

[Me₂Si] *Ansa* bridged complexes of permethyltitanocene: synthesis and structural characterization of fulvene derivatives with trialkyldienemethane character †

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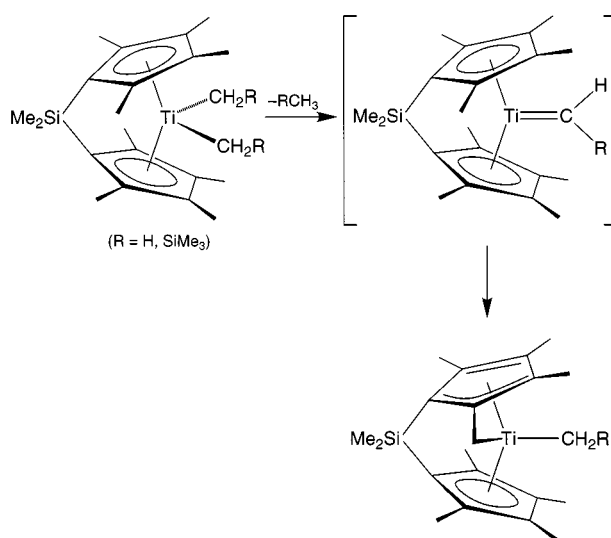
A series of permethylated [Me₂Si] *ansa* bridged titanocene complexes has been synthesized and structurally characterized by X-ray diffraction; the dialkyl complexes [Me₂Si(C₅Me₄)₂]TiR₂ are thermally unstable towards elimination of alkane (RH), thereby yielding fulvene derivatives [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]TiR.

We have recently reported how incorporation of the [Me₂Si] *ansa* bridge may have a profound effect on the chemistry of the permethylzirconocene system by increasing the electrophilicity of the metal center.¹ In this paper, we describe chemistry of the corresponding titanium system, [Me₂Si(C₅Me₄)₂]TiX₂, which includes (i) an unusual coupling reaction to form a biphenyl derivative and (ii) the synthesis of fulvene derivatives that possess trialkyldienemethane character.

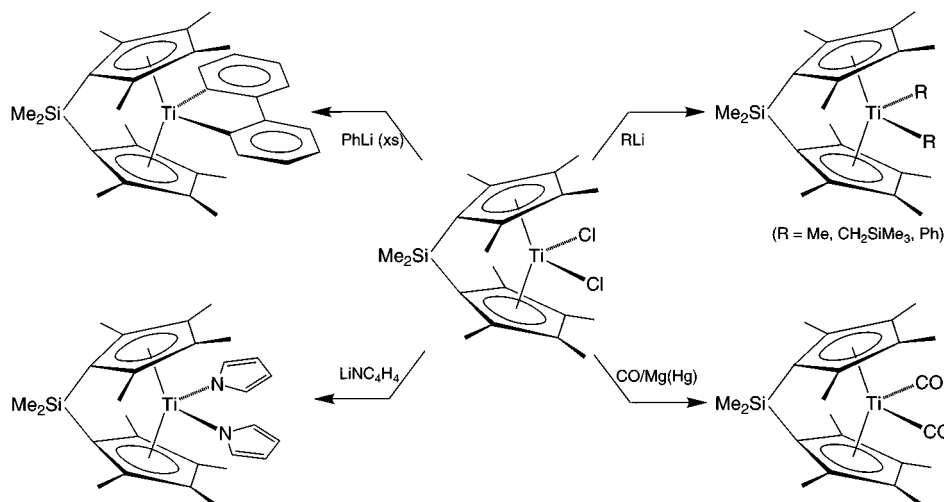
The dichloride [Me₂Si(C₅Me₄)₂]TiCl₂² provides a convenient entry to a series of *ansa* titanocene complexes (Scheme 1).³ For example, reduction of [Me₂Si(C₅Me₄)₂]TiCl₂ with Mg(Hg) under an atmosphere of CO gives the dicarbonyl, [Me₂Si(C₅Me₄)₂]Ti(CO)₂, while reactions with RLi (R = Me, Ph, CH₂SiMe₃) and LiNC₄H₄ yield [Me₂Si(C₅Me₄)₂]TiR₂⁴ and [Me₂Si(C₅Me₄)₂]Ti(NC₄H₄)₂, respectively. Most interestingly, however, the reaction of [Me₂Si(C₅Me₄)₂]TiCl₂ with excess PhLi results in C–C coupling and the formation of the biphenyl-2,2'-diyl complex, [Me₂Si(C₅Me₄)₂]Ti[(C₆H₄)₂] (Scheme 1).⁵

