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Preparation of Dimeric Monopentamethylcyclopentadienyltitanium(III) Dihalides and Related Derivatives

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Dedicated to the memory of Prof. Dr. Catalina Ruiz-Pérez, who passed away in August 2019.

Synopsis:

Half-sandwich titanium(III) dihalide complexes with a dimeric structure [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl, Br, I) have been structurally characterized. The chloride compound reacts with isocyanides to form dinuclear titanium(III) adducts with long Ti–Ti distances and weak antiferromagnetic coupling of the d^1 titanium centers. Subsequently, the *tert*-butylisocyanide ligands of the dinuclear adduct undergo a reductive coupling reaction to give a titanium(IV) iminoacyl derivative.
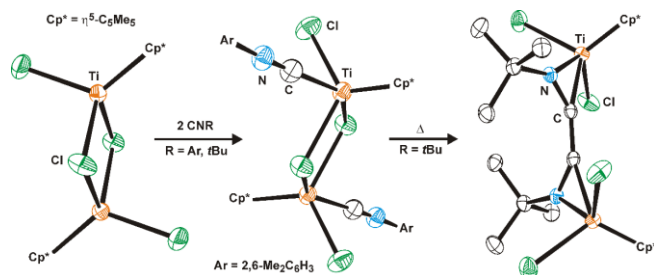
Abstract:

The synthesis, crystal structure, and reactivity of a series of half-sandwich titanium(III) dihalide complexes [Ti(η^5-C$_5$Me$_5$)X$_2$] (X = Cl, Br, I) and several of its Lewis base derivatives have been investigated. The reaction of the trihalides [Ti(η^5-C$_5$Me$_5$)X$_3$] (X = Cl (**1**), Br (**2**), I (**3**)) with LiAlH$_4$ ($\geq$1 equiv) in toluene at room temperature results in the formation of the halide-bridged dimers [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl (**4**), Br (**5**), I (**6**)). The treatment of **4** with [Li{N(SiMe$_3$)$_2$}] ($\geq$2 equiv) at room temperature affords the precipitation of the amido titanium(III) complex [{Ti(η^5-C$_5$Me$_5$)(μ-Cl){N(SiMe$_3$)$_2$}}$_2$] (**7**), but analogous reactions of **4** with other lithium reagents [LiR] (R = Me, CH$_2$SiMe$_3$, NMe$_2$) lead to disproportionation into titanium(IV) [Ti(η^5-C$_5$Me$_5$)R$_3$] and presumably titanium(II) derivatives. Similarly, complex **4** in solution at temperatures higher than 100 ºC undergoes disproportionation as demonstrated by its reactions with cobaltocene and *N*-(4-methylbenzylidene)aniline yielding the ionic paramagnetic compound [Co(η^5-C$_5$H$_5$)$_2$][Ti(η^5-C$_5$Me$_5$)Cl$_3$] (**8**) and the diamagnetic diazatitanacyclopentane [Ti(η^5-C$_5$Me$_5$)Cl{N(Ph)CH(*p*-tolyl)}$_2$], respectively. Treatment of complex **4** with 2 equiv of 2,6-dimethylphenylisocyanide or *tert*-butylisocyanide in toluene at room temperature affords the paramagnetic titanium(III) dinuclear adducts [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(CNR)}$_2$] (R = 2,6-Me$_2$C$_6$H$_3$ (**9**), *t*Bu (**10**)). Magnetic studies for polycrystalline **9** show that it displays a weak intramolecular antiferromagnetic coupling between the Ti ions, which is consistent with the long Ti–Ti distance of 3.857(1) Å determined by X-ray diffraction. The isocyanide ligands in complex **10** undergo a reductive coupling reaction in toluene to give the titanium(IV) iminoacyl derivative [{Ti(η^5-C$_5$Me$_5$)Cl$_2$}$_2$(μ-η^2:η^2-*t*BuN=C-C=N*t*Bu)] (**11**). Whereas an analogous dinuclear structure was found in the aqua titanium(III) complex [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(OH$_2$)}$_2$] (**12**), resulting from the reaction of **4** with adventitious

amounts of water, compound **4** reacts with excess ammonia to give a mononuclear adduct

[Ti(η^5-C$_5$Me$_5$)Cl$_2$(NH$_3$)$_2$] (**13**) with a robust layered pattern in the solid-state.

Introduction

Low-valent early transition-metal complexes are receiving increasing attention due to their implication in bond-forming reactions useful in synthesis and catalysis.[1] Traditionally, the preparation of these highly-reactive compounds involves the reduction of high-valent metal halides with a variety of reducing agents, such as alkali/alkaline-earth metals or their derivatives (e.g., KC_8, $NaC_{10}H_8$), zinc or manganese in ethereal solvents. However, salt-free reduction methods exhibit clear advantages such as the easier removal of the by-products or the use of non-coordinating solvents, which are critical for productive chemistry of the reduced compounds.[2] In particular, titanium(III) species are frequently used in catalytic single-electron transfers for organic synthesis and small-molecule activation.[1] Over the last decades, the Nugent-RajanBabu reagent (bis(cyclopentadienyl)titanium(III) chloride derivative $[Ti(\eta^5-C_5H_5)_2Cl]$) has become a common reagent for promoting single-electron transfers in organic synthetic transformations.[3,4] This compound and its derivatives with small R substituents on the cyclopentadienyl rings show a chloride-bridged dimeric structure $[\{Ti(\eta^5-C_5H_{5-n}R_n)_2(\mu-Cl)\}_2]$,[5] and exhibit some degree of antiferromagnetic coupling between the titanium atoms. In solution, both dimeric $[\{Ti(\eta^5-C_5H_{5-n}R_n)_2(\mu-Cl)\}_2]$ and monomeric $[Ti(\eta^5-C_5H_{5-n}R_n)_2Cl]$ derivatives are involved in a solvent-assisted equilibrium in which half-open dimeric systems $[\{Cl(\eta^5-C_5H_{5-n}R_n)_2Ti\}(\mu-Cl)\{Ti(\eta^5-C_5H_{5-n}R_n)_2\}]$ are acting as intermediates.[6]

There are fewer examples of applications of monocyclopentadienyltitanium(III) halides $[Ti(\eta^5-C_5R_5)X_2]$, but these compounds are attracting considerable interest as catalysts in organic synthesis.[7] For instance, $[Ti(\eta^5-C_5Me_5)Cl_2]$ has been recently suggested to be the active species in radical chemistry of catalyzed organic transformations wherein the Nugent–RajanBabu reagent or its derivative $[Ti(\eta^5-C_5Me_5)_2Cl]$ were substantially less

reactive.[7c] While the synthesis of these half-sandwich derivatives was described several decades ago, their structures and properties remain poorly described in the literature.[8] In 1961, Bartlett reported the precipitation of $[Ti(\eta^5-C_5H_5)Cl_2]$ from the reaction mixture of $[Ti(\eta^5-C_5H_5)_2Cl_2]$ with $[Al(iBu)_2Cl]$ in a toluene-heptane solution.[9] In rational procedures, $[Ti(\eta^5-C_5H_5)X_2]$ (X = Cl, Br, I) complexes were obtained by dissolving the cyclopentadienyltitanium(IV) trihalides in tetrahydrofuran and using zinc as reductant.[10] Later, adducts $[Ti(\eta^5-C_5H_5)Cl_2(thf)_n]$ (n = 1, 2)[11] were prepared by reaction of $[Ti(\eta^5-C_5H_5)Cl_3]$ with Li_3N[12] or $K[H_2BC_8H_{14}]$[13] in tetrahydrofuran. The physical properties of the dihalide complexes $[Ti(\eta^5-C_5H_5)X_2]$ (X = Cl, Br) suggested an oligomeric structure but the compounds are paramagnetic with magnetic moments consistent with one unpaired electron per titanium atom, and no decrease of the magnetic moment with decreasing temperature was observed in the 100–300 K range.[10]

The reduction of the pentamethylcyclopentadienyl trichloride complex $[Ti(\eta^5-C_5Me_5)Cl_3]$ with zinc,[14] manganese,[15] or $KPPh_2$[16] in tetrahydrofuran affords the analogous derivatives $[Ti(\eta^5-C_5Me_5)Cl_2(thf)]$ and $[Ti(\eta^5-C_5Me_5)Cl_2]$. In a seminal contribution, Mashima and co-workers used electron-rich organosilicon compounds as salt-free reductants for generating group 4-6 species, including $[Ti(\eta^5-C_5Me_5)Cl_2]$ and $[Ti(\eta^5-C_5Me_5)Cl_2(thf)]$.[17] We have recently reported that thermolysis or hydrogenolysis of $[Ti(\eta^5-C_5Me_5)Cl_2Me]$ in hydrocarbon solvents leads to the clean formation of half-sandwich titanium(III) dichloride species $[Ti(\eta^5-C_5Me_5)Cl_2]$ along with volatile by-products.[18] Dimeric $[\{Ti(\eta^5-C_5Me_5)Cl(\mu-Cl)\}_2]$ and trimeric $[\{Ti(\eta^5-C_5Me_5)(\mu-Cl)_2\}_3]$ complexes were characterized by means of X-ray diffraction determinations, and the electronic structures and stabilities of several aggregates were established by computational calculations. Since these salt-free routes provide the dichloride complex in good yield and high purity, we

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decided to explore the reactivity of this titanium(III) species. Here also are described the syntheses and crystal structures of the bromide and iodide titanium(III) analogues [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$].

Results and Discussion

Synthesis and characterization of [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl, Br, I) complexes.

The treatment of titanium(IV) halides [TiX$_4$] with 1 equiv of pentamethylcyclopentadienyltrimethylsilane [Si(C$_5$Me$_5$)Me$_3$] in toluene afforded the trihalide derivatives [Ti(η^5-C$_5$Me$_5$)X$_3$] (X = Cl (**1**), Br (**2**), I (**3**)) via [SiMe$_3$X] elimination.[19] Given the absence of structurally documented examples of cyclopentadienyltitanium triiodide species, an X-ray diffraction study was undertaken for red single-crystals of **3**. The molecular structure reveals a three-legged piano-stool disposition for monocyclopentadienyltitanium(IV) complexes (Figure S1 and Table S3 in the Supporting Information) similar to that found in the chloride complex [Ti(η^5-C$_5$Me$_5$)Cl$_3$].[20] Despite the larger steric bulk of the iodide ligands, the separation between titanium and the centroid of the cyclopentadienyl ring (2.029 Å) in **3** is very similar to that of the chloride analogue (2.021 Å).

