diffractometer was funded in part by the National Science Foundation [Grant No. CHE-8520787). The loan of $IrCl_3$ from Johnson Matthey, Inc., is greatly appreciated. We thank David Miller for preparing the thiaalkynes.

Registry No. 1, 122424-96-8; 2, 132462-17-0; 3, 138180-44-6; 4, 138180-45-7; MeSC≡CSMe, 59507-56-1; MeSC≡CMe, 22174-51-2.

Supplementary Material Available: Tables of additional bond angles, displacement parameters, and least-squares planes (4 pages); a listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

Titanium/Magnesium Complexes: Intermediates in the Reduction of Titanocene Dichloride by Magnesium

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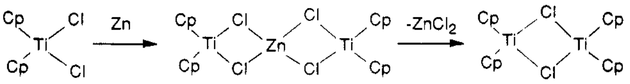
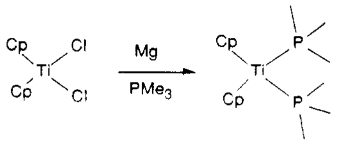
Summary: $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mg(THF)_2$ (**1**) and $(Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl)_2)_2$ (**2**) have been isolated from the reaction of Cp_2TiCl_2 with Mg in THF and in the presence of P donors. A more convenient synthesis of **1** is derived from the reaction of $(Cp_2Ti(\mu\text{-}Cl))_2$ with anhydrous $MgCl_2$. These species have been structurally characterized. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 8.104 (2) Å, b = 11.371 (4) Å, c = 16.282 (9) Å, β = 91.53 (3)°, Z = 2, and V = 1500 (1) Å^3, while compound **2** crystallizes in the tetragonal space group $I4_1/a$ with a = 24.018 (6) Å, c = 14.927 (7) Å, Z = 8, and V = 8611 (5) Å^3. These species react with PMe_3 to yield the Ti(III) species $Cp_2Ti(PMe_3)Cl$ (**3**) and $MgCl_2$. The species **3** reacts further with Mg in the presence of PMe_3 to give the "stabilized titanocene" $Cp_2Ti(PMe_3)_2$. These observations support the notion that Ti(III)/Mg compounds such as **1** and **2** are intermediates in the reduction of Cp_2TiCl_2 to Ti(II).

The reduction of Cp_2TiCl_2 to $[Cp_2Ti(\mu\text{-}Cl)]_2$ can be effected by a number of metallic reagents, including Zn, Na, Al, Na/Hg, Li/Hg, and K.[1] In addition, organolithium, organoaluminum, and Grignard reagents and metal hydrides such as MgH_2, $NaBH_4$, and $LiAlH_4$ have been employed to obtain Ti(III) species.[1] Electrochemical[2] and photochemical[3] procedures have also been studied. In some cases, intermediate adducts are observed. For example, Zn reduction affords the well-characterized intermediate $(Cp_2Ti(\mu\text{-}Cl)_2)_2$ Zn, which degrades to $[Cp_2Ti(\mu\text{-}Cl)]_2$ and $ZnCl_2$ in a donor solvent (eq 1).[4,5] Alternatively, borohydride reductions afford complexes of the form $Cp_2Ti((\mu\text{-}H)_2BH_2)$.[6] Reduction of Cp_2TiCl_2 to the Ti(II) species $Cp_2Ti(CO)_2$ was first achieved with Mg in the presence of CO.[7] Similarly, Rausch and co-workers[8] have developed a convenient, high-yield route to stabilize "titanocene" employing Mg reduction of Cp_2TiCl_2 in the presence of phosphine ligands, which affords complexes such as $Cp_2Ti(PMe_3)_2$ (eq 2). This work has prompted numerous studies in which titanocene is employed to effect organic transformations.[9-14] Such applications have been recently reviewed.[1]



(1)



(2)

