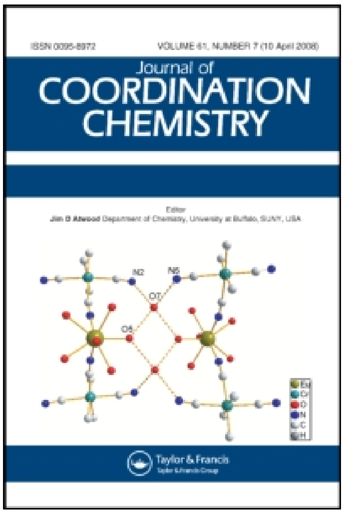

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<i>m</i>-Terphenyl derivative of titanium(III): Cp_2TiR ($Cp=C_5H_5$; <i>R</i>=2,6-(4-$MeC_6H_4)_2C_6H_3$)

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m-Terphenyl derivative of titanium(III): Cp_2TiR ($Cp = C_5H_5$; $R = 2,6\text{-}(4\text{-}MeC_6H_4)_2C_6H_3$)

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The title compound, Cp_2TiR ($Cp = C_5H_5$; $R = 2,6\text{-}(4\text{-}MeC_6H_4)_2C_6H_3$), **1**, was prepared by reaction of RLi with $[Cp_2TiCl]_2$. Compound **1** was characterized by elemental analysis, EPR, and single crystal X-ray crystallography. The title compound crystallizes in the monoclinic space group C2/c with the following unit cell dimensions: $a = 11.1466(7)$ Å, $b = 16.4429(11)$ Å, $c = 13.0786(8)$ Å; $b = 106.2040(10)^\circ$; $V = 2301.9(3)$ $Å^3$. The EPR spectrum of **1** displays two signals, a high field signal at $g = 1.979$ and a lower field signal at $g = 1.959$. Significantly, **1** is a sterically encumbered *m*-terphenyl-stabilized trivalent titanocene paramagnetic complex and may be a practical one-electron reducing reagent.

Keywords: EPR; Radical; *m*-terphenyl; Titanium

1. Introduction

Recent investigations by this laboratory of the organometallic chemistry at the transition metal-main group metal interface have garnered significant results. In particular, sodium reduction of organogroup 13 halides, $RECl_2$ ($E = Ga$, In; $R = 2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$), in the presence of group 4 metallocene dichlorides, Cp_2MCl_2 ($M = Ti$, Zr), has afforded a series of interesting $Cp_2M(ER)_2$ compounds with a "V-shaped" E-M-E structural motif [1, 2]. Notably, the :ER fragments in these $Cp_2M(ER)_2$ compounds mimic the two-electron donor properties of the carbonyl ligand, :CO. Additionally, these $Cp_2M(ER)_2$ compounds were the first examples of Ga-Zr, Ga-Ti, In-Zr, and In-Ti bonds. Recently we reported a trimetallic fulvalene-bridged dizirconocene-gallium complex, $(C_{10}H_8)(ZrCp)_2(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}GaR)$ ($R = 2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3$) [3]. Employing a slightly modified synthetic strategy, we also prepared an interesting group 4-group 15 organometallic complex, $Cp_2Zr(BiR)_2$ ($R = 2,6\text{-}Mes_2C_6H_3$) [4], which contained the first Bi-Zr bonds and a $Zr(Bi)_2$ three-membered ring. These discoveries initiated interest in the steric effects of the bulky *m*-terphenyl ligand on group 4 metallocenes. Herein, we report the synthesis and molecular structure of the first *m*-terphenyl stabilized, trivalent titanocene,

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Cp_2TiR ($R = 2,6\text{-}(4\text{-}MeC_6H_4)_2C_6H_3$), **1**. Significantly, **1** is a sterically encumbered *m*-terphenyl-stabilized trivalent titanocene paramagnetic complex.

Low-valent titanium species find utility in many important transformations including olefin hydrogenation [5–7], isomerization reactions [8], and dehalogenation of organic halides [9–11]. In addition, low-valent titanocenes are used to couple ketones and aldehydes to form pinacols [12, 13], dials [14, 15], and alkenes [16, 17], and can transform carbonyls into terminal alkenes by methylene transfer [18–20]. Monomeric trivalent Cp_2TiR complexes are also well known for their ability to reduce molecular nitrogen, producing dinitrogen complexes, $(Cp_2TiR)_2N_2$ [21, 22].

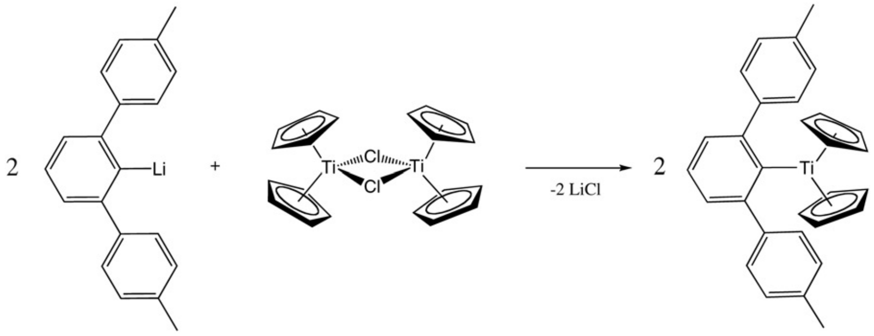
Routine syntheses of monomeric trivalent titanocenes generally involve either the reaction of $[Cp_2TiCl]_2$ with a Grignard reagent [23] or electrochemical reduction of $Cp_2TiCl(R)$ using elemental aluminum or zinc [24].