The treatment of complexes **1**-**3** with lithium tetrahydridoaluminate(III) ($\geq$ 1 equiv) in toluene at room temperature led to green solutions from which the dinuclear titanium(III) dihalide derivatives [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl (**4**), Br (**5**), I (**6**)) were obtained (Scheme 1). Compounds **4**-**6** were isolated after workup in 40-66% yields as highly air-sensitive green solids, which exhibit a good solubility in aromatic hydrocarbon solvents but are poorly soluble in hexane. We have recently described the synthesis of crystals of the chloride complex **4** in higher yield (90%) by thermolysis of [Ti(η^5-C$_5$Me$_5$)Cl$_2$Me] in hexane.[18] Crystals of compounds **5** and **6** were isolated after recrystallization in hot toluene and those samples were used for X-ray crystal structure determinations and magnetic measurements.

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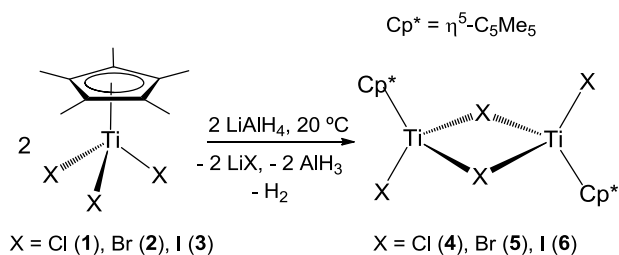
Scheme 1. Synthesis of dinuclear titanium(III) complexes 4-6.

The molecular structure of 6 is shown in Figure 1, whereas that of 5 is presented in Figure S2 of the Supporting Information. Selected distances and angles of complexes 4-6 are compared in Table 1. The crystal structures of complexes 4-6 show dimers with two $[Ti(\eta^5-C_5Me_5)X]$ units linked by two bridging halide ligands. The $\eta^5-C_5Me_5$ ligands are disposed in a transoid mode about the central $Ti_2(\mu-X)_2$ core. A three-legged piano-stool geometry is defined around each titanium, with one terminal halide and two bridging halide ligands at the legs. Within each molecule, the titanium–halide bond distances of the terminal ligands are ca. 0.1 Å shorter than those related with the bridging ligands.
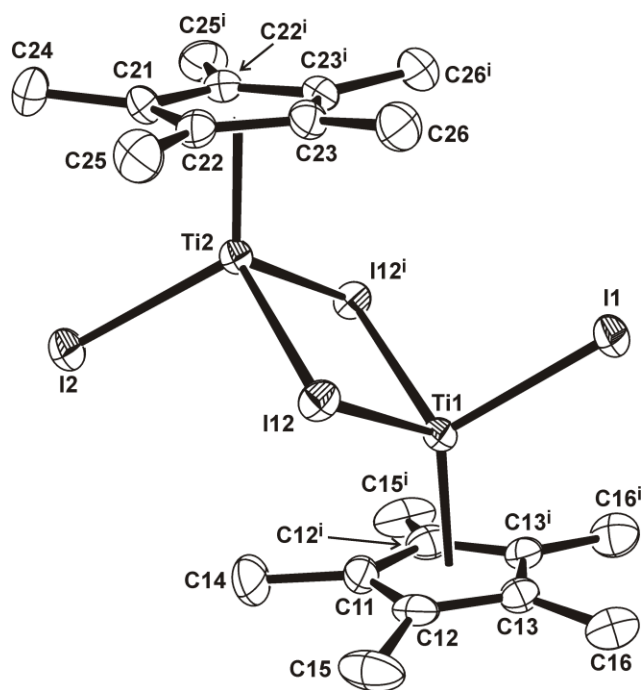

Figure 1. ORTEP diagram (thermal ellipsoids at the 50% probability level) of 6. Hydrogen atoms are omitted for clarity. Symmetry code: (i) x, 1/2 − y, z.

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Table 1. Selected Averaged Lengths (Å) and Angles (deg) for Complexes **4-6**

	4 (X = Cl)[18]	**5** (X = Br)	**6** (X = I)
Ti–Ti	3.266(1)	3.407(1)	3.592(2)
Ti–$X_{terminal}$	2.274(1)	2.430(5)	2.659(7)
Ti–$X_{bridging}$	2.392(4)	2.534(3)	2.732(5)
$X_{bridging}$···$X_{bridging}$	3.495(2)	3.750(1)	4.118(1)
Ti–Cm^a	2.004(1)	2.008(1)	2.016(1)
$X_{bridging}$–Ti–$X_{bridging}$	93.9(1)	95.5(1)	97.8(3)
Ti–$X_{bridging}$–Ti	86.1(2)	84.5(1)	82.2(1)

^{a} Cm = Centroid of cyclopentadienyl carbon atoms

The titanium–titanium distance increases from 3.266(1) Å in the chloride complex **4** to 3.407(1) Å and 3.592(2) Å in the bromide and iodide analogues **5** and **6**, respectively. This is primarily due to the increase of the Ti–$X_{bridging}$ bond lengths from 2.392(4) Å in **4** to 2.534(3) Å in **5** and 2.732(5) Å in **6**. However, within the central $Ti_2(\mu\text{-}X)_2$ cores, the Ti–X–Ti angle decreases and the X–Ti–X angle increases from complex **4** to complexes **5** and **6**, which could be attributed in part to the larger van der Waals radius of the halogen atoms causing halogen–halogen repulsion. Similar trends in structural features have been found in the crystal structures of the bis(cyclopentadienyl)titanium(III) derivatives [{Ti(η^5-$C_5H_4Me)_2(\mu\text{-}X)$}$_2$] (X = Cl, Br) and rationalized by X···X repulsions.[5a] Additionally, these structural trends could be the result of the resistance of the titanium atoms to get away from each other, because of a direct Ti–Ti orbital interaction.

Computational studies for the chloride-bridged dimer **4** showed a singlet ground state and a relatively large singlet–triplet energy gap.[18] In accord with this strong antiferromagnetic interaction, diamagnetism is expected in the NMR spectra of complex **4** in a fashion similar to those suggested by NMR and EPR spectroscopies in solution for the

analogous dimeric complexes [{Ti(η^5-C$_5$Me$_4$Ph)Cl(μ-Cl)}$_2$] and [{Ti(η^5-C$_5$(CH$_2$Ph)$_5$)Cl(μ-Cl)}$_2$], which show slightly longer Ti–Ti distances (3.335(1) and 3.374(2) Å, respectively).[21] However, the ^{1}H NMR spectrum at room temperature of a solution of crystals of the chloride complex **4** in benzene-d$_6$ revealed one broad resonance at $\delta = 6.88$ ($\Delta\nu_{1/2} = 24$ Hz) and one sharp resonance signal at $\delta = 2.09$ in a 40:60 intensity ratio.[18] ^{1}H NMR spectra at different temperatures and concentrations, along with DFT calculations for several [{Ti(η^5-C$_5$Me$_5$)Cl$_2$}$_n$] aggregates, led us to suggest that the diamagnetic dimer **4** and a paramagnetic tetramer [{Ti(η^5-C$_5$Me$_5$)(μ-Cl)$_2$}$_4$] are in equilibrium in solution. Indeed, the magnetic moment of **4**, determined in a benzene-d$_6$ solution by the Evans Method[22] ($\mu_{eff} = 1.37$ μ_B per dimer), is consistent with the presence of an additional paramagnetic compound in solution.

In contrast, the ^{1}H NMR spectra of complexes **5** and **6** in benzene-d$_6$ at room temperature are very simple and only show a singlet resonance signal at $\delta = 2.21$ and 2.47, respectively. The ^{13}C{^{1}H} NMR spectra at room temperature show two sharp resonance signals for the η^5-C$_5$Me$_5$ ligands at $\delta = 139.8$ and 16.2 for **5** and at $\delta = 143.6$ and 19.5 for **6**. These resonances are only slightly shifted downfield with respect to those found in the parent titanium(IV) compounds [Ti(η^5-C$_5$Me$_5$)X$_3$] (X = Br (**2**), $\delta_H = 1.95$ and $\delta_C = 138.2$ and 15.4; X = I (**3**), $\delta_H = 2.09$ and $\delta_C = 138.9$ and 18.0) in benzene-d$_6$. However, the magnetic moment measurements for complexes **5** and **6** in benzene-d$_6$ at ambient temperature by the Evans Method gave $\mu_{eff} = 1.30$ and 1.50 μ_B per dimer, respectively. We suggest that other paramagnetic aggregates could be present in solutions of **5** and **6**, but the broadening of the signals of these species precludes their detection in the NMR spectra.

The magnetization towards temperature of polycrystalline compounds [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl (**4**), Br (**5**), I (**6**)) has been measured at 1 T between 2 and 300 K.

The plots of the magnetic susceptibility versus temperature for complexes **4** (Figure 2), **5** and **6** (Figures S7 and S8 of the Supporting Information, respectively) are similar. In all cases, a continuous increase in susceptibility as the temperature decreases is observed. However, the curves for derivatives **4** and **5** show a decrease at very low temperature (maximum in susceptibility at 6.4 K and 5.0 K, respectively), whereas in that for complex **6** the inversion point is absent (Figure S8).

