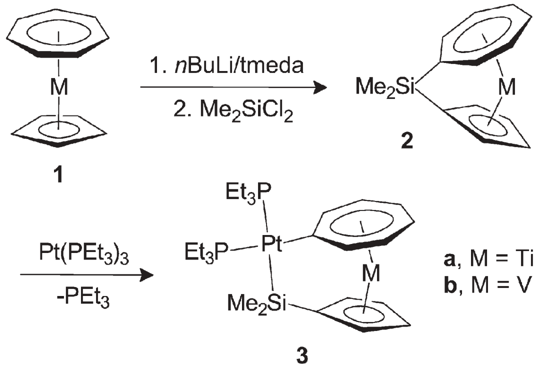
**On treatment with [Pt(PEt$_3$)$_3$], silicon-bridged *ansa*-cycloheptatrienyl-cyclopentadienyl Ti and V complexes, [1]silatroticenophane and [1]silatrovacenophane, undergo oxidative addition and regioselective insertion of a Pt(PEt$_3$)$_2$ moiety into the silicon–carbon bond to the seven-membered ring; the resulting complexes, [2]platinasilatroticenophane and [2]platinasilatrovacenophane, can be partly used as single-source catalysts for the ring-opening polymerization (ROP) of the original highly strained sandwich molecules.**

Poly(ferrocenes) represent the most important class of transition metal-containing macromolecules and are playing an important role in the development of novel polymers with intriguing structural, conductive, magnetic, optical, or redox properties.[1] In most cases, these polymers are accessed by ring-opening polymerization (ROP) of strained [1]ferrocenophanes, which can be initiated thermally or by anionic or transition metal catalysis.[2] In stark contrast, metallocyclophanes containing bridged sandwich moieties other than ferrocene have been much less thoroughly studied. Alternative examples of strained and potentially polymerizable metallocenes comprise [2]cobaltocenophanes[3] as well as [1]- and [2]ruthenocenophanes.[4] In addition, several single atom-bridged bis(benzene)chromium and -vanadium sandwich complexes have been synthesized,[5,6] and their polymerization behaviour has been partly investigated.[5a,5c]

Only recently, the first *ansa*-complexes containing a bridging unit between a cycloheptatrienyl (Cht) and a cyclopentadienyl (Cp) unit have been reported, which could be obtained by the reaction of [(η-C$_7$H$_7$)Ti(η-C$_5$H$_5$)] (troticene, **1a**) or [(η-C$_7$H$_7$)V(η-C$_5$H$_5$)] (trovacene, **1b**) with two equivalents of *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) followed by treatment of the intermediate dilithio complexes with Me$_2$SiCl$_2$ (Scheme 1).[7,8] The resulting [1]silatroticenophane **2a** and [1]silatrovacenophane **2b** are highly strained molecules, which should be strongly susceptible to strain release by undergoing ring-opening polymerization reactions. In fact, a differential scanning calorimetry (DSC) study of **2a** indicated the formation of poly(troticenylsilanes) at about 140–160 °C.[8] Characterization of the resulting material is hampered by its air- and moisture-sensitivity as well as by its poor solubility in common organic solvents. NMR experiments, however, suggest that an irregular polymer is formed, which includes all possible Cp–Si–Cp, Cht–Si–Cht and Cp–Si–Cht linkages.

Alternatively, transition metal-catalyzed ROP would allow the study of polymer formation under milder conditions[2] and might result in regioselective Si–C bond activation as demonstrated by the polymerization of an unsymmetric [1]silaferrocenophane containing bridged C$_5$H$_4$ and C$_5$Me$_4$ rings.[9] As it has also been demonstrated before that the reaction of [1]silaferrocenophanes with stoichiometric amounts of platinum(0) complexes results in oxidative addition and formation of isolable [2]platinasilaferrocenophanes,[10] we set out to investigate similar insertion reactions with complexes **2**. Thus, addition of equimolar amounts of **2a** to a solution of [Pt(PEt$_3$)$_3$][11] in toluene led to the isolation of a green crystalline compound after stirring at room temperature for 15 h and recrystallization from hexane (Scheme 1). The $^{31}$P NMR spectrum exhibits two resonance signals with a P–P coupling of 17 Hz and with Pt–P couplings of 994 and 2108 Hz, respectively, revealing that insertion of a Pt(PEt$_3$)$_2$ moiety into one of the Si–C bonds in **2a** must have occurred. Furthermore, the observation of Pt satellites ($^3J_{\mathrm{HPt}}$ = 67 Hz) for the α-C$_7$H$_6$ proton resonance unequivocally confirms the regioselective cleavage of the bond between silicon and the seven-membered ring. In agreement with the formation of the [2]platinasilatroticenophane **3a**, strong couplings to the Pt-195 and P-31 nuclei are only detected for the $^{13}$C NMR resonances of the cycloheptatrienyl carbon atoms.†

