Organometallics 1992, *11*, 3301–3306

= 14 Hz, 3 H), 5.34 (s, 5 H)) (ca. 80%) along with ca. 20% of the trans isomer (δ 0.42 (d, *J* = 2.6 Hz, 3 H), 4.87 (d, *J* = 1.4 Hz, 5 H)). A spectrum recorded 10 min later showed a ca 1:10 ratio of the cis and trans isomers. Phosphorus–Cp couplings are generally observed for trans, but not for cis, four-legged piano stool structures $CpM(CO)_2(PR_3)X$.[21]

Acknowledgment. We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters (stipend to V.S.), and from the Norwegian Council for Science and the Humanities, NAVF.

Note Added in Proof. The general coordination geometry of **3a** has been confirmed by an X-ray crystallographic analysis of **3a**$(PF_6)_2$ by Professor Christian Rømming. The crystal quality did not allow for an accurate structural analysis.

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Fulvalene Derivatives of Titanium: X-ray Structures of $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ and $[\{Ti(CH_2C_6H_5)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$

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Dithalliofulvalene and bis(trimethylsilyl)fulvalene were used as alkylating reagents to transfer the fulvalene group to $TiCl_4$, leading to $[(TiCl_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**1**; 30% yield). This extremely moisture-sensitive compound is quantitatively hydrolyzed to the μ-oxo dinuclear complex $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**2**) when the reaction to synthesize **1** is carried out in wet toluene or chloroform. The transformation of **2** into **1** can also be done by reacting the μ-oxo derivative with $AlEtCl_2$ in toluene. Alkylation of **1** with $[Mg(CH_2Ph)_2]\cdot THF$ led to $[\{Ti(CH_2Ph)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**3**; 97% yield). The crystal structures of **2** and **3** have been determined by X-ray diffraction methods. Crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 9.305$ (3) Å, $b = 12.387$ (4) Å, $c = 12.821$ (4) Å, and $\beta = 110.31$ (2)°. Crystals of **3** are monoclinic, space group $P2_1/n$, with $Z = 2$ in a unit cell of dimensions $a = 16.976$ (6) Å, $b = 11.022$ (5) Å, $c = 11.238$ (4) Å, and $\beta = 101.15$ (2)°. Both structures were solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1662 (**2**) and 2126 (**3**) observed reflections to R and R_w values of 0.0397 and 0.0482 (**2**) and 0.0490 and 0.0609 (**3**), respectively. In both compounds each fulvalene cyclopentadienyl ring is η^5-bound to one titanium atom. The remaining coordination sites of titanium are occupied by two chlorines and one bridging oxygen in **2** or by three benzyl ligands in **3**, each showing a different bonding system.

Introduction

The electron deficiency of monocyclopentadienyl complexes of the early transition metals is partially compensated by using the permethylated ring, which gives rise to similarly reactive although thermally more stable compounds. An even more reactive and structurally interesting type of complex is to be expected by using the fulvalene group, whose electron-donor capacity is lower than that of the unsubstituted cyclopentadienyl ring. Also, this $\eta^5{:}\eta^5$ bridging fulvalene group would permit the access to homo- or heterodinuclear compounds containing independent or nonindependent metal fragments. Fulvalene complexes are known for many transition metals,[1] including derivatives of group 4d elements. However, the known group 4d fulvalene complexes contain some additional cyclopentadienyl rings, being usually metallocene type compounds. A new synthetic route leading to $[(\eta^5\text{-}C_5Me_5)MCl_3]$ (M = Ti, Zr, Hf)[2a] and extended to Nb and Ta[2b,c] was developed in our laboratory by using $[(C_5Me_5)SiMe_3]$ as an alkylating agent. A variety of titanium alkyls and oxo alkyls have been synthesized previously[2d] from these starting materials, and many of these compounds show structural features that confirm the presence of electron-deficient metal centers.

The already known early-transition-metal fulvalene complexes have been previously isolated through two synthetic methods: (i) activating C–H bonds in cyclopentadienyl rings with transformations of two cyclopentadienyl units into a fulvalene group;[1] (ii) using dithalliofulvalene salts prepared by reaction of dihydrofulvalene with TlOEt.[3]

We have, previously, isolated the mono(trimethylsilyl)- and bis(trimethylsilyl)fulvalene derivatives,[4] and we report

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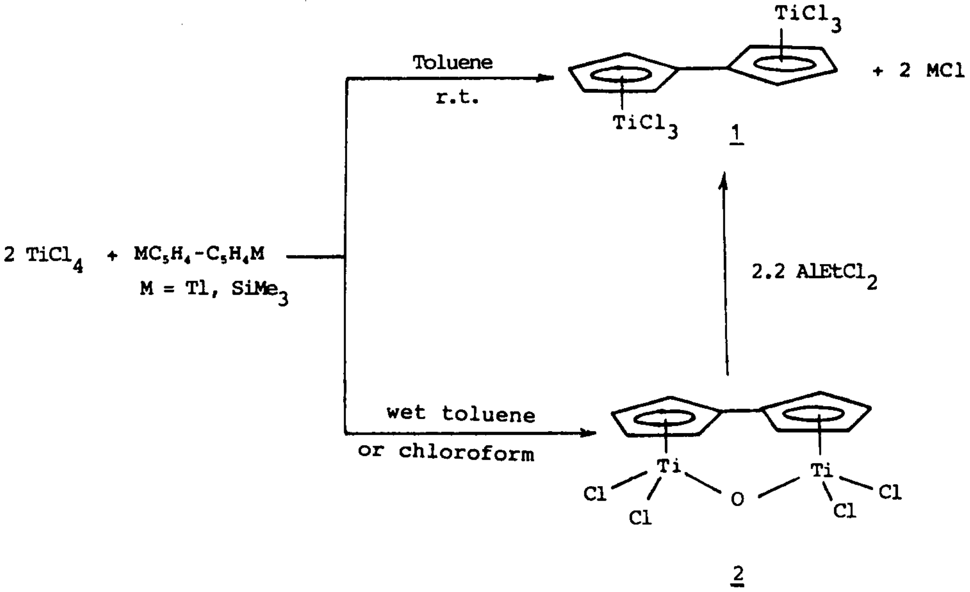
[1] Wielstra, Y.; Meetsma, A.; Gambarotta, S.; Khan, S. *Organometallics* **1990**, *9*, 876 and references therein.