The dialkyl complexes [Me₂Si(C₅Me₄)₂]TiR₂ may be used as

precursors to other derivatives *via* reaction at the Ti–C bond; for example, [Me₂Si(C₅Me₄)₂]Ti(OAc)₂ and [Me₂Si(C₅Me₄)₂]Ti(NC₄H₄)Me, accompanied by elimination of methane, are obtained upon treatment of [Me₂Si(C₅Me₄)₂]TiMe₂ with AcOH and C₄H₄NH, respectively.⁶ In the absence of a substrate, the dialkyls [Me₂Si(C₅Me₄)₂]TiR₂ (R = Me, Ph, CH₂SiMe₃) eliminate alkane (RH) to give the corresponding fulvene derivatives [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]TiR (Scheme 2).^{7,8} The molecular structure of the phenyl derivative [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]TiPh has been determined by X-ray diffraction



Scheme 2



Scheme 1

† Supplementary data available: tables of analytical and spectroscopic data, and preparative details. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/1365/>, otherwise available from BLDS (No. SUP 57522, 19 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

(Fig. 1),[‡] thereby confirming that metallation occurs adjacent to the *ansa* bridge. Furthermore, the diffraction study indicates that the fulvene moiety is coordinated in a most asymmetric manner, with individual Ti–C bond lengths ranging from 2.16 Å to 2.57 Å, with the shortest being that adjacent to the methylene group, and the longest being those most distant from the methylene group.⁹ For comparison, the longest Ti–C bond length in the diphenylfulvene complex (C₅H₄CPh₂)₂Ti is only 2.40 Å.^{10,11} The fulvene moiety of [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]-TiPh is thus slipped, such that the principal interaction is with four carbon atoms, namely C11, C12, C13 and C32 (Fig. 1). In this regard, the complex is perhaps better represented as a trialkyldienemethane, *i.e.* C(CR₂)₃, derivative,¹² with the bonding supplemented by a weak olefin (C14 and C15) interaction (see Fig. 2). Supporting this notion, trialkyldienemethane character is indicated by the observation that the Ti–C12 bond is effectively perpendicular to the C11–C13–C32 plane, passing through its centroid.¹³ It is important to note that this view of the metal–fulvene interaction as possessing trialkyldienemethane character has not previously been offered as a description for fulvene complexes; specifically, bonding in transition metal fulvene complexes is typically only discussed

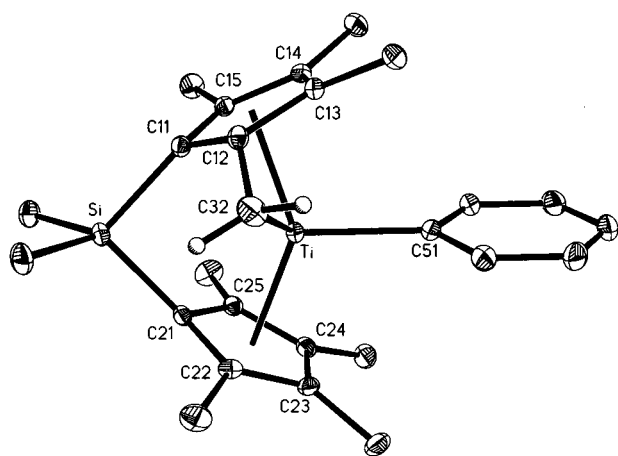


Fig. 1 Selected bond lengths (Å): Ti–C11 2.250(4), Ti–C12 2.156(4), Ti–C13 2.395(4), Ti–C14 2.572(4), Ti–C15 2.491(4), Ti–C21 2.294(4), Ti–C22 2.370(4), Ti–C23 2.459(4), Ti–C24 2.447(4), Ti–C25 2.336(4), Ti–C32 2.328(5), C12–C32 1.408(6).

in terms of whether the interaction is better described as coordination of a neutral η^6 -fulvene (*i.e.* a “diene-olefin”) or as that of a dianionic η^5, η^1 -ligand (Fig. 2).^{10,11,14} The trialkyldienemethane-olefin view of the interaction, therefore, provides an alternative description that may more appropriately describe the bonding in certain fulvene complexes.¹⁵

