New Preparative Methods for the Halides of Titanium(II) and Vanadium(II): Reduction of Titanium(IV) Halides with Sodium and Oxidation of Bis(mesitylene)vanadium(0)

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Titanium(II) Chloride, Vanadium(II) Chloride, Sodium Reduction

$TiCl_4(THF)_2$ reacts with two equivalents of sodium in THF to afford the soluble $TiCl_2(THF)_n$ (**1**), which has been characterized analytically and by spectroscopic and magnetic measurements. By redox reactions, $TiCl_2(THF)_n$ gives $TiCl_2(9,10\text{-}C_{10}H_8O_2)$ (**2**), or $TiCl_2(benzoate)_2$ (**3**), with 9,10-phenanthrenequinone or dibenzoylperoxide in toluene, respectively. By operating in 1,2-dimethoxyethane (DME), $Na(DME)_{1.5}[TiCl_4(DME)]$ (**4**), or $NaTiCl_3(DME)_2$ have been isolated from the reaction of $TiCl_4(DME)$ with one or two equivalents of sodium, respectively. From **4,** by cation exchange, PPN[$TiCl_4$(DME)] [PPN = bis(triphenylphosphine)iminium] (**5**), has been obtained and characterized analytically, spectroscopically and by X-ray diffraction methods. Crystal data: $C_{40}H_{40}Cl_4NO_2P_2Ti$, MW = 818.4, space group: $Pna2_1$ (N° 33), $a = 14.445(2)$, $b = 15.690(2)$, $c = 17.544(2)$ Å, V = 3976(2) Å^3, Z = 4, F(000) = 1692, $R = 0.041$, $Rw = 0.0420$. The titanium(III) atom in the anion has the expected *cis*-octahedral, slightly distorted, geometry. By reaction of $TiBr_4(DME)_{0.5}$ with sodium in DME, $TiBr_3(DME)_{1.5}$.1.5 DME (**7**), is the product. Bis(mesitylene)vanadium(0), $Vmes_2$, reacts with two equivalents of CPh_3Cl in DME, to give $VCl_2(DME)_n$.

Introduction

The anhydrous dihalides of 3d transition metals are known from titanium to zinc. They are polynuclear compounds with bridging halides; for example, $TiCl_2$ [1] and VCl_2 [1] have layered structures with hexacoordinate metals . The dichlorides of groups 4 to 6 are highly reducing, their preparation therefore involving the *syn*-proportionation of higher chlorides with the metal itself, the disproportionation in the solid state (*e.g.*, $TiCl_2$ from $TiCl_3$), or the reduction with dihydrogen at elevated temperatures [2]. Coordination of the dihalides of the 3d transition elements with ethers usually decreases the molecular complexity and leads to low-nuclearity molecular complexes of general formula $MX_2(ether)_n$: compounds of this type with coordinated tetrahydrofuran (THF) are known for zinc(II) [3], copper(II) [3], nickel(II) [3], cobalt(II) [3], iron(II) [3], manganese(II) [3, 4], chromium(II) [4]. X-ray crystallography of the tetranuclear iron(II) THF-adduct, $Fe_4Cl_8(THF)_6$, has shown [5] the compound to contain chloride-bridged pentacoordinate and hexacoordinate iron atoms.

Also in view of the apparently substitutional inertness of titanium(II) (a d^2 system) and of vanadium(II) (a d^3 system), the preparation of the ether-substituted dihalides of titanium(II) requires the preliminary addition of acetonitrile to the anhydrous dihalide, followed by displacement by the ether [6]. As an additional example, anhydrous VCl_2 was observed [7] to be completely unreactive towards pyridine after heating for several months in the neat amine.

Conventional syntheses of Lewis base adducts of $TiCl_2$ [8] and VCl_2 [9] by reduction in organic solvents of higher titanium halides or by chlorination of vanadium complexes in low oxidation states are still relatively unexplored. This paper re-

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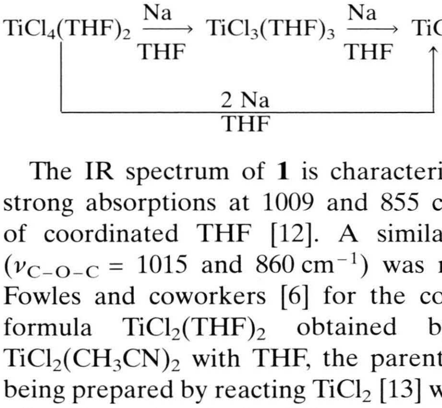
ports the preparation of ether adducts of titanium(II) and vanadium(II), $MCl_2(ether)_n$, obtained, respectively, by sodium reduction of $TiCl_4$ in THF as medium or by oxidation of bis(mesitylene) vanadium(0) with CPh_3Cl in DME. Also, the effect of the halide and of the reaction medium on these reactions has been studied. The crystal and molecular structure of an intermediate reduction product, PPN[$TiCl_4$(DME)] is also reported. Part of this work was communicated in a preliminary form [10]. Between our preliminary communication and the submission of this paper, the preparation of $TiCl_2(THF)_2$ [11], obtained by a different method, has appeared, the compound being used essentially for the reductive coupling of organic halides, ketones and aldehydes. Thus, our results should be regarded as complementary to those by Eisch and coworkers which recently appeared in print in this Journal.