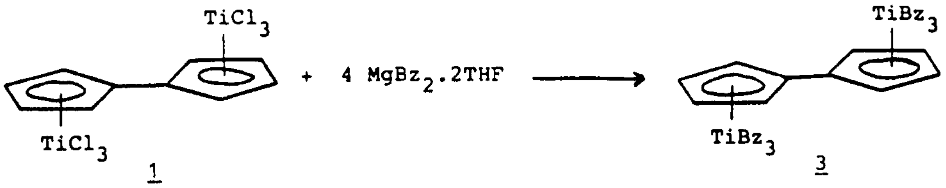
[2] (a) Hidalgo, G.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. (b) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organomet. Synth.* **1988**, *4*, 20. (c) De la Mata, J.; Fandos, R.; Gomez, M.; Gomez-Sal, P.; Martinez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 1846. (d) Gomez-Sal, P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

[3] Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1986**, *308*, C-1.

Scheme I



Scheme II



in this paper the use of the latter to synthesize $[(TiCl_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (1), which is alternatively synthesized with the dithalliofulvalene salts and is the first dinuclear titanium complex with two "titanium trichloride" units joined through the fulvalene ligand. The hydrolysis of this compound in wet toluene or chloroform leads to the μ-oxo dimer $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (2), which reacts with $AlEtCl_2$ to generate 1 quantitatively. The reaction of 1 with $MgBz_2{\cdot}2THF$ (Bz = CH_2Ph) gives $[(TiBz_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (3). All these compounds were characterized by the usual analytical methods, and the structures of 2 and 3 have been fully elucidated by X-ray diffraction studies.

Results and Discussion

Treatment of $TiCl_4$ with dithalliofulvalene[3] or bis(trimethylsilyl)fulvalene[4] in very dry toluene produces the new titanium complex $[(TiCl_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (1) in the reaction shown in Scheme I.

The mass spectrum of 1 is consistent with the proposed dinuclear structure (m/z 437 (M^+)), having the correct isotopic distribution. The spectral behavior of 1 indicates the presence of the fulvalene group. The ^1H NMR spectrum, in C_6D_6 at room temperature, shows two pseudotriplets corresponding to the fulvalene protons at δ 6.35 (t) and 5.95 (t) with a coupling constant of J = 2.77 Hz (toluene-d_8: δ 6.43 (t) and 6.07 (t) with a coupling constant of J = 2.77 Hz).

The $^{13}C\{^1H\}$ NMR spectrum in THF-d_8, at room temperature, shows the presence of the fulvalene carbons at δ 129.2 for C_1 and δ 125.6, 122.5 for C_{2-5}.

Unfortunately, the yield in the preparation of 1 is low in toluene (30%). In polar solvents, complete decomposition is observed, leading rapidly to reduced titanium species with oxidation of the fulvalene group.[5] In THF the decomposition process gives the stable green $TiCl_3{\cdot}3THF$ as the major product.

For this reason the use of bis(trimethylsilyl)fulvalene to synthesize compound 1 does not improve the yield. In addition, the low reactivity of the silyl derivative means that if the reaction mixture is heated polymerization of the silyl reagent takes place.

Complex 1 is extremely sensitive to moisture and must be manipulated under rigorous anhydrous conditions to avoid the formation of the μ-oxo dinuclear complex $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (2), which is difficult to separate. When the reaction to synthesize 1 is carried out under not sufficiently dry conditions, the final product 1 is always obtained with impurities of the μ-oxo complex, as deduced from the NMR spectroscopy studies. If the solvent used in the reaction is wet chloroform, compound 2 is obtained as a pure compound (30% yield). The ^1H NMR spectrum of 2, in C_6D_6 at room temperature, shows the expected two pseudotriplets due to the fulvalene protons at δ 6.26 (t) and 6.04 (t) (toluene-d_8 δ 6.33 (t) and 6.14 (t); CD_3CN δ 7.68 (t) and 7.12 (t); $CDCl_3$ δ 7.34 (t) and 6.99 (t); CD_2Cl_2 δ 7.14 (t) and 7.05 (t)). The ^{13}C NMR spectrum, in C_6D_6, at room temperature, shows signals at δ 121.31 and 117.04 for C_{2-5} (C_1 not observed) ($CDCl_3$ δ 135.5 and 116.56 for C_{2-5} and δ 111.04 for C_1). The structure of 2 was determined by an X-ray diffraction study.

