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Journal of Organometallic Chemistry 584 (1999) 286–292

Journal of Organometallic Chemistry

Bis(μ-η^5:η^5-1,4-bis(trimethylsilyl)cyclooctatetraene)dititanium — the first compound with a strong Ti–Ti bond

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Received 26 February 1999

Abstract

The reduction of $\{[\eta^8\text{-}1,4\text{-}(SiMe_3)_2C_8H_6]Ti(\mu\text{-}Cl)\}_2(THF)$ by magnesium in the presence of bis(trimethylsilyl)acetylene in tetrahydrofuran affords diamagnetic bis[μ-η^5:η^5-1,4-bis(trimethylsilyl)cyclooctatetraenetitanium](Ti–Ti) (**1**) in low yield. The X-ray crystal analysis of **1** revealed that bridging cyclooctatetraene ligands in the centrosymmetric dimer are concave-bent. An extremely short Ti–Ti distance of 2.326(2) Å is compatible with the presence of a double Ti–Ti bond. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Bridging 1,4-bis(trimethylsilyl)cyclooctatetraene dianion; Titanium–titanium bond; Crystal structure

1. Introduction

Cyclooctatetraene (COT) and its dianion (COT^{2-}) are versatile ligands capable of coordinating to transition metals in various η^n-modes. In mononuclear complexes COT^{2-} coordinates exclusively in an η^8-mode while COT acquires one of the η^6-, η^4- or η^2-coordination modes. Both COT^{2-} and COT ligands also act as metal-bridging ligands, most currently COT^{2-} in μ-η^5:η^5- and COT in μ-η^4:η^4-modes [1]. In the transition metal complexes of general composition $(COT)_3M_2$ the bridging μ-η^5:η^5-COT^{2-} ligand occurs in all complexes containing the metal–metal bond $[(\eta^4\text{-COT})M]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-COT}^{2-})$(M–M) (M = Cr [2a], Mo [2b], W [2b,c]); the only complex containing bridging COT ligand is $(\eta^8\text{-COT})Ti]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-COT})$ [3].

Recently, 1,4-bis(trimethylsilyl)cyclooctatetraene (COT″) was introduced into organometallic chemistry as a much cheaper alternative to the very expensive COT [4]. This ligand behaves in many respects analogously to COT, coordinating as η^8-COT''^{2-} and η^4-COT″ in most transition metal and lanthanide complexes [5]. The basic mononuclear complex in the COT″–Ti chemistry $(\eta^8\text{-COT}''^{2-})(\eta^4\text{-COT}'')Ti$ coordinates the ligands in both the modes [6]. The bridging behavior of COT″ and COT''^{2-} ligands in the $(COT'')_3M_2$ complexes is so far unknown, however.

In this paper we report on the products arising from the recently described $[(\eta^8\text{-COT}''^{2-})Ti(\mu\text{-Cl})]_2(THF)$ [7] by the reduction with magnesium in the presence or the absence of bis(trimethylsilyl)acetylene (BTMSA).

2. Experimental

All manipulations, syntheses, and most of the spectroscopic measurements were carried out under vacuum

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PII: S0022-328X(99)00165-5

using all-sealed glass devices equipped with breakable seals. The adjustment of single crystals into capillaries for X-ray analysis, preparation of KBr pellets and distributing crystals into capillaries for EI MS measurements were performed in a glove-box under an atmosphere of nitrogen or argon.

2.1. Chemicals

The solvents THF, hexane, toluene, and benzene-d_6 were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [8]. BTMSA (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h and distilled into ampoules. Starting material $[(COT''^{2-})Ti(\mu\text{-}Cl)]_2(THF)$ was obtained from $(COT''^{2-})2Li^+$ and $TiCl_3{\cdot}3THF$ as recently reported [7].

2.2. Methods

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were measured on a Varian Unity Inova 400 spectrometer (399.95, 100.58, and 79.46 MHz, respectively) in C_6D_6 at 25°C. ^{29}Si-NMR spectra were obtained using a standard DEPT pulse sequence. Chemical shifts (δ, ppm) are referenced to the solvent signal (δ_H 7.15, δ_C 128.0) or to a solution of $SiMe_4$ in C_6D_6 (external reference, δ_{Si} 0). UV–vis spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). EI MS spectra were measured on a VG-7070E double-focusing mass spectrometer (70 eV, 50 μA, 200°C). Samples in capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance not below 5% and by important peaks of lower intensity. IR spectra were registered on a Specord 75 IR (Carl Zeiss, Jena, Germany). KBr pellets from estimated amounts of crystalline samples were prepared in a glovebox under purified nitrogen and were measured under a nitrogen atmosphere in a closed cell. ESR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined using an Mn^{2+} ($M_I = -1/2$ line) standard at $g = 1.9860$. A variable temperature unit STT-3 was used for measurements in the range 133–296 K.

