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[Me_2Si] *Ansa* bridged complexes of permethyltitanocene: synthesis and structural characterization of fulvene derivatives with trialkylidenemethane character †

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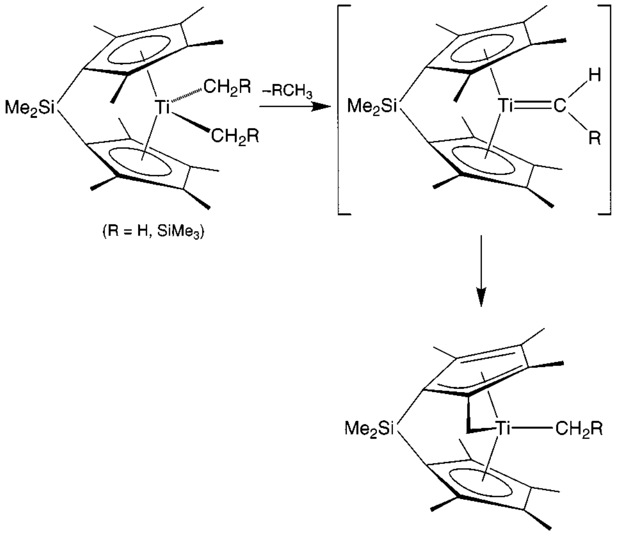
A series of permethylated [Me_2Si] *ansa* bridged titanocene complexes has been synthesized and structurally characterized by X-ray diffraction; the dialkyl complexes [$Me_2Si(C_5Me_4)$]TiR_2 are thermally unstable towards elimination of alkane (RH), thereby yielding fulvene derivatives [$Me_2Si(C_5Me_4)(C_5Me_3CH_2)$]TiR.

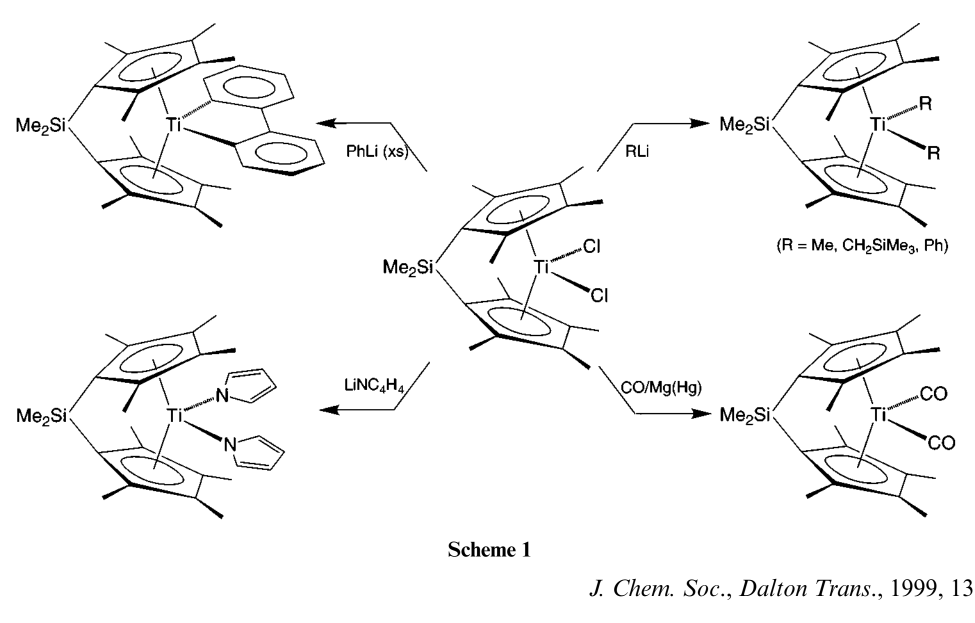
We have recently reported how incorporation of the [Me_2Si] *ansa* bridge may have a profound effect on the chemistry of the permethylzirconocene system by increasing the electrophilicity of the metal center.[1] In this paper, we describe chemistry of the corresponding titanium system, [$Me_2Si(C_5Me_4)_2$]TiX_2, which includes (*i*) an unusual coupling reaction to form a biphenyl derivative and (*ii*) the synthesis of fulvene derivatives that possess trialkylidenemethane character.