To date, only a few unambiguously structurally characterized monomeric trivalent cyclopentadienyl titanium(III) derivatives have been reported [25–29]. Notably, only one of these compounds incorporates unsubstituted Cp rings, Cp_2TiR ($R = 2,6\text{-}Me_2C_6H_3$) [26]. To our knowledge, 2,6-dimethylphenyl is the bulkiest ligand used to stabilize a Cp_2TiR complex [26]. Could a *m*-terphenyl ligand stabilize a similar complex or would its degree of steric bulk impede formation of a metal carbon bond.

2. Discussion

1 was obtained as greenish-brown needles in good yield (50%) by reaction of RLi with $[Cp_2TiCl]_2$ (scheme 1) [30]. Although **1** is air- and moisture- sensitive, decomposing gradually when exposed to air, turning orange-brown in colour, it is stable for months under an inert atmosphere.

The structure of **1** (figure 1) confirms a three-coordinate, trivalent titanium that is shielded by the sterically encumbered *m*-terphenyl ligand and two Cp rings. The *m*-terphenyl ligand staggers the $Cp_{(cen)}$–Ti(1)–$Cp_{(cen)}$ plane (torsion angle of $Cp_{(cen)}$–Ti(1)–C(1)–C(2) = 70.98°). Moreover, the independent Cp rings stagger each other and are bent away from the *m*-terphenyl ligand to further reduce steric interactions. The central titanium of **1** resides in a trigonal planar environment, with respect to Cp ring centroids ($Cp_{(cen)}$-Ti(1)–C(1) bond angle = 112.54°; $Cp_{(cen)}$–Ti(1)–$Cp_{(cen)}$ bond



Scheme 1.

angle = 134.93°). **1** possesses a two-fold axis that passes through the Ti-C(1) bond and bisects the central phenyl ring of the *m*-terphenyl ligand. The Ti(1)–C(1) bond length in **1** of 2.242(2) Å compares well with other trivalent titanocenes such as $Cp_2{}^*TiCH_2CMe_3$ ($Cp^* = C_5Me_5$) (2.231(5) Å) [25], and Cp_2TiR ($R = 2,6\text{-}Me_2C_6H_3$), (2.178(7) Å) [26], and surprising similar to tetravalent titanocenes, $(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2Ti$ (2.332(2) Å) [31], and the 17-electron complex, $Cp_2Ti[2\{(CH_3)_2NCH_2\}C_6H_4]$, (2.22(3) Å) [32].

As **1** is monomeric with a neutral trivalent titanium center without an observable counter ion, it is reasonable to consider the oxidation state as (III) with a d^1 electron configuration. Indeed, it has been reported that compounds of $Cp_2{}^*TiR$ ($Cp^* = Me_5C_5$, R = aryl, alkyl, halide) are paramagnetic, 15-electron species, with one unpaired electron residing on the titanium [25]. The ESR spectrum of **1** (figure 2) shows a characteristic high-field singlet signal at g = 1.959 (line width 12 G), which represents an unassociated paramagnetic species. This strongly supports paramagnetic properties of **1**.

It has been observed that electron-deficient, 15-electron, $Cp_2{}^*TiR$ compounds are reluctant to dimerize, or form adducts with solvents or salts [25, 29]. Compound **1** deviates from this observation, as the ESR spectrum shows a smaller low-field signal at g = 1.979 (line width of 6 G), caused by a solvent effect indicating THF coordination of