2.3. Preparation of $\{[\mu\text{-}\eta^5{:}\eta^5\text{-}1,4\text{-}(SiMe_3)_2C_8H_6]Ti\}_2$ (1)

Solid $\{[\eta^8\text{-}1,4\text{-}(SiMe_3)_2C_8H_6]Ti(\mu\text{-}Cl)\}_2(THF)$ (1.0 g, 1.36 mmol) was dissolved in 30 ml of THF, and this solution was added to Mg turnings (0.24 g, 10 mmol) and BTMSA (2.0 ml, 9.0 mmol). The mixture was heated to 60°C for 8 h. The green–brown solution obtained was separated from excess magnesium and evaporated under a vacuum. The dark residue was repeatedly extracted by 80 ml of hexane in a closed system to give a greenish brown solution. The combined extracts were concentrated (to ca. 10 ml) until some solid precipitated out. The solid was dissolved upon heating and the warm solution was slowly cooled in a thermally isolated box. A crop of brown–red prismatic crystals was obtained. The mother liquor was concentrated to about half volume and the crystallization procedure was repeated to give another crop of crystals. Both crops were combined and recrystallized from hexane by the same procedure. Yield of brown–red prisms of **1** was 0.10 g (12%), m.p. 214°C. Compound **1**: EI MS (direct inlet, 70 eV, 170–180°C; m/z (%)): 596(5), 595(13), 594(31), 593(46), 592(M^+, 71), 591(23), 590(16), 297(6), 296(17), 248(5), 160(23), 145(15), 135(10), 74(8), 73(100), 45(14), 43(6). ^{1}H-NMR (C_6D_6): −0.01 (36H, s, 4 × $SiMe_3$), 5.04 (6H, m), 5.27 (2H, m), 6.51 (2H, m), 6.57 (2H, m). All 'multiplets' are lacking any fine structure and are very broad. ^{13}C-NMR (C_6D_6): −0.5 q (12C, $SiMe_3$), 95.8 s (4C), 96.4 d (4C), 99.2 d (4C), 120.7 d (4C). UV–NIR (λ_{max}, hexane): $310 > 470 > 560 > 670 > 770 > 1010$ (br) nm. IR (KBr, cm^{-1}): 3020 (w), 2945 (s), 2888 (m), 1927 (vw), 1867 (vw), 1803 (vw), 1737 (vw), 16140 (vw), 1584 (w), 1500 (w), 1465 (w), 1439 (w), 1400 (m)1365 (w), 1317 (w), 1243 (vs), 1038 (s), 1008 (s), 988 (m), 945 (m), 932 (w), 908 (m), 865 (sh), 833 (vs), 775 (s), 760 (m), 741 (s), 682 (m), 637 (m), 625 (m), 561 (w), 542 (m), 518 (w), 417 (m). Anal. Calc. for $C_{28}H_{48}Si_4Ti_2$: C, 56.73; H, 8.16. Found: C, 56.59; H, 8.08%.

2.4. Isolation of $(\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)\{(\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6)Ti\}_2$ (2)