The dichloride [$Me_2Si(C_5Me_4)_2$]$TiCl_2$[2] provides a convenient entry to a series of *ansa* titanocene complexes (Scheme 1).[3] For example, reduction of [$Me_2Si(C_5Me_4)_2$]$TiCl_2$ with Mg(Hg) under an atmosphere of CO gives the dicarbonyl, [$Me_2Si(C_5Me_4)_2$]$Ti(CO)_2$, while reactions with RLi (R = Me, Ph, CH_2SiMe_3) and $LiNC_4H_4$ yield [$Me_2Si(C_5Me_4)_2$]TiR_2[4] and [$Me_2Si(C_5Me_4)_2$]$Ti(NC_4H_4)_2$, respectively. Most interestingly, however, the reaction of [$Me_2Si(C_5Me_4)_2$]$TiCl_2$ with excess PhLi results in C–C coupling and the formation of the biphenyl-2,2′-diyl complex, [$Me_2Si(C_5Me_4)_2$]$Ti[(C_6H_4)_2]$ (Scheme 1).[5]

The dialkyl complexes [$Me_2Si(C_5Me_4)_2$]TiR_2 may be used as precursors to other derivatives *via* reaction at the Ti–C bond; for example, [$Me_2Si(C_5Me_4)_2$]$Ti(OAc)_2$ and [$Me_2Si(C_5Me_4)_2$]$Ti(NC_4H_4)Me$, accompanied by elimination of methane, are obtained upon treatment of [$Me_2Si(C_5Me_4)_2$]$TiMe_2$ with AcOH and C_4H_4NH, respectively.[6] In the absence of a substrate, the dialkyls [$Me_2Si(C_5Me_4)_2$]TiR_2 (R = Me, Ph, CH_2SiMe_3) eliminate alkane (RH) to give the corresponding fulvene derivatives [$Me_2Si(C_5Me_4)(C_5Me_3CH_2)$]TiR (Scheme 2).[7,8] The molecular structure of the phenyl derivative [$Me_2Si(C_5Me_4)(C_5Me_3CH_2)$]TiPh has been determined by X-ray diffraction



Scheme 2



Scheme 1

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† *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 BLDSC (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 $(C_5H_4CPh_2)_2Ti$ is only 2.40 Å.[10,11] The fulvene moiety of $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiPh$ 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 trialkylidenemethane, *i.e.* $C(CR_2)_3$, derivative,[12] with the bonding supplemented by a weak olefin (C14 and C15) interaction (see Fig. 2). Supporting this notion, trialkylidenemethane 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 trialkylidenemethane character has not previously been offered as a description for fulvene complexes; specifically, bonding in transition metal fulvene complexes is typically only discussed 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 trialkylidenemethane-olefin view of the interaction, therefore, provides an alternative description that may more appropriately describe the bonding in certain fulvene complexes.[15]

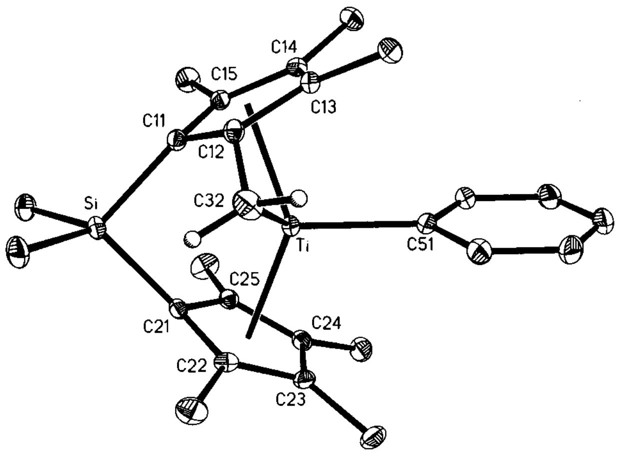


Fig. 1 Selected bond lengths (Å): Ti–C11 2.250(4), Ti–C12 2.156(4), Ti–C13 2.395(4), Ti–C14 2.572(4), Ti–C15 2.491(4), Ti–C21 2.294(4), Ti–C22 2.370(4), Ti–C23 2.459(4), Ti–C24 2.447(4), Ti–C25 2.336(4), Ti–C32 2.328(5), C12–C32 1.408(6).