In a similar fashion as described for the synthesis of **3a**, treatment of the [1]silatrovacenophane **2b** with [Pt(PEt$_3$)$_3$] affords the [2]platinasilatrovacenophane **3b** as blue-grey crystals after recrystallization from hexane/thf solution (Scheme 1). Since **2b** and **3b** are paramagnetic and contain one unpaired electron, both compounds have been characterized by means of elemental analysis and EPR spectroscopy.†



**Scheme 1**

---

† Electronic supplementary information (ESI) available: experimental section including the syntheses, full characterization, and spectroscopic data of all the new compounds. See http://www.rsc.org/suppdata/cc/b4/b417884j/

*matthias.tamm@ch.tum.de

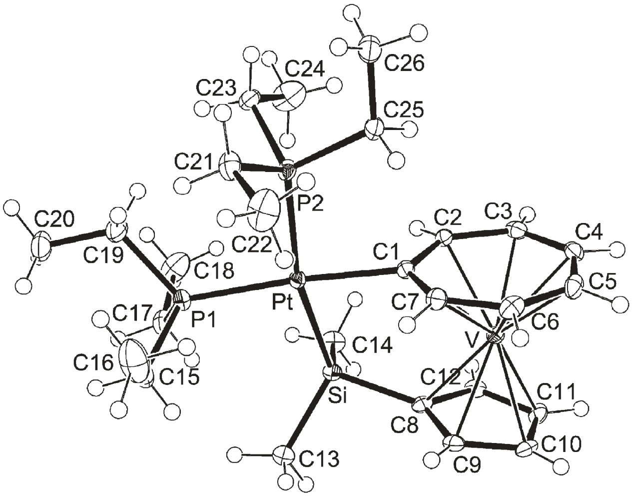


**Fig. 1** ORTEP drawing of **3b** with thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°) of **3a** (M = Ti); values for **3b** (M = V) are given in square brackets: Pt–P1 2.2962(9) [2.3020(7)], Pt–P2 2.3874(6) [2.3849(6)], Pt–Si 2.3881(8) [2.3900(6)], Pt–C1 2.096(3) [2.092(2)], M–C1 2.196(3) [2.191(2)], M–C2 2.199(3) [2.183(3)], M–C3 2.212(3) [2.186(3)], M–C4 2.215(3) [2.189(3)], M–C5 2.216(3) [2.192(3)], M–C6 2.196(3) [2.176(3)], M–C7 2.184(3) [2.168(3)], M–C8 2.280(3) [2.209(3)], M–C9 2.293(3) [2.222(3)], M–C10 2.333(3) [2.267(3)], M–C11 2.333(3) [2.274(3)], M–C12 2.301(3) [2.236(3)], Si–C8 1.890(3) [1.894(3)]; P1–Pt–P2 99.42(3) [99.38(2)], P1–Pt–Si 92.42(3) [92.37(2)], P2–Pt–C1 84.66(9) [84.89(7)], Si–Pt–C1 83.70(9) [83.59(7)].

To unambiguously confirm the formation of Pt–Si-bridged *ansa*-Cht–Cp complexes, the molecular structures of **3a** and **3b** were determined by X-ray diffraction (Fig. 1).‡ Both compounds are isostructural and crystallize in the orthorhombic space group $P2_12_12_1$. As expected, all Ti–C bond distances in **3a** are slightly longer than the corresponding V–C distances in **3b**. Accordingly, **3a** shows a slightly stronger deviation from an unstrained sandwich structure than **3b** with a larger tilt angle $\alpha$ (13.5 *versus* 10.6°) between the $C_7H_6$ and $C_5H_4$ planes together with a smaller angle $\delta$ at the metal atom defined by the ring centroids (169.1 *versus* 171.9°). Comparison with the molecular structure of **2a** ($\alpha = 24.1°$, $\delta = 160.5°$)[8] reveals that oxidative addition to platinum produces a considerable strain release. Since **2a** additionally exhibits large distortions from planarity at the *ipso*-carbon atoms bonded to silicon, with the largest angle $\beta$ being observed between the $C_7$ plane and the Si–C1 bond ($\beta = 41.1°$ *versus* $\beta' = 28.7°$), the observation of a regioselective insertion into this specific bond can be conclusively explained. Naturally, the analogous angles $\beta$ and $\beta'$ between the ring planes and the Pt–C1 and Si–C8 bond axes are much smaller in **3a** (3.8, 6.8°) and in **3b** (5.7, 7.0°). The platinum centres in both complexes are in a slightly distorted square-planar environment with two different $PEt_3$ ligands. Due to the strong *trans* influence of the silyl substituent, the Pt–P2 distances are significantly longer than the Pt–P1 distances. These distances as well as the Pt–C1 and Pt–Si bond lengths are in reasonable agreement with the values obtained from structural characterization of related [2]platinasilaferrocenophanes (Fig. 1).[10a,10b,10d]