Deuterium kinetic isotope and labeling studies¹⁶ indicate that elimination of methane from [Me₂Si(C₅Me₄)₂]TiMe₂ occurs *via* rate determining α -H abstraction of one of the titanium methyl groups giving {[Me₂Si(C₅Me₄)₂]Ti=CH₂}, followed by rapid transfer of a ring methyl hydrogen to the methylene group (Scheme 2). Such a mechanism is preceded by Bercaw’s detailed study of methane elimination from Cp*₂TiMe₂ to give Cp*(C₅Me₄CH₂)TiMe.¹⁷ In view of the structural changes introduced by incorporating a [Me₂Si] *ansa* bridge (see below), it is perhaps surprising that the rate of methane elimination is virtually unaffected by this modification,¹⁸ the primary kinetic isotope for elimination from [Ti(CD₃)₂] is, however, considerably greater for the *ansa* system [$k_H/k_D = 5.16$ at 100 °C] than that for the permethyltitanocene system [$k_H/k_D = 2.92$ at 98.3 °C].¹⁹

Elimination of benzene from [Me₂Si(C₅Me₄)₂]TiPh₂ presumably occurs *via* a similar mechanism involving a benzyne intermediate,^{20,21} although the reaction is significantly more facile than elimination of methane from [Me₂Si(C₅Me₄)₂]TiMe₂.²² Evidence for the presence of a benzyne intermediate is provided by the observation that {[Me₂Si(C₅Me₄)₂]Ti(η^2 -C₆H₄)} may be trapped by C₂H₄ or C₂H₂ to give [Me₂Si(C₅Me₄)₂]Ti(η^2 -C₆H₄CH₂CH₂) and [Me₂Si(C₅Me₄)₂]Ti(η^2 -C₆H₄CH=CH), respectively (Scheme 3). Furthermore, the fulvene complex [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]TiPh also reacts with C₂H₄ to yield [Me₂Si(C₅Me₄)₂]Ti(η^2 -C₆H₄CH₂CH₂), suggesting that isomerization of [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]-TiPh to {[Me₂Si(C₅Me₄)₂]Ti(η^2 -C₆H₄)} is kinetically facile.

The molecular structures of the majority of the above [Me₂Si(C₅Me₄)₂]TiXX’ complexes have been determined by

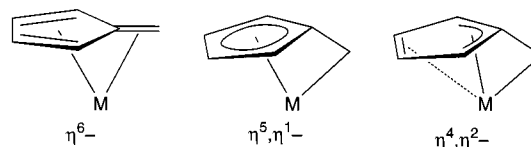
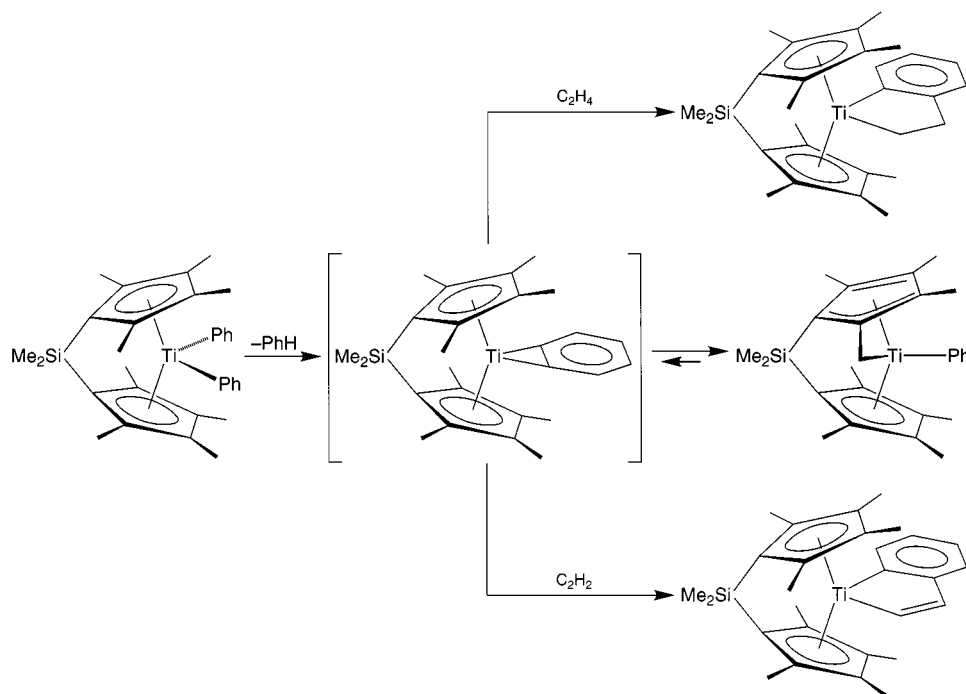


Fig. 2 Coordination modes of fulvene ligands.