Deuterium kinetic isotope and labeling studies[16] indicate that elimination of methane from $[Me_2Si(C_5Me_4)_2]TiMe_2$ occurs *via* rate determining α-H abstraction of one of the titanium methyl groups giving $\{[Me_2Si(C_5Me_4)_2]Ti{=}CH_2\}$, followed by rapid transfer of a ring methyl hydrogen to the methylene group (Scheme 2). Such a mechanism is precedented by Bercaw's detailed study of methane elimination from $Cp^*_2TiMe_2$ to give $Cp^*(C_5Me_4CH_2)TiMe$.[17] In view of the structural changes introduced by incorporating a [Me_2Si] *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 $[Ti(CD_3)_2]$ 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 $[Me_2Si(C_5Me_4)_2]TiPh_2$ presumably occurs *via* a similar mechanism involving a benzyne intermediate,[20,21] although the reaction is significantly more facile than elimination of methane from $[Me_2Si(C_5Me_4)_2]TiMe_2$.[22] Evidence for the presence of a benzyne intermediate is provided by the observation that $\{[Me_2Si(C_5Me_4)_2]Ti(\eta^2\text{-}C_6H_4)\}$ may be trapped by C_2H_4 or C_2H_2 to give $[Me_2Si(C_5Me_4)_2]Ti(\eta^2\text{-}C_6H_4CH_2CH_2)$ and $[Me_2Si(C_5Me_4)_2]Ti(\eta^2\text{-}C_6H_4CH{=}CH)$, respectively (Scheme 3). Furthermore, the fulvene complex $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiPh$ also reacts with C_2H_4 to yield $[Me_2Si(C_5Me_4)_2]Ti(\eta^2\text{-}C_6H_4CH_2CH_2)$, suggesting that isomerization of $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiPh$ to $\{[Me_2Si(C_5Me_4)_2]Ti(\eta^2\text{-}C_6H_4)\}$ is kinetically facile.

The molecular structures of the majority of the above $[Me_2Si(C_5Me_4)_2]TiXX'$ complexes have been determined by

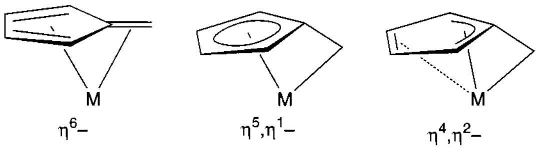
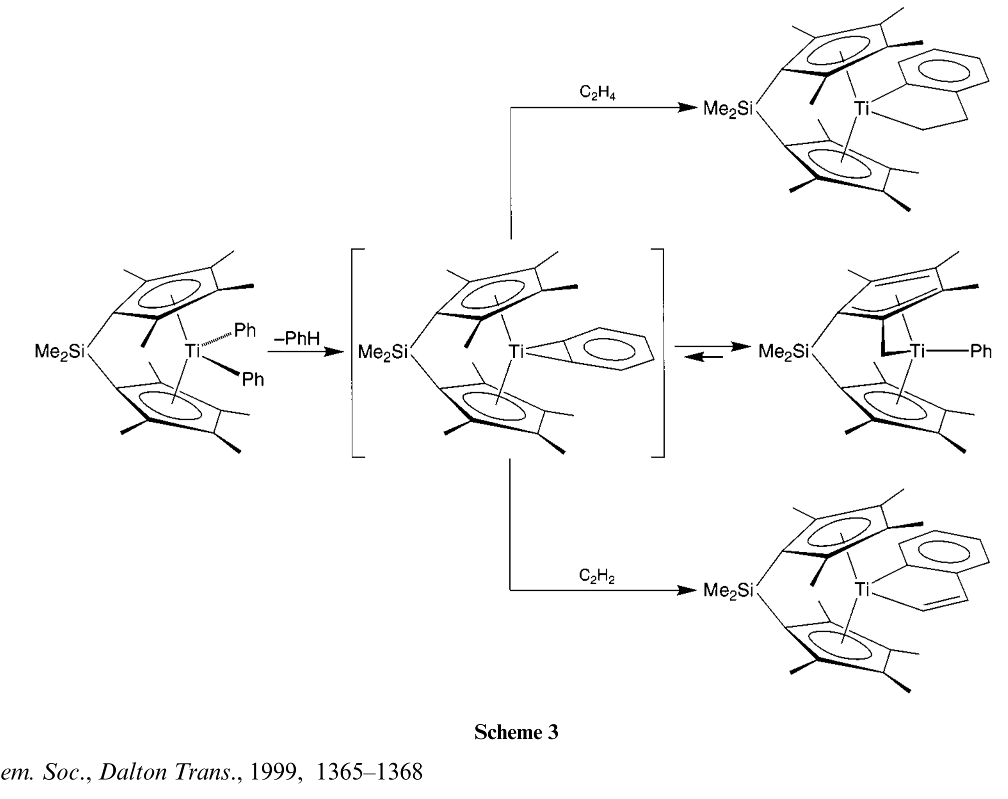