A brown–green mother liquor from the isolation of **1** was further concentrated to a volume of 2 ml. Cooling to −18°C for 4 days afforded green crystals of **2** which were slightly washed by condensing hexane vapor and separated. Estimated yield of **2** was 30 mg. As the crystals were very poorly X-ray diffracting the structure of **2** has been established from MS and NMR spectra. Compound **2**: ^{1}H-NMR: −0.09 (s, 18H, $(Me_3Si)_2C_2$), 0.56 (s, 36H, $(\mathit{Me}_3Si)_2C_8H_6$); 6.59, 7.09 (2 × m, 4H, $(Me_3Si)_2C_8\mathit{H}_6$; H-5, H-6, H-7, H-8), 7.58 (s, $(Me_3Si)_2C_8\mathit{H}_6$; H-2, H-3). ^{13}C-NMR (all signals singlets): 0.7 ($(\mathit{Me}_3Si)_2C_8H_6$), 3.6 ($(\mathit{Me}_3Si)_2C_2$); 96.7, 100.6, 102.4, 110.0 (4 × CH $(Me_3Si)_2C_8H_6$); 297.0 ($(Me_3Si)_2\mathit{C}_2$). ^{29}Si-NMR: −25.9 ($(Me_3\mathit{Si})_2C_2$), 8.8 ($(Me_3\mathit{Si})_2C_8H_6$). MS (direct inlet, 70 eV, 230°C; m/z (%)): 762 (M^+, 3), 594(7), 593(11), 592($[M-BTMSA]^+$, 17), 591(5), 298(10), 297(18), 296($[COT''Ti]^+$, 54), 295(8), 294(6), 160(16), 157(7), 156(14), 155(89), 145(10), 135(6), 97(5), 83(6), 74(8), 73(100), 70(9), 59(5), 57(6), 45(16), 43(8). UV–vis (λ_{max}, hexane): 370 ≫ 650 (br) nm.

2.5. *The reaction in the absence of BTMSA*

The reduction of [(COT″$^{2-}$)Ti(μ-Cl)]$_2$(THF) by magnesium in THF was carried out as described above. The obtained dark brown solution was evaporated and the residue was extracted by hexane. A yellow powder compound was obtained, moderately soluble in hexane. The compound contained paramagnetic impurities that could not be removed by fractional crystallization, and their presence precluded investigations by NMR spectroscopy. The EI MS spectrum of the yellow powder revealed that the compound of the (COT″)$_3$Ti$_2$ composition is the main volatile component. EI MS (direct inlet, 70 eV, 260°C; m/z (%)): 842 (6.7), 841 (9.4), 840 (M$^+$, 11.6), 592 (5.3), 545 (7.9), 544 (11.4), 472 (5.7), 471 (11.4), 448 (11.0), 447 (18.7), 446 (37.7), 445 (5.9), 298 (18.0), 297 (34.6), 296 (100), 295 (14.6), 294 (13.7), 248 (8.3), 222 (5.5), 208 (5.0), 160 (19.2), 145 (12.8), 135 (6.6), 74 (7.4), 73 (83.8), 57 (7.3), 45 (14.5), 43 (6.2). UV–NIR (hexane, 22°C, nm): 355 ≫ 780 > 960(sh) ~ 1270. The ESR spectra were irreproducible, showing a single line at $g = 1.972$–1.974, $\Delta H = 10$–15 G; at −140°C in toluene glass the spectra indicated a mixture of a monomeric species and probably two binuclear species in the electronic triplet state showing maximum zero-field splitting D about 0.018 cm^{-1}. This value of D roughly corresponds to the Ti(III)–Ti(III) distance 4.5–5.0 Å, however, no suggestion of a particular structure can be drawn from these data.

2.6. *X-ray crystal structure of compound* ***1***

A crystal fragment of **1** was fixed in a Lindenmann glass capillary under purified nitrogen in a glovebox (Labmaster 130, mBraun). The capillary was closed with sealing wax. The X-ray measurements were carried out at room temperature (r.t.). The diffraction data were collected on a Philips PW1100 four-circle diffractometer updated by STOE using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The intensity data were collected at r.t. by ω/2θ scans and were corrected for the Lorentz and polarization effects. An absorption correction was applied by using ψ-scans. The structure was solved using the Patterson method. The refinement was performed with full-matrix least-squares methods based on F^2 using the SHELXL-97 program [9]. The non hydrogen atoms were refined anisotropically. The hydrogen atoms were included at their calculated positions.

Crystal data, details of data collection and refinement are given in Table 1.