The representation of magnetic moment versus temperature for complexes **4** and **5** remains almost constant from room temperature until about 75 K and then a sudden decreasing is observed giving a final magnetic moment close to zero. The representation for compound **6** is slightly different, showing a continuous decrease from 300 K to very low temperature (Figure S8). The magnetic moments at 300 K are 1.13, 0.98 and 1.10 μ_B for **4**, **5** and **6**, respectively. These magnetic moments are significantly lower than the expected (2.45 μ_B) for a dimer with two magnetically isolated Ti(III) ions (S = 1/2), whereas at 2 K the compounds are almost diamagnetic.
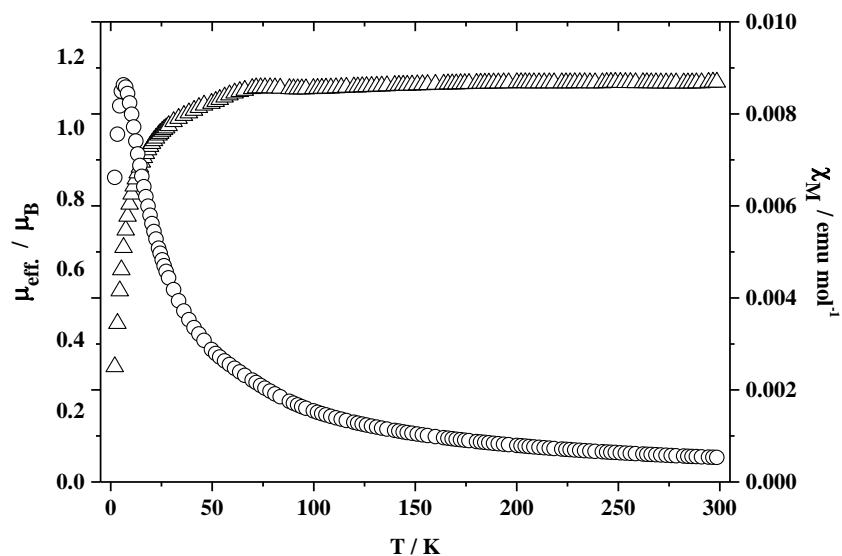

Figure 2. Temperature dependence of the molar magnetic susceptibility χ_M (o) and μ_{eff} (Δ) in crushed crystals of **4**.

The low magnetic moment from 300 to 2 K and the decrease with temperature in **4–6** compounds could be due to a strong intramolecular antiferromagnetic interaction in accordance with the short Ti–Ti distance that favors the direct magnetic interaction between the titanium ions. However, the magnetic interaction through the bridging halide must be also important. Thus, the better magnetic communication through the iodide bridging ligand respect to the chloride and bromide ligands could explain the different profile observed in the magnetic moment curve.

The magnetic properties of the analogous bis(cyclopentadienyl)titanium(III) dimers [{Ti(η^5-C$_5$H$_5$)$_2$(μ-X)}$_2$] (X = F, Cl, Br, I) were initially measured to liquid nitrogen temperatures, and the existence of a strong antiferromagnetic coupling between the Ti(III) atoms was suggested.[23] Later, Stucky and co-workers measured the magnetic susceptibility to liquid helium temperature, and calculated the magnetic data of complexes [{Ti(η^5-C$_5$H$_4$R)$_2$(μ-X)}$_2$] (R = H, X = Cl, $J = -111$ cm^{-1}; R = Me, X = Cl, $J = -160$ cm^{-1}; R = H, X = Br, $J = -138$ cm^{-1}).[5a] Other similar dinuclear titanium(III) complexes such as [PPh$_4$][Ti$_2$Cl$_4$(μ-Cl)$_3$(PEt$_3$)$_2$]·2CH$_2$Cl$_2$ ($J = -552$ cm^{-1}),[24] and [(η^5-1,3-(tBu)$_2$C$_5$H$_3$)$_2$Ti(μ-N$_2$)Ti(η^5-1,3-(tBu)$_2$C$_5$H$_3$)$_2$][25] ($J = -105$ cm^{-1}) also show strong antiferromagnetic interactions. The magnetic data of all these complexes were fitted using the Hamiltonian $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = \frac{1}{2}$) and the following expression of the molar magnetic susceptibility derived by Bleaney and Bowers (equation 1), where N, β, k, and T have the usual meanings and J represents the singlet–triplet separation.[26]

$$\chi_M = \frac{2N\,g^2\,\beta^2}{kT[3+\exp(-J/kT)\ ]} \quad (1)$$

However, the fit of the magnetic data of complexes **4–6** with equation 1 has not been possible or leads to unacceptable magnetic parameters. The inclusion of a term corresponding to the temperature independent paramagnetism (TIP) and another one due to the presence of a paramagnetic impurity did not improve the fit. Thus, X-ray powder diffraction studies for the halide complexes **4–6** were carried out to check the purity of the samples. The experimental diffractograms of the crystalline materials **4–6** used in the magnetic measurements are very similar to those calculated in the single crystal studies (see Figures S9–S11). As a consequence, the samples used in the magnetic measurements seem to be pure compounds although the presence of an amorphous paramagnetic compound or the existence of two magnetic different phases in these complexes cannot be ruled out. In fact, the curved baseline of the experimental diffratograms of **5** and **6** strongly suggests the presence of amorphous substances.

The impossibility of fitting the magnetic data of **4–6**, which should have a simple magnetic behavior similar to those found in the dimers aforementioned, could be consistent with the sample containing other paramagnetic species different from the dimer complexes. Thus, this magnetic study could be compatible with the diamagnetic nature of dimeric complexes **4–6** and the presence of some additional paramagnetic species as the tetramer proposed above in the NMR studies of **4**. However, all attempts to fit the magnetic data using a mixture of the diamagnetic complexes **4–6** and the paramagnetic compounds were unsuccessful.

Reactivity of [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (4)

The replacement of chloride ligands of complex **4** by reaction with 1:4 molar ratios of conventional lithium reagents LiR (R = Me, CH$_2$SiMe$_3$, NMe$_2$) in toluene at room temperature led to solutions containing the known titanium(IV) derivatives [Ti(η^5-C$_5$Me$_5$)R$_3$] as the only diamagnetic compounds determined by ^{1}H NMR spectroscopy.[27,28] Apparently, disproportionation occurred into the titanium(IV) complexes and an unknown titanium(II) species. Analogous results on the preparation of monocyclopentadienyltitanium(III) alkyl species has been noted by Green and Lucas,[29] while Teuben and co-workers were able to isolate the bis(allyl) [Ti(η^5-C$_5$R$_5$)(C$_3$H$_5$)$_2$] (R = H, Me) and benzyl [Ti(η^5-C$_5$H$_5$)(CH$_2$Ph)$_2$] derivatives.[14] In contrast, treatment of **4** with [Li{N(SiMe$_3$)$_2$}] ($\geq$2 equiv) in toluene at room temperature led to the precipitation of the amido titanium(III) complex [{Ti(η^5-C$_5$Me$_5$)(μ-Cl){N(SiMe$_3$)$_2$}}$_2$] (**7**) (Scheme 2). Compound **7** was isolated in 95% yield as purple crystals, which are not soluble in unreactive solvents hampering the characterization of complex **7** by NMR spectroscopy. Most likely, the lack of solubility of complex **7** in the reaction solvent along with the steric bulk of the bis(trimethylsilyl)amido ligands prevent further substitution of chloride groups and no disproportionation was observed.
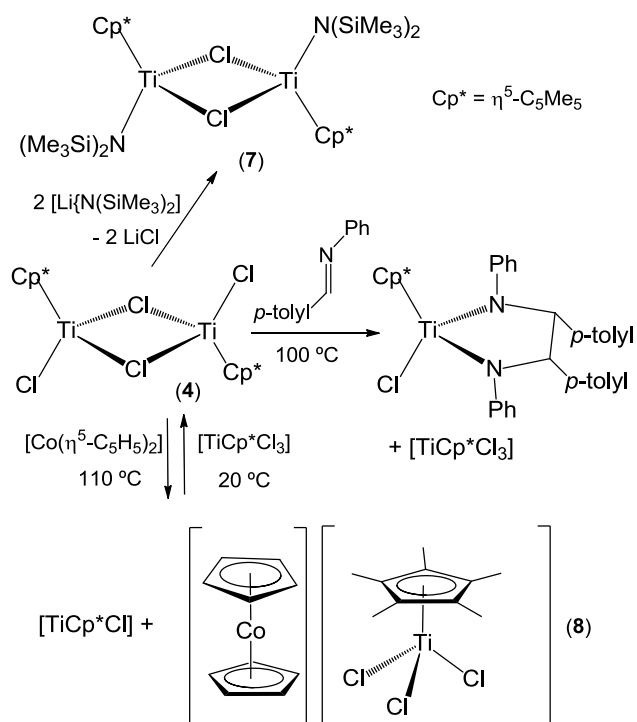
Scheme 2. Reactivity of complex **4**.

The X-ray crystal structure of **7** reveals two independent molecules in the asymmetric unit with no significant differences between them. The structure of one of them is shown in Figure 3. Molecules of **7** lie on an inversion center in the midpoint between the titanium atoms. Each molecule contains a central $Ti_2(\mu\text{-}Cl)_2$ core with the $\eta^5\text{-}C_5Me_5$ ligands in a transoid fashion similar to that of the parent complex **4**. However, the presence of the bulky bis(trimethylsilyl)amido ligands bonded to the titanium atoms produces a significant lengthening of the Ti–Ti and Ti–Cl$_{bridging}$ distances (averaged 3.853(4) and 2.482(13) Å, respectively) when compared with those found in **4** (averaged 3.266(1) and 2.392(4) Å) and the analogous hydroborate complex $[\{Ti(\eta^5\text{-}C_5Me_5)(BH_4)(\mu\text{-}Cl)\}_2]$ (3.452(1) and 2.440(2) Å).[30] Thus, complex **7** exhibits narrower Cl–Ti–Cl and wider Ti–Cl–Ti angles than those found in the aforementioned chloride-bridged dimers. The Ti–N bond length of averaged

1.983(4) Å is characteristic for bis(trimethylsilyl)amido ligands bonded to titanium(III) centers.[31]
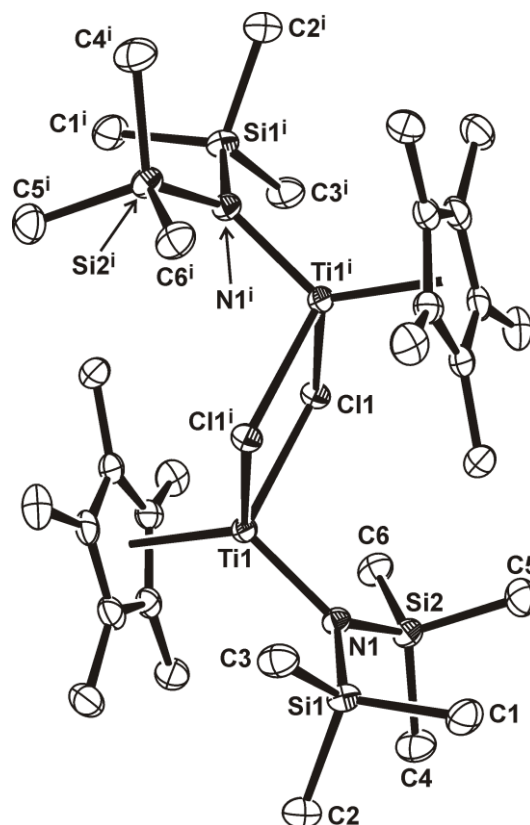
Figure 3. ORTEP diagram (thermal ellipsoids at the 50% probability level) of one of the two cristallographically independent molecules of complex **7**. Hydrogen atoms are omitted for clarity. Selected averaged lengths (Å) and angles (deg): Ti–Ti 3.853(4), Ti–Cl 2.482(13), Ti–N 1.983(4), Cl–Ti–Cl 78.2(1), Ti–Cl–Ti 101.8(1), N–Ti–Cl 108(2). Symmetry code: (i) $1 - x, -y, -z$.