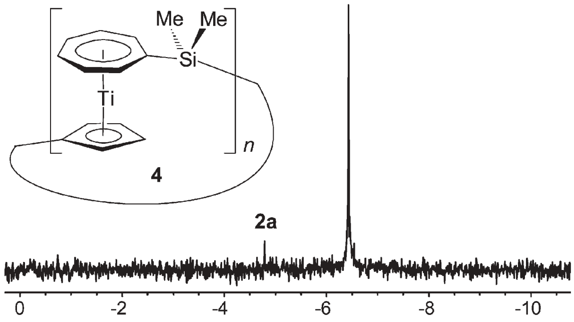


**Fig. 2** $^{29}Si$ NMR spectrum ($\delta$/ppm, $C_6D_6$, 25 °C) of a mixture of oligomers **4** ($n \approx 5$–23).

The observation of regioselective Si–C bond activation in **2a** and **2b** suggests that their metal-catalyzed ring-opening polymerization might result in the formation of regioregular poly(troticenylsilanes) and poly(trovacenylsilanes), respectively, in which the Cp–Cht-sandwich moieties are exclusively linked *via* Cp–Si–Cht bridges. To test this hypothesis, a catalytic amount of **3a** (3 mol%) was added to a solution of **2a** in $C_6D_6$, and the mixture was heated for 64 h at 80 °C. The consumption of **2a** was followed by $^1H$ NMR spectroscopy revealing a gradual increase of broad resonance signals, which can tentatively be assigned to the $C_7H_6$, $C_5H_4$ and $SiMe_2$ protons of a polymeric reaction product. As only one new resonance is observed at −6.43 ppm in the $^{29}Si$ NMR spectrum, it can be concluded that cyclic polymers of type **4** with a single Cp–Si–Cht environment should have formed (Fig. 2).† This assumption can be supported by a MALDI-TOF mass spectrometric characterization of the polymeric material, which was isolated as a light-green powder after extraction with $CH_2Cl_2$ and subsequent precipitation with hexane. Molecular peaks for oligomers **4** can be detected between $m/z = 1301$ ($n = 5$) and 5985 ($n = 23$), and the formation of low molecular weight polymers with a large molecular weight distribution is in agreement with the reported formation of cyclic poly(ferrocenylsilanes) by use of catalytic amounts of a corresponding [2]platinasilaferrocenophane. In contrast to our system, however, $BH_3$-activation was required to remove the inhibiting $PEt_3$ ligands.[10d]

With this contribution, we could demonstrate in principle that regioselective Si–C bond activation and regioregular oligomerization of *ansa*-Cht–Cp complexes can be achieved with Pt(0) complexes. Based on these findings, it can be envisaged that novel metallopolymers might derive from the metal-catalyzed ring-opening polymerization of Lewis-acidic **2a**[8] and of paramagnetic **2b** as well as from their incorporation into other polymeric materials.

**Matthias Tamm,* Andreas Kunst and Eberhardt Herdtweck**
*Lehrstuhl für Anorganische Chemie, Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany. E-mail: matthias.tamm@ch.tum.de; Fax: +49 (89) 289-13473; Tel: +49 (89) 289-13080*

## Notes and references

‡ *Crystal data*: **3a**: $C_{26}H_{46}P_2PtSiTi$, $M$ = 691.61, orthorhombic, $a$ = 7.8446(1), $b$ = 17.6912(1), $c$ = 20.2936(1) Å, $U$ = 2816.35(4) Å$^3$, $T$ = 123 K, space group $P2_12_12_1$ (no. 19), $Z$ = 4, $D_c$ = 1.631 g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 5.414 mm$^{-1}$, 68763 reflections measured, 5155 unique ($R_{int}$ = 0.065) which were used in all calculations. The final $wR(F^2)$ was 0.0366 (all data). CCDC 257302. **3b**: $C_{26}H_{46}P_2PtSiV$, $M$ = 694.68, orthorhombic, $a$ = 7.8629(1), $b$ = 17.7086(1), $c$ = 20.1938(1) Å, $U$ = 2811.80(4) Å$^3$, $T$ = 123 K, space group $P2_12_12_1$ (no. 19), $Z$ = 4, $D_c$ = 1.641 g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 5.471 mm$^{-1}$, 58165 reflections measured,

5129 unique ($R_{\mathrm{int}} = 0.055$) which were used in all calculations. The final $wR(F^2)$ was 0.0294 (all data). CCDC 257303. See http://www.rsc.org/suppdata/cc/b4/b417884j/ for crystallographic data in .cif or other electronic format.