Scheme 3

Table 1 Geometrical data for [Me₂Si(C₅Me₄)₂]TiXX' derivatives

	$d(\text{M}-\text{C}_{\text{pcent}})/\text{\AA}$	$d(\text{M}-\text{C})/\text{\AA}$	$d(\text{M}-\text{C}) \text{ range}/\text{\AA}$	α°	β°	$\gamma^a/\text{\AA}$
Cp* ₂ TiCl ₂ ^b	2.128	2.404–2.484	0.080	137.4	135.4	1.0
[Me ₂ Si(C ₅ Me ₄) ₂]TiCl ₂ ^c	2.136	2.365–2.552	0.187	132.2	120.6	5.8
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(CO) ₂	2.046	2.281–2.465	0.184	139.7	128.1	5.8
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(CH ₂ SiMe ₃) ₂	2.167	2.392–2.574	0.182	130.4	119.9	5.3
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(NC ₄ H ₄) ₂	2.154	2.386–2.557	0.171	130.6	120.6	5.0
[Me ₂ Si(C ₅ Me ₄) ₂]TiMe ₂	2.138	2.371–2.530	0.159	132.8	123.3	4.8
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(NC ₄ H ₄)Me	2.133	2.375–2.517	0.142	132.3	123.1	4.6
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(C ₆ H ₄ C ₂ H ₄)	2.129	2.383–2.521	0.138	132.5	124.5	4.0
[Me ₂ Si(C ₅ Me ₄) ₂]TiPh ₂	2.143	2.396–2.521	0.125	131.1	124.2	3.5
[Me ₂ Si(C ₅ Me ₄) ₂]Ti(C ₆ H ₄ C ₂ H ₂)	2.090	2.363–2.470	0.107	134.5	128.1	3.2
[Me ₂ Si(C ₅ Me ₄) ₂]Ti[(C ₆ H ₄) ₂]	2.095	2.366–2.468	0.102	134.4	128.1	3.2

^a $\gamma = (\alpha - \beta)/2$. ^b From ref. 27. ^c From ref. 3.

X-ray diffraction ‡ and details of the coordination of the *ansa* ligands are summarized in Table 1. By comparison with the non-bridged Cp*₂TiCl₂ derivative, in which the Cp* ligands are coordinated in a symmetric η⁵-fashion, with individual Ti–C bond lengths differing by less than 0.08 Å, the cyclopentadienyl groups in [Me₂Si(C₅Me₄)₂]TiXX' derivatives are coordinated much less symmetrically. Thus, individual Ti–C bond lengths in [Me₂Si(C₅Me₄)₂]TiX₂ differ by up to 0.19 Å for each complex, increasing in the sequence Ti–C₁ < Ti–C_{2,5} < Ti–C_{3,4},²³ such that the [Me₂Si(C₅Me₄)₂] ligand adopts a modified geometry which approaches an η³,η³-coordination mode. This modification is accompanied by a small tilting (γ) of the cyclopentadienyl groups away from the normal of the M–C_{pcent} vector towards the *ansa*-bridge, i.e. the C_{pcent}–M–C_{pcent} angle (α) is greater than the angle between the Cp ring normals (β). As with the corresponding zirconium system, the modified η³,η³-coordination geometry creates a more electrophilic metal center, as judged by the greater ν(CO) stretching frequencies of the dicarbonyl complex [Me₂Si(C₅Me₄)₂]Ti(CO)₂ (1879 and 1955 cm⁻¹) compared to those for Cp*₂Ti(CO)₂ (1858 and 1940 cm⁻¹).^{24–26}

In summary, a variety of permethylated *ansa*-titanocene complexes has been synthesized. The dialkyl complexes [Me₂Si(C₅Me₄)₂]TiR₂ are thermally unstable towards elimination of alkane (RH), thereby yielding fulvene derivatives [Me₂Si(C₅Me₄)₂](C₅Me₃CH₂)TiR. Interestingly, the titanium–fulvene interaction in these complexes may be considered to possess character analogous to that of a metal–trialkylidenemethane derivative.

