Electron-deficient (pentamethylcyclopentadienyl)titanium trialkyls: evidence of [cyclic] Ti.cntdot..cntdot..cntdot.H-C and [cyclic] Ti.cntdot..cntdot..cntdot.C-C interactions. Crystal and molecular structure of .mu.-[o-(CH2)2C6H4]{(.eta.5-C5Me5)Ti[o-(CH2)2C6H4]}2

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Electron-Deficient (Pentamethylcyclopentadienyl)titanium Trialkyls: Evidence of Ti···H–C and Ti···C–C Interactions. Crystal and Molecular Structure of μ-[o-$(CH_2)_2C_6H_4$]{(η^5-C_5Me_5)Ti[o-$(CH_2)_2C_6H_4$]}$_2$

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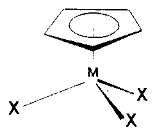
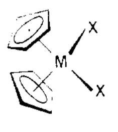
(η^5-C_5Me_5)$TiCl_3$ (1) reacts with 3 equiv of lithium or Grignard reagents to form (η^5-C_5Me_5)TiR_3 (R = Me, CH_2Ph, CH_2SiMe_3, and C_6F_5) and with 2 equiv to give (η^5-C_5Me_5)$TiClR_2$ (R = Me, CH_2Ph, and CH_2SiMe_3). If 1 is reacted with [o-$(CH_2)_2C_6H_4$]$Mg(THF)_2$ in a 2:3 molar ratio, μ-[o-$(CH_2)_2C_6H_4$]{(η^5-C_5Me_5)Ti[o-$(CH_2)_2C_6H_4$]}$_2$ is obtained; its structure has been fully elucidated by X-ray diffraction methods. Crystals are monoclinic of space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 11.207$ (1) Å, $b = 34.520$ (6) Å, $c = 10.460$ (1) Å, and $\beta = 113.83$ (1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by blocked-matrix least squares to $R = 0.0694$ and $R_w = 0.0743$ for 2096 observed reflections. Of the three o-xylylene groups two act as chelating ligands to the Ti atoms, while the third one acts as a bridge between the two metals. An interaction between the Ti atoms and the C ring atoms of the chelating o-xylylene groups is evident. This situation is compared with that of (η^5-C_5Me_5)$Ti(CH_2Ph)_3$, where an agostic interaction has been proposed.

Introduction

The organometallic chemistry of the group 4 elements is now well developed and has given rise to a series of interesting new reaction patterns. We do not intend a review of the whole known chemistry, but the reader is referred to general treatises.[1] The vast majority of this chemistry is associated with the Cp_2M fragment (Cp = η^5-C_5H_5). By contrast the chemistry of the CpM fragment is poorly documented. A d^0-Cp_2MX_2 complex (I) has one vacant orbital ($2a_1$) lying in the plane that contains both X substituents and bisecting the angle between the normals to the two Cp ring planes.[2] The d^0-Cp_2MX_2 complexes are formally 16-electron species, and their chemistry is clearly influenced by this empty orbital. A d^0-$CpMX_3$ complex (II) has, however, three vacant not coplanar coordination sites, corresponding to the 1e + a_1 orbitals, which are mainly metal d_{z^2}, $d_{x^2-y^2}$, d_{xy} orbitals.[3] These compounds are therefore formally 12-electron species, and this electron deficiency along with the energy and nature of the vacant orbitals should make possible the appearance of structural and reactivity patterns different to those known for the analogous Cp_2MX_2 compounds. This idea prompted us to undertake the study of the chemical and structural features of monopentamethylcyclopentadienyl complexes of the group 4 elements, to which little attention has been paid up to date. The permethylated Cp ring should have important stabilizing effects, as noted previously in the $Cp^*{}_2M$ systems.[4] In this paper we report the synthesis and structural characterization of a series of (pentamethylcyclopentadienyl)titanium tri- and dialkyls. A preliminary account of part of this work has appeared.[5]



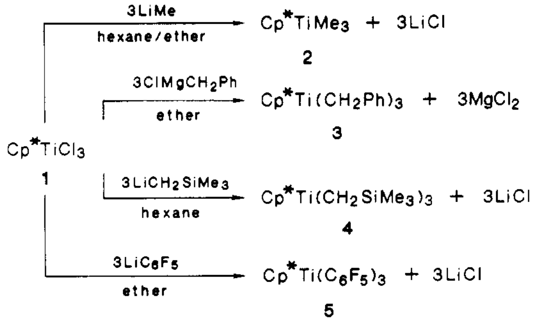
(II)



(I)

Results

Cp^*TiCl_3 (1) (Cp^* = η^5-C_5Me_5) serves as an adequate starting compound for the synthesis of a number of (pentamethylcyclopentadienyl)titanium alkyls. 1 reacts cleanly with 3 equiv of LiMe, $LiCH_2SiMe_3$, LiC_6F_5, or $ClMgCH_2Ph$ in hexane, diethyl ether, or a mixture of both affording the trialkyl (2–4) and -aryl (5) derivatives in high yield (70–98%).



(1)

The high solubility of 2 and 4 in hexanes lowers the yield of the crystallized compounds, but the crude product has

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[1] (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., and Abel, E. W. Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 271–646. (b) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic: Oxford, 1974. (c) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-zirconium and Hafnium Compounds*; Ellis-Horwood Ltd.: Chichester, 1986.

[2] Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[3] Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585 and references therein.

[4] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

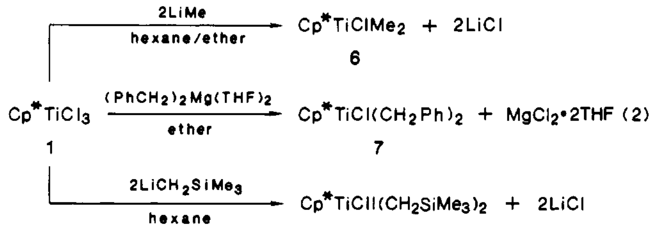
[5] Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.

0276-7333/89/2308-0476$01.50/0

exactly the same ^1H NMR spectrum as the crystalline material and can be used without further purification. Compounds **2**–**5** are rather stable, **5** being the least stable, decomposing at room temperature overnight in C_6D_6 solution or in a week in the solid to unidentified products. **2** darkens in the solid and in solution if exposed to the light, but no change is observed in the ^1H NMR spectrum.

The X-ray structure of **3** has been determined[5] and showed evidence for an agostic $CH_2 \cdots Ti$ interaction with one of the benzyl groups. The molecule nevertheless is not rigid in solution, and only one peak for the benzylic protons can be observed in the ^1H NMR spectrum even down to −70 °C. Such fluxional behavior is also responsible for the normal value of $^1J_{CH}$ (121 Hz) observed for the benzylic carbons, as it has been previously reported in other systems.[6] Similarly in the case of **2** and **4** no changes are observed in the range +30 to −70 °C, and only one peak is observed for the CH_3 and CH_2 groups. In the ^{13}C spectrum of **4** a rather low value for $^1J_{CH}$ (105 Hz) will be indicative of an agostic interaction.