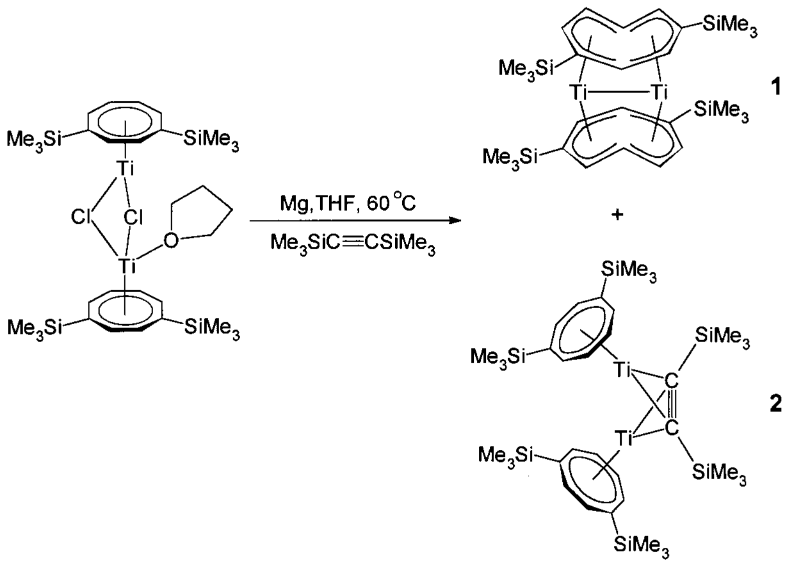
3. Results and discussion

The reduction of [(COT″$^{2-}$)TiCl]$_2$(THF) in THF by magnesium in the presence of BTMSA afforded two products which were isolated by fractional crystallization from hexane. The main product **1**, crystallizing in nearly rectangular prisms of yellow–brown color, was obtained in poorly reproducible yields ranging from 5 to 15%. The minor product **2** was obtained in very low yield from the mother liquor of **1** as bright green crystals highly soluble in hexane (Scheme 1).

Compound **1** is a thermally robust compound showing a high melting point of 214°C and a high abundance of its molecular ion, however, it is extremely sensitive towards air in solution, as well as in the solid phase. The composition of **1** was inferred from the mass spectrum showing, besides the most abundant [SiMe$_3$]$^+$ ion, the molecular ion M$^+$ with 71% intensity, [M/2]$^+$ ion, [COT″]$^+$ and its fragment ions. ^{1}H- and ^{13}C-NMR spectra revealed that the two COT″ ligands as well as the trimethylsilyl groups and pairs of ring carbon atoms within one ligand are equivalent. The multiplets due to CH protons of the COT″ rings are broad and, hence, their fine structure cannot be analyzed. This points to dynamic exchange processes taking place in solution at r.t. The electronic absorption spectrum of **1** is very rich in bands extending to 1000 nm. This is compatible with the presence of two d-elec-

Table 1
Crystallographic data and structure refinement parameters for compound **1**

Crystal data	
Empirical formula	$C_{28}H_{48}Si_4Ti_2$
Molecular weight	592.82
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	12.0714(5)
b (Å)	6.9489(5)
c (Å)	19.9570(7)
β (°)	101.944(3)
V (Å^3)	1637.81(15)
Z	2
D_{calc} (g cm^{-3})	1.202
μ (Mo–K$_\alpha$)(mm^{-1})	0.649
F(000)	632
Crystal size (mm^3)	0.2 × 0.4 × 0.5
Data collection and refinement	
θ Range for data collection (°)	3.11–24.99
Index ranges	$-14 \leq h \leq 14$, $0 \leq k \leq 8$, $-23 \leq l \leq 0$
Reflections collected	3143
Independent reflections	2880
Data/restraints/parameters	2880/0/154
Goodness-of-fit on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0512$, $wR_2 = 0.1034$
R indices (all data)	$R_1 = 0.0864$, $wR_2 = 0.1252$



Scheme 1.

trons which are involved in the metal–metal bond [10]. The IR spectrum of **1** in KBr pellet is dominated by strong bands corresponding to the presence of trimethylsilyl groups. Weak bands at 3020 and at 1600 cm^{-1} can be attributed to C–H and C=C bonds in the COT″ dianion, respectively. Very weak bands in the range 1737–1927 cm^{-1} may be attributed to ‘aromatic’ overtones in a highly symmetrical complex. All these data are compatible with the centrosymmetric structure of **1** which has been established by the X-ray crystal analyses (vide infra).