Since disproportionation at room temperature was observed in solutions of the putative titanium(III) alkyl species, we decided to explore the possibility of an analogous process in the chloride complex **4**. We speculated that the asymmetric rupture of the dimer may lead to formation of titanium(IV) $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ and titanium(II) $[Ti(\eta^5\text{-}C_5Me_5)Cl]$ species. Thus, we performed several reactivity studies with solutions of **4** in

hydrocarbon solvents. The treatment of a toluene solution of **4** with 1 equiv of cobaltocene [Co(η^5-C$_5$H$_5$)$_2$] at 110 °C for 3 days gave green crystals of the ion pair [Co(η^5-C$_5$H$_5$)$_2$][Ti(η^5-C$_5$Me$_5$)Cl$_3$] (**8**) in 20% isolated yield (Scheme 2). The crystal structure consists of well-separated cobaltocenium [Co(η^5-C$_5$H$_5$)$_2$]$^+$ and titanate [Ti(η^5-C$_5$Me$_5$)Cl$_3$]$^-$ ions (Figure S4 and Table S7 in the Supporting Information). The bond lengths and angles in the titanate anion of **8** are essentially identical to those reported for the chromocenium analogue [Cr(η^5-C$_5$Me$_5$)$_2$][Ti(η^5-C$_5$Me$_5$)Cl$_3$].[32] Likewise, the cation of **8** is also similar to those found in several crystal structures containing this fragment,[33] including [Co(η^5-C$_5$H$_5$)$_2$][Ti(η^5-C$_5$H$_5$)Cl$_3$].[34] Compound **8** is only slightly soluble in chloroform-d$_1$ and its ^{1}H NMR spectrum shows two broad resonances at δ = 8.1 ($\Delta\nu_{1/2}$ = 313 Hz) and 6.5 ($\Delta\nu_{1/2}$ = 45 Hz) assignable to the η^5-C$_5$Me$_5$ and η^5-C$_5$H$_5$ ligands, respectively. Compound **8** was prepared independently in higher yield (76%) by the direct reaction of [Ti(η^5-C$_5$Me$_5$)Cl$_3$] (**1**) with [Co(η^5-C$_5$H$_5$)$_2$] (1 equiv) in toluene at room temperature. Cyclic voltammetry of [Ti(η^5-C$_5$Me$_5$)Cl$_3$] in thf at 22 °C revealed one chemically reversible redox event at −1.20 V vs. ferrocene/ferrocenium (Fc/Fc$^+$) (Figure S12 in the Supporting Information),[35] which was assigned to the [Ti(η^5-C$_5$Me$_5$)Cl$_3$]/[Ti(η^5-C$_5$Me$_5$)Cl$_3$]$^-$ couple. This value is in agreement with the electron transfer reaction between the mild reducing agent [Co(η^5-C$_5$H$_5$)$_2$] (E ≈ −1.3 V)[36] and [Ti(η^5-C$_5$Me$_5$)Cl$_3$].

While the reaction of authentic [Ti(η^5-C$_5$Me$_5$)Cl$_3$] with cobaltocene in benzene-d$_6$ is immediate at room temperature to give the precipitation of **8**, the analogous treatment of a solution of **4** in benzene-d$_6$ with [Co(η^5-C$_5$H$_5$)$_2$] is slow and requires an excess of reducing agent and high temperatures (120 °C for 2 days) for the complete consumption of the resonance signals assignable to the equilibrium of **4** in the ^{1}H NMR spectrum. After filtration to remove the green solid of **8** of the NMR tube, the spectrum of the resultant

solution showed only a broad resonance assignable to cobaltocene ($\delta = -51.39$, $\Delta\nu_{1/2} = 99$ Hz) by comparison with the spectra of authentic $[Co(\eta^5\text{-}C_5H_5)_2]$ material in benzene-d$_6$, and the data reported in the literature in other solvents.[37] Excess of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ was added to this solution at room temperature until the cobaltocene signal disappeared of the spectra. The solution was filtered to eliminate **8**, and the ^{1}H NMR spectrum showed the signals characteristic of **4** in solution, $\delta = 6.88$ (broad) and $\delta = 2.09$, along with the resonance at $\delta = 1.87$ due to the $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ excess.

Since we could not observe any resonance signal attributable to the titanium(II) species $[Ti(\eta^5\text{-}C_5Me_5)Cl]$, we decided to study its conversion to a known diamagnetic product as a diagnostic evidence. Beckhaus and co-workers have reported on the formation of a broad range of titanaaziridines and larger titanacycles by C–C coupling reaction of imines in low-valent titanium cyclopentadienyl species generated *in situ*.[38] In particular, the authors described the formation of the diamagnetic diazatitanacyclopentane $[Ti(\eta^5\text{-}C_5Me_5)Cl\{N(Ph)CH(p\text{-}tolyl)\}_2]$ by reduction of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ with magnesium in the presence of *N*-(4-methylbenzylidene)aniline. Indeed, addition of this imine to a benzene-d$_6$ solution of **4** led to the formation of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ and $[Ti(\eta^5\text{-}C_5Me_5)Cl\{N(Ph)CH(p\text{-}tolyl)\}_2]$ complexes in a 1:1 ratio according to ^{1}H NMR spectroscopy (Scheme 2). The reaction is slow at room temperature (ca. 25% conversion after 6 days) and the complete consumption of the resonances due to **4** in solution was only observed after heating the NMR tube at 100 ºC for 12 days. The characteristic NMR spectroscopic data in benzene-d$_6$ for the N-CH unit of the diazatitanacyclopentane ring ($\delta_H = 5.88$ and $\delta_C = 73.8$) were found in the ^{1}H and ^{13}C\{^{1}H\} NMR spectra as reported in the literature.[38]

On the basis of experimental evidences obtained from the reactions of $[Co(\eta^5\text{-}C_5H_5)_2]$ and *N*-(4-methylbenzylidene)aniline with solutions of **4** in aromatic hydrocarbon solvents,

we suggest that disproportionation of the titanium(III) complex **4** in solution occurs at high temperatures to formally give monomeric titanium(IV) [Ti(η^5-C$_5$Me$_5$)Cl$_3$] and titanium(II) [Ti(η^5-C$_5$Me$_5$)Cl] species.

Since we have already reported that the dimeric complex **4** readily dissolves in tetrahydrofuran to give the mononuclear adduct [Ti(η^5-C$_5$Me$_5$)Cl$_2$(thf)],[18] we decided to study the reactivity of **4** with other donor molecules (Scheme 3). Treatment of complex **4** with 2 equiv of 2,6-dimethylphenylisocyanide or *tert*-butylisocyanide in toluene at room temperature affords the titanium(III) dinuclear adducts [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(CNR)}$_2$] (R = 2,6-Me$_2$C$_6$H$_3$ (**9**), *t*Bu (**10**)) (Scheme 3). Compounds **9**·C$_7$H$_8$ and **10** were isolated as air-sensitive green solids in 76 and 60% yields, respectively. While complex **9**·C$_7$H$_8$ dissolves poorly in hydrocarbon solvents, the *tert*-butylisocyanide adduct **10** shows a good solubility in hexane and toluene.
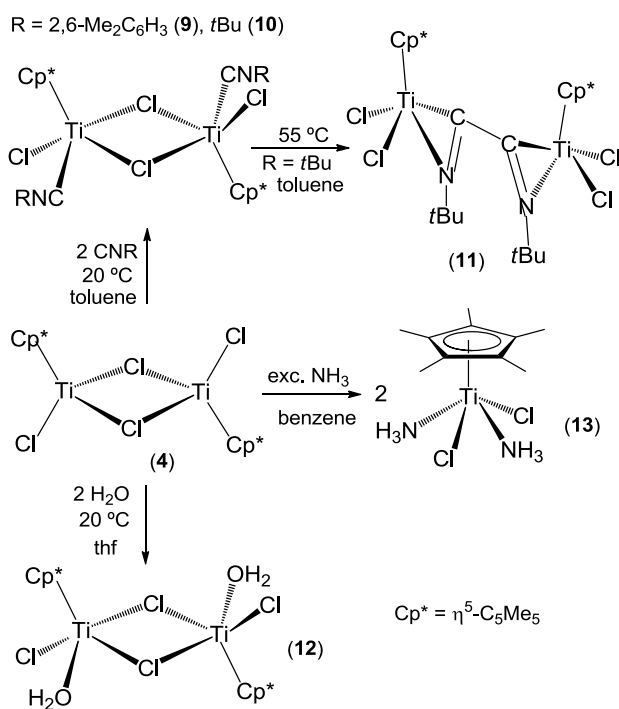
Scheme 3. Reactions of **4** with Lewis bases.