Fig. 2 Coordination modes of fulvene ligands.



Scheme 3

Table 1 Geometrical data for $[Me_2Si(C_5Me_4)_2]TiXX'$ derivatives

	$d(M–Cp_{cent})$/Å	d(M–C)/Å	d(M–C) range/Å	α/°	β/°	γ^a/°
$Cp^*{}_2TiCl_2$ [b]	2.128	2.404–2.484	0.080	137.4	135.4	1.0
$[Me_2Si(C_5Me_4)_2]TiCl_2$ [c]	2.136	2.365–2.552	0.187	132.2	120.6	5.8
$[Me_2Si(C_5Me_4)_2]Ti(CO)_2$	2.046	2.281–2.465	0.184	139.7	128.1	5.8
$[Me_2Si(C_5Me_4)_2]Ti(CH_2SiMe_3)_2$	2.167	2.392–2.574	0.182	130.4	119.9	5.3
$[Me_2Si(C_5Me_4)_2]Ti(NC_4H_4)_2$	2.154	2.386–2.557	0.171	130.6	120.6	5.0
$[Me_2Si(C_5Me_4)_2]TiMe_2$	2.138	2.371–2.530	0.159	132.8	123.3	4.8
$[Me_2Si(C_5Me_4)_2]Ti(NC_4H_4)Me$	2.133	2.375–2.517	0.142	132.3	123.1	4.6
$[Me_2Si(C_5Me_4)_2]Ti(C_6H_4C_2H_4)$	2.129	2.383–2.521	0.138	132.5	124.5	4.0
$[Me_2Si(C_5Me_4)_2]TiPh_2$	2.143	2.396–2.521	0.125	131.1	124.2	3.5
$[Me_2Si(C_5Me_4)_2]Ti(C_6H_4C_2H_2)$	2.090	2.363–2.470	0.107	134.5	128.1	3.2
$[Me_2Si(C_5Me_4)_2]Ti[(C_6H_4)_2]$	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 $Cp^*{}_2TiCl_2$ derivative, in which the Cp* ligands are coordinated in a symmetric η^5-fashion, with individual Ti–C bond lengths differing by less than 0.08 Å, the cyclopentadienyl groups in $[Me_2Si(C_5Me_4)]TiXX'$ derivatives are coordinated much less symmetrically. Thus, individual Ti–C bond lengths in $[Me_2Si(C_5Me_4)]TiX_2$ differ by up to 0.19 Å for each complex, increasing in the sequence $Ti–C_1 < Ti–C_{2,5} < Ti–C_{3,4}$,[23] such that the $[Me_2Si(C_5Me_4)]$ ligand adopts a modified geometry which approaches an η^3,η^3-coordination mode. This modification is accompanied by a small tilting (γ) of the cyclopentadienyl groups away from the normal of the $M–Cp_{cent}$ vector towards the *ansa*-bridge, *i.e.* the $Cp_{cent}–M–Cp_{cent}$ angle (α) is greater than the angle between the Cp ring normals (β). As with the corresponding zirconium system, the modified η^3,η^3-coordination geometry creates a more electrophilic metal center, as judged by the greater ν(CO) stretching frequencies of the dicarbonyl complex $[Me_2Si(C_5Me_4)_2]Ti(CO)_2$ (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 $[Me_2Si(C_5Me_4)]TiR_2$ are thermally unstable towards elimination of alkane (RH), thereby yielding fulvene derivatives $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiR$. 