Compound **2** was identified on the basis of EI MS and ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra to be a COT″ analogue of recently prepared $[(\eta^8\text{-}C_8H_8)Ti]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ [11]. The EI MS spectrum shows a low abundant molecular ion which easily fragmentates via elimination of BTMSA to $[COT''_2Ti_2]^+$ and $[COT''Ti]^+$; fragment ions of COT″ and BTMSA are also observed. According to the NMR spectra, the molecule exhibits a two-fold axis or a plane of symmetry showing only one half of the principal signals. This most likely reflects a time averaging of the NMR signals due to an intramolecular motion fast on the NMR time scale at 294 K. The ^{13}C and ^{1}H chemical shifts of **2** are in good agreement with those reported for non-silylated analogue of **2**, $(\mu\text{-}\eta^2\text{:}\eta^2\text{-BTMSA})[(\eta^8\text{-}C_8H_8)Ti]_2$, a significantly down-field shifted signal of triple bond carbons (δ_C 297.0) being indicative of a ‘butterfly’-like structure with $\mu\text{-}\eta^2\text{:}\eta^2$-bridging BTMSA [11]. The ^{29}Si-NMR signal of the acetylenic trimethylsilyl group has also been found very close to that of the analogous $[(COT)Ti]_2\cdot$BTMSA complex (δ_{Si} −26.9). The electronic absorption spectrum of **2** is very similar to the spectrum of $[(COT)Ti]_2\cdot$BTMSA in the position and relative intensity of the absorption bands. Compound **2** did not give crystals suitable for X-ray crystal analysis.

In the absence of BTMSA, a yellow product, highly soluble in hexane, was obtained in low yield. It contained paramagnetic impurities which could not be removed by fractional crystallization. This circumstance precluded the investigation by NMR spectroscopy. The ESR spectra of the impurities differed in various experiments whereas the mass spectra of the solid product always contained ions compatible with the $(COT'')_3Ti_2$ composition (m/z 840 M^+; 592 $[COT''_2Ti_2]^+$; 296 $[COT''Ti]^+$(100%)). This indicates that the $(COT'')_3Ti_2$ compound is the main volatile product, however, the mode of coordination, $[(COT'')Ti]_2(\mu\text{-}COT''^{2-})$(Ti–Ti) versus $[(COT''^{2-})Ti]_2(\mu\text{-}COT'')$, remains unknown.

The formation of **1** in the system containing BTMSA may be imagined as proceeding through complex **2** by the elimination of the bridging BTMSA. The thermolysis of **2** at the temperature of the reduction by magnesium (60°C) was not observed, and thus one has to assume that the elimination of BTMSA is magnesium-assisted. Examples of such magnesium-assisted reactions are known in titanocene chemistry [12]. If this mechanism is valid the titanium atoms in **2** have to be much more reactive than in $[(COT^{2-})Ti]_2(\mu\text{-BTMSA})$ which proved to be highly unreactive also in the presence of Mg [11]. On the other hand, the trimethylsilyl substituents in COT″ are apparently responsible for the high stability of **1**, as no compound of such type is known in COT–transition metal complexes except $[(\mu\text{-}COT)Ni]_2$. The latter compound, although characterized by single crystal X-ray diffraction, appeared to be fluxional in the solid state so that the structure of the COT ligands is only tentatively described [13].

*3.1. Crystal structure of **1***

The molecule of **1** is a centrosymmetric dimer in which the titanium atoms are bridged by two COT''^{2-} ligands which are bent across the C(2)–C(6) interconnection to form two planes (Fig. 1). The important bond lengths and angles of **1** are listed in Table 2. The two halves of bent COT''^{2-} ligands are approximately planar. Their carbon atoms form least squares planes with maximum deviations of 0.05 Å, and their dihedral angle is 38.2°. The Si atoms deviate from these planes by ca. 0.1 Å towards the Ti atoms. The centroids of pentadienyl fragments CE(1) and CE(2) and titanium atoms Ti(1) and Ti(1′) define the least squares plane with maximum deviations of ± 0.002 Å. The mode of coordination of the COT″ dianions can be discussed on the basis of the C–C and Ti–C bond lengths, as denoted in Fig. 2. The bonds connecting the bending atoms C(2) and C(6) are 0.03–0.05 Å longer than the bonds to the most distant atoms C(4) and C(8). Correspondingly, the Ti–C bond lengths to the C(2) and C(6) atoms are longer by ca. 0.2 Å than the other Ti–C bonds. The asymmetrical position of the Si(1) atom in COT''^{2-} noticeably extends the Ti′–C(6) distance (Fig. 2). The distance of 3.16 Å between C(2) and C(6) atoms excludes the formation of a bridging pentalene ligand. Such an unexpected transformation of COT''^{2-} ligand was recently reported [14], and transition metal pentalene complexes were reviewed [15]. The electronic structure of the bent ligand can be plausibly drawn as a resonance structure of pentadienyl and allyl anions as it was suggested for such a bent COT ligand in the $[(\mathrm{COT})\mathrm{M}]_2(\mu\text{-}\mathrm{COT}^{2-})$ (M = Cr [2a], Mo [2b], and W [2b,c] complexes, $(\mathrm{CpM})_2(\mu\text{-}\mathrm{COT}^{2-})$ (Cp = η^5-C_5H_5, M = V [16a], Cr [16b]) and $[(\mathrm{Me_2N})_2\mathrm{W}]_2(\mu\text{-}\mathrm{COT}^{2-})$ [17].