Acknowledgements

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Notes and references

‡ Crystal data. [Me₂Si(C₅Me₄)₂]TiMe₂, C₂₂H₃₆SiTi, *M* 376.50, orthorhombic, *Pnma*, *a* 10.1151(9), *b* 14.966(2), *c* 13.7309(12) Å, *U* 2078.6(3) Å³, *Z* 4, μ 0.471 mm⁻¹, *T* 293(2) K, *R* 1 0.0878, *wR* 2 0.1427 for 2494 reflections collected. [Me₂Si(C₅Me₄)₂]Ti(CH₂SiMe₃)₂, C₂₈H₅₂Si₃Ti, *M* 520.87, monoclinic, *P2₁/n*, *a* 9.322(4), *b* 15.914(8), *c* 20.647(9) Å, β 98.715(11)°, *U* 3027(2) Å³, *Z* 4, μ 0.415 mm⁻¹, *T* 203(2) K, *R* 1 0.1029, *wR* 2 0.1152 for 20564 reflections collected. [Me₂Si(C₅Me₄)₂]TiPh₂, C₃₂H₄₀SiTi, *M* 500.63, monoclinic, *P2₁/n*, *a* 11.518(5), *b* 15.820(7), *c* 15.041(7) Å, β 98.815(13)°, *U* 2708(2) Å³, *Z* 4, μ 0.379 mm⁻¹, *T* 203(2) K, *R* 1 0.0583, *wR* 2 0.0992 for 20007 reflections collected. [Me₂Si(C₅Me₄)₂]Ti[(C₆H₄)₂], C₃₂H₃₈SiTi, *M* 498.61, triclinic, *P1*, *a* 9.5788(10), *b* 10.0927(12), *c* 14.3197(16) Å, α 81.039(2), β 77.790(2), γ 74.042(2)°, *U* 1293.9(3) Å³, *Z* 2, μ 0.396 mm⁻¹, *T* 203(2) K, *R* 1 0.0862, *wR* 2 0.1302 for 9737 reflections collected. [Me₂Si(C₅Me₄)₂]Ti(C₆H₄C₂H₂), C₂₈H₃₆SiTi, *M* 448.56, monoclinic, *P2₁/n*, *a* 10.2119(7), *b* 13.8023(8), *c* 17.0937(11) Å, β 100.3010(10)°, *U* 2370.5(3) Å³, *Z* 4, μ 0.424 mm⁻¹, *T* 203(2) K, *R* 1 0.0624, *wR* 2 0.1175 for 17424 reflections collected. [Me₂Si(C₅Me₄)₂]Ti(C₆H₄C₂H₄), C₂₈H₃₈SiTi, *M* 450.57, monoclinic, *P2₁/n*, *a* 10.3168(5), *b* 13.9236(6), *c* 16.7155(8) Å, β 100.6990(10)°, *U* 2359.39(19) Å³, *Z* 4, μ 0.427 mm⁻¹, *T* 203(2) K, *R* 1 0.0499, *wR* 2 0.1039 for 17101 reflections collected. [Me₂Si(C₅Me₄)₂]Ti(CO)₂,

C₂₂H₃₆O₂SiTi, *M* 402.45, monoclinic, *P2₁/c*, *a* 9.7826(10), *b* 23.523(3), *c* 10.0518(11) Å, β 115.319(6)°, *U* 2090.8(4) Å³, *Z* 4, μ 0.480 mm⁻¹, *T* 298(2) K, *R* 1 0.1258, *wR* 2 0.1518 for 3024 reflections collected. [Me₂Si(C₅Me₄)₂]TiMe(NC₄H₄), C₂₅H₃₇NSiTi, *M* 427.55, monoclinic, *C2/m*, *a* 17.078(7), *b* 10.981(5), *c* 13.495(5) Å, β 114.27(2)°, *U* 2307(2) Å³, *Z* 4, μ 0.433 mm⁻¹, *T* 293(2) K, *R* 1 0.0546, *wR* 2 0.1202 for 2288 reflections collected. [Me₂Si(C₅Me₄)₂]Ti(NC₄H₄)₂, C₂₈H₃₈N₂SiTi, *M* 478.59, tetragonal, *P4₃2₁2*, *a* 11.2367(6), *b* 11.2367(6), *c* 19.998(2) Å, *U* 2525.0(3) Å³, *Z* 4, μ 0.405 mm⁻¹, *T* 293(2) K, *R* 1 0.0814, *wR* 2 0.1105 for 2791 reflections collected. [Me₂Si(C₅Me₄)₂](C₅Me₃CH₂)TiPh, C₂₆H₃₄SiTi, *M* 422.52, triclinic, *P1*, *a* 8.7542(8), *b* 9.0925(8), *c* 15.4375(14) Å, α 76.673(2), β 83.731(2), γ 69.141(2)°, *U* 1116.83(17) Å³, *Z* 2, μ 0.446 mm⁻¹, *T* 213(2) K, *R* 1 0.1364, *wR* 2 0.1747 for 8338 reflections collected. CCDC reference number 186/1397.