Despite the convenience of employing Cp_2TiCl_2/Mg as a source of titanocene species, little is known about intermediates in the reduction process. In this paper, we describe two Ti/Mg complexes obtained from reactions of Cp_2TiCl_2 with Mg. These species react with PMe_3 to yield the Ti(III) species $Cp_2Ti(PMe_3)Cl$ and $MgCl_2$, suggesting that these Ti/Mg compounds are intermediates in the Mg reduction of Cp_2TiCl_2 and that further reduction of such Ti(III) species in the presence of PMe_3 affords the "stabilized titanocene" $Cp_2Ti(PMe_3)_2$.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres inter-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. EPR spectra were recorded using a Varian E-12 EPR spectrometer employing DPPH as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2, Mg, P_4, and $MgCl_2$ were purchased from the Aldrich Chemical Co., while $PhPH_2$ and $CyPH_2$ were purchased from Pressure Chemical. $(Cp_2Ti(\mu\text{-}Cl))_2$ was prepared by the literature method.[15]

Synthesis of $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mg(THF)_2$ (1). (i) Cp_2TiCl_2 (100 mg, 0.403 mmol) was dissolved in 5 mL of THF. Fivefold molar excesses of fine Mg turnings and P_4 were added. The mixture stood for 18 h and was filtered, and hexane (1–2 mL) was added. Small green crystals of 1 formed on standing for 24–48 h; yield 5%.

(ii) $(Cp_2Ti(\mu\text{-}Cl))_2$ (100 mg, 0.235 mmol) and $MgCl_2$ (22.3 mg, 0.235 mmol) were suspended in 5 mL of toluene, and 1 mL of THF

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Table I. Crystallographic Parameters

	1	2
formula	$C_{28}H_{36}Cl_4MgO_2Ti_2$	$C_{36}H_{52}Cl_6Mg_2O_4Ti_2$
cryst color, form	green blocks	aquamarine blocks
a, Å	8.104 (2)	24.018 (6)
b, Å	11.371 (4)	
c, Å	16.282 (9)	14.927 (7)
β, deg	91.53 (3)	
cryst syst	monoclinic	tetragonal
space group	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)
V, $Å^3$	1500 (1)	8611 (5)
calcd density, g cm^{-3}	1.48	1.40
Z	2	8
cryst dimens, mm	0.40 × 0.30 × 0.50	0.30 × 0.35 × 0.45
abs coeff, μ, cm^{-1}	9.310	8.054
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	24	24
scan speed, deg min^{-1}	32.0 ($\theta/2\theta$)	16.0 ($\theta/2\theta$)
scan range, deg	1.0 below Kα_1 to 1.0 above Kα2	1.0 below Kα_1 to 1.0 above Kα_2
bkgd/scan time ratio	0.5	0.5
no. of data collected	3008	4168
2θ range, deg	4.5–50.0	4.5–50.0
index range	$h,k,\pm l$	h,k,l
no. of data with $F_o^2 > 3\sigma(F_o^2)$	1172	930
no. of variables	169	126
R, %	4.36	7.32
R_w, %	4.26	7.58
largest Δ/σ in final least-squares cycle	0.007	0.005
goodness of fit	1.211	1.780

was added. The mixture stood for 36 h and was filtered, and hexane (1–2 mL) was added. Small green crystals of **1** formed on standing; yield 25%. EPR (THF, 298 K): $g = 1.981$, $\langle a(^{47}Ti)\rangle = 10.5$ G.

Synthesis of $(Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl))_2$ (2). Cp_2TiCl_2 (100 mg, 0.403 mmol) was dissolved in 5 mL of THF. Fivefold molar excesses of fine Mg turnings and either $PhPH_2$ or $CyPH_2$ were added. The mixture stood for 18 h and was filtered, and hexane (1–2 mL) was added. Small aquamarine crystals of **2** formed on standing for 24–48 h; yield 5%. EPR (THF, 298 K): $g = 1.964$, $\langle a(^{47}Ti)\rangle = 20.0$ G.

Generation of $Cp_2Ti(PMe_3)Cl$ (3). To solutions of **1** or **2** in THF was added PMe_3. The reaction was monitored by EPR spectroscopy. Comparison of the observed resonances to that of an authentic sample of $Cp_2Ti(PMe_3)Cl$ confirmed its formation.[16]

Synthesis of $Cp_2Ti(PMe_3)_2$. To a solution of **3** generated by the reaction of $(Cp_2Ti(\mu\text{-}Cl))_2$ (100 mg, 0.235 mmol) with excess PMe_3 in THF was added excess Mg. The solution stood overnight. The product was isolated as per the literature workup of $Cp_2Ti(PMe_3)_2$. Comparison of the ^1H NMR spectrum of the product to that of an authentic sample of $Cp_2Ti(PMe_3)_2$ confirmed the formulation (yield 75%).