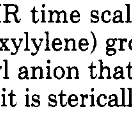
Cp^*TiCl_3 can also be partially alkylated just by using the stoichiometric amount of the corresponding magnesium or lithium reagent (eq 2). Other (pentamethylcyclopentadienyl)titanium trihalides also can be employed.



$$\underset{\mathbf{9}}{Cp^*TiBr_3} + (PhCH_2)Mg(THF)_2 \rightarrow \underset{\mathbf{10}}{Cp^*TiBr(CH_2Ph)_2} + MgBr_2{\cdot}2THF \quad (3)$$

We have not attempted anymore combinations of halogen and alkyls. The ^1H NMR spectrum of **6** shows a singlet for the Ti–Me groups, but the CH_2 protons of **7**, **8**, and **10** are diastereotopic and give rise to two AB doublets. All these ^1H NMR spectra are invariable up to 80–85 °C where the compounds start to decompose. In the gated decoupled spectrum a 1:2:1 triplet is observed for the CH_2 carbon atoms of **7** and **10** which indicates that $^1J_{CH_A}$ and $^1J_{CH_B}$ are equal, but in the case of **8** these couplings constants are different: $^1J_{CH_A}$ = 105 Hz and $^1J_{CH_B}$ = 113 Hz (a doublet of doublets is obtained). Therefore we can at least say that **7**, **8**, and **10** are stereochemically rigid, pseudotetrahedral species on the ^1H NMR time scale up to 80 °C.

The *o*-xylenediyl (*o*-xylylene) group **11** can be regarded as a substituted benzyl anion that can act as a chelating or bridging group, and it is sterically rather undemanding.



11

For these reasons and in view of the structure of **3** we set out to prepare similar *o*-xylylene derivatives. With use of the magnesium compound **12** to introduce the chelating dialkyl **11**, the expected $Cp^*TiCl[o\text{-}(CH_2)_2C_6H_4]$ is obtained when the molar ratio of **1**/**12** is 1:1, but in some instances $\mu\text{-}[o\text{-}(CH_2)_2C_6H_4](\mu\text{-}Cl)_2(Cp^*Ti)_2$ is also isolated. This surprising result has been mentioned elsewhere.[7] When a 2:3 molar ratio is used, we obtain **13** according to eq 4.

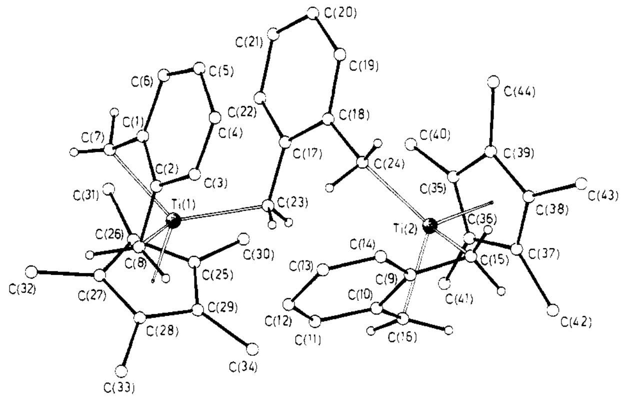


Figure 1. View of the structure of **13** with the atomic labeling scheme.

$$\underset{\mathbf{1}}{2Cp^*TiCl_3} + \underset{\mathbf{12}}{3[o\text{-}(CH_2)_2C_6H_4]Mg(THF)_2} \rightarrow \underset{\mathbf{13}}{\mu\text{-}[o\text{-}(CH_2)_2C_6H_4]\{Cp^*Ti[o\text{-}(CH_2)_2C_6H_4]\}_2} + 3MgCl_2{\cdot}2THF \quad (4)$$

The structure of **13**, determined by X-ray, shows two $Cp^*Ti[o\text{-}(CH_2)_2C_6H_4]$ titanacycles, formed by chelating *o*-xylylene ligands, bridged by a third *o*-xylylene ligand. (see Figure 1). The NMR spectroscopy shows two types of *o*-xylylene groups to be present: in the ^1H spectrum the bridging group gives rise to a singlet at 0.68 ppm (CH_2) and two multiplets centered at 6.68 and 5.76 ppm (C_6H_4) while the chelating $o\text{-}(CH_2)_2C_6H_4$ groups originate two AB doublets (1.30 and 2.46 ppm ($^2J_{HH}$ = 10.7 Hz)) for the CH_2 protons and two multiplets at 7.07 and 7.16 ppm for the ring protons. Some differences are again evident in the ^{13}C NMR spectrum although an unambiguous assignment requires a careful comparison of the ^1H-coupled and -uncoupled ^{13}C NMR spectra. The resonance due to the methylene carbons of the chelating dialkyl appears at 76.4 ppm with an anomalous high coupling constant ($^1J_{CH}$ = 140 Hz) whereas the methylene carbons of the bridging *o*-xylylene gives a signal at 82.2 ppm with $^1J_{CH}$ = 121 Hz. At the same time the $C_{\beta,\beta'}$ signals of the chelating *o*-xylylene group seem to appear at higher field than those of the bridging group (134.1 vs 129.2 ppm). All these data could be indicative of electronic differences between both types of *o*-xylylene groups, as confirmed by the X-ray determination.

X-ray Structure of μ-[*o*-$(CH_2)_2C_6H_4$]{Cp^*Ti[*o*-$(CH_2)_2C_6H_4$]}$_2$ (13). The structure of the binuclear complex **13** is depicted in Figure 1; the most representative bond distances and angles are given in Tables I and II, respectively and a selection of planes and dihedral angles in Table III. The structure consists of two $Cp^*Ti[o\text{-}(CH_2)_2C_6H_4]$ units containing a titanacyclic system, formed by a chelating *o*-xylylene ligand, that are bridged by a third $o\text{-}(CH_2)_2C_6H_4$ ligand. This structure is undoubtly dictated by the bridging *o*-xylylene group and the bulky Cp* rings. Molecular models show nevertheless that simultaneous rotation around the Ti–C_α(bridging) and bridging C_α–C_β bonds is possible. This process must take place in solution and explains the appearance of a singlet for the methylene

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[6] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[7] Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1988**, *7*, 258.