Complexes **9** and **10** were characterized by spectroscopic and analytical methods, and crystals of **9**·C_7H_8 suitable for an X-ray crystallographic determination were obtained by cooling a toluene solution at –35 °C. The molecular structure reveals that **9** forms a dimer with two $\{Ti(\eta^5\text{-}C_5Me_5)Cl(CNC_6H_3Me_2)\}$ units connected by two bridging chloride ligands (Figure 4). Molecules of **9** lie on an inversion center in the midpoint between the titanium atoms. A distorted four-legged piano-stool arrangement is defined around each titanium, with one terminal chloride, the *sp*-carbon atom of one isocyanide group, and two bridging chloride ligands at the legs. The titanium–chlorine bond distances of the terminal ligands (Ti(1)–Cl(1) 2.377(1) Å) are shorter than those related with the bridging ligands (Ti(1)–Cl(2) 2.466(1) Å and Ti(1)–Cl(2)^i 2.520(1) Å, symmetry code: (i) 2 – x, 1 – y, –z). The planar central $Ti_2(\mu\text{-}Cl)_2$ core shows Cl(2)–Ti(1)–Cl(2)^i and Ti(1)–Cl(2)–Ti(1)^i angles of 78.6(1) and 101.4(1)°, respectively. When compared with **4**, coordination of the isocyanide ligands to the titanium(III) atoms produces a significant lengthening of the titanium–chlorine and the titanium–titanium distances similar to those cited above for the amido complex **7**. Thus, the Ti–Ti length of 3.857(1) Å is almost identical to that of **7** (averaged 3.853(4) Å) and is 0.59 Å longer than that found in **4**. The Ti(1)–C(1) of 2.204(3) Å is similar to those found in the titanium(III) complex $[Ti(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2)_2I_2]$ (averaged 2.183(3) Å).[39] The isocyanide ligand is linear with a Ti(1)–C(1)–N(1) angle of 178.7(3)° and possesses a normal C≡N bond length (1.156(4) Å),[40] very similar to that found in the free 2,6-dimethylphenylisocyanide (1.163(3) Å).[41]

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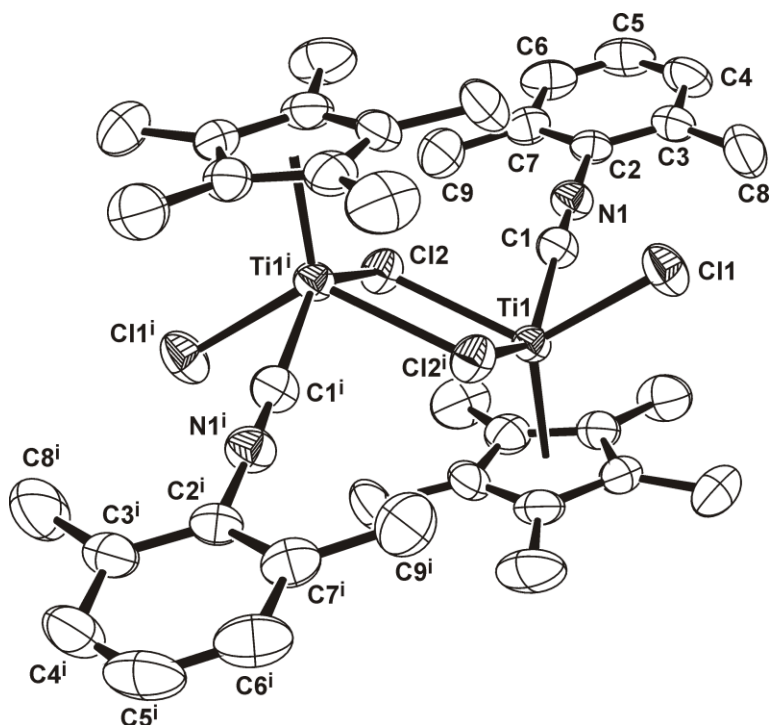
Figure 4. ORTEP diagram (thermal ellipsoids at the 50% probability level) of **9**·C_7H_8. The toluene solvent molecule and hydrogen atoms are omitted for clarity. Selected lengths (Å) and angles (deg): Ti(1)–Ti(1)^i 3.857(1), Ti(1)–C(1) 2.204(3), Ti(1)–Cl(1) 2.377(1), Ti(1)–Cl(2) 2.466(1), Ti(1)–Cl(2)^i 2.520(1), C(1)–N(1) 1.156(4), Cl(2)–Ti(1)–Cl(2)^i 78.6(1), Ti(1)–Cl(2)–Ti(1)^i 101.4(1), Ti(1)–C(1)–N(1) 178.7(3). Symmetry code: (i) 2 − x, 1 − y, −z.

The magnetic susceptibility of complex **9**·C_7H_8 measured at 1 T shows a continuous increase as temperature is reduced, which is typical of paramagnetic compounds (Figure 5).
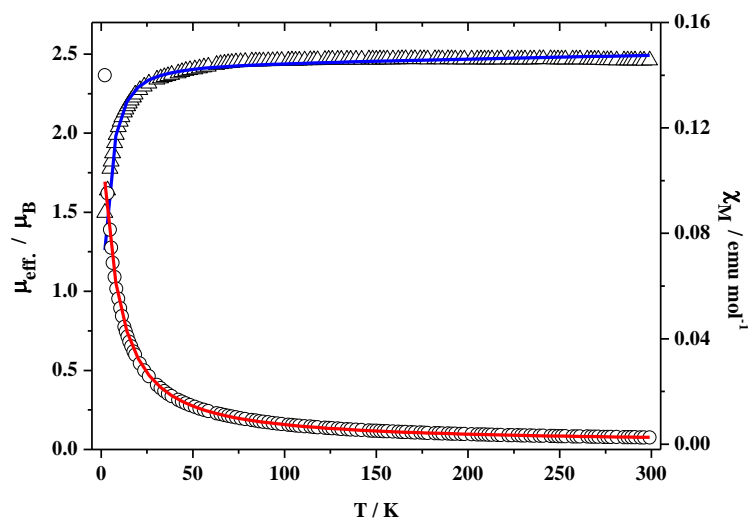
Figure 5. Temperature dependence of the molar magnetic susceptibility χ_M (o) and μ_{eff} (Δ) for **9**·C_7H_8. Solid lines result from least-squares fits using the model described in the text.

The magnetic moment of **9**·C_7H_8 at 300 K is 2.46 μ_B, as expected (2.45 μ_B) for a dimer with two magnetically isolated Ti(III) ions. The representation of magnetic moment versus temperature remains almost constant from 300 to 50 K, whereas a sharp decrease appears at very low temperatures to give a final value at 2 K of 1.50 μ_B. This sharp decrease could be ascribed to an antiferromagnetic coupling between the titanium centers of each dimer molecule. However, the shape of this curve at very low temperature also suggests the existence of additional interdimer antiferromagnetic interactions. Thus, the magnetic data of complex **9**·C_7H_8 have been fitted using the Bleaney-Bowers equation (equation 1) including a term with the temperature independent paramagnetism (TIP). The additional intermolecular interaction (zJ') has been introduced as a perturbation of the molecular field approximation (equation 2).[26]

$$\chi_M = \frac{\chi_{Ti}}{1 - \left[\ 2\,zJ'/N\,g^2\,\beta^2\ \right]\chi_{Ti}} \qquad \text{(equation 2)}$$

where

$$\chi_{Ti} = \frac{2N\,g^2\,\beta^2}{kT\left[3 + \exp(-J/kT)\ \right]} + TIP$$

Using this model, a good agreement between the experimental and calculated values for the magnetic moment and the molar magnetic susceptibility is observed (Figure 5). The refined parameters are: g = 1.92, J = –7.5 cm⁻¹, zJ' = –4.1 cm⁻¹ and TIP = 1.4 × 10⁻⁴ emu mol⁻¹. The agreement factor calculated as $\sigma^2 = \Sigma(\mu_{\text{eff. calc.}} - \mu_{\text{eff. exp.}})^2\ /\ \Sigma\mu_{\text{eff. exp.}}^2$ is σ^2 = 8.5 × 10⁻⁴. The intradimer J value indicates a weak antiferromagnetic coupling between the Ti ions compared with compound **4** and with other similar [{Ti(η^5-C$_5$H$_4$R)$_2$(μ-Cl)}$_2$] compounds.[5a] As above described, the incorporation of one isocyanide ligand to the environment of each titanium atom produces a significant lengthening of the titanium–titanium distance, which is consistent with a strong decrease, or even disappearance, of the direct magnetic interchange and bond between the titanium atoms. Thus, the magnetic interaction could take place by a super-exchange mechanism through the bridging chloride ligands.[42,43] The g and TIP values are typical of titanium(III) complexes.[5] The intermolecular magnetic coupling zJ' = –4.1 cm⁻¹ is also similar to those found in other molecular complexes. In summary, the magnetic properties of compound **9** are consistent with the existence of inter- and intramolecular antiferromagnetic coupling.

IR spectra (KBr) of complexes **9** and **10** show ν(C≡N) stretching vibrations at 2158 and 2185 cm⁻¹, respectively. Those values are higher than those found for the free 2,6-dimethylphenylisocyanide (2122 cm⁻¹) or *tert*-butylisocyanide (2138 cm⁻¹), indicating principally σ-type Ti-CNR interactions.[39,44] ¹H NMR spectra of complexes **9** and **10** are

silent according to their paramagnetic nature and only a broad resonance at $\delta = 2.48$ ($\Delta\nu_{1/2}$ = 190 Hz) could be tentatively assigned to the *tert*-butyl group in the spectrum of **10**. The magnetic moment measurements in pyridine-d_5 or benzene-d_6 at room temperature by the Evans Method gave $\mu_{eff} = 2.33$ μ_B for **9** and $\mu_{eff} = 2.38$ μ_B for **10** per dimer. The effective magnetic moment for **9** in solution at 295 K is in good agreement with the solid-state data obtained by SQUID magnetometry ($\mu_{eff} = 2.46$ μ_B, 300 K).

Complex **9** appears to be stable in benzene-d_6 solutions at temperatures below 120 ºC according to ^{1}H NMR spectroscopy, while resonances assigned to [Ti(η^5-C$_5$Me$_5$)Cl$_3$] were found in the spectra of the sample heated at higher temperatures. In contrast, a benzene-d_6 solution of **10** turned from green to orange color after 3 days at room temperature. The ^{1}H NMR spectrum of the resultant solution showed a new set of sharp resonances assignable to the titanium(IV) iminoacyl derivative [{Ti(η^5-C$_5$Me$_5$)Cl$_2$}$_2$(μ-η^2:η^2-*t*BuN=C-C=N*t*Bu)] (**11**) (Scheme 3). The formation of compound **11** is the result of the reductive C–C coupling of the two isocyanide ligands and the generation of the bridging *N,N´*-di-*tert*-butyl-1,4-diaza-1,3-butadiene-2,3-diyl ligand between the two titanium centers. The conversion of compound **10** to **11** is faster in solutions heated at 55 ºC, but at temperatures higher than 60 ºC the NMR spectra showed resonance signals due to [Ti(η^5-C$_5$Me$_5$)Cl$_3$]. Thus, complex **11** was isolated as an orange solid in 65% yield upon heating at 55 ºC a toluene solution of **10** for 4 days. In contrast to compounds **9** and **10**, complex **11** is stable in chloroform-d_1 solutions and shows decreased air-sensitivity as expected for a titanium(IV) derivative.