The reaction of 2 with 2 equiv of $AlEtCl_2$ in toluene produces the quantitative metathesis of oxygen by chlorine, leading to the formation of 1 (100% yield). This is the best method to obtain the compound 1 in pure form.

Alkylation of 1 with an excess of dibenzylmagnesium ($MgBz_2{\cdot}2THF$) proceeds cleanly, and the resulting hexabenzyl compound $[\{Ti(CH_2Ph)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (3) can be isolated in quantitative yield.

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(4) Cuenca, T.; Flores, J. C.; Royo, P. Unpublished results.

(5) Garrat, P. J. *Aromaticity*; Wiley-Interscience: New York, 1986.

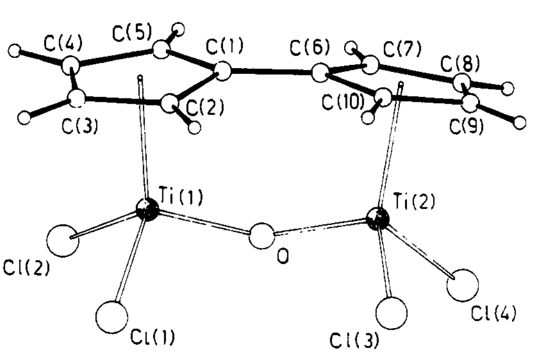

Figure 1. View of the molecular structure of $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (2) with the atomic labeling scheme.

Table I. Selected Bond Distances (Å) and Angles (deg) for Compound 2[a]

Distances			
Ti(1)–CE(1)	2.037 (7)	Ti(2)–CE(2)	2.029 (7)
Ti(1)–Cl(1)	2.233 (2)	Ti(2)–Cl(3)	2.233 (2)
Ti(1)–Cl(2)	2.235 (2)	Ti(2)–Cl(4)	2.227 (2)
Ti(1)–O	1.806 (3)	Ti(2)–O	1.817 (3)
C(1)–C(2)	1.422 (7)	C(6)–C(7)	1.409 (8)
C(2)–C(3)	1.409 (7)	C(7)–C(8)	1.397 (9)
C(3)–C(4)	1.401 (8)	C(8)–C(9)	1.387 (11)
C(4)–C(5)	1.415 (8)	C(9)–C(10)	1.398 (10)
C(1)–C(5)	1.403 (7)	C(6)–C(10)	1.411 (8)
C(1)–C(6)	1.449 (7)		
Angles			
CE(1)–Ti(1)–Cl(1)	114.7 (2)	CE(2)–Ti(2)–Cl(3)	115.4 (2)
CE(1)–Ti(1)–Cl(2)	115.9 (2)	CE(2)–Ti(2)–Cl(4)	117.8 (2)
CE(1)–Ti(1)–O	111.1 (2)	CE(2)–Ti(2)–O	110.6 (2)
Cl(1)–Ti(1)–Cl(2)	105.2 (1)	Cl(3)–Ti(2)–Cl(4)	103.3 (1)
Cl(1)–Ti(1)–O	105.5 (1)	Cl(3)–Ti(2)–O	103.7 (1)
Cl(2)–Ti(1)–O	103.2 (1)	Cl(4)–Ti(2)–O	104.6 (1)
C(2)–C(1)–C(5)	107.0 (5)	C(7)–C(6)–C(10)	106.5 (5)
C(6)–C(1)–C(2)	126.5 (5)	C(1)–C(6)–C(7)	125.8 (5)
C(6)–C(1)–C(5)	125.9 (5)	C(1)–C(6)–C(10)	127.0 (5)
Ti(1)–O–Ti(2)	138.6 (2)		

[a] Estimated standard deviations are given in parentheses. CE(1) and CE(2) are the centroids of the C(1)—···C(5) and C(6)···C(10) rings, respectively.

The new compound 3 has been characterized by infrared and ^1H NMR spectroscopy and by an X-ray diffraction study. The ^1H NMR spectrum shows the fulvalene protons as two triplets at δ 5.52 and 5.61 ppm (J = 2.67 Hz) corresponding to an A_2B_2 system. The methylene benzyl protons appear as one singlet at δ 2.89 ppm.

Description of the X-ray Structure of $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (2). The structure of 2 is shown in Figure 1 along with the atomic labeling system; selected bond distances and angles are given in Table I. Each Ti atom interacts in a η^5 fashion with one cyclopentadienyl ring of the fulvalene ligand, thus acting as a bridge between two *cis*-$TiCl_2$ units. The Ti–C distances are in the range 2.350 (7)–2.373 (7) Å for Ti(1) and 2.333 (8)–2.373 (6) Å for Ti(2), and the titanium–cyclopentadienyl centroid (CE) distances are 2.037 (7) and 2.029 (7) Å, respectively. Each cyclopentadienyl ring is strictly planar, whereas the fulvalene as a whole is slightly bent, the dihedral angle between the two rings being 14.5 (3)°. The two titanium atoms are also joined through a symmetric oxo bridge (Ti–O bond lengths 1.806 (3) and 1.817 (3) Å and Ti–O–Ti angle 138.6 (2)°). The Ti···Ti separation is rather short (3.388 (1) Å), as expected for a doubly bridged binuclear complex. The coordination around each titanium can be described as "three-legged piano stool" with two terminal Cl atoms and the bridging O atom occupying the legs. Each plane through the three legs is almost parallel to the mean plane of the cyclopentadienyl ring, the dihedral angles being 6.8 (2) and 8.8 (2)° for Ti(1) and Ti(2), respectively. The CE–Ti–leg angles are nearly equal (111.1 (2), 114.7 (2), and 115.9 (2)° for Ti(1) and 110.6 (2), 115.4 (2), and 117.8 (2)° for Ti(2)), as are the angles between the legs (103.2 (1), 105.2 (1), and 105.5 (1)° for Ti(1) and 103.3(1), 103.7 (1), and 104.6 (1)° for Ti(2)).