Table I. Important Interatomic Distances (Å) for 13[a]

Ti(1)–C(1)	2.47 (1)	C(9)–C(15)	1.46 (2)
Ti(1)–C(2)	2.45 (2)	C(10)–C(11)	1.44 (2)
Ti(1)–C(7)	2.12 (1)	C(10)–C(16)	1.46 (2)
Ti(1)–C(8)	2.11 (1)	C(11)–C(12)	1.33 (2)
Ti(1)–C(23)	2.13 (1)	C(12)–C(13)	1.41 (3)
Ti(1)–C(25)	2.38 (1)	C(13)–C(14)	1.34 (2)
Ti(1)–C(26)	2.41 (1)	C(17)–C(18)	1.42 (2)
Ti(1)–C(27)	2.39 (1)	C(17)–C(22)	1.42 (2)
Ti(1)–C(28)	2.37 (2)	C(17)–C(23)	1.46 (2)
Ti(1)–C(29)	2.39 (2)	C(18)–C(19)	1.41 (2)
Ti(1)–CE(1)	2.06 (2)	C(18)–C(24)	1.49 (2)
		C(19)–C(20)	1.37 (2)
Ti(2)–C(9)	2.47 (1)	C(20)–C(21)	1.37 (3)
Ti(2)–C(10)	2.47 (1)	C(21)–C(22)	1.40 (2)
Ti(2)–C(15)	2.13 (1)	C(25)–C(26)	1.44 (1)
Ti(2)–C(16)	2.13 (1)	C(25)–C(29)	1.38 (2)
Ti(2)–C(24)	2.13 (1)	C(26)–C(27)	1.43 (2)
Ti(2)–C(35)	2.40 (1)	C(27)–C(28)	1.41 (2)
Ti(2)–C(36)	2.36 (1)	C(28)–C(29)	1.41 (1)
Ti(2)–C(37)	2.36 (1)	C(25)–C(30)	1.53 (2)
Ti(2)–C(38)	2.36 (1)	C(26)–C(31)	1.52 (2)
Ti(2)–C(39)	2.38 (1)	C(27)–C(32)	1.53 (2)
Ti(2)–CE(2)	2.06 (1)	C(28)–C(33)	1.55 (2)
		C(29)–C(34)	1.51 (2)
C(1)–C(2)	1.42 (2)	C(35)–C(36)	1.40 (2)
C(1)–C(6)	1.44 (2)	C(35)–C(39)	1.40 (2)
C(1)–C(7)	1.48 (2)	C(36)–C(37)	1.40 (2)
C(2)–C(3)	1.41 (2)	C(37)–C(38)	1.34 (2)
C(2)–C(8)	1.45 (2)	C(38)–C(39)	1.39 (2)
C(3)–C(4)	1.37 (3)	C(35)–C(40)	1.52 (2)
C(4)–C(5)	1.36 (3)	C(36)–C(41)	1.54 (3)
C(5)–C(6)	1.36 (3)	C(37)–C(42)	1.57 (3)
C(9)–C(10)	1.43 (2)	C(38)–C(43)	1.59 (3)
C(9)–C(14)	1.40 (2)	C(39)–C(44)	1.55 (2)

[a] CE(1) and CE(2) are the centroids of the two C(25)–C(29) and C(35)–C(39) rings, respectively.

Table II. Important Interatomic Angles (deg) for 13[a]

C(23)–Ti(1)–CE(1)	112.0 (5)	C(17)–C(18)–C(19)	120 (1)
C(8)–Ti(1)–CE(1)	113.5 (6)	Ti(2)–C(24)–C(18)	128.9 (8)
C(7)–Ti(1)–CE(1)	114.1 (6)	C(6)–C(1)–C(7)	124 (1)
C(8)–Ti(1)–C(23)	108.5 (6)	C(2)–C(1)–C(7)	117 (1)
C(7)–Ti(1)–C(23)	122.3 (6)	C(2)–C(1)–C(6)	119 (1)
C(7)–Ti(1)–C(8)	82.8 (6)	C(1)–C(2)–C(8)	120 (1)
Ti(1)–C(7)–C(1)	84.7 (8)	C(1)–C(2)–C(3)	116 (1)
Ti(1)–C(8)–C(2)	85.0 (8)	C(3)–C(2)–C(8)	124 (1)
Ti(1)–C(23)–C(17)	113.9 (8)	C(2)–C(3)–C(4)	124 (1)
C(24)–Ti(2)–CE(2)	119.2 (5)	C(3)–C(4)–C(5)	118 (2)
C(16)–Ti(2)–CE(2)	112.8 (5)	C(4)–C(5)–C(6)	122 (2)
C(15)–Ti(2)–CE(2)	113.0 (6)	C(1)–C(6)–C(5)	120 (2)
C(16)–Ti(2)–C(24)	116.5 (5)	C(14)–C(9)–C(15)	124 (1)
C(15)–Ti(2)–C(24)	106.9 (5)	C(10)–C(9)–C(15)	116 (1)
C(15)–Ti(2)–C(16)	82.4 (5)	C(10)–C(9)–C(14)	119 (1)
Ti(2)–C(15)–C(9)	84.9 (7)	C(9)–C(10)–C(16)	120 (1)
Ti(2)–C(16)–C(10)	84.7 (8)	C(9)–C(10)–C(11)	116 (1)
C(23)–C(17)–C(18)	124 (1)	C(11)–C(10)–C(16)	123 (1)
C(23)–C(17)–C(22)	120 (1)	C(10)–C(11)–C(12)	123 (1)
C(18)–C(17)–C(22)	116 (1)	C(11)–C(12)–C(13)	119 (1)
C(24)–C(18)–C(17)	120 (1)	C(12)–C(13)–C(14)	121 (1)
C(24)–C(18)–C(19)	119 (1)	C(9)–C(14)–C(13)	122 (1)

[a] CE(1) and CE(2) are the centroids of the two C(25)–C(29) and C(35)–C(39) rings, respectively.

Table III

plane	atoms
1	C(1), C(2), C(3), C(4), C(5), C(6)
2	C(1), C(2), C(7), C(8)
3	C(9), C(10), C(11), C(12), C(13), C(14)
4	C(9), C(10), C(15), C(16)
5	C(17), C(18), C(19), C(20), C(21), C(22)
6	C(17), C(18), C(23), C(24)
7	Ti(1), C(7), C(8)
8	Ti(2), C(15), C(16)
9	C(25), C(26), C(27), C(28), C(29)
10	C(35), C(36), C(37), C(38), C(39)

plane–plane	dihedral angle (deg)[a]	plane–plane	dihedral angle (deg)[a]
1–2	174.0 (6)	4–8	109.4 (6)
1–5	172.9 (4)	5–6	175.9 (5)
1–7	103.6 (5)	5–9	66.8 (5)
1–9	71.3 (4)	5–10	21.8 (5)
1–10	25.5 (5)	7–9	147.7 (5)
2–7	109.5 (7)	8–10	149.6 (5)
3–4	172.0 (6)	9–10	77.8 (5)
3–5	92.0 (4)		
3–8	101.5 (5)		
3–9	100.1 (5)		
3–10	71.1 (5)		

[a] Estimated standard deviations in parentheses.

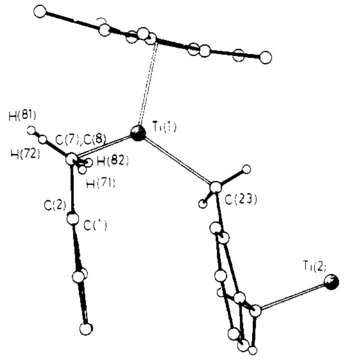

Figure 2. Projection of a part of the structure of 13 along the line through C(7) and C(8), showing the orientation of the chelating xylylene ligand around the Ti(1) atom.

hydrogens of the bridging *o*-xylylene and the Cp* methyls in the ^{1}H NMR spectrum.