- H. Lee, P. J. Desrosiers, I. Guzei, A. L. Rheingold and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 3255.
- P. Jutzki and R. Dickbreder, *Chem. Ber.*, 1986, **119**, 1750.
- Other [Me₂Si(C₅Me₄)₂]TiX₂ derivatives include [Me₂Si(C₅Me₄)₂]TiCl and [Me₂Si(C₅Me₄)₂]Ti[η²-C₂(SiMe₃)₂]. See: V. Varga, J. Hiller, R. Gyepes, M. Polasek, P. Sedmera, U. Thewalt and K. Mach, *J. Organomet. Chem.*, 1997, **538**, 63.
- For unsubstituted analogs, [Me₂Si(C₅H₄)₂]TiR₂, see: (a) R. Gómez, T. Cuenca, P. Royo, W. A. Herrmann and E. Herdtweck, *J. Organomet. Chem.*, 1990, **382**, 103; (b) R. Gómez, T. Cuenca, P. Royo and E. Hovestreydt, *Organometallics*, 1991, **10**, 2516.
- Alternatively, [Me₂Si(C₅Me₄)₂]Ti[(C₆H₄)₂] may also be obtained by reaction of [Me₂Si(C₅Me₄)₂]TiPh₂ with PhLi.
- H. Lee, J. Cordaro and J. B. Bonanno, unpublished work.
- Non-bridged fulvene analogs Cp*(C₅Me₄CH₂)TiR (R = H, Me, CH₂CMe₃, CH₂SiMe₃, Ph, CH=CH₂) have also been reported. See, for example: (a) C. McDade, J. C. Green and J. E. Bercaw, *Organometallics*, 1982, **1**, 1629; (b) G. A. Luinstra, P. H. P. Brinkmann and J. H. Teuben, *J. Organomet. Chem.*, 1997, **532**, 125; (c) G. A. Luinstra and J. H. Teuben, *Organometallics*, 1992, **11**, 1793; (d) J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1996, **118**, 8737; (e) J. L. Polse, A. W. Kaplan, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 6316; (f) R. Beckhaus, J. Oster and T. Wagner, *Chem. Ber.*, 1994, **127**, 1003; (g) R. Beckhaus, J. Oster, I. Sang, I. Strauß and M. Wagner, *Synlett*, 1997, 241.
- The CH₂ groups in [Me₂Si(C₅Me₄)₂](C₅Me₃CH₂)TiR are characterized by ¹³C NMR signals at *ca.* δ 80, with ¹J_{C–H} coupling constants of *ca.* 150 Hz: Me (δ 78.3, 149 and 154 Hz), Ph (δ 82.5, 150 and 153 Hz) and CH₂SiMe₃ (δ 80.2 ppm, 149 and 151 Hz). These values are comparable to those for Cp*(C₅Me₄CH₂)TiR derivatives (see, for example, ref. 7).
- The Ti–C bond lengths for the unmetallated cyclopentadienyl group range from 2.29 Å to 2.46 Å.
- For a review of bonding in fulvene complexes, see: J. A. Bandy, V. S. B. Mtetwa, K. Prout, J. C. Green, C. E. Davies, M. L. H. Green, N. J. Hazel, A. Izquierdo and J. J. Martin-Polo, *J. Chem. Soc., Dalton Trans.*, 1985, 2037.
- For further comparison, the longest Ti–C bond length in the Ti(III) complex Cp*(C₅Me₄CH₂)Ti is 2.47 Å. See: J. M. Fischer, W. E. Piers and V. G. Young, Jr., *Organometallics*, 1996, **15**, 2410.
- For trialkylidene methane derivatives of zirconium, see: G. Rodriguez and G. C. Bazan, *J. Am. Chem. Soc.*, 1997, **119**, 343.
- Thus, the Ti–C12 bond deviates by only 2.5° from the Ti–centroid vector.
- (a) L. E. Schock, C. P. Brock and T. J. Marks, *Organometallics*, 1987, **6**, 232; (b) A. R. Bulls, W. P. Schaefer, M. Serfas and J. E. Bercaw, *Organometallics*, 1987, **6**, 1219.