Complex **11** was characterized by spectroscopic and analytical methods, and its structure was elucidated by a single-crystal X-ray diffraction experiment. The molecular structure shows two {Ti(η^5-C$_5$Me$_5$)Cl$_2$} moieties held together by one {μ-η^2:η^2-*t*BuN=C-C=N*t*Bu} ligand (Figure 6). Molecules of **11** present a C_2 axis which crosses the midpoint

of the C(1)–C(1)^i bond (symmetry code: (i) –x, y, 1/2 – z). The titanium atoms exhibit distorted four-legged piano-stool geometries with two terminal chloride and the carbon and nitrogen atoms of one iminoacyl group at the legs. The titanium–chlorine bond distances of 2.290(1) and 2.320(1) Å are comparable to those determined in the acyl derivatives [Ti(η^5-C$_5$Me$_5$)Cl$_2$(η^2-COMe)][45] and [Ti(η^5-C$_5$Me$_5$)Cl$_2$(η^2-COCHPPh$_3$)].[46] The 1,4-diazabutadiene-2,3-diyl ligand of complex **11** is coordinated in an η^2-fashion to each metal center through the carbon and nitrogen atoms. While several examples of 1,4-diazabutadiene-2,3-diyl ligands bridging two metal centers have been reported before,[47,48,49] the symmetric coordination mode of this moiety in complex **11** is unprecedented. The C(1)–Ti(1)–N(1) angle of 35.6(1)º along with the Ti(1)–C(1) and Ti(1)–N(1) bond lengths of 2.122(3) and 2.034(2) Å respectively, compare well with those observed in other organotitanium iminoacyl complexes.[50] Within the 1,4-diazabutadiene ligand, the C(1)–C(1)^i and C(1)–N(1) distances of 1.414(5) and 1.274(3) Å are indicative of single- and double-bond character, respectively.[47] Thus, the C–N distance in **11** is clearly longer than that determined for the C≡N fragment of the isocyanide ligand in complex **9** (1.156(4) Å). Finally, the sum of angles subtended at the C(1) and N(1) atoms, 359.8 and 359.3º respectively, are consistent with an *sp*^{2} hybridization of both atoms.
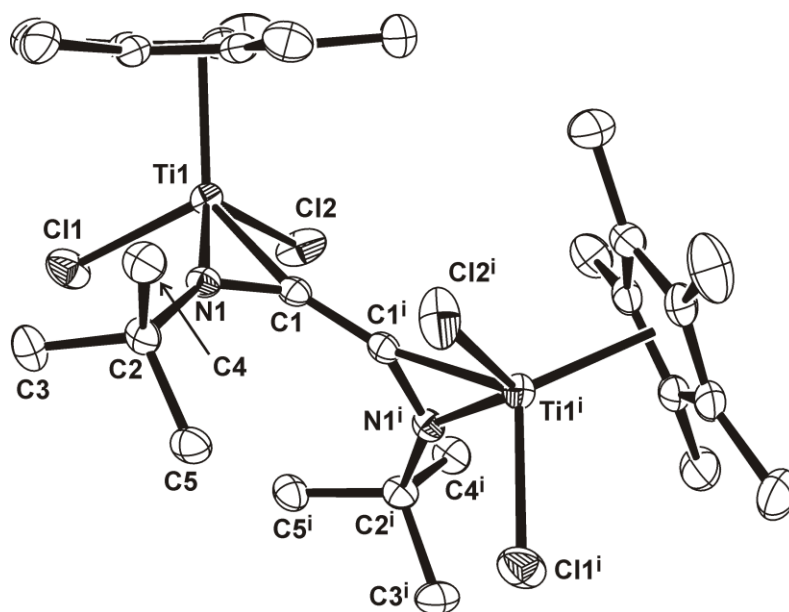
Figure 6. ORTEP diagram (thermal ellipsoids at the 50% probability level) of **11**. Hydrogen atoms are omitted for clarity. Selected lengths (Å) and angles (deg): Ti(1)–Cl(1) 2.290(1), Ti(1)–Cl(2) 2.320(1), Ti(1)–C(1) 2.122(3), Ti(1)–N(1) 2.034(2), C(1)–N(1) 1.274(3), C(1)–C(1)^i 1.414(5), C(1)–Ti(1)–N(1) 35.6(1). Symmetry code: (i) –x, y, 1/2 – z.

The IR (KBr) spectrum of **11** shows the ν(C=N) stretching vibration at 1611 cm^{-1}, a value characteristic of the dihapto coordination mode of the iminoacyl ligands to the metallic atoms.[45,50] The ^{1}H NMR spectra of **11** in benzene-d$_6$ or chloroform-d$_1$ at room temperature show two singlet resonances for the η^5-C$_5$Me$_5$ and CMe$_3$ groups in accordance with the C_2 symmetry determined in the solid-state. The ^{13}C{^{1}H} NMR spectrum in chloroform-d$_1$ displays one resonance at $\delta = 214.0$, which can be attributed to the C=N carbon of the 1,4-diazabutadiene ligand. This value is slightly shifted to higher field compared to those observed for other η^2-iminoacyl ligands bound to titanium(IV) centers ($\delta = 230.5$–245.0).[45,50]

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A molecular structure similar to that of **9** was also determined for the aqua titanium(III) complex [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(OH$_2$)}$_2$]·2C$_4$H$_8$O (**12**·2C$_4$H$_8$O) (see Figure S5 and Table S10 in the Supporting Information). The Ti–Ti separation of 3.851(1) Å and the Ti$_2$(μ-Cl)$_2$ core are essentially identical to those of **9**. The Ti–O bond length (2.083(2) Å) is analogous to that found in complex [{Ti(η^5-C$_5$Me$_5$)Cl$_2$(thf)],[16,18] and those determined in the dinuclear titanium(III) complex [Ti$_2$Cl$_4$(μ-Cl)$_2$(thf)$_4$] (2.082(4) and 2.099(6) Å).[51] A few green crystals of this aqua complex were isolated in the treatment of [Ti(η^5-C$_5$Me$_5$)Cl$_3$] with zinc powder in tetrahydrofuran at room temperature and subsequent slow evaporation of the solvent. The OH$_2$ ligands in complex **12** most likely come from adventitious water occluded in the zinc powder. Treatment of solutions of **4** with water in different molar ratios afforded complicated mixture of products and a rational synthesis of **12** could not be obtained. In contrast, when a benzene solution of **4** was exposed to NH$_3$ (1 atm) at room temperature, precipitation of the mononuclear ammonia adduct [{Ti(η^5-C$_5$Me$_5$)Cl$_2$(NH$_3$)$_2$]·0.5C$_6$H$_6$ (**13**·0.5C$_6$H$_6$) occurred (Scheme 3). Compound **13**·0.5C$_6$H$_6$ was isolated in 78% yield as a blue green powder, which is not soluble in common organic solvents. The IR spectrum (KBr) of **13** shows several bands for the ν_{NH} vibrations, between 3358 and 3168 cm^{-1}, and a very strong absorption at 1604 cm^{-1} assignable to the NH$_3$ bending mode.[52] Crystals of **13**·0.5C$_6$D$_6$ were obtained by slow cooling at room temperature of a benzene-d$_6$ solution heated at 100 ºC. Compound **13** shows a monomeric structure with a four-legged piano-stool disposition with a mirror plane passing through the Ti and N atoms and the carbon atoms C(11) and C(16) of the η^5-C$_5$Me$_5$ ligand (Figure S6). The titanium–chlorine bond length of 2.444(1) Å is slightly longer than that found for the monomeric titanium(III) derivative [Ti(η^5-C$_5$H$_5$)Cl$_2$(methylimidazol)$_2$] (2.407(2) Å),[53] whereas the titanium–nitrogen distances of 2.215(4) and 2.222(4) Å are

similar to those found in the ammine titanium(III) complexes $[Ti(\eta^5\text{-}C_5Me_4SiMe_3)_2(NH_3)]^+$ (2.208(3) Å),[54] and $[Ti(\eta^5\text{-}C_5H_5)_2(NH_3)_2]^+$ (2.197(2) and 2.221(2) Å).[55] Ammine and chloride ligands of **13** participate in the building of a robust layered pattern with N–H···Cl hydrogen bonds, whilst the layers are connected by the benzene molecules through C–H···Cl interactions (Figure 7 and Table S12). The strong intermolecular interactions may explain the insolubility of **13** even in donor solvents (i.e., pyridine-d_5, tetrahydrofuran-d_8), precluding its characterization by NMR spectroscopy.
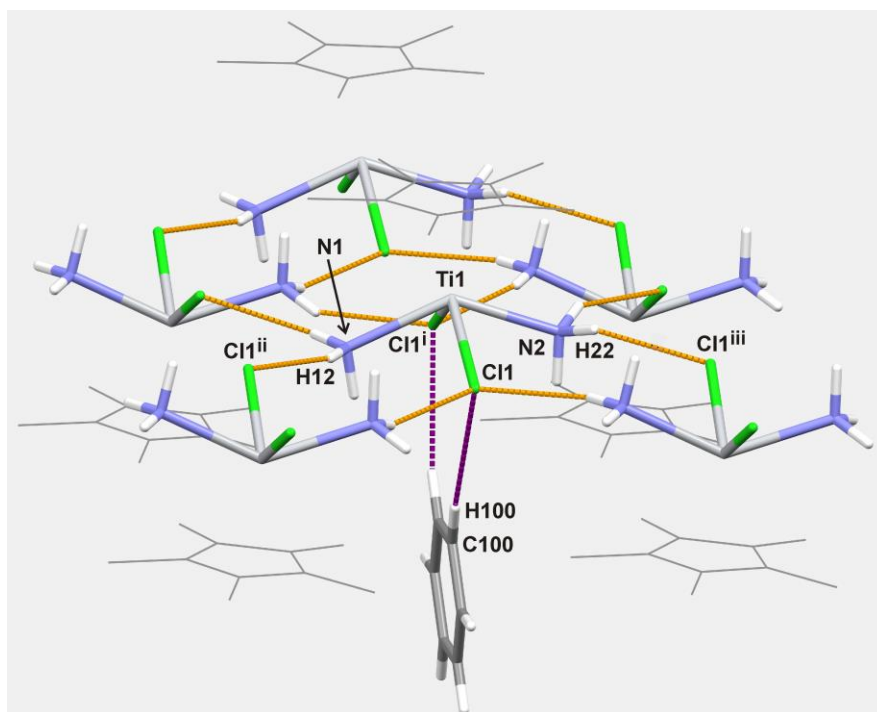

Figure 7. Perspective view of a layer in **13**·0.5C_6D_6 constituted by N–H···Cl hydrogen bonds (drawn in orange). C–H···Cl interactions connecting layers are drawn in purple. Hydrogen atoms of methyl fragments are omitted for clarity. Symmetry code: (i) x, y, 1 – z; (ii) 1/2 – x, 1/2 + y, 1/2 – z; (iii) 1/2 – x, –1/2 + y, 1/2 – z.