Each Ti atom is in an environment that can be described as a distorted three-legged piano stool, the distortion being imposed by the small bite of the chelating *o*-xylylene ligand. The angles between the legs [C(7), C(8), and C(23) for Ti(1) and C(15), C(16), and C(24) for Ti(2)] vary from 82.8 (6) (bite angle) to 122.3 (6)° for Ti(1) and from 82.4 (5) (bite angle) to 116.5 (5)° for Ti(2). The angles formed between these legs and the corresponding Ti–Cp* centroid axis are in the range 112.0 (5)–114.1 (6)° for Ti(1) and 112.8 (5)–119.2 (5)° for Ti(2).

Distances and angles within the pentamethylcyclopentadienyl ligands are unexceptional:[8] the ring C–C distances vary from 1.38 (2) to 1.44 (1) Å in Cp*(1) and from 1.34 (2) to 1.40 (2) Å in Cp*(2). The methyl groups are slightly bent away from the planes through the five carbon atoms of the ring, the maximum deviation being 0.16 (2) Å in Cp*(1) and 0.22 (1) Å in Cp*(2), this latter corresponding to the C(40) atom, which is placed over the bridging *o*-xylylene group.

The ring Ti–C distances vary from 2.37 (1) to 2.41 (1) Å in the case of Ti(1) and from 2.36 (1) to 2.40 (1) Å for Ti(2), and the Cp* centroid–Ti distances are both equal, 2.06 (2) and 2.06 (1) Å, all being quite normal values for η^5-C_5Me_5 ligands.[9]

The Ti–C distances, involving the methylene C(7), C(8), C(23) and C(15), C(16), C(24) carbon atoms of the legs, are very similar, varying from 2.11 (1) to 2.13 (1) Å for Ti(1) and being 2.13 (1) Å for Ti(2). These values are comparable to those found in monopentamethylcyclopentadienyl compounds: $Cp^*Ti(CH_2Ph)_3$ (2.08 (1)–2.16 (1) Å[5]) or

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[8] (a) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (b) Sanner, R. D.; Duggan, M. D.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358. (c) Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51. (d) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457.

[9] See ref 5, 7, 8, and 10.

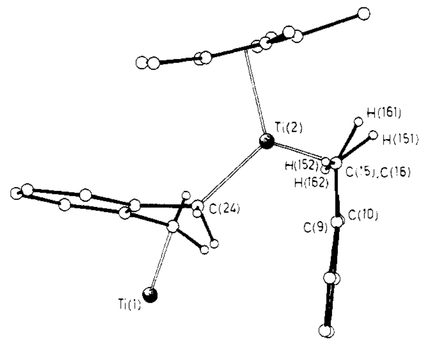

Figure 3. Projection of a part of the structure of **13** along the line through C(15) and C(16), showing the orientation of the chelating xylylene ligand around the Ti(2) atom.

$[Cp^*TiMe(\mu\text{-}O)]_3$ (2.08 (1)–2.10 (1) Å[10]).

The three *o*-xylylene groups are nearly planar, and there is no bond alternation. Note that the chelating *o*-xylylene groups are bent in such a way that their rings are situated within the hole created by the three legs (Figures 2 and 3). Moreover, the distances of the metals to the β-carbons are rather short: Ti(1)–C(1) = 2.47 (1), Ti(1)–C(2) = 2.45 (2), and Ti(2)–C(9) = Ti(2)–C(10) = 2.47 (1) Å. The Ti–C_α–C_β angles vary from 84.7 (8) to 85.0 (8)°, much smaller than the tetrahedral angle, and the fold angles (the dihedral angles between the Ti–C_α–$C_{\alpha'}$ and C_α–C_β–$C_{\beta'}$–$C_{\alpha'}$ planes) also are unusually narrow in both cases (109.5 (7)° for Ti(1) and 109.4 (6)° for Ti(2)). All these data are indicative of an interaction between the Ti atoms and the ring systems.

Discussion

The use of the Cp* ligand has allowed once more the isolation of a series of compounds whose Cp analogues, although prepared some years ago,[11] have been barely studied because their instability. The increased thermal stability imparted by the Cp* ring becomes evident when comparing both series of compounds: $CpTiMe_3$ melts and decomposes at 20 °C while **2** has a melting point of 75–76 °C (without decomposition), and $CpTi(CH_2SiMe_3)_3$ melts at 60–62 °C while **4** melts at 83–84 °C. Provided that water is absolutely avoided (otherwise a series of oxo compounds are immediately formed[10]), all the aforementioned compounds can be easily handled. They are nevertheless electron-deficient compounds (formally 12 electrons), and we wondered what the titanium atom could do in order to cope with this electron deficiency. For this reason we carried out an X-ray analysis of the tribenzyl derivative **3** and a determination of its structure, which has been discussed elsewhere.[5] Both hydrogen atoms of one benzyl group interact with the Ti atom [Ti–H distances: 2.32 and 2.37 Å, Ti–C(8)–H angles: 94 and 97°]. This interaction generates distortions in this benzylic skeleton [Ti–C(8)–C(9) = 139.0 (7)°] (see Figure 4).

We prepared **13** assuming that it should present a similar electronic distribution around the metal but in a considerably less crowded environment. What we have found (see X-ray discussion) is that the chelating *o*-xylylene ligands are located in the hole created by the legs.

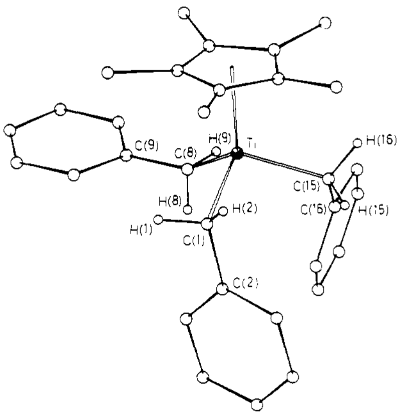

Figure 4. View of the structure of $Cp^*Ti(CH_2Ph)_3$.

Table IV

compound	Δd (Å)[a]	M–C_α–C_β angle (deg)	$^1J_{CH}$ (Hz)	ref
$Ti(CH_2Ph)_4$	–0.47	98 (2)	132	13
	–0.48	88 (2)		
	–0.66	88 (2)		
	–1.03	116 (2)		
$Zr(CH_2Ph)_4$	–0.47	85 (1),	136	25
	(mean)	90 (1),		
		92 (1),		
		101 (1)		
$Cp^*Ti(CH_2Ph)_3$	–0.91	113.8 (6)	126	5
	–0.91	114.0 (7)		
	–1.26	139.0 (7)		
$Cp^*Th(CH_2Ph)_3$	–0.29	86 (1)	134	18
	–0.33	87 (1)		
	–0.40	91 (1)		
$(2,6\text{-}Bu^t_2C_6H_3O)Zr(CH_2Ph)_3$	–0.31	84.3 (9)	132	17
		97.9 (12)		
		115.1 (11)		
$[Cp_2Zr(NCMe)(CH_2Ph)]^+$	–0.31	84.9 (4)	*b*	26
$Cp_2Ti[o\text{-}(CH_2)_2C_6H_4]$	–0.71	102.4 (3)	*b*	12
$Cp_2Zr[o\text{-}(CH_2)_2C_6H_4]$	–0.61	95.5 (4)	*b*	12
13	–1.14[c]	128.9 (8)	121	this work
	–0.90[c]	113.9 (8)	121	
	–0.34[d]	84.8 (8)	140	
	–0.35[d]	84.8 (8)	140	

[a] Defined by $[d(M\text{–}C_\alpha) + d(M\text{–}C_{\alpha'})]/2 - [d(M\text{–}C_\beta) + d(M\text{–}C_{\beta'})]/2$ in *o*-xylylene complexes and $[d(M\text{–}C_\alpha) - d(M\text{–}C_\beta)]$ in benzyl complexes. [b] Not published. [c] Bridging *o*-xylylene. [d] Chelating *o*-xylylenes.