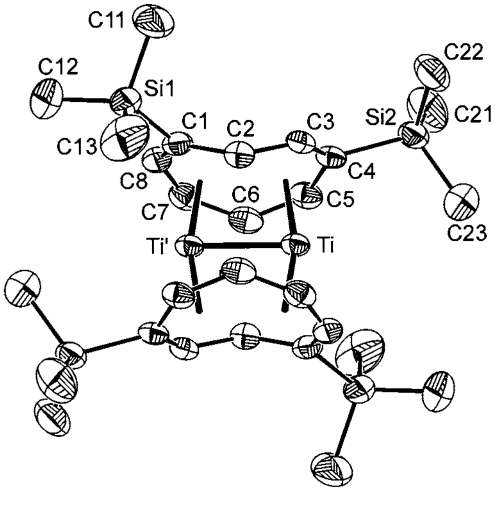


Fig. 1. ORTEP drawing of **1** with 30% probability ellipsoids and atom numbering scheme.

Table 2
Selected bond distances (Å) and angles (°) for **1**[a]

Bond distances			
Ti(1)–CE(2)	1.808(4)	Ti(1)′–CE(1)	1.810(4)
Ti(1)–C(2)	2.456(4)	Ti(1)–C(3)	2.286(3)
Ti(1)–C(4)	2.320(3)	Ti(1)–C(5)	2.270(4)
Ti(1)–C(6)	2.462(4)	Ti(1)′–C(1)	2.294(4)
Ti(1)′–C(2)	2.429(4)	Ti(1)′–C(6)	2.492(4)
Ti(1)′–C(7)	2.292(4)	Ti(1)′–C(8)	2.298(4)
C(1)–C(8)	1.396(6)	C(1)–Si(1)	1.873(4)
C(1)–C(2)	1.458(5)	C(2)–C(3)	1.456(5)
C(3)–C(4)	1.404(5)	C(4)–C(5)	1.405(5)
C(4)–Si(2)	1.887(4)	C(5)–C(6)	1.435(5)
C(6)–C(7)	1.433(5)	C(7)–C(8)	1.401(5)
Ti(1)–Ti(1)′	2.326(2)	Si–C_{Me}(av)	1.858(6)
Bond angles			
CE(1)–Ti(1)′–CE(2)′	164.5(2)	CE(2)–Ti(1)–CE(1)′	164.2(2)
C(2)–C(1)–C(8)	125.1(4)	C(2)–C(1)–Si(1)	114.9(3)
C(8)–C(1)–Si(1)	119.8(3)	C(3)–C(2)–C(1)	136.9(4)
C(4)–C(3)–C(2)	131.5(4)	C(3)–C(4)–C(5)	123.7(4)
C(3)–C(4)–Si(2)	117.4(3)	C(5)–C(4)–Si(2)	118.0(3)
C(4)–C(5)–C(6)	131.4(4)	C(7)–C(6)–C(5)	136.4(4)
C(8)–C(7)–C(6)	130.3(4)	C(1)–C(8)–C(7)	129.0(4)

[a] Operator for generating equivalent atoms: ( )′ $-x$, $-y$, $-z$.

The extraordinary feature of compound **1** is the Ti–Ti distance, 2.326(2) Å. This distance is considerably shorter than the Ti–Ti distance in the metal (2.8956 Å in Ti(α) at 25°C [18]). The comparison of intermetallic distances in the metals (Δ_1) with intermetallic distances in binuclear complexes bridged via

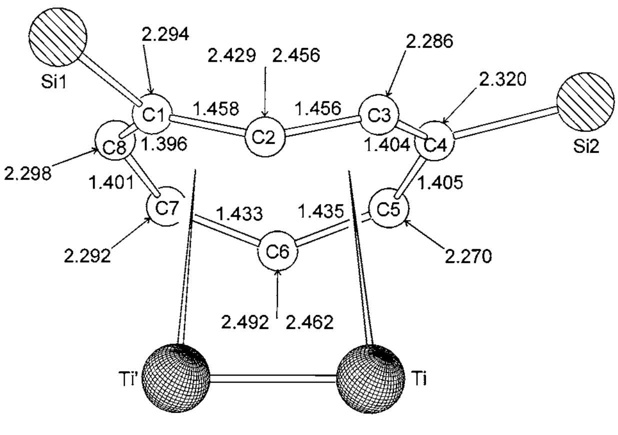


Fig. 2. Schematic description of C–C and Ti–C (at arrows) bond lengths in **1**.