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. $[Me_2Si(C_5Me_4)_2]TiMe_2$, $C_{22}H_{36}SiTi$, *M* 376.50, orthorhombic, *Pnma*, *a* 10.1151(9), *b* 14.966(2), *c* 13.7309(12) Å, *U* 2078.6(3) Å^3, *Z* 4, μ 0.471 mm^{-1}, *T* 293(2) K, *R*1 0.0878, *wR*2 0.1427 for 2494 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti(CH_2SiMe_3)_2$, $C_{28}H_{52}Si_3Ti$, *M* 520.87, monoclinic, $P2_1/n$, *a* 9.322(4), *b* 15.914(8), *c* 20.647(9) Å, β 98.715(11)°, *U* 3027(2) Å^3, *Z* 4, μ 0.415 mm^{-1}, *T* 203(2) K, *R*1 0.1029, *wR*2 0.1152 for 20564 reflections collected. $[Me_2Si(C_5Me_4)_2]TiPh_2$, $C_{32}H_{40}SiTi$, *M* 500.63, monoclinic, $P2_1/n$, *a* 11.518(5), *b* 15.820(7), *c* 15.041(7) Å, β 98.815(13)°, *U* 2708(2) Å^3, *Z* 4, μ 0.379 mm^{-1}, *T* 203(2) K, *R*1 0.0583, *wR*2 0.0992 for 20007 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti[(C_6H_4)_2]$, $C_{32}H_{38}SiTi$, *M* 498.61, triclinic, $P\bar{1}$, *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) Å^3, *Z* 2, μ 0.396 mm^{-1}, *T* 203(2) K, *R*1 0.0862, *wR*2 0.1302 for 9737 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti(C_6H_4C_2H_2)$, $C_{28}H_{36}SiTi$, *M* 448.56, monoclinic, $P2_1/n$, *a* 10.2119(7), *b* 13.8023(8), *c* 17.0937(11) Å, β 100.3010(10)°, *U* 2370.5(3) Å^3, *Z* 4, μ 0.424 mm^{-1}, *T* 203(2) K, *R*1 0.0624, *wR*2 0.1175 for 17424 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti(C_6H_4C_2H_4)$, $C_{28}H_{38}SiTi$, *M* 450.57, monoclinic, $P2_1/n$, *a* 10.3168(5), *b* 13.9236(6), *c* 16.7155(8) Å, β 100.6990(10)°, *U* 2359.39(19) Å^3, *Z* 4, μ 0.427 mm^{-1}, *T* 203(2) K, *R*1 0.0499, *wR*2 0.1039 for 17101 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti(CO)_2$, $C_{22}H_{30}O_2SiTi$, *M* 402.45, monoclinic, $P2_1/c$, *a* 9.7826(10), *b* 23.523(3), *c* 10.0518(11) Å, β 115.319(6)°, *U* 2090.8(4) Å^3, *Z* 4, μ 0.480 mm^{-1}, *T* 298(2) K, *R*1 0.1258, *wR*2 0.1518 for 3024 reflections collected. $[Me_2Si(C_5Me_4)_2]TiMe(NC_4H_4)$, $C_{25}H_{37}NSiTi$, *M* 427.55, monoclinic, *C*2/*m*, *a* 17.078(7), *b* 10.981(5), *c* 13.495(5) Å, β 114.27(2)°, *U* 2307(2) Å^3, *Z* 4, μ 0.433 mm^{-1}, *T* 293(2) K, *R*1 0.0546, *wR*2 0.1202 for 2288 reflections collected. $[Me_2Si(C_5Me_4)_2]Ti(NC_4H_5)_2$, $C_{28}H_{38}N_2SiTi$, *M* 478.59, tetragonal, $P4_32_12$, *a* 11.2367(6), *b* 11.2367(6), *c* 19.998(2) Å, *U* 2525.0(3) Å^3, *Z* 4, μ 0.405 mm^{-1}, *T* 293(2) K, *R*1 0.0814, *wR*2 0.1105 for 2791 reflections collected. $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiPh$, $C_{26}H_{34}SiTi$, *M* 422.52, triclinic, $P\bar{1}$, *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) Å^3, *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.