The fold angle (as defined above) of these two xylylene groups is about 30° smaller than that encountered in $Cp_2Ti[o\text{-}(CH_2)_2C_6H_4]$ (139°), which is a 16-electron compound;[12] at the same time the mean value of the difference in Ti–C distances to the α- and β-carbon atoms [Δd, defined as $[d(Ti\text{–}C_\alpha) + d(Ti\text{–}C_{\alpha'})]/2 - [d(Ti\text{–}C_\beta) + d(Ti\text{–}C_{\beta'})]/2$] amounts to –0.71 Å in the titanocene complex and to –0.34 and –0.35 Å in our case. The distances Ti(1)–C(1) and Ti(1)–C(2) (2.47 (1) and 2.45 (2) Å, respectively) and Ti(2)–C(9) and Ti(2)–C(10 (2.47 (1) Å) are even notably shorter than the two "short" Ti–C distances found in $Ti(CH_2Ph)_4$ (2.61 and 2.81 Å) where a "benzallyl"-type distortion was proposed.[13]

If Δd is taken as indicative of the magnitude of the metal–C_β interaction in benzyl and *o*-xylylene metal complexes, it is clear that **13** represents one of the most pronounced examples within the reported derivatives of the group 4 elements and most of the Ti derivatives (see Table IV, in which the complexes of the middle to late transition elements have not been included because they are more adequately described as true η^3-allyl[14] or η^4-diene[15] com-

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plexes). At the same time as the interaction increases, the value of the $^1J_{\mathrm{C_\alpha H}}$ coupling constant also increases from the value of 125 Hz typical for sp^3 C atoms.[16] This trend has been noted earlier,[17] and the 140 Hz for **13** is the higher value reported to date. Following this argument we can suppose a similar interaction in $\mathrm{Cp^*TiCl[\mathit{o}\text{-}(CH_2)_2C_6H_4]}$ that also has a value of 140 Hz.[7]

Thus, the chelating *o*-xylylene group in **13** interacts with the Ti atom so as to reduce its electronic deficiency, whereas the Ti atom of **3** compensates for this deficiency by interacting with the C–H bonds of the "anomalous" benzyl ligand. The questions that arise are why is there a $\overline{\mathrm{Ti\cdots C{-}C}}$ interaction in **13** and a $\overline{\mathrm{Ti\cdots H{-}C}}$ in **3** and why do we not observe in **3** the "benzallyl"-type distortion found in $\mathrm{Ti(CH_2Ph)_4}$[13] or $\mathrm{Cp^*Th(CH_2Ph)_3}$.[18] We cannot give a definitive answer, but we feel that steric effects produced by the Cp* ring may play an important role. Molecular models show for **3** that a structure similar to that of the thorium derivative is sterically unfeasible.

Experimental Section

All manipulations were carried out under dry argon in Vacuum Atmospheres drybox. Solvents were distilled from drying agents as follows and stored in the drybox: sodium benzophenone ketyl for diethyl ether and tetrahydrofuran, sodium for toluene, and sodium–potassium amalgam for hexane. $\mathrm{Cp^*TiCl_3}$,[19] $\mathrm{Cp^*TiBr_3}$,[19] and $\mathrm{[\mathit{o}\text{-}(CH_2)_2C_6H_4]Mg(THF)_2}$[20] were prepared according to literature methods. ^{1}H NMR spectra were recorded on a Varian FT-80 A instrument; the ^{1}H and ^{13}C chemical shifts are referenced to residual protons or carbons of the solvent or to TMS as an internal standard. ^{19}F chemical shifts are referenced to $\mathrm{CFCl_3}$ taking downfield shifts as negatives. C, H analyses were done with a Perkin-Elmer 240B microanalyzer.

$\mathrm{Cp^*TiMe_3}$ (2). A 1.6 M solution (6.5 mL) of LiMe in diethyl ether is slowly added to an ice-cooled suspension of 1 g (3.46 mmol) of $\mathrm{Cp^*TiCl_3}$ in 40 mL of hexane; the mixture is left to reach room temperature with stirring for 4 h and then is filtered. Upon elimination of the solvent under reduced pressure, 0.77 g (98%) of yellow **2** is obtained as a microcrystalline but spectroscopically and analytically pure solid. Recrystallization from pentane at −78 °C gives **2** as beautiful yellow prisms. Anal. Calcd for $\mathrm{C_{13}H_{24}Ti}$: C, 68.41; H, 10.60. Found: C, 68.30; H, 10.49. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 1.74 (s, 15 H, Cp*), 0.99 (s, 9 H, Ti–Me). ^{1}H NMR (ppm in $\mathrm{CDCl_3}$): 1.93 (s, 15 H, Cp*), 0.73 (s, 9 H, Ti–Me). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 122.3 (s, $\mathit{C}_5\mathrm{Me}_5$), 61.2 (q, $^1J_{\mathrm{CH}} = 119$ Hz, Ti–Me), 12.0 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C}_5\mathit{Me}_5$).

$\mathrm{Cp^*Ti(CH_2Ph)_3}$ (3). A freshly prepared solution of 4.66 mmol of $\mathrm{PhCH_2MgBr}$ in diethyl ether is added dropwise to a stirred suspension of 0.45 g (1.55 mmol) of $\mathrm{Cp^*TiCl_3}$ in 15 mL of $\mathrm{Et_2O}$ at −10 °C. The mixture is allowed to warm to room temperature and stirred for 1 h, and the solvent is then stripped under reduced pressure. The solid residue is treated with several portions of hexane (10 mL each), and the combined extracts are concentrated under vacuum and cooled overnight to −40 °C to yield 0.63 g (90%) of orange-red crystals of **3**. Anal. Calcd for $\mathrm{C_{31}H_{36}Ti}$: C, 81.56; H, 7.95. Found: C, 81.10; H, 8.14. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 7.36–6.84 (m, 15 H, Ph), 2.73 (s, 6 H, $\mathrm{CH_2}$), 1.61 (s, 15 H, Cp*). ^{1}H NMR (ppm in $\mathrm{CDCl_3}$): 7.16–6.57 (m, 15 H, Ph), 2.61 (s, 6 H, $\mathrm{CH_2}$), 1.85 (s, 15 H, Cp*). ^{13}C NMR (gated decoupled; ppm in $\mathrm{CDCl_3}$): 150.0 (m, ipso-$\mathrm{C_6H_5}$), 128.2 (dd, $^1J_{\mathrm{CH}} = 159$ Hz, $^2J_{\mathrm{CH}} = 8$ Hz, *o*-$\mathrm{C_6H_5}$), 126.7 (dm, $^1J_{\mathrm{CH}} = 156$ Hz, *m*-$\mathrm{C_6H_5}$), 123.9 (s, $\mathit{C}_5\mathrm{Me}_5$), 122.3 (dt, $^1J_{\mathrm{CH}} = 160$ Hz, $^2J_{\mathrm{CH}} = 8$ Hz, *p*-$\mathrm{C_6H_5}$), 94.1 (tt, $^1J_{\mathrm{CH}} = 122$ Hz, $^3J_{\mathrm{CH}} = 4$ Hz, $\mathrm{CH_2}$), 11.9 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C}_5\mathit{Me}_5$).