Table II. Selected Bond Distances (Å) and Angles (deg) for Compound 3[a]

Distances			
Ti–CE	2.049 (5)	C(3)–C(4)	1.398 (7)
Ti–C(6)	2.100 (5)	C(4)–C(5)	1.398 (7)
Ti–C(13)	2.153 (5)	C(1)–C(5)	1.409 (6)
Ti–C(20)	2.180 (5)	C(6)–C(7)	1.488 (6)
C(1)–C(1′)[b]	1.460 (6)	C(13)–C(14)	1.445 (6)
C(1)–C(2)	1.410 (6)	C(20)–C(21)	1.478 (6)
C(2)–C(3)	1.392 (7)		
Angles			
CE–Ti–C(6)	113.5 (2)	C(1′)–C(1)–C(5)	126.8 (4)
CE–Ti–C(13)	111.0 (2)	C(8)–C(7)–C(12)	117.1 (4)
CE–Ti–C(20)	112.4 (2)	C(6)–C(7)–C(8)	122.1 (4)
C(6)–Ti–C(13)	101.1 (2)	C(6)–C(7)–C(12)	120.8 (4)
C(6)–Ti–C(20)	93.6 (2)	C(15)–C(14)–C(19)	117.0 (4)
C(13)–Ti–C(20)	119.0 (2)	C(13)–C(14)–C(15)	120.4 (4)
Ti–C(6)–C(7)	128.0 (3)	C(13)–C(14)–C(19)	122.3 (4)
Ti–C(13)–C(14)	90.9 (3)	C(22)–C(21)–C(26)	116.2 (4)
Ti–C(20)–C(21)	118.5 (3)	C(20)–C(21)–C(22)	121.7 (4)
C(2)–C(1)–C(5)	106.7 (4)	C(20)–C(21)–C(26)	122.1 (4)
C(1′)–C(1)–C(2)	126.5 (4)		

[a] Estimated standard deviations are given in parentheses. CE is the centroid of the C(1)···C(5) ring. [b] The symmetry operation indicated by the prime sign is $-x, -y, -z$.

It is interesting to compare the structure of 2 with those of the two modifications of the complex $[\{\eta^5\text{-}C_5H_5)\text{-}TiCl_2\}(\mu\text{-}O)]$ (the former with a trans (A)[6] and the latter with a cis configuration (B)[7], in which two more flexible cyclopentadienyl rings are substituted for the fulvalene ligand. The Ti–C (in the range 2.288 (9)–2.336 (9) Å in A and 2.29 (2)–2.39 (2) Å in B), Ti–CE (2.010 Å in A and 2.031 Å in B), Ti–Cl (2.239 (2) Å in A and 2.233 (5)–2.256 (5) Å in B), and Ti–O (1.777 (1) in A, 1.801 (9) and 1.809 (9) Å in B) bond lengths are practically equal, whereas a remarkable difference can be noted in the Ti–O–Ti angle of the oxo bridge, which is 180° in A (having an imposed C_i symmetry) and 167.5 (6)° in B, and consequently in the larger Ti···Ti separation (3.554 Å in A, and 3.576 Å in B).

The structure of 2 can be also compared to that of the zirconium complex $[\{ZrCl(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$, in which a cyclopentadienyl group substitutes a chlorine ligand, but the same two fulvalene–oxo bridges are present.[8] This complex has an imposed C_2 symmetry and displays Zr–O bond lengths of 1.943 (1) Å, a larger Zr–O–Zr angle (156.0 (2)°), and a much longer Zr···Zr separation (3.801 (1) Å).

Description of the X-ray Structure of $[\{Ti(CH_2Ph)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (3). The structure of 3 is shown in Figure 2 along with the atomic labeling system; selected bond distances and angles are given in Table II. The complex has a crystallographically imposed C_i symmetry with the inversion center lying on the middle of the C(1)–C(1′) bond joining the two cyclopentadienyl rings of the fulvalene ligand. Each titanium atom interacts in a slightly asymmetric η^5 fashion with one cyclopentadienyl ring, the Ti–C distances ranging from 2.329 (5) to 2.403 (4) Å. The titanium–cyclopentadienyl centroid (CE) dis-

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[6] (a) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 5510. (b) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169.

[7] Gowik, P.; Klapotke, T.; Pickardt, J. *J. Organomet. Chem.* **1990**, *393*, 343.

[8] Ashworth, T. V.; Cuenca, T.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 289.