- 15 For example, the wide range of M–C bond lengths in the zirconium and hafnium complexes, Cp*(C₅Me₄CH₂)ZrPh (2.28–2.62 Å)^{14a} and Cp*(C₅Me₄CH₂)HfCH₂Ph (2.25–2.60 Å),^{14b} suggests that they may also be considered to possess trialkylidenemethane character.
- 16 Specifically, [Me₂Si(C₅Me₄)₂Ti(CD₃)₂] yields principally the isotopomers [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]Ti(CD₂H) and CD₄, rather than [Me₂Si(C₅Me₄)(C₅Me₃CH₂)]Ti(CD₃) and CD₃H.
- 17 C. McDade, J. C. Green and J. E. Bercaw, *Organometallics*, 1982, **1**, 1629.
- 18 For [Me₂Si(C₅Me₄)₂TiMe₂]: $\Delta H^\ddagger = 27.8(8)$ kcal mol⁻¹, $\Delta S^\ddagger = -5(2)$ e.u. (1 e.u. = 4.184 J K⁻¹ mol⁻¹). For Cp*₂TiMe₂: $\Delta H^\ddagger = 27.6(3)$ kcal mol⁻¹, $\Delta S^\ddagger = -2.9(7)$ e.u. (ref. 17).
- 19 Interestingly, values of $k_H/k_D \approx 5$ have also been observed for elimination of methane from Cp*₂Ti(CH₃)(C₆D₅) (5.7 at 33 °C) and Cp*₂Ti(CH₃)(CD=CD₂) (5.1 at 80 °C). See ref. 7(c).
- 20 A benzyne intermediate has also been proposed in the formation of Cp*(C₅Me₄CH₂)ZrPh by thermal elimination of PhH and H₂ from Cp*₂ZrPh₂^{14a} and Cp*₂Zr(Ph)H (F. D. Miller and R. D. Sanner, *Organometallics*, 1998, **7**, 818), respectively.
- 21 Cp₂TiPh₂ has been proposed to decompose *via ortho*-hydrogen abstraction by the other phenyl group, generating a benzyne intermediate, [Cp₂Ti(η²-C₆H₄)]. See: (a) J. Dvorak, R. J. O'Brien and W. Santo, *Chem. Commun.*, 1970, 411; (b) C. P. Boekel, J. H. Teuben and H. J. de Liefde Meijer, *J. Organomet. Chem.*, 1975, **102**, 161.
- 22 At 40 °C, the rate constants for elimination of RH from [Me₂-Si(C₅Me₄)₂TiR₂] are: Ph [$1.30(1) \times 10^{-4}$ s⁻¹], CH₂SiMe₃ [$9.85(9) \times 10^{-5}$ s⁻¹] and Me [2.0×10^{-8} s⁻¹]. The value for the methyl derivative is that determined by the activation parameters listed in ref. 18.
- 23 The numbering system is such that C₁ is the ring carbon attached to silicon.
- 24 D. J. Sikora, M. D. Rausch, R. D. Rogers and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 1265.
- 25 ESR spectroscopic studies suggest that 2-methyltetrahydrofuran binds more strongly to [Me₂Si(C₅Me₄)₂TiCl] than to Cp*₂TiCl, providing further evidence for enhanced electrophilicity of the *ansa* titanocene system. See ref. 3.
- 26 It should, however, be noted that computational studies suggest that ring slippage and tilt introduced by incorporation of bulky substituents are not the principal factors responsible for modification of the electron density at a metal center in a series of *non-bridged* titanocene complexes; rather the changes in electron density merely reflect the inductive effects of the various substituents. See: B. E. Bursten, M. R. Callstrom, C. A. Jolly, L. A. Paquette, M. R. Sivik, R. S. Tucker and C. A. Wartchow, *Organometallics*, 1994, **13**, 127.
- 27 T. C. McKenzie, R. D. Sanner and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.

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