X-ray Data Collection and Reduction. X-ray-quality crystals of **1** and **2** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6-S four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 reflections located by an autosearch routine. These data were used to determine the crystal systems. An automated check of the Laue symmetry confirmed the crystal system as monoclinic and tetragonal for **1** and **2**, respectively. Ultimately, 25 reflections (15° < 2θ < 35°) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions and subsequent refinements confirmed the space groups as $P2_1/c$ and $I4_1/a$ for **1** and **2**, respectively. The data sets were collected in four shells (4.5° < 2θ < 50.0°), and three standard reflections were recorded every 150 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN software program package on a VAX 3520 workstation located in the Department of Chemistry and Biochemistry at the University of Windsor. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in each of the refinements.

Table II. Positional Parameters

atom	*x*	*y*	*z*
		Compound 1	
Ti(1)	0.7436 (2)	0.1934 (1)	0.14088 (8)
Cl(1)	0.7232 (2)	0.0971 (2)	−0.0015 (1)
Cl(2)	1.0270 (2)	0.0926 (2)	0.1393 (1)
Mg	1.0000	0	0
O	1.1055 (5)	0.1523 (4)	−0.0500 (3)
C(1)	0.492 (1)	0.165 (1)	0.2098 (6)
C(2)	0.613 (1)	0.1764 (8)	0.2699 (5)
C(3)	0.718 (1)	0.084 (1)	0.2630 (5)
C(4)	0.663 (1)	0.0141 (7)	0.1980 (6)
C(5)	0.519 (1)	0.065 (1)	0.1662 (5)
C(6)	0.874 (1)	0.3482 (7)	0.0741 (5)
C(7)	0.906 (1)	0.3654 (7)	0.1564 (6)
C(8)	0.763 (2)	0.3908 (9)	0.1921 (6)
C(9)	0.639 (1)	0.3893 (8)	0.1337 (8)
C(10)	0.707 (1)	0.3648 (7)	0.0584 (6)
C(11)	1.2584 (9)	0.2072 (7)	−0.0220 (4)
C(12)	1.282 (1)	0.3119 (9)	−0.0721 (6)
C(13)	1.148 (1)	0.318 (1)	−0.1315 (6)
C(14)	1.0389 (9)	0.2163 (7)	−0.1197 (4)
		Compound 2	
Ti(1)	0.0691 (1)	0.0847 (1)	0.2114 (2)
Cl(1)	0.0851 (2)	0.0097 (2)	0.3301 (3)
Cl(2)	−0.0311 (2)	0.0605 (2)	0.2484 (3)
Cl(3)	−0.0111 (2)	0.0685 (2)	0.4966 (3)
Mg	−0.0131 (2)	−0.0050 (3)	0.3780 (4)
O(1)	−0.0187 (5)	−0.0759 (5)	0.2942 (8)
O(2)	−0.1005 (5)	−0.0116 (6)	0.3915 (8)
C(1)	0.093 (1)	0.1791 (8)	0.198 (1)
C(2)	0.1338 (9)	0.1548 (9)	0.247 (2)
C(3)	0.111 (1)	0.139 (1)	0.325 (2)
C(4)	0.055 (1)	0.1500 (9)	0.327 (1)
C(5)	0.0423 (9)	0.1776 (9)	0.244 (2)
C(6)	0.077 (1)	0.093 (1)	0.052 (2)
C(7)	0.128 (1)	0.078 (1)	0.083 (2)
C(8)	0.1242 (9)	0.0263 (9)	0.123 (1)
C(9)	0.070 (1)	0.0081 (9)	0.114 (1)
C(10)	0.0434 (9)	0.050 (1)	0.068 (1)
C(11)	0.019 (1)	−0.122 (1)	0.294 (2)
C(12)	−0.011 (1)	−0.169 (1)	0.254 (2)
C(13)	−0.045 (1)	−0.144 (1)	0.189 (2)
C(14)	−0.058 (1)	−0.085 (1)	0.221 (2)
C(15)	−0.131 (1)	−0.056 (1)	0.433 (2)
C(16)	−0.184 (1)	−0.032 (1)	0.462 (2)
C(17)	−0.188 (1)	0.024 (1)	0.423 (2)
C(18)	−0.134 (1)	0.036 (1)	0.391 (2)