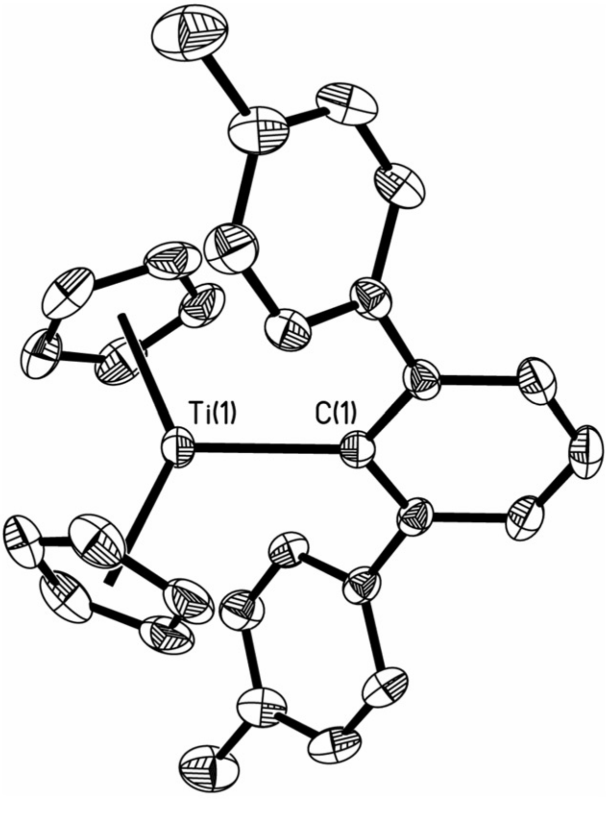


Figure 1. Molecular structure of **1** (30% probability ellipsoids, hydrogen atoms omitted), selected bond lengths (Å) and angles(degrees): Ti(1)–C(1), 2.242(2); $Cp_{(cen)}$–Ti(1)–C(1) 112.54°, $Cp_{(cen)}$–Ti(1)–$Cp_{(cen)}$, 134.93°.

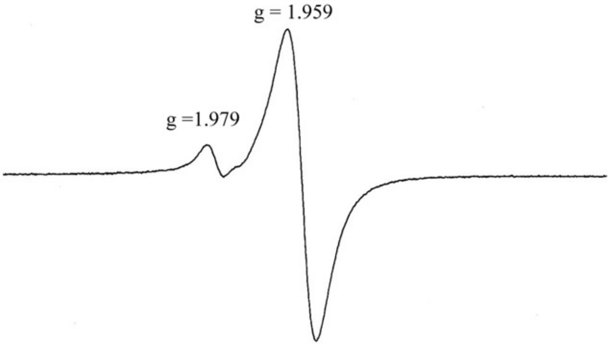


Figure 2. ESR spectrum of **1** in THF at 298 K

1 in solution. A similar phenomenon was observed for $(C_5HPh_4)_2TiCl$ [27]. The ^1H NMR spectrum of **1** showed a series of broad and ill-defined signals, which were insufficient for integration and characterization.

We have reported the synthesis and characterization of the first *m*-terphenyl stabilized titanium (III) radical and its single crystal X-ray structure. We are currently exploring the reactivity of **1** as a one-electron reducing agent, and its viability as a pinacol coupling reagent.

3. Experimental

All manipulations were performed under purified argon using Schlenk techniques in conjunction with an inert atmosphere dry-box (MBraun LabMaster 130). 2,6-(4-$MeC_6H_4)_2C_6H_3I$ [33] and 2,6-(4-$MeC_6H_4)_2C_6H_3Li$ [34] were prepared by using modified literature procedures. Cp_2TiCl_2 (Aldrich) was used as received. The ESR spectrum was recorded with a Bruker 300E EPR spectrometer.

1: RLi (1.25 g, 4.7 mmol) in THF (25 mL) was slowly added to $[Cp_2TiCl]_2$ (1.0 g, 4.7 mmol) in THF (25 mL) at ca. −78°C. The reaction was allowed to warm to room temperature and stirred overnight. All solvent was removed *in vacuo*, and the residue was extracted with toluene (25 mL). The toluene solution was removed *in vacuo*, and the residue was extracted with diethyl ether (25 mL). The solution was filtered and reduced by half then placed in a −25°C freezer. Overnight green-brown needles of **1** were isolated (1.03 g, 50%), mp. 180–182°C. Anal.: Calc (Found) for $C_{30}H_{27}Ti$ (435.40): C, 82.76 (82.93); H, 6.25 (6.27).

3.1. *Data Collection*

Dark brown-green crystals of **1** were mounted and sealed in a glass capillary under argon. The X-ray intensity data were measured at room temperature on a Bruker SMART TM CCD-based X-ray diffractometer system with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by the omega/phi-scan technique.

The crystalline compound is monoclinic, space group C2/c (No. 15) and the final residual values based on 142 variable parameters and 1654 observed reflections ($I > 2\ \sigma(I)$) are $R1 = 0.0373$, $wR2 = 0.1058$, and those for all unique reflections are $R1 = 0.0477$, $wR2 = 0.1157$. The goodness-of-fit indicator for all data is 1.029. Peaks on the final difference map ranged from 0.188 to $-0.306\, e/\text{Å}^3$, which are of no chemical significance. Crystallographic data: $C_{15}H_{13.5}Ti_{0.5}$: $a = 11.1466(7)$ Å, $b = 16.4429(11)$ Å, $c = 13.0786(8)$ Å, $\beta = 106.2040(10)^\circ$, $V = 2301.9(3)$ Å^3, Z = 8, F.W. = 217.71, $\mu = 0.386\,\text{mm}^{-1}$, $d = 1.256\,\text{g cm}^{-3}$, $F(000) = 916$. Of the 2025 unique reflections collected, 1654 were observed ($I > 2\ \sigma(I)$). The linear absorption coefficient for Mo Kα radiation is $0.386\,\text{mm}^{-1}$. The data were corrected for Lorentz and polarization effects and integrated with SAINT software. Absorption corrections were applied with SADABS. Subsequent solution and refinement was performed using the SHELXTL 6.1 solution package operating on a Pentium computer. The structure was solved by direct methods using the SHELXTL 6.1 software package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy atom positions were determined using direct methods employing SHELXTL. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, the non-hydrogen atoms were refined anisotropically.

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