Conclusions

Halide-bridged dimeric structures [{Ti(η^5-C$_5$Me$_5$)X(μ-X)}$_2$] (X = Cl, Br, I) have been structurally characterized for monopentamethylcyclopentadienyltitanium(III) dihalides. The chloride compound [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] reacts with lithium reagents [LiR] via metathesis of chloride ligands and subsequent disproportionation, and only by using the bulky group N(SiMe$_3$)$_2$ the titanium(III) species [{Ti(η^5-C$_5$Me$_5$)(μ-Cl){N(SiMe$_3$)$_2$}}$_2$] could be isolated. Similarly, the dimeric dichloride titanium(III) complex in aromatic hydrocarbon solutions at temperatures higher than 100 ºC undergoes disproportionation into titanium(IV) [Ti(η^5-C$_5$Me$_5$)Cl$_3$] and titanium(II) [Ti(η^5-C$_5$Me$_5$)Cl] species, as demonstrated by its reactions with cobaltocene and *N*-(4-methylbenzylidene)aniline. Complex [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] reacts with Lewis bases (ammonia, water or isocyanides) to give mononuclear species [Ti(η^5-C$_5$Me$_5$)Cl$_2$(NH$_3$)$_2$] or dinuclear adducts [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(L)}$_2$] (L = H$_2$O, CNR) with long Ti–Ti separations. The titanium centers in the arylisocyanide dimer [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(CNC$_6$H$_3$Me$_2$)}$_2$] are weakly antiferromagnetically coupled as determined by magnetic susceptibility measurements at different temperatures. The *tert*-butylisocyanide titanium(III) adduct undergoes a reductive C–C coupling of the two isocyanide ligands with generation of a bridging *N,N´*-di-*tert*-butyl-1,4-diaza-1,3-butadiene-2,3-diyl ligand between the two titanium(IV) centers. The simple and clean syntheses of monopentamethylcyclopentadienyltitanium(III) dihalides may allow the study of challenging organic transformations with unsaturated substrates.

Experimental Section

General Comments. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene, benzene, and hexane were distilled from Na/K alloy just before use. Tetrahydrofuran was distilled from purple solutions of sodium benzophenone just prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$, C_5D_5N) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Thermolyses in solution at high temperatures were carried out by heating flame-sealed NMR or Carius tubes in a Roth autoclave model III. $[Co(\eta^5\text{-}C_5H_5)_2]$ was purchased from ABCR and used as received. Electronic grade ammonia (purity > 99.995%, O_2 < 2 ppm, and H_2O < 10 ppm) was purchased from Sociedad Española del Oxígeno, and used as received. Lithium tetrahydridoaluminate(III) ($LiAlH_4$, 95%), lithium bis(trimethylsilyl)amide $[Li\{N(SiMe_3)_2\}]$, *N*-(4-methylbenzylidene)aniline, and *tert*-butylisocyanide were purchased from Aldrich and used as received. 2,6-Dimethylphenylisocyanide was purchased from FLUKA and sublimed under vacuum prior to use. $[Ti(\eta^5\text{-}C_5Me_5)X_3]$ (X = Cl, (**1**), Br (**2**), I (**3**)),[19] and $[\{Ti(\eta^5\text{-}C_5Me_5)Cl\}_2(\mu\text{-}Cl)\}_2]$[18] (**4**) were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using an FT-IR Perkin-Elmer SPECTRUM 2000 spectrophotometer. Microanalyses (C, H, N) were performed in a Heraeus CHN-O Rapid or a Leco CHNS-932 microanalyzer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300, Mercury-300, or Unity-500 Plus spectrometers. Chemical shifts (δ) in the ^1H and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to carbon of the solvent, C_6D_6 (^1H: δ = 7.15; ^{13}C: δ = 128.0) or $CDCl_3$ (^1H: δ = 7.24; ^{13}C: δ = 77.0). The effective magnetic

moments in solution were determined by the Evans NMR method at 295 K (using a 300 MHz instrument with a field strength of 7.05 Tesla).[22]

The variable-temperature magnetization data were acquired on polycrystalline samples obtained from crushed crystals with a Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) magnetometer over a temperature range of 2 to 300 K at the constant field of 1 T. Gelatin capsules were charged with the samples in an argon-filled glovebox and were handled under argon atmosphere until inserted in the magnetometer. Each raw data set was corrected for the diamagnetic contribution of both the sample holder and the complex to the susceptibility. The molar diamagnetic corrections were calculated on the basis of Pascal´s constants.[22c]

The cyclic voltammograms were taken with a potentiostat/galvanostat CH Instruments CHI620E. All experiments were carried out using a conventional three electrode cell. Platinum was used as working electrode, a platinum wire as counter electrode, and a silver wire as pseudo reference electrode. Potentials were internally referenced to the ferrocene/ferrocenium redox couple at 0 mV. Measurements were made under a purified argon atmosphere in a glovebox using tetrahydrofuran solutions of [nBu$_4$N][PF$_6$] (0.1 M).

Synthesis of [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (4). A 150 mL Schlenk tube was charged with [Ti(η^5-C$_5$Me$_5$)Cl$_3$] (0.60 g, 2.07 mmol), LiAlH$_4$ (0.08 g, 2.07 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 3 days. After filtration, the volatile components of the resultant brown solution were removed under reduced pressure to give **4** as a green solid (0.21 g, 40%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, δ): 6.88 (s br., $\Delta\nu_{1/2}$ = 24 Hz; C$_5$Me$_5$), 2.09 (s; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 °C, δ): 136.5 (*C*$_5$Me$_5$), 90.5 (br.; *C*$_5$Me$_5$), 48.0 (br.; C$_5$*Me*$_5$), 14.5 (C$_5$*Me*$_5$). The effective magnetic

moment of **4** was determined to be 1.37 μ_B (based on a unit formula of $C_{20}H_{30}Cl_4Ti_2$) on a C_6D_6 solution.[18]

Synthesis of [{Ti(η⁵-C₅Me₅)Br(μ-Br)}₂] (5). In a fashion similar to the preparation of **4**, [Ti(η⁵-C₅Me₅)Br₃] (0.60 g, 1.42 mmol) and LiAlH₄ (0.057 g, 1.42 mmol) were reacted in toluene (60 mL) for 20 h to give **5** as a dark-green solid (0.27 g, 56%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 2959 (m), 2908 (vs), 2861 (m), 1485 (w), 1429 (m), 1377 (s), 1260 (w), 1022 (s), 800 (w), 728 (w), 618 (w), 424 (s). ¹H NMR (C_6D_6, 20 °C, δ): 2.21 (s; C_5Me_5). ¹³C{¹H} NMR (C_6D_6, 20 °C, δ): 139.8 (*C*₅Me₅); 16.2 (C₅*Me*₅). Anal. Calcd for $C_{20}H_{30}Br_4Ti_2$ (M_w = 685.81): C 35.03, H 4.41. Found: C 35.41, H 4.30. The effective magnetic moment of **5** was determined to be 1.30 μ_B (based on a unit formula of $C_{20}H_{30}Br_4Ti_2$) on a C_6D_6 solution.

Synthesis of [{Ti(η⁵-C₅Me₅)I(μ-I)}₂] (6). In a fashion similar to the preparation of **4**, [Ti(η⁵-C₅Me₅)I₃] (0.60 g, 1.06 mmol) and LiAlH₄ (0.042 g, 1.06 mmol) were reacted in toluene (30 mL) for 2 days to afford **6** as a green solid (0.30 g, 66%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 2976 (m), 2952 (m), 2904 (s), 2854 (w), 1482 (m), 1451 (m), 1424 (m), 1378 (s), 1261 (w), 1066 (m), 1022 (vs), 802 (w), 730 (w), 546 (w), 418 (m). ¹H NMR (C_6D_6, 20 °C, δ): 2.47 (s; C_5Me_5). ¹³C{¹H} NMR (C_6D_6, 20 °C, δ): 143.6 (*C*₅Me₅); 19.5 (C₅*Me*₅). Anal. Calcd for $C_{20}H_{30}I_4Ti_2$ (M_w = 873.79): C 27.49, H 3.46. Found: C 27.64, H 4.01. The effective magnetic moment of **6** was determined to be 1.50 μ_B (based on a unit formula of $C_{20}H_{30}I_4Ti_2$) on a C_6D_6 solution.

Synthesis of [{Ti(η⁵-C₅Me₅)(μ-Cl){N(SiMe₃)₂}}₂] (7). A toluene solution (10 mL) of [Li{N(SiMe₃)₂}] (0.33 g, 1.97 mmol) was carefully added to a solution of **4** (0.50 g, 0.98 mmol) in toluene (20 mL). The mixture was allowed to react without any stirring at room temperature for 3 days to give the precipitation of huge purple crystals of **7** and a fine white powder. After elimination of the solution by decantation, the crystals were rinsed with

several portions of toluene to remove the powder and characterized as **7** (0.66 g, 95%). IR

(KBr, cm^{-1}): $\tilde{\nu}$ 2955 (m), 2910 (m), 1437 (w), 1403 (w), 1378 (m), 1259 (s), 1248 (vs),

1024 (w), 891 (vs), 853 (vs), 837 (vs), 792 (s), 760 (m), 709 (m), 670 (m), 636 (w), 421

(m). Anal. Calcd for $C_{32}H_{66}Cl_2N_2Si_4Ti_2$ (M_w = 757.87): C 50.71, H 8.78, N 3.70. Found: C

50.71, H 9.00, N 3.69.