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[17,18] The heavy-atom positions for each structure were determined using direct methods employing the Mithril option of the TEXSAN package. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix, least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight, *w*, is defined as $1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement all the non-hydrogen atoms in **1** were refined as individual anisotropic atoms. For **2**, only the Ti, Cl, and Mg atoms were refined anisotropically in order to maintain a reasonable data to variable ratio. The remaining non-hydrogen atoms were refined isotropically. In all cases, hydrogen atom positions were calculated

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Table III. Selected Bond Distances (Å) and Angles (deg)

Compound 1			
Ti(1)–Cl(1)	2.565 (2)	O–C(11)	1.450 (8)
Ti(1)–Cl(2)	2.568 (2)	O–C(14)	1.441 (8)
Ti(1)–C(1)	2.372 (8)	C(1)–C(2)	1.37 (1)
Ti(1)–C(2)	2.384 (8)	C(1)–C(5)	1.36 (1)
Ti(1)–C(3)	2.360 (8)	C(2)–C(3)	1.36 (1)
Ti(1)–C(4)	2.340 (8)	C(3)–C(4)	1.39 (1)
Ti(1)–C(5)	2.375 (8)	C(4)–C(5)	1.39 (1)
Ti(1)–C(6)	2.337 (8)	C(6)–C(7)	1.37 (1)
Ti(1)–C(7)	2.366 (8)	C(6)–C(10)	1.38 (1)
Ti(1)–C(8)	2.40 (1)	C(7)–C(8)	1.34 (1)
Ti(1)–C(9)	2.386 (9)	C(8)–C(9)	1.36 (1)
Ti(1)–C(10)	2.381 (8)	C(9)–C(10)	1.39 (1)
Cl(1)–Mg	2.500 (2)	C(11)–C(12)	1.46 (1)
Cl(2)–Mg	2.504 (2)	C(12)–C(13)	1.44 (1)
Mg–O	2.105 (4)	C(13)–C(14)	1.47 (1)
Cl(1)–Ti(1)–Cl(2)	80.59 (7)	Cl(2)–Mg–O	88.7 (1)
Cl(2)–Mg–O	91.3 (1)	Cl(1)–Mg–Cl(2)	83.10 (6)
Cl(1)–Mg–Cl(2)	96.90 (6)	Cl(1)–Mg–O	90.4 (1)
Cl(1)–Mg–O	89.6 (1)	Mg–O–C(11)	125.8 (4)
Ti(1)–Cl(1)–Mg	98.25 (7)	Ti(1)–Cl(2)–Mg	98.06 (6)
Mg–O–C(14)	125.0 (4)	C(11)–O–C(14)	109.2 (5)
C(2)–C(1)–C(5)	109.3 (9)	C(1)–C(2)–C(3)	107.6 (8)
C(2)–C(3)–C(4)	108.7 (8)	C(3)–C(4)–C(5)	107.0 (8)
C(1)–C(5)–C(4)	107.4 (8)	C(7)–C(6)–C(10)	108.6 (8)
C(6)–C(7)–C(8)	108.2 (9)	C(7)–C(8)–C(9)	108.8 (9)
C(8)–C(9)–C(10)	108.4 (9)	C(6)–C(10)–C(9)	106.0 (8)
O–C(11)–C(12)	107.4 (6)	C(11)–C(12)–C(13)	107.9 (8)
C(12)–C(13)–C(14)	108.7 (7)	O–C(14)–C(13)	106.7 (6)
Compound 2			
Ti(1)–Cl(1)	2.556 (6)	Ti(1)–Cl(2)	2.535 (5)
Ti(1)–C(1)	2.35 (2)	Ti(1)–C(2)	2.35 (2)
Ti(1)–C(3)	2.36 (2)	Ti(1)–C(4)	2.35 (2)
Ti(1)–C(5)	2.37 (2)	Ti(1)–C(6)	2.39 (2)
Ti(1)–C(7)	2.39 (2)	Ti(1)–C(8)	2.34 (2)
Ti(1)–C(9)	2.34 (2)	Ti(1)–C(10)	2.38 (2)
Cl(1)–Mg	2.490 (8)	Cl(2)–Mg	2.529 (8)
Cl(3)–Mg	2.499 (8)	Cl(3)′–Mg	2.484 (8)
Mg–O(1)	2.12 (1)	Mg–O(2)	2.11 (1)
O(1)–C(11)	1.44 (2)	O(1)–C(14)	1.46 (2)
O(2)–C(15)	1.43 (2)	O(2)–C(18)	1.40 (2)
Cl(1)–Ti(1)–Cl(2)	80.2 (2)	Cl(3)–Mg–Cl(3)′	84.0 (3)
Cl(3)–Mg–O(1)	170.9 (5)	Cl(3)–Mg–O(2)	90.3 (4)
Cl(3)′–Mg–O(1)	88.1 (4)	Cl(3)′–Mg–O(2)	96.6 (4)
O(1)–Mg–O(2)	86.1 (5)	Cl(1)–Mg–Cl(2)	81.6 (2)
Cl(1)–Mg–Cl(3)	94.9 (3)	Cl(1)–Mg–Cl(3)′	94.7 (3)
Cl(1)–Mg–O(1)	90.2 (4)	Cl(1)–Mg–O(2)	168.0 (5)
Cl(2)–Mg–Cl(3)	96.1 (3)	Cl(2)–Mg–Cl(3)′	176.2 (3)
Cl(2)–Mg–O(1)	92.1 (4)	Cl(2)–Mg–O(2)	87.2 (4)
Ti(1)–Cl(1)–Mg	99.0 (2)	Ti(1)–Cl(2)–Mg	98.5 (2)
Mg–Cl(3)–Mg′	96.0 (3)	Mg–O(1)–C(11)	126 (1)
Mg–O(1)–C(14)	127 (1)	C(11)–O(1)–C(14)	107 (2)
Mg–O(2)–C(15)	127 (1)	Mg–O(2)–C(18)	120 (1)
C(15)–O(2)–C(18)	109 (2)		