Results and Discussion

By reaction of $TiCl_4(THF)_2$ with two equivalents of sodium in THF at room temperature the black-brown $TiCl_2(THF)_n$, (**1**), was obtained through the probable intermediacy of the light blue $TiCl_3(THF)_3$ as evidenced by the blue-green colour of the solution in the initial stages of the reaction (sequence 1).



$$\begin{tikzcd} \mathrm{TiCl_4(THF)_2} \arrow[r, "Na", "THF"'] \arrow[rr, bend right, "\substack{2\ Na\\ THF}"'] & \mathrm{TiCl_3(THF)_3} \arrow[r, "Na", "THF"'] & \mathrm{TiCl_2(THF)}_n \ \mathbf{1} \end{tikzcd} \qquad (1)$$

The IR spectrum of **1** is characterized by two strong absorptions at 1009 and 855 cm^{-1} typical of coordinated THF [12]. A similar spectrum (ν_{C-O-C} = 1015 and 860 cm^{-1}) was reported by Fowles and coworkers [6] for the compound of formula $TiCl_2(THF)_2$ obtained by reacting $TiCl_2(CH_3CN)_2$ with THF, the parent compound being prepared by reacting $TiCl_2$ [13] with acetonitrile. Even though the infrared spectra and the magnetic behaviour *(vide infra)* of our compound and that reported in the literature [6] are similar, compound **1** is soluble in THF with a deep brown colour and slightly soluble in aromatic hydrocarbons, while the product isolated by Fowles is described as substantially insoluble in THF and in non-polar solvents [6].

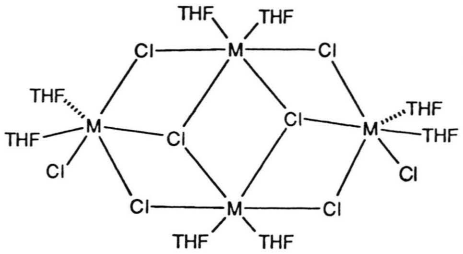


Fig. 1. A sketch of the suggested molecular structure of $M_4Cl_8(THF)_6$, based on the results of the diffractometric study [6] of the iron(II) compound. Dashed lines indicate the positions possibly occupied by additional THF groups in $M_4Cl_8(THF)_8$.

By taking into consideration the molecular structure of $TiCl_2$ (CdI_2-type, *i. e.,* while hexacoordinate titanium centres and triply bridging chlorides) [1], the possibility exists for $TiCl_2(THF)_n$ of a molecular arrangement similar to that reported for the iron(II) derivative, $Fe_2Cl_8(THF)_6$ [5], which contains hexacoordinate and pentacoordinate atoms bonded to terminal, doubly- and triply-bridging chlorides. Such a structure, see Fig. 1, could explain both the variable content of THF (addition of one THF to each of the pentacoordinate metal atoms would lead to a formula with a THF/Ti molar ratio of **2**) and the solubility of our titanium complex. Presumably, Fowles' compound corresponds to another structural polynuclear modification of the type suggested [4] for the THF adduct of manganese(II), $MnCl_2(THF)_2$.

The magnetic behaviour of **1** in the solid state has been examined in the temperature range 70–290 K, the $1/\chi_M^{corr}$ *vs.* T plot being in Fig. 2. The magnetic moment of 1.33 BM at 290 K, well below the value of 2.88 BM expected for magnetically diluted octahedral titanium(II) with d^2 configura-

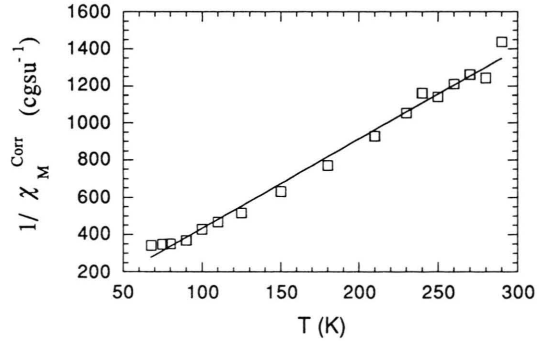


Fig. 2. Plot of $1/\chi_M^{corr}$ *vs.* T for $TiCl_2(THF)_n$ (**1**).

tion, confirms the oligonuclear structure of the compound. Halide-bridging is known in low-valent titanium halides [1] giving rise to low magnetic moments [14]. It has to be noted that $TiCl_2$ shows a χ_M^{corr} of 570×16^{-6} cgsu at 288 K [15] corresponding to a magnetic moment of 1.15 BM. The higher value of magnetic moment found for compound **1,** with respect to $TiCl_2$, is in agreement with a lower degree of spin pairing due to the cleavage of the polynuclear structure of $TiCl_2$ allegedly operated by THF.

As shown by the $1/\chi_M^{corr}$ *vs.* T plot (Fig. 2) for **1,** the Curie-Weiss law is obeyed with a Weiss constant $\theta = 9.8$ K, which is in the range of values obtained by Fowles and coworkers [6] for $TiCl_2$-(*o*-phenanthroline) ($\theta = 24$ K), $TiCl_2(CH_3CN)_2$ ($\theta = 44$ K) and $TiBr_2(CH_3CN)_2$ ($\theta =$ *ca.* 100 K).

As a consequence of the paramagnetism of the molecule, the ^1H NMR spectrum of **1** shows broad signals downfield with respect to uncomplexed THF. However, once the paramagnetic centre is oxidized by treatment with D_2O and air, sharp signals due to free THF at 3.57 and 1.42 ppm were observed.

Compound **1** shows a rather surprising low reactivity in substitution reactions: it does not react with nitrogen bases such as pyridine or N,N-tetramethylethylenediamine at room temperature; it reacts slowly with DME to give $TiCl_2(DME)_n$ (eq. (2)) and with the cyclopentadienyl anion in the presence of CO (eq. (3)). The latter reaction produces $TiCp_2(CO)_2$ in good yields, thus definitely showing the oxidation state II of titanium in the THF adduct.

$$TiCl_2(THF)_n \xrightarrow{DME} TiCl_2(DME)_n \qquad (2)$$

$$TiCl_2(THF)_n + 2\ NaCp + 