1 H. Lee, P. J. Desrosiers, I. Guzei, A. L. Rheingold and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 3255.

2 P. Jutzi and R. Dickbreder, *Chem. Ber.*, 1986, **119**, 1750.

3 Other $[Me_2Si(C_5Me_4)_2]TiX_2$ derivatives include $[Me_2Si(C_5Me_4)_2]TiCl$ and $[Me_2Si(C_5Me_4)_2]Ti[\eta^2\text{-}C_2(SiMe_3)_2]$. See: V. Varga, J. Hiller, R. Gyepes, M. Polasek, P. Sedmera, U. Thewalt and K. Mach, *J. Organomet. Chem.*, 1997, **538**, 63.

4 For unsubstituted analogs, $[Me_2Si(C_5H_4)_2]TiR_2$, 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.

5 Alternatively, $[Me_2Si(C_5Me_4)_2]Ti[(C_6H_4)_2]$ may also be obtained by reaction of $[Me_2Si(C_5Me_4)_2]TiPh_2$ with PhLi.

6 H. Lee, J. Cordaro and J. B. Bonanno, unpublished work.

7 Non-bridged fulvene analogs $Cp^*(C_5Me_4CH_2)TiR$ (R = H, Me, CH_2CMe_3, CH_2SiMe_3, Ph, $CH{=}CH_2$) 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.

8 The CH_2 groups in $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]TiR$ are characterized by ^{13}C 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 CH_2SiMe_3 (δ 80.2 ppm, 149 and 151 Hz). These values are comparable to those for $Cp^*(C_5Me_4CH_2)TiR$ derivatives (see, for example, ref. 7).

9 The Ti–C bond lengths for the unmetallated cyclopentadienyl group range from 2.29 Å to 2.46 Å.

10 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.

11 For further comparison, the longest Ti–C bond length in the Ti(III) complex $Cp^*(C_5Me_4CH_2)Ti$ is 2.47 Å. See: J. M. Fischer, W. E. Piers and V. G. Young, Jr., *Organometallics*, 1996, **15**, 2410.

12 For trialkylidene methane derivatives of zirconium, see: G. Rodriguez and G. C. Bazan, *J. Am. Chem. Soc.*, 1997, **119**, 343.

13 Thus, the Ti–C12 bond deviates by only 2.5° from the Ti–centroid vector.

14 (*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, $Cp^*(C_5Me_4CH_2)ZrPh$ (2.28–2.62 Å)[14a] and $Cp^*(C_5Me_4CH_2)HfCH_2Ph$ (2.25–2.60 Å),[14b] suggests that they may also be considered to possess trialkylidenemethane character.

16 Specifically, $[Me_2Si(C_5Me_4)_2]Ti(CD_3)_2$ yields principally the isotopomers $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]Ti(CD_2H)$ and CD_4, rather than $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]Ti(CD_3)$ and CD_3H.

17 C. McDade, J. C. Green and J. E. Bercaw, *Organometallics*, 1982, **1**, 1629.

18 For $[Me_2Si(C_5Me_4)_2]TiMe_2$: $\Delta H^\ddagger = 27.8(8)$ kcal mol^{-1}, $\Delta S^\ddagger = -5(2)$ e.u. (1 e.u. = 4.184 J K^{-1} mol^{-1}). For $Cp^*_2TiMe_2$: $\Delta H^\ddagger = 27.6(3)$ 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 $Cp^*_2Ti(CH_3)(C_6D_5)$ (5.7 at 33 °C) and $Cp^*_2Ti(CH_3)(CD{=}CD_2)$ (5.1 at 80 °C). See ref. 7(*c*).

20 A benzyne intermediate has also been proposed in the formation of $Cp^*(C_5Me_4CH_2)ZrPh$ by thermal elimination of PhH and H_2 from $Cp^*_2ZrPh_2$[14a] and $Cp^*_2Zr(Ph)H$ (F. D. Miller and R. D. Sanner, *Organometallics*, 1998, **7**, 818), respectively.

21 Cp_2TiPh_2 has been proposed to decompose *via ortho*-hydrogen abstraction by the other phenyl group, generating a benzyne intermediate, $[Cp_2Ti(\eta^2\text{-}C_6H_4)]$. 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 $[Me_2Si(C_5Me_4)_2]TiR_2$ are: Ph [$1.30(1) \times 10^{-4}$ s^{-1}], CH_2SiMe_3 [$9.85(9) \times 10^{-5}$ 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 C_1 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 $[Me_2Si(C_5Me_4)_2]TiCl$ 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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