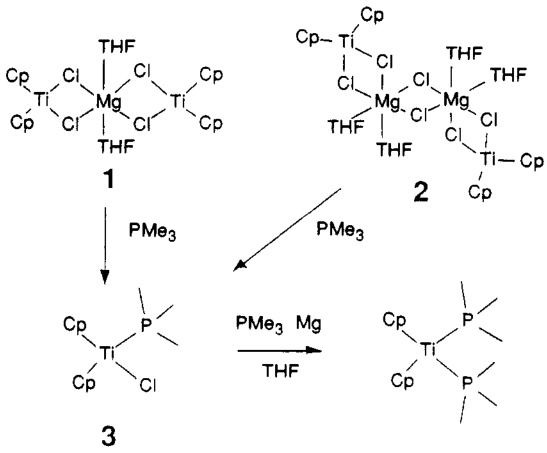
by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final refinement data are given in Table I. The largest peaks in the final difference Fourier map calculations showed residual electron densities of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and values of $10F_o$ and $10F_c$ (Table S3) have been deposited as supplementary material.

Results and Discussion

The reaction of Cp_2TiCl_2 with Mg in THF in the presence of excess PMe_3 is known to give $Cp_2Ti(PMe_3)_2$ in excellent yield.[8] In an analogous manner we examined the reaction of Cp_2TiCl_2 with Mg in the presence of excess P_4. The solution becomes dark initially and gradually lightens to a light red-brown. Light green crystals of 1 are isolated from the solution upon adding hexane and cooling. The yield of 1 from this mixture is low, and the nature of the other products is as yet unknown. Nonetheless, the isolated product was characterized. It proves to be paramagnetic at 25 °C, exhibiting a single EPR resonance at $g = 1.981$ with $\langle a(^{47/49}Ti)\rangle = 10.5$ G. An X-ray structural study was performed to determine the precise molecular architecture (vide infra). This showed 1 to be $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mg(THF)_2$. Knowing the precise formulation, a more conventional procedure for the preparation of 1 was contrived. Reaction of $(Cp_2Ti(\mu\text{-}Cl))_2$ and anhydrous $MgCl_2$ in toluene/THF affords 1 in a low but nevertheless improved yield (25%).