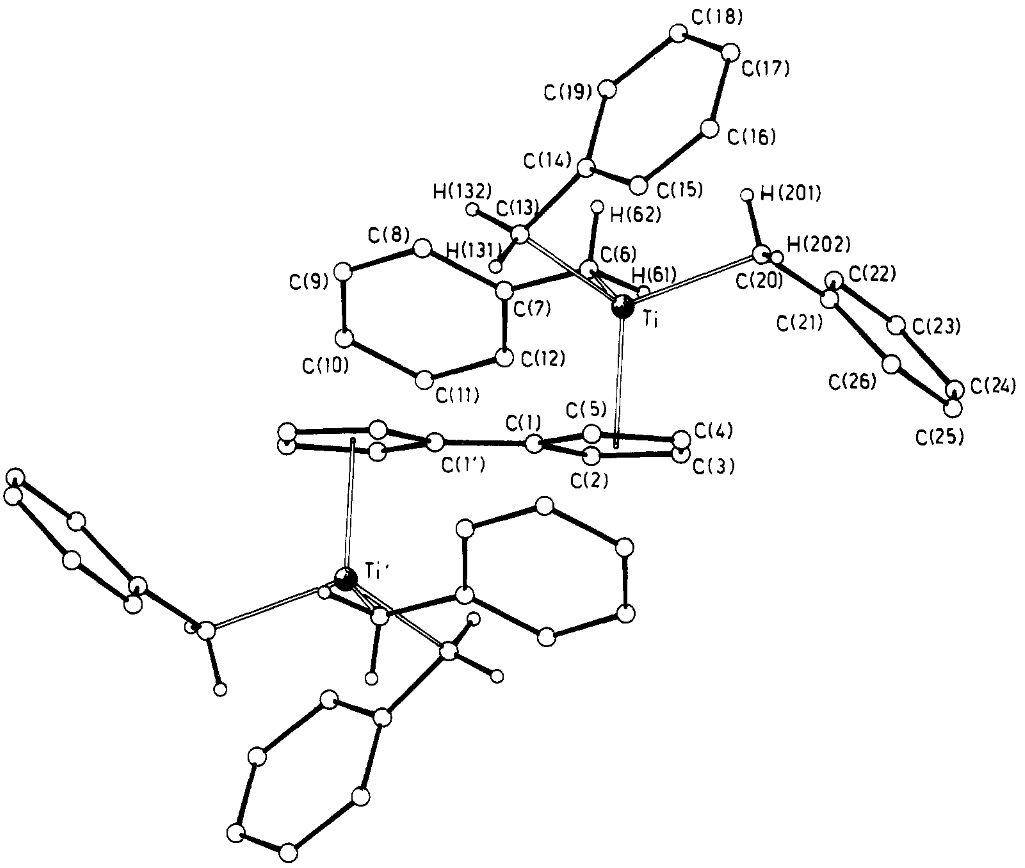

Figure 2. View of the molecular structure of $[\{Ti(CH_2Ph)_3\}_2(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)]$ (**3**) with the atomic labeling scheme.

tance is 2.049 (5) Å, and the fulvalene as a whole is strictly planar. Each titanium atom is also bound to three benzyl groups, and fulvalene can be regarded as a "bridge" between two *trans*-$TiBz_3$ units. The Ti⋯Ti separation is very long (5.715 (2) Å), as might be expected for the trans configuration. The coordination around each titanium can be described as three-legged piano stool with the α-carbons C(6), C(13), and C(20) of Bz ligands occupying the legs. The plane through the three α-carbons (legs) is almost parallel to the mean plane of the cyclopentadienyl ring, the dihedral angle being 1.1 (1)°. Although the CE–Ti–leg angles are nearly equal (111.0 (2), 112.4 (2), and 113.5 (2)°), the distances involving titanium with the α-carbons (Ti–C(6) = 2.100 (5), Ti–C(13) = 2.153 (5), and Ti–C(20) = 2.180 (5) Å) and the angles between the legs (98.6 (2), 101.1 (2), and 119.0 (2)°) vary remarkably, reflecting a different disposition and interaction of each Bz ligand. Bz(1) and Bz(2), with C(6) and C(20), respectively, point toward the fulvalene ligand, whereas Bz(3) with C(13) points away from it (see Figure 3). Bz(1), the benzyl with the shortest Ti–C_α distance, is unique. The angle Ti–C(6)–C(7) is 128.0 (3)°, much larger than those usually found for Ti–C_α–C_β angles in benzyl complexes. An interesting example of this behavior has been found in $[(\eta^5\text{-}C_5Me_5)TiBz_3]$, in which this angle is even larger, 139.0 (7)°.[9] This distortion was attributed to a double CH_2⋯Ti "agostic" interaction, which should alleviate the electronic deficiency of titanium.[10] In fact Ti–H distances were found to be 2.32 and 2.37 Å, which are much shorter than those involving the CH_2 hydrogen atoms of "normal" benzyl groups (2.57–2.66 Å). A similar, although weaker, double agostic interaction can also be postulated for Bz(1) in **3**, the Ti–H distances being 2.46 (7) and 2.48 (6) Å.