Table 3
Comparison of intermetallic distances in some transition metals and their complexes bridged by the COT^{2-} ligand

Element	M–M distance in metals Δ_1 (Å)[a]	Complex	M–M distance in complexes Δ_2 (Å)	Δ_1/Δ_2	Ref.
Ti	2.8956	$[(COT^{2-})Ti]_2$	2.326	1.245	[b]
V	2.6224	$(CpV)_2(COT^{2-})$	2.439	1.075	[16a]
Cr	2.4980	$(CpCr)_2(COT^{2-})$	2.390	1.045	[16b]
		$[(COT)Cr]_2(COT^{2-})$	2.214	1.128	[2a]
Ni	2.4916	$[(COT^{2-})Ni]_2$	av. 2.91	0.856	[13]
Mo	2.7251	$[(COT)Mo]_2(COT^{2-})$	2.302	1.184	[2b]
W	2.7409	$[(COT)W]_2(COT^{2-})$	2.375	1.154	[2b,c]
		$[NMe_2)_2W]_2(COT^{2-})$	2.430	1.128	[17]
Fe	2.4823	$(Me_2N)_3TiFeCp(CO)_2$	2.567	1.047[c]	[21a]
Co	2.5061	$(t\text{-}BuO)_3TiCo(CO)_4$	2.565	1.064[c]	[21b]

[a] Ref. [18].

[b] This work.

[c] The value of Δ_1 is taken as $[\Delta_1(Ti)+\Delta_1(M)]/2$.

COT^{2-} ligands (Δ_2) (Table 3) shows that complex **1** exerts the largest shortening of the M–M distance with respect to the metal (Δ_1/Δ_2 ratio). The complexes listed in Table 3 except the Ni complex were assumed to contain triple or quadruple M–M bonds, depending on the number of available electrons [10]. The electron-deficient titanium atom in **1** can supply only two d-electrons into the intermetallic bond to form the double bond Ti=Ti. By constituting this bond a formal electron count at the Ti atom increases from 12 to 14 electrons. The other dititanium compounds with a short intermetallic distance contain folded $Ti(\mu\text{-}H)_2Ti$ fragment and a cyclopentadienyl-derived bridging ligand like (μ-η^4:η^3-1,4-dimethyl-2,3-dimethylenecyclopentadienyl) [d(Ti–Ti) 2.732 Å] [19a], (μ-η^5:η^6-indenyl) [d(Ti–Ti) 2.745 Å] [19b] or (μ-η^5:η^5-fulvalenide) [d(Ti–Ti) 2.989 Å] [19c]. The intermetallic compounds of titanium are very rare and a few known examples contain a late transition metal counterpart [20]. Particularly short intermetallic bonds were found in $(Me_2N)_3Ti{-}FeCp(CO)_2$ [d(Ti–Fe) = 2.567 Å [21a]] and $(t\text{-}BuO)_3Ti{-}Co(CO)_4$ [d(Ti–Co) = 2.565 Å [21b]. In this case, the metallic reference distance (Δ_1) was taken as one half of the sum of M–M distances for Ti and the relevant metal. The bimetallic complexes containing carbyl bridging ligands extend the intermetallic distances Ti–Pt [22a], Ti–Rh [22b,c] close to 2.83 Å, which slightly exceeds the average metallic distances. The exact evaluation of 'shortness of intermetallic bonds', however, suffers from the lack of reference metal size (for discussion see Ref. [23]).

4. Supplementary material

Crystallographic data for the structural analysis and the atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1139 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www.http://www.ccdc.cam.ac.uk).

Acknowledgements

This investigation was supported by the Grant Agency of the Czech Republic, Grant No. 203/96/0948 and by the Volkswagen Stiftung. The Grant Agency of the Czech Republic also sponsored an access to Cambridge Structure Data Base (grant No. 203/99/0067).

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