$\mathrm{Cp^*Ti(CH_2SiMe_3)_3}$ (4). Solid $\mathrm{LiCH_2SiMe_3}$ (0.36 g, 3.82 mmol) is added to a stirred suspension of 0.37 g (1.27 mmol) of $\mathrm{Cp^*TiCl_3}$ in 20 mL hexane at −40 °C; the mixture is warmed to room temperature, stirred for 1 h, filtered, and taken to dryness under reduced pressure. A dark brown-yellow oil that exhibits the ^{1}H NMR spectra of pure **4** is obtained this way. Crystallization from pentane at −78 °C affords yellow crystals of **4** in ca. 60% yield. Anal. Calcd for $\mathrm{C_{22}H_{48}Si_3Ti}$: C, 59.41; H, 10.88. Found: C, 60.20; H, 11.06. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 1.86 (s, 15 H, Cp*), 1.37 (s, 6 H, $\mathrm{CH_2}$), 0.28 (s, 27 H, $\mathrm{SiMe_3}$). ^{1}H NMR (ppm in $\mathrm{CDCl_3}$): 2.01 (s, 15 H, Cp*), 1.21 (s, 6 H, $\mathrm{CH_2}$), 0.07 (s, 27 H, $\mathrm{SiMe_3}$). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 122.6 (s, $\mathit{C}_5\mathrm{Me}_5$), 84.4 (t, $^1J_{\mathrm{CH}} = 105$ Hz, $\mathrm{CH_2}$), 12.9 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C}_5\mathit{Me}_5$), 2.95 (q, $^1J_{\mathrm{CH}} = 118$ Hz, $\mathrm{SiMe_3}$).

$\mathrm{Cp^*Ti(C_6F_5)_3}$ (5). A freshly prepared solution of $\mathrm{LiC_6F_5}$ (5.48 mmol) in diethyl ether is added to a suspension of 0.53 g (1.83 mmol) of $\mathrm{Cp^*TiCl_3}$ in 20 mL of $\mathrm{Et_2O}$ at −78 °C. After the solution is warmed to room temperature and stirred for 1 h, the solvent is stripped and the red residue is extracted with 20 mL of warm toluene. Crystalline dark-red **5** (0.87 g, 70%) is obtained upon cooling at −40 °C overnight. Anal. Calcd for $\mathrm{C_{28}H_{15}F_{15}Ti}$: C, 49.15; H, 2.21. Found: C, 48.73; H, 2.80. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 1.79 (s, Cp*). ^{19}F NMR (ppm in $\mathrm{C_6D_6}$): −160.7 (m, *m*-$\mathrm{C_6F_5}$), −149.8 (t, $^3J_{\mathrm{FF}} = 19.9$ Hz, *p*-$\mathrm{C_6F_5}$), −122.0 (d, $^3J_{\mathrm{FF}} = 19.3$ Hz, *o*-$\mathrm{C_6F_5}$).

$\mathrm{Cp^*TiClMe_2}$ (6). The procedure to obtain **2** is followed except that 0.46 g (1.59 mmol) of $\mathrm{Cp^*TiCl_3}$ and 1.98 mL (3.18 mmol) of LiMe are reacted in 20 mL hexane to yield 0.34 g of light yellow **6** (85% yield). Anal. Calcd for $\mathrm{C_{12}H_{21}ClTi}$: C, 57.97; H, 8.51. Found: C, 58.01; H, 8.50. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 1.70 (s, 15 H, Cp*), 1.15 (s, 6 H, Ti–Me). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 126.3 (s, $\mathit{C}_5\mathrm{Me}_5$), 68.0 (q, $^1J_{\mathrm{CH}} = 123$ Hz, Ti–Me), 12.3 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C}_5\mathit{Me}_5$).

$\mathrm{Cp^*TiCl(CH_2Ph)_2}$ (7). The procedure to obtain **3** is followed except that 0.39 g (1.35 mmol) of $\mathrm{Cp^*TiCl_3}$ and 0.47 g (1.35 mmol) of $\mathrm{(PhCH_2)_2Mg(THF)_2}$ are used. Crystallization from hexane yielded red **7** (85%). Anal. Calcd for $\mathrm{C_{24}H_{29}ClTi}$: C, 71.91; H, 7.29. Found: C, 71.80; H, 7.28. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 7.14–6.95 (m, 10 H, Ph), 3.04 (d, $^2J_{\mathrm{HH}} = 10.5$ Hz, 2 H, $\mathrm{CH_2}$), 2.20 (d, $^2J_{\mathrm{HH}} = 10.5$ Hz, 2 H, $\mathrm{CH_2}$), 1.66 (s, 15 H, Cp*). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 148.0 (m, ipso-Ph), 128.5 (dd, $^1J_{\mathrm{CH}} = 157$ Hz, $^2J_{\mathrm{CH}} = 7$ Hz, *o*-Ph), 129.1 (dm, $^1J_{\mathrm{CH}} = 158$ Hz, *m*-Ph), 127.2 (s, $\mathit{C}_5\mathrm{Me}_5$), 123.7 (dm, $^1J_{\mathrm{CH}} = 126$ Hz, *p*-Ph), 97.2 (d, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{CH_2}$), 12.3 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C}_5\mathit{Me}_5$).

$\mathrm{Cp^*TiCl(CH_2SiMe_3)_2}$ (8). The procedure to obtain **4** is followed except that 1.11 g (3.83 mmol) of $\mathrm{Cp^*TiCl_3}$ and 0.72 (7.67 mmol) of $\mathrm{LiCH_2SiMe_3}$ are reacted in 40 mL of hexane to yield 1 g of yellow **8** (66% yield). Anal. Calcd for $\mathrm{C_{18}H_{37}ClSi_2Ti}$: C, 55.01; H, 9.49. Found: C, 54.79; H, 9.40. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 2.03 (d, $^2J_{\mathrm{HH}} = 11$ Hz, 2 H, $\mathrm{CH_2}$), 1.83 (s, 15 H, Cp*), 1.41 (d, $^2J_{\mathrm{HH}} = 11$ Hz, $\mathrm{CH_2}$), 0.35 (s, 18 H, $\mathrm{SiMe_3}$). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 125.7 (s, $\mathit{C}_5\mathrm{Me}_5$), 90.0 (dd, $^1J_{\mathrm{CH_a}} = 113$ Hz, $^1J_{\mathrm{CH_b}} = 105$ Hz, $\mathrm{CH_2}$), 13.0 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C}_5\mathit{Me}_5$), 2.6 (q, $^1J_{\mathrm{CH}} = 118$ Hz, $\mathrm{SiMe_3}$).