Synthesis of [Co(η^5-C₅H₅)₂][Ti(η^5-C₅Me₅)Cl₃] (8). *Method A:* A 100 mL ampule (Teflon

stopcock) was charged with **4** (0.30 g, 0.59 mmol), [Co(η^5-C₅H₅)₂] (0.11 g, 0.58 mmol),

and toluene (20 mL). The reaction mixture was heated at 110 °C for 3 days. The resultant

solution was allowed to cool to ambient temperature to afford green crystals of **8** (0.055 g,

20%). *Method B:* A 100 mL Schlenk tube was charged with **1** (0.20 g, 0.69 mmol), [Co(η^5-

C₅H₅)₂] (0.13 g, 0.69 mmol), and toluene (25 mL). The reaction mixture was stirred at room

temperature for 16 h to give a green solution and a green solid. The solid was isolated by

filtration onto a glass frit and vacuum-dried to afford **8** as a green powder (0.25 g, 76%). IR

(KBr, cm^{-1}): $\tilde{\nu}$ 3094 (vs), 2968 (m), 2946 (m), 2909 (s), 1493 (w), 1414 (vs), 1375 (m),

1114 (w), 1069 (w), 1009 (s), 880 (m), 864 (vs), 821 (w), 804 (w), 756 (w), 503 (m), 464

(vs), 422 (vs). ^{1}H NMR (CDCl₃, 20 °C, δ): 8.1 (s br., $\Delta\nu_{1/2}$ = 313 Hz, 15H; C₅Me₅), 6.5 (s

br., $\Delta\nu_{1/2}$ = 45 Hz, 10H; C₅H₅). Anal. Calcd for $C_{20}H_{25}Cl_3CoTi$ (M_w = 478.57): C 50.19, H

5.27. Found: C 50.32, H 5.28.

Synthesis of [{Ti(η^5-C₅Me₅)Cl(μ-Cl)(CN-2,6-Me₂C₆H₃)}₂] (9). A 100 mL Schlenk tube

was charged with **4** (0.30 g, 0.59 mmol), 2,6-dimethylphenylisocyanide (0.15 g, 1.14

mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 1.5

h. The volume of the resultant brown suspension was reduced under reduced pressure to ca.

10 mL to give a green solid and a brown solution. The solid was isolated by filtration onto a

glass frit and vacuum-dried to afford **9·**C₇H₈ as a green powder (0.37 g, 76%). The toluene

filtrate was cooled to –35 ºC for 7 days to give a few suitable single crystals for X-ray diffraction of complex **9**·C$_7$H$_8$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3025 (w), 2979 (m), 2952 (m), 2904 (s), 2158 (vs), 1603 (w), 1495 (m), 1474 (m), 1449 (m), 1381 (m), 1264 (w), 1175 (w), 1166 (w), 1083 (w), 1023 (m), 783 (s), 742 (s), 720 (w), 699 (w), 468 (w), 418 (m). Anal. Calcd for C$_{45}$H$_{56}$Cl$_4$N$_2$Ti$_2$ (M_w = 862.48): C 62.67, H 6.54, N 3.25. Found: C 62.50, H 6.64, N 3.72. The effective magnetic moment of **9**·C$_7$H$_8$ was determined to be 2.33 μ_B (based on a unit formula of C$_{45}$H$_{56}$Cl$_4$N$_2$Ti$_2$) on a C$_5$D$_5$N solution.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)Cl(μ-Cl)(CN*t*Bu)}$_2$] (10). The reaction mixture of **4** (0.15 g, 0.30 mmol) and *tert*-butylisocyanide (0.050 g, 0.60 mmol) in toluene (20 mL) was stirred for 45 min at room temperature to give a dark green solution. The volatile components of the solution were removed under reduced pressure to afford **10** as a green powder (0.12 g, 60%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2976 (s), 2909 (s), 2185 (vs), 1475 (s), 1456 (s), 1373 (s), 1202 (s), 1069 (w), 1029 (s), 858 (m), 761 (m), 715 (m), 517 (w), 415 (s). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, δ): 2.48 (s br., $\Delta\nu_{1/2}$ = 190 Hz; CMe$_3$). Anal. Calcd for C$_{30}$H$_{48}$Cl$_4$N$_2$Ti$_2$ (M_w = 674.26): C 53.44, H 7.18, N 4.16. Found: C 53.93, H 6.93, N 4.17. The effective magnetic moment of **10** was determined to be 2.38 μ_B (based on a unit formula of C$_{30}$H$_{48}$Cl$_4$N$_2$Ti$_2$) on a C$_6$D$_6$ solution.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)Cl$_2$}$_2$(μ-η^2:η^2-*t*BuN=C-C=N*t*Bu)] (11). A 100 mL ampule (Teflon stopcock) was charged with **4** (0.30 g, 0.59 mmol), *tert*-butylisocyanide (0.098 g, 1.18 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 1 h and the resultant dark green solution was heated at 55 ºC for 4 days to give an orange precipitate and a brown solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **11** as an orange powder (0.26 g, 65%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2988 (s), 2909 (s), 1611 (s), 1545 (m), 1450 (s), 1369(s), 1226 (m), 1178 (vs), 1097 (w), 1066 (w),

1018 (m), 927 (w), 867 (w), 829 (w), 802 (w), 681 (m), 586 (w), 525 (s). ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 2.06 (s, 30H; C$_5$Me$_5$), 1.48 (s, 18H; CMe$_3$). ^{1}H NMR (CDCl$_3$, 20 °C, δ): 2.19 (s, 30H; C$_5$Me$_5$), 1.53 (s, 18H; CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C, δ): 214.0 (CN), 131.2 (*C*$_5$Me$_5$), 69.1 (*C*Me$_3$), 30.5 (C*Me*$_3$), 14.3 (C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{48}$Cl$_4$N$_2$Ti$_2$ (M_w = 674.26): C 53.44, H 7.18, N 4.16. Found: C 53.75, H 6.78, N 4.47.

Synthesis of [Ti(η^5-C$_5$Me$_5$)Cl$_2$(NH$_3$)$_2$] (13). A 25 mL ampule (Teflon stopcock) was charged with **4** (0.10 g, 0.20 mmol) and benzene (15 mL) to give a brown solution. The argon atmosphere was changed by ammonia, and the reaction mixture was allowed to react without any stirring for 3 d to give **13**·0.5C$_6$H$_6$ as a blue-green powder (0.10 g, 78%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3358 (m), 3329 (s), 3255 (m), 3192 (w), 3168 (m), 2971 (w), 2950 (w), 2910 (m), 2857 (w), 1604 (vs), 1496 (w), 1433 (m), 1410 (m), 1378 (m), 1234 (vs), 1068 (w), 1027 (w), 792 (m), 731 (m), 606 (w), 465 (w). Anal. Calcd for C$_{13}$H$_{24}$Cl$_2$N$_2$Ti (M_w = 327.12): C 47.73, H 7.39, N 8.56. Found: C 46.32, H 7.16, N 8.79.

X-ray crystal structure determinations. Dark-red crystals of **3** and dark-green crystals of **5** and **6** were obtained by slow cooling at room temperature of toluene solutions heated at 100 °C. Purple crystals of **7** were grown from the reaction mixture in toluene at ambient temperature as described above. Green crystals of **8** were obtained by slow cooling at room temperature of a toluene solution heated at 100 °C as described in the Experimental Section. Green crystals of **9**·C$_7$H$_8$ were obtained from a toluene solution as described above. Orange crystals of **11** were obtained by slow cooling at room temperature of a chloroform-d$_1$ solution of the compound heated at 45 °C in a NMR tube. Green crystals of complex **12**·2C$_4$H$_8$O were obtained from a tetrahydrofuran solution as described above. Blue crystals of **13**·0.5C$_6$D$_6$ were grown by slow cooling at room temperature of a benzene-d$_6$ solution heated at 100 °C in a NMR tube. The crystals were removed from the Schlenk

or NMR tubes and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 150 or 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Tables S1 and S2 of the Supporting Information.

The structures were solved, using the WINGX package,[56] by direct methods (**7**, **11** and **13**) (SHELXS-2013),[57] or intrinsic phasing methods (the rest) (SHELXT),[58] and refined by least-squares against F^2 (SHELXL-2014/7).[57] Compound **6** was refined as a two-component inversion twin using TWIN and BASF instructions. The final value of the BASF parameter was 0.357. Crystals of complex **7** contained half of two independent molecules in the asymmetric unit, but there were no significant differences between them.

Crystals of **8** presented disorder for the carbon atoms C(21)-C(25) and C(31)-C(35) of the cyclopentadienyl rings linked to cobalt. These disorders were conventionally treated by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command of the SHELXL program. The final values were 73 and 27% for the atoms C(21)-C(25), and 66 and 34% for the atoms C(31)-C(35). Moreover, carbon atoms C(21)'-C(25)', C(31)-C(35) and C(31)'-C(35)' of the disordered cyclopentadienyl ligands were restrained with DELU instructions.

Compound **9** crystallized with a molecule of toluene, which was found in the difference Fourier map, but it was not possible to obtain a chemically sensible model for it, so the Squeeze[59] procedure was used to remove its contribution to the structural factors. On the other hand, complex **12** crystallized with two molecules of tetrahydrofuran, whereas **13** did it with a half molecule of benzene.

In all the crystallographic studies, all non-hydrogen atoms were anisotropically refined. Moreover all hydrogen atoms were included, positioned geometrically and refined by using a riding model, except those of the water molecules (H(1) and H(2)) in complex **12**, which were located in the difference Fourier map and refined isotropically. Additionally, SADI restraints were applied to the lengths O(1)-H(1) and O(1)-H(2) in refinement of compound **12**.

Associated Content:

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.2021/acs.inorg-chem.xxxxxx.

Experimental crystallographic data of complexes **3**, **5**–**9**, and **11**–**13**; perspective views of the crystal structure of complexes **3**, **5**, **7**, **8**, **12** and **13**; tables for selected lengths and angles of the crystal structures of **3**, **5**–**9**, and **11**–**13**; plots of the temperature dependence of the molar magnetic susceptibility χ_M and μ_{eff} for complexes **5** and **6**; powder X-ray diffractogram for compound **4**; cyclic voltammogram of **1**; selected ^1H and $^{13}C\{^1H\}$ NMR spectra for complexes **5**, **6**, and **11** (PDF).

Accession Codes:

CCDC 1965497–1965505 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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