1 I. Manners, *Science*, 2001, **294**, 1664.

2 (*a*) I. Manners, *Chem. Commun.*, 1999, 857; (*b*) P. Nguyen, P. Gómez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515; (*c*) I. Manners and U. Vogel, in *Modern Cyclophane Chemistry*, eds. R. Gleiter and H. Hopf, Wiley-VCH, Weinheim, 2004, p. 415.

3 (*a*) M. J. Drewitt, S. Barlow, D. O'Hare, J. M. Nelson, P. Nguyen and I. Manners, *Chem. Commun.*, 1996, 2153; (*b*) S. Fox, J. P. Dunne, M. Tacke, D. Schmitz and R. Dronskowski, *Eur. J. Inorg. Chem.*, 2002, 3039.

4 (*a*) U. Vogel, A. J. Lough and I. Manners, *Angew. Chem*, 2004, **116**, 3383; U. Vogel, A. J. Lough and I. Manners, *Angew. Chem. Int. Ed.*, 2004, **43**, 3321; (*b*) J. M. Nelson, A. J. Lough and I. Manners, *Angew. Chem*, 1994, **106**, 1019; J. M. Nelson, A. J. Lough and I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 989.

5 (*a*) A. Berenbaum and I. Manners, *Dalton Trans.*, 2004, 2057; (*b*) H. Braunschweig, M. Homberger, C. Hu, X. Zheng, E. Gullo, G. Clentsmith and M. Lutz, *Organometallics*, 2004, **23**, 1968; (*c*) K. C. Hultzsch, J. M. Nelson, A. J. Lough and I. Manners, *Organometallics*, 1995, **14**, 5496; (*d*) C. Elschenbroich, J. Hurley, B. Metz, W. Massa and G. Baum, *Organometallics*, 1990, **9**, 889.

6 (*a*) C. Elschenbroich, E. Schmidt, R. Gondrum, B. Metz, O. Burghaus, W. Massa and S. Wocadlo, *Organometallics*, 1997, **16**, 4589; (*b*) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, A. Behrendt, W. Massa, S. Wocadlo and E. Reijerse, *Inorg. Chem.*, 1995, **34**, 743; (*c*) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, W. Massa, S. Wocadlo and J. Pebler, *Inorg. Chem.*, 1993, **32**, 5421.

7 C. Elschenbroich, F. Paganelli, M. Nowotny, B. Neumüller and O. Burghaus, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1599.

8 M. Tamm, A. Kunst, T. Bannenberg, E. Herdtweck, P. Sirsch, C. J. Elsevier and J. M. Ernsting, *Angew. Chem.*, 2004, **116**, 5646; M. Tamm, A. Kunst, T. Bannenberg, E. Herdtweck, P. Sirsch, C. J. Elsevier and J. M. Ernsting, *Angew. Chem. Int. Ed.*, 2004, **43**, 5530.

9 (*a*) P. Gómez-Elipe, R. Resendes, P. M. Macdonald and I. Manners, *J. Am. Chem. Soc.*, 1998, **120**, 8348; (*b*) P. Gómez-Elipe, P. M. Macdonald and I. Manners, *Angew. Chem.*, 1997, **109**, 780; P. Gómez-Elipe, P. M. Macdonald and I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 762.

10 (*a*) J. B. Sheridan, A. J. Lough and I. Manners, *Organometallics*, 1996, **15**, 2195; (*b*) N. P. Reddy, N. Choi, S. Shimada and M. Tanaka, *Chem. Lett.*, 1996, 649; (*c*) J. B. Sheridan, K. Temple, A. J. Lough and I. Manners, *J. Chem. Soc., Dalton Trans.*, 1997, 711; (*d*) K. Temple, A. J. Lough, J. B. Sheridan and I. Manners, *J. Chem. Soc., Dalton Trans.*, 1998, 2799; (*e*) K. Temple, F. Jäkle, J. B. Sheridan and I. Manners, *J. Am. Chem. Soc.*, 2001, **123**, 1355; (*f*) W. Y. Chan, A. Berenbaum, S. B. Clendenning, A. J. Lough and I. Manners, *Organometallics*, 2003, **22**, 3796.

11 T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, **28**, 119.