$\mathrm{Cp^*TiBr(CH_2Ph)_2}$ (10). The procedure to obtain **3** is followed except that 0.76 g (1.80 mmol) of $\mathrm{Cp^*TiBr_3}$ and $\mathrm{(PhCH_2)_2Mg(THF)_2}$ are used. Crystallization from hexane gave 0.68 g of red **10** (85% yield). Anal. Calcd for $\mathrm{C_{24}H_{29}BrTi}$: C, 64.73; H, 6.56. Found: C, 64.49; H, 6.85. ^{1}H NMR (ppm in $\mathrm{C_6D_6}$): 7.11–6.96 (m, 10 H, Ph), 3.10 (d, $^2J_{\mathrm{HH}} = 10.3$ Hz, 2 H, $\mathrm{CH_2}$), 2.16 (d, $^2J_{\mathrm{HH}} = 10.3$ Hz, $\mathrm{CH_2}$), 1.67 (s, 15 H, Cp*). ^{13}C NMR (gated decoupled; ppm in $\mathrm{C_6D_6}$): 147.7 (m, ipso-Ph), 129.4 (dm, $^1J_{\mathrm{CH}} = 157$ Hz, *m*-Ph), 128.5 (dd, $^1J_{\mathrm{CH}} = 158$ Hz, $^2J_{\mathrm{CH}} = 6$ Hz, *o*-Ph), 127.6 (s, $\mathit{C}_5\mathrm{Me}_5$), 123.9 (dm, $^1J_{\mathrm{CH}} = 157$ Hz, *p*-Ph), 100.6 (t, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{CH_2}$), 12.8 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C}_5\mathit{Me}_5$).

$\mu\text{-}[\mathit{o}\text{-}\mathrm{(CH_2)_2C_6H_4}]\{\mathrm{Cp^*Ti}[\mathit{o}\text{-}\mathrm{(CH_2)_2C_6H_4}]\}_2$ (13). *o*-$\mathrm{(CH_2)_2C_6H_4Mg(THF)_2}$ (0.99 g, 3.63 mmol) are added portionwise to a cooled (−40 °C) solution of 0.70 g (2.42 mmol) of $\mathrm{Cp^*TiCl_3}$

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Table V. Experimental Data for the X-ray Diffraction Study on 13

mol formula	$C_{44}H_{54}Ti_2$
mol wt	678.71
cryst system	monoclinic
space group	$P2_1/a$
a, Å	11.207 (1)
b, Å	34.520 (6)
c, Å	10.460 (1)
β, deg	113.83 (1)
V, Å^3	3701.6 (9)
Z	4
D_{calcd}, g cm^{-3}	1.218
$F(000)$	1448
cryst dimens, mm	0.20 × 0.22 × 0.25
linear abs, cm^{-1}	38.83
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, deg	3–12
scan width	$(\theta - 0.6) - (\theta + 0.6 + 0.142 \tan \theta)$
radiatn	Ni-filtered Cu Kα (λ = 1.541 838 Å)
2θ range	6–140
reflectns measd	$\pm h,k,l$
std reflctn	one measd after 50 reflctns
unique total data	6949
unique obsd data $[I \geq 2\sigma(I)]$	2096
R	0.0694
R_w	0.0743

in 40 mL diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred 1.5 h. The ether was then removed under reduced pressure and replaced by 20 mL of hexane; the dark red solution was filtered, the precipitate was washed two times with 10-mL portions of hexane, and the combined extracts were concentrated and cooled overnight at −40 °C. Brown-red crystals of **13** (0.41 g) are obtained (50% yield). Anal. Calcd for $C_{44}H_{54}Ti_2$: C, 77.90; H, 7.96. Found: C, 78.00; H, 7.90. ^{1}H NMR (ppm in C_6D_6): 7.16 (m, 4 H, chelating C_6H_4), 7.07 (m, 4 H, chelating C_6H_4), 6.68 (m, 2 H, bridging C_6H_4), 5.76 (m, 2 H, bridging C_6H_4), 2.46 (d, $^2J_{HH}$ = 10.6 Hz, 4 H, chelating CH_2), 1.70 (s, 30 H, Cp*), 1.30 (d, $^2J_{HH}$ = 10.6 Hz, 4 H, chelating CH_2), 0.68 (s, 4 H, bridging CH_2). ^{13}C NMR (gated decoupled, ppm in C_6D_6): 135.1 (s, β-*o*-$(CH_2)_2C_6H_4$), 134.1 (d, $^1J_{CH}$ = 158 Hz, C_6H_4), 129.2 (s, β-*o*-$(CH_2)_2CH_6H_4$), 128.3 (d, $^1J_{CH}$ = 164 Hz, C_6H_4), 125.2 (d, $^1J_{CH}$ = 160 Hz, C_6H_4), 122.5 (d, $^1J_{CH}$ = 164 Hz, C_6H_4), 121.4 (s, C_5Me_5), 82.3 (t, $^1J_{CH}$ = 121 Hz, CH_2), 76.4 (t, $^1J_{CH}$ = 140 Hz, CH_2), and 11.8 (q, $^1J_{CH}$ = 126 Hz, $C_5\mathit{Me}_5$).

X-ray Data Collection, Structure Determination, and Refinement for μ-[*o*-$(CH_2)_2C_6H_4$]{Cp*Ti[*o*-$CH_2)_2C_6H_4$]}$_2$ (13). A crystal of **13** was sealed in a Lindemann glass capillary under dry argon and used for data collection. The crystallographic data are summarized in Table V. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having $15 < \theta < 41°$. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[21] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[22] A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.1056 and 0.8735, respectively).[23] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by standard Patterson and Fourier methods and refined by blocked-matrix least squares first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms excepting the carbon atoms of the pentamethylcyclopentadienyl rings. All the hydrogen atoms (excepting those of the methyl groups) were clearly localized in the final difference Fourier map and refined isotropically. The first cycles of refinement were carried out on the basis of 411 variables; after the last cycle, no parameters shifted by more than 0.4 esd. The biggest remaining peak in the final difference map was equivalent to about 0.55 e/Å^3; unit weights were used in all the stages of the refinement as a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, with K and g values to be refined, in the last cycles of the refinement did not give better results. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 24. The final atomic coordinates for the non-hydrogen atoms are given in Table VI. The atomic coordinates of the hydrogen atoms are given in Table SI and the thermal parameters in Table SII.