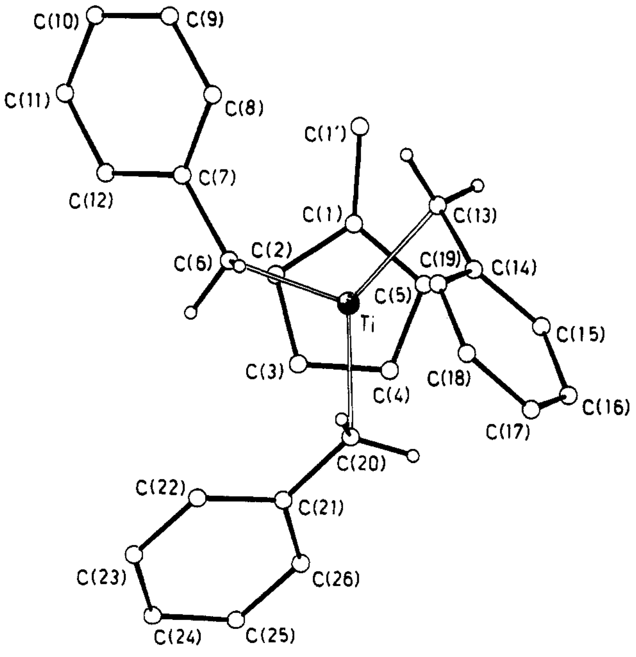

Figure 3. Projection of a moiety of the structure of **3** along the line joining titanium to the centroid of one cyclopentadienyl ring.

The Ti–C(20)–C(21) angle with Bz(2) is 118.5 (3)° and corresponds to a normal benzyl group. In $[(\eta^5\text{-}C_5Me_5)TiBz_3]$ the Ti–C_α–C_β angles and the Ti–C_α distances involving the regular benzyl groups were found to be 114.0 (7) and 113.9 (6)°, and 2.156 (10) and 2.140 (10) Å. The

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

[10] (a) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802. (b) Obaras, S.; Koga, N.; Morokuma, K. *J. Organomet. Chem.* **1984**, *270*, C33. (c) Koga, N.; Obaras, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625. (d) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Pront, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629.

Ti–H distances in Bz(2) are 2.45 (7) and 2.59 (7) Å, so that a weak agostic CH···Ti interaction can be postulated.

An interesting feature can be noted with Bz(3) of 3. The Ti–H distances (2.66 (7) and 2.68 (7) Å) are similar to those found in normal benzyl groups, but the Ti–C(14) distance (2.611 (4) Å) is shorter and the Ti–C(13)–C(14) angle (90.9 (3)°) of the same magnitude as those found for Ti–Cβ distances and for Ti–C_α–C_β angles with benzyl groups in which benzallylic interactions were observed.[11] This type of interaction with Bz(3) can be confirmed also by the Ti–C(15) and Ti–C(19) distances (3.239 (4) and 3.276 (5) Å), showing the same trend as in [$(\eta^5$-$C_5Me_5)ThBz_3$], in which a benzallylic interaction has been observed.[11]

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere by using Schlenk and high-vacuum-line techniques or a Model HE-63P glovebox (Pedetrol). Solvents were distilled from drying agents as follows: sodium–benzophenone for tetrahydrofuran and diethyl ether, sodium for toluene, and sodium–potassium alloy for hexane. $Na(C_5H_5)\cdot DME$,[12] $Mg(PhCH_2)_2\cdot 2THF$,[13] $Tl_2(\mu$-$C_{10}H_8)$,[3] and $(SiMe_3)_2(\mu$-$C_{10}H_8)$[4] were prepared by literature methods. $AlEtCl_2$ was purchased from Aldrich. ^1H and ^{13}C NMR spectra were recorded on Varian FT-80A and UNITY FT-300 spectrometers. ^1H and ^{13}C chemical shifts were referenced to Me_4Si. Mass spectra were recorded on a Hewlett-Packard 5890 spectrometer. C and H analyses were done with a Perkin-Elmer 240B microanalyzer.

Preparation of [$(TiCl_3)_2(\mu$-η^5:η^5-$C_{10}H_8)$] (1). Method a. A suspension of $Tl_2(\mu$-$C_{10}H_8)$ (4.15 g, 7.73 mmol) in toluene (200 mL) was cooled to −78 °C, and $TiCl_4$ (1.67 mL, 15.46 mmol) was immediately added by syringe. With stirring, the reaction mixture was slowly warmed to 80 °C and left for 6 h. In order to finish the reaction, the dark mixture was refluxed over 2 h; then, this mixture was cooled to room temperature, the dark gray solid was decanted and the red solution was filtered. The evaporation of the solvent gave the product, which was washed with hexane (2 × 40 mL) (yield 1.00 g, 30%).

Method b. To a solution of $TiCl_4$ (5.14 mL, 46.76 mmol) in toluene (200 mL) cooled to −10 °C was added another solution of recently prepared $(SiMe_3)_2(\mu$-$C_{10}H_8)$ (6.42 g, 23.38 mmol) dropwise over 2 h with an addition funnel connected to a gas bubbler. The resulting mixture was allowed to reach room temperature and stirred overnight. The dark gray insoluble impurities were decanted, the red solution was filtered, the solvent was removed, and the red-brown solid was washed with *n*-hexane (2 × 50 mL) (yield 1.53 g, 15%).

Anal. Calcd for $C_{10}H_8Cl_6Ti_2$: C, 27.47; H, 1.83. Found: C, 27.92; H, 2.05. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 6.35 (t, 4 H, C_5H_4, J = 2.77 Hz), 5.95 (t, 4 H, C_5H_4, J = 2.77). ^1H NMR (toluene-d_8, 300 MHz, 25 °C): δ 6.43 (t, 4 H, C_5H_4, J = 2.77 Hz), 6.07 (t, 4 H, C_5H_4, J = 2.77). ^{13}C NMR (THF-d_8, 75 MHz, 25 °C): δ 129.2 (C_1), 125.6 and 122.5 (C_{2-5}). EI-MS (70 eV): m/z 437 ([M^+]).