In an analogous manner we examined the reactions of Cp_2TiCl_2 and Mg in the presence of excess $PhPH_2$ or $CyPH_2$. In either case, the solutions become purple after several hours. Upon addition of hexane and cooling aquamarine crystals of 2 are obtained. Once again, the yield is low and the nature of the other species remaining in solution has not been determined. The compound 2 is a paramagnetic Ti(III) species, as evidenced by the EPR resonance at $g = 1.964$ and the $\langle a(^{47/49}Ti)\rangle$ value of 20.0 G. The structure of 2 was determined crystallographically (vide infra) to be $(Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl))_2$. Attempts to prepare 2 in a more direct manner via reaction of $(Cp_2Ti(\mu\text{-}Cl))_2$ and 2 equiv of anhydrous $MgCl_2$ were unsuccessful.

The immediate reaction of compounds 1 and 2 with PMe_3 in THF is indicated by the formation of the white precipitate $MgCl_2$. The Ti product of both reactions is the same, and it exhibits a doublet EPR resonance at $g = 1.985$ with $\langle a(^{31}P)\rangle = 16.5$ G and $\langle a(^{47/49}Ti)\rangle = 10.0$ G. This species is formulated as the Ti(III) species $Cp_2Ti(PMe_3)Cl$ (3) by comparison of the spectral data to that of an authentic sample. Subsequent reaction of 3 with Mg in the presence of excess PMe_3 afforded the Ti(II) species $Cp_2Ti(PMe_3)_2$.



Structure Studies. The crystallographic study of 1 confirmed the trimetallic nature. An ORTEP drawing of 1 is shown in Figure 1. Two pseudotetrahedral $Cp_2Ti(\mu\text{-}Cl)_2$ units are bridged by a central Mg atom. The pseudooctahedral coordination sphere of the Mg atom is completed by two molecules of THF, which occur in a trans disposition. The crystallographic symmetry requires that Mg sit on a center of symmetry. This molecules is, in fact, isostructural with the Mn analogue $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mn(THF)_2$, studied by Stucky and co-workers some time ago.[19,20]

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(20) Sekutowski, D.; Stucky, G. *Inorg. Chem.* **1975**, *14*, 2192.

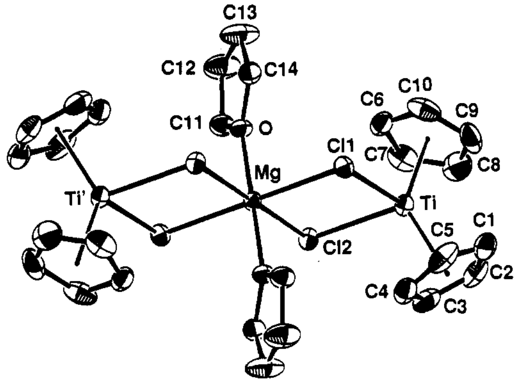

Figure 1. ORTEP drawing of 1. Thermal ellipsoids at the 30% level are shown; hydrogen atoms are omitted for clarity.

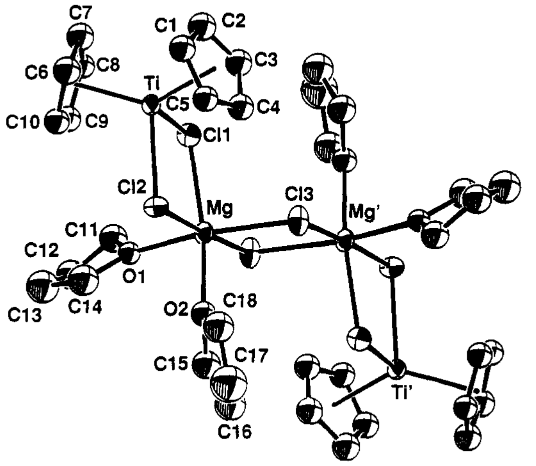

Figure 2. ORTEP drawing of 2. Thermal ellipsoids at the 30% level are shown; hydrogen atoms are omitted for clarity.