Table VI. Fractional Atomic Coordinates (×10^4) with ESD's in Parentheses for the Non-Hydrogen Atoms

atom	x	y	z
Ti(1)	3275 (2)	946 (1)	3186 (2)
Ti(2)	−1847 (2)	1689 (1)	319 (2)
C(1)	2806 (12)	615 (4)	5026 (12)
C(2)	2851 (12)	1018 (4)	5293 (13)
C(3)	1812 (15)	1170 (4)	5575 (14)
C(4)	845 (15)	951 (5)	5688 (15)
C(5)	846 (14)	562 (6)	5460 (15)
C(6)	1785 (16)	386 (4)	5154 (15)
C(7)	3788 (13)	461 (4)	4546 (14)
C(8)	3815 (13)	1255 (4)	5073 (13)
C(9)	−1428 (12)	2187 (3)	2151 (14)
C(10)	−302 (13)	2175 (3)	1838 (14)
C(11)	939 (13)	2160 (4)	3016 (16)
C(12)	1064 (14)	2159 (4)	4336 (15)
C(13)	−75 (17)	2160 (4)	4604 (15)
C(14)	−1258 (13)	2178 (3)	3554 (14)
C(15)	−2688 (12)	2164 (3)	964 (14)
C(16)	−449 (12)	2117 (4)	395 (14)
C(17)	374 (11)	786 (3)	1874 (11)
C(18)	−826 (11)	869 (3)	1972 (11)
C(19)	−1653 (12)	565 (3)	2012 (12)
C(20)	−1342 (16)	186 (4)	1900 (15)
C(21)	−224 (17)	95 (4)	1734 (15)
C(22)	626 (12)	391 (4)	1715 (14)
C(23)	1305 (11)	1083 (4)	1889 (12)
C(24)	−1248 (11)	1278 (3)	1974 (12)
C(25)	3666 (11)	943 (3)	1111 (12)
C(26)	4622 (11)	690 (3)	2082 (12)
C(27)	5419 (12)	930 (4)	3217 (12)
C(28)	4940 (12)	1312 (4)	2909 (13)
C(29)	3867 (12)	1319 (4)	1607 (13)
C(30)	2689 (13)	800 (4)	−317 (14)
C(31)	4797 (14)	257 (4)	1930 (15)
C(32)	6641 (15)	801 (4)	4472 (15)
C(33)	5608 (15)	1677 (5)	3769 (16)
C(34)	3138 (14)	1676 (4)	861 (15)
C(35)	−2353 (12)	1212 (4)	−1488 (12)
C(36)	−2084 (12)	1564 (4)	−1986 (13)
C(37)	−3045 (13)	1832 (4)	−2069 (14)
C(38)	−3876 (14)	1654 (4)	−1628 (14)
C(39)	−3477 (12)	1273 (4)	−1246 (13)
C(40)	−1669 (15)	829 (4)	−1454 (15)
C(41)	−996 (16)	1626 (5)	−2503 (17)
C(42)	−3186 (19)	2245 (6)	−2735 (20)
C(43)	−5187 (19)	1823 (5)	−1611 (20)
C(44)	−4233 (16)	960 (5)	−813 (18)

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Supplementary Material Available: Table SI, coordinates and isotropic thermal parameters for the hydrogen atoms, and Table SII, thermal parameters for the non-hydrogen atoms (2 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Neopentylarsenic Chemistry: Synthesis and Characterization of $As(CH_2CMe_3)_nBr_{3-n}$ (n = 1–3) and $As(CH_2CMe_3)_nBr_{5-n}$ (n = 2 or 3). Crystal and Molecular Structure of $As(CH_2CMe_3)_3$ and $As(CH_2CMe_3)_3Br_2$

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The new compound $As(CH_2CMe_3)_3$ has been prepared in 91% yield from the reaction of $(Me_3CCH_2)MgCl$ with $AsCl_3$ in ether solution. Addition of bromine to a pentane solution of $As(CH_2CMe_3)_3$ yielded $As(CH_2CMe_3)_3Br_2$ as a colorless, crystalline solid. Reductive elimination of neopentyl bromide, at 190–195 °C, from $As(CH_2CMe_3)_3Br_2$ produced the pale yellow liquid $As(CH_2CMe_3)_2Br$. Reaction of $As(CH_2CMe_3)_2Br$ with bromine resulted in formation of the yellow solid $As(CH_2CMe_3)_2Br_3$. The arsorane reductively eliminates neopentyl bromide at room temperature, but more readily at 50 °C, yielding $As(CH_2CMe_3)Br_2$ as a pale yellow liquid. The neopentylarsines and -arsoranes have been fully characterized according to physical and solubility properties and IR and ^1H and ^{13}C NMR spectroscopic properties. Also, single-crystal X-ray diffraction studies of $As(CH_2CMe_3)_3$ and $As(CH_2CMe_3)_3Br_2$ have been carried out. The compound $As(CH_2CMe_3)_3$ crystallizes in the hexagonal space group $P6_3$ with unit-cell parameters a = 9.929 (2) Å, b = 9.929 (2) Å, c = 10.373 (3) Å, V = 885.7 (4) Å^3, and Z = 2. The geometry about arsenic is pyramidal with the C–As–C angle equal to 94.6 (4)° and As–C distances of 1.998 (10) Å. The addition compound $As(CH_2CMe_3)_3Br_2$ crystallizes in the monoclinic space group Cc with unit-cell parameters a = 9.894 (3) Å, b = 17.038 (5) Å, c = 12.147 (3) Å, V = 1947.9 (9) Å^3, and Z = 4. A nearly regular trigonal-bipyramidal geometry is observed about As with the Br–As–Br angle equal to 179.6 (1)° and an average C–As–C equal to 120 (1)°. The average As–C bond distance is 1.98 (1) Å, and As–Br bond distances range from 2.530 (2) to 2.597 (2) Å.

Introduction

There has been considerable interest in the effect of sterically demanding ligands on the synthesis and properties of organometallic derivatives of the main-group elements. Organometallic compounds incorporating such ligands have been shown to exhibit some unusual properties. For example, aluminum compounds incorporating neopentyl[1] and mesityl[2] ligands have been shown to be monomeric in the solid state. Also, mesityl,[3] pentamethylcyclopentadienyl,[4] and neopentyl[5] derivatives of gallium exhibit significantly reduced Lewis acidities. In addition, sterically demanding ligands have been used to stabilize a variety of low-valent group 14 and group 15 derivatives.[6] In arsenic chemistry, Lappert and co-workers[7] have examined the utility of the bis(trimethylsilyl)methyl and (trimethylsilyl)amino ligands in stabilizing radicals of the type $^\bullet AsR_2$. The effect of the bulky mesityl group on rotation about the As–C bond has also been investigated.[8] Particular interest has focused on arsenic derivatives incorporating the (trimethylsilyl)methyl moiety. Tris[(trimethylsilyl)methyl]arsine and bis[(trimethylsilyl)methyl]arsenic(III) chloride were first described by Seyferth.[9] Reactivity patterns of arsenic(V) compounds incorporating the (trimethylsilyl)methyl ligand have also been examined.[10] More recently, Wells and co-workers have investigated a route to the silylarsine $(Me_3SiCH_2)_2AsSiMe_3$ from reaction of $(Me_3SiCH_2)_2AsLi$ and Me_3SiCl.[11] The silylarsine was then used to prepare a series of novel (arsino)gallanes.[11,12]

Substituting the neopentyl moiety for the (trimethylsilyl)methyl ligand in aluminum[1,13] and gallium[5,14] compounds resulted in pronounced differences in properties

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