Preparation of [$(TiCl_2)_2(\mu$-O$)(\mu$-η^5:η^5-$C_{10}H_8)$] (2). The same procedure described for 1 using wet chloroform produces compound 2 (0.89 g, 30% yield). Anal. Calcd for $C_{10}H_8Cl_4Ti_2O$: C, 31.46; H, 2.11. Found: C, 31.33; H, 2.27. ^1H NMR (C_6D_6, 300 MHz, 25 °C); δ 6.26 (t, 4 H, C_5H_4, J = 2.68 Hz), 6.04 (t, 4 H, C_5H_4, J = 2.44). ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34 (t, 4 H, C_5H_4, J = 2.68 Hz), 6.99 (t, 4 H, C_5H_4, J = 2.68 Hz). ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 7.14 (t, 4 H, C_5H_4, J = 2.68 Hz), 7.05 (t, 4 H, C_5H_4, J = 2.68). ^1H NMR (CD_3CN, 300 MHz, 25 °C): δ 7.68 (t, 4 H, C_5H_4), 7.12 (t, 4 H, C_5H_4). ^{13}C NMR (C_6D_6, 75 MHz, 25 °C): δ 121.31, 117.04 (C_{2-5}, C_5H_4). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ 135, 116.56 (C_{2-5}, C_5H_4), 111.04 (C_1, C_5H_4).

Reaction of [$(TiCl_2)_2(\mu$-O$)(\mu$-η^5:η^5-$C_{10}H_8)$] (2) with $AlEtCl_2$. A 0.14-g (0.35-mmol) amount of [$(TiCl_2)_2(\mu$-η^5:η^5-$C_{10}H_8)$] was dissolved in 100 mL of toluene, and the solution was cooled to −78 °C. A 0.80-mmol amount of $AlEtCl_2$ (0.46 mL of a 1.8 M solution in toluene) was added dropwise, and the mixture was stirred while room temperature was reached. A black-red solution was obtained. After filtration and evaporation of the solvent, the residue was extracted with dry chloroform. By concentration of the resulting solution and cooling to −35 °C compound 1 was obtained almost quantitatively.

Table III. Summary of Crystallographic Data for 2 and 3

	2	3
formula	$C_{10}H_8Cl_4OTi_2$	$C_{52}H_{50}Ti_2$
mol wt	381.79	770.77
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	9.305 (3)	16.976 (6)
b, Å	12.387 (4)	11.022 (5)
c, Å	12.821 (4)	11.238 (4)
β, deg	110.31 (2)	101.15 (2)
V, Å^3	1385.9 (8)	2063 (1)
Z	4	2
D_{calcd}, g cm^{-3}	1.830	1.241
$F(000)$	752	812
cryst size, mm	0.20 × 0.25 × 0.32	0.15 × 0.22 × 0.28
μ, cm^{-1}	19.00 (Mo Kα)	35.49 (Cu Kα)
rflns measd	$\pm h,k,l$	$\pm h,k,l$
total no. of unique data	3048	3924
no. of unique obsd data ($I \geqslant 2\sigma(I)$)	1662	2126
R	0.0397	0.0490
R_w	0.0482	0.0609

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms of 2

	x/a	y/b	z/c	U^a
Ti(1)	529 (1)	1089 (1)	2439 (1)	33.3 (3)
Ti(2)	3668 (1)	2497 (1)	3984 (1)	33.2 (3)
Cl(1)	1576 (2)	−260 (1)	1794 (2)	72.5 (8)
Cl(2)	−1293 (2)	1768 (2)	945 (1)	76.2 (7)
Cl(3)	5400 (2)	1293 (1)	3882 (2)	70.4 (7)
Cl(4)	4471 (2)	4034 (1)	3470 (1)	61.3 (6)
O	1957 (4)	2144 (3)	2821 (3)	36.6 (12)
C(1)	880 (6)	1232 (4)	4358 (4)	35.7 (18)
C(2)	965 (7)	122 (4)	4102 (4)	41.9 (23)
C(3)	−486 (7)	−200 (4)	3366 (5)	49.1 (25)
C(4)	−1460 (7)	699 (5)	3135 (5)	51.2 (22)
C(5)	−608 (6)	1581 (5)	3745 (4)	43.7 (22)
C(6)	2144 (6)	1913 (4)	4998 (4)	40.8 (19)
C(7)	2149 (7)	3051 (5)	5000 (5)	51.2 (23)
C(8)	3635 (8)	3400 (6)	5600 (6)	65.9 (30)
C(9)	4573 (8)	2505 (7)	5957 (5)	65.9 (28)
C(10)	3663 (7)	1588 (6)	5588 (5)	53.7 (24)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Preparation of [$\{Ti(CH_2Ph)_3\}_2(\mu$-η^5:η^5-$C_{10}H_8)$] (3). A recently prepared solution of $Mg(CH_2Ph)_2\cdot 2THF$ in diethyl ether (0.30 g, 0.84 mmol in 20 mL) was added dropwise to a suspension of [$(TiCl_3)_2(\mu$-η^5:η^5-$C_{10}H_8)$] (0.12 g, 0.28 mmol) in ether (20 mL); the reaction mixture was cooled to −10 °C and left for 3 h. The solvent was removed under vacuum and the bright red product extracted with toluene (2 × 15 mL). The resulting solution was concentrated and cooled to −40 °C for 2 days, affording a bright red monocrystalline solid as the product 2 (yield 0.21 g, 97%). Anal. Calcd for $C_{52}H_{50}Ti_2$: C, 81.06; H, 6.50. Found: C, 80.64; H, 6.89. ^1H NMR (C_6D_6, 28 °C): δ 2.89 (s, 12 H, Ti–CH_2), 5.52 (t, 4 H, $C_{10}H_8$, J = 2.67 Hz), 5.61 (t, 4 H, $C_{10}H_8$, J = 2.67 Hz), 6.7–7.2 (m, Ph).