The structural study of the aquamarine compound 2 showed that it contains two Ti and two Mg atoms. An ORTEP drawing of 2 is shown in Figure 2. Two pseudotetrahedral $Cp_2Ti(\mu\text{-}Cl)_2$ fragments are chloride-bridged to two Mg atoms. Two more chloride bridges further link the two Mg atoms. Two THF molecules complete the pseudooctahedral coordination sphere of the Mg atoms; however, in contrast to 1, the THF molecules are in a cis orientation. The crystallographic symmetry demands that the entire molecule have 2-fold symmetry.

The structural details of the cores of molecules 1 and 2 are depicted in Figure 3. In both molecules the $Ti(\mu\text{-}Cl)_2Mg$ fragments are planar with Ti–Cl distances of 2.565 (2), 2.568 (2) Å and 2.535 (5), 2.556 (6) Å for molecules 1 and 2, respectively. These distances are slightly shorter than those found in $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mn(THF)_2$ (2.572 (2) and 2.578 (2) Å)[19] and significantly longer than the bridging Ti–Cl distances found in $TiCl_4(\mu\text{-}Cl)_2(C_2H_5O_2CCH_3)_4$[21] and $TiCl_3(\mu\text{-}Cl)_2(\mu\text{-}O_2CCH_2Cl)Mg(C_2H_5O_2CCH_2Cl)_3$.[22] The Mg–Cl distances in 1 are not significantly different, averaging 2.502 (3) Å. In 2, Mg–Cl distances are found to be 2.529 (8) and 2.490 (8) Å. This difference is consistent with the relative trans influences of chloride and THF. Cl(3) of 2 forms the chloride bridge between the Mg centers, and as expected the Mg–Cl(3) distance in 3 of 2.484 (8) Å is shorter than the other Mg–Cl bonds in which the chloride atoms bridge to Ti. In any case, these bridging Mg–Cl distances fall within the range seen in the cation $[(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]^+$.[23] The angles about the core are similar in the two molecules again, with differences reflecting the differing relative geometries at Mg. The relatively small Cl–Ti–Cl angles of 80.59 (7) and 80.2 (2)° found in 1 and 2, respectively, are typical of d^1 systems. Mg–O and Ti–C distances in both molecules are also typical.

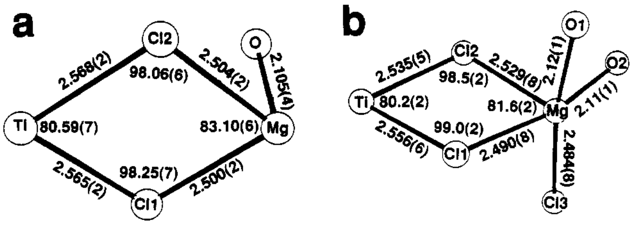

Figure 3. Structural details of the Ti/Mg cores of (a) 1 and (b) 2.

Implications. The isolation of these two Ti(III)/Mg species from reactions of Cp_2TiCl_2 and Mg in THF in the presence of P donors has some implications regarding the mechanism of the reduction process. We suggest that 1 and/or 2 and perhaps other related Ti/Mg aggregates are formed upon initial reduction of Ti(IV) to Ti(III). Such Ti(III) species react rapidly with PMe_3 to give $Cp_2Ti(PMe_3)Cl$, which apparently reacts further with Mg to yield the Ti(II) species, that is, the "stabilized titanocene" $Cp_2Ti(PMe_3)_2$. In the absence of strong σ-donors such Ti/Mg compounds are isolated and may in fact be the initial reactive species, affording intermediates in various organic reactions in which Cp_2TiCl_2/Mg is employed as a catalyst.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters (3 pages); a table of $10F_o$ and $10F_c$ values (15 pages). Ordering information is given on any current masthead page.

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