X-ray Data Collection, Structure Determination, and Refinement for [$(TiCl_2)_2(\mu$-O$)(\mu$-η^5:η^5-$C_{10}H_8)$] (2) and [$\{Ti(CH_2Ph)_3\}_2(\mu$-η^5:η^5-$C_{10}H_8)$] (3). Single crystals of 2 and 3 were sealed in Lindemann glass capillaries under dry nitrogen and used for data collections. The crystallographic data are summarized in Table III. Unit cell parameters were determined from the θ values of 30 carefully centered reflections having 10 < θ < 18° (2) and 23 < θ < 40° (3). Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using niobium-filtered Mo Kα radiation (λ = 0.71073 Å) (2) and nickel-filtered Cu Kα radiation (λ = 1.54184 Å) (3) and θ/2θ scans. The reflections were

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Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of 3

	x/a	*y/b*	*z/c*	U^a
Ti	149 (1)	1694 (1)	1955 (1)	43.6 (2)
C(1)	−197 (2)	74 (4)	518 (4)	44.7 (15)
C(2)	−887 (2)	775 (4)	553 (4)	51.5 (15)
C(3)	−1073 (3)	673 (4)	1703 (4)	61.6 (17)
C(4)	−508 (3)	−95 (4)	2395 (4)	61.5 (18)
C(5)	32 (3)	−464 (4)	1671 (4)	52.8 (16)
C(6)	−193 (3)	3245 (4)	896 (4)	54.8 (15)
C(7)	−258 (3)	3391 (4)	−435 (4)	50.6 (15)
C(8)	413 (3)	3464 (4)	−964 (4)	61.4 (19)
C(9)	342 (4)	3549 (4)	−2213 (6)	81.8 (29)
C(10)	−400 (6)	3576 (5)	−2956 (5)	96.3 (30)
C(11)	−1062 (4)	3520 (5)	−2448 (5)	89.8 (28)
C(12)	−1007 (3)	3440 (4)	−1210 (4)	66.9 (19)
C(13)	1369 (3)	1466 (4)	1719 (4)	56.8 (16)
C(14)	1668 (2)	1890 (4)	2940 (4)	50.2 (15)
C(15)	1759 (3)	1079 (4)	3923 (4)	61.7 (18)
C(16)	1941 (3)	1495 (6)	5104 (5)	80.7 (24)
C(17)	2048 (3)	2713 (6)	5355 (5)	81.5 (23)
C(18)	1980 (3)	3517 (5)	4410 (5)	76.1 (21)
C(19)	1793 (3)	3121 (5)	3214 (4)	61.9 (18)
C(20)	−73 (3)	2372 (4)	3683 (4)	61.0 (16)
C(21)	−909 (3)	2631 (4)	3796 (4)	50.3 (16)
C(22)	−1303 (3)	3687 (4)	3320 (4)	60.1 (17)
C(23)	−2091 (3)	3902 (5)	3383 (4)	69.0 (20)
C(24)	−2523 (3)	3085 (5)	3913 (5)	69.2 (20)
C(25)	−2152 (3)	2055 (5)	4402 (5)	70.9 (22)
C(26)	−1358 (3)	1822 (4)	4347 (4)	61.9 (18)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.6)°$ to $(\theta + 0.6 + 0.346 \tan \theta)°$ (**2**) and $(\theta + 0.6 + 0.142 \tan \theta)°$ (**3**). One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed by following Lehmann and Larsen.[14] Intensities were collected for Lorentz and polarization effects. A correction for absorption was applied to the data for **3** (maximum and minimum values for the transmission factors were 1.1651 and 0.7891).[15] Only the observed reflections were used in the structure solution and refinement.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were clearly located in the ΔF map and refined isotropically. The final cycles of refinement were carried out on the basis of 186 (**2**) and 344 (**3**) variables; after the last cycles, no parameters shifted by more than 0.46 (**2** and **3**) esd. The largest remaining peak in the final difference map was equivalent to about 0.54 (**2**) and 0.32 (**3**) e/Å^3. In the final cycles of refinement the weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 1.0 and 0.0034 (**2**) and 0.4484 and 0.0033 (**3**), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 16. All calculations were carried out on the Cray X-MP/48 computer of the "Centro di Calcolo Elettronico interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[17] The final atomic coordinates for the non-hydrogen atoms are given in Tables IV (**2**) and V (**3**).

The atomic coordinates of the hydrogen atoms are given in Tables SI (**2**) and SII (**3**) and the thermal parameters in Tables SIII (**2**) and SIV (**3**) (Tables SI–SIV are given in the supplementary material).

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Supplementary Material Available: Tables of hydrogen atom positional and isotropic thermal parameters, non-hydrogen atom anisotropic thermal parameters, and all bond distances and angles for **2** and **3** (7 pages). Ordering information is given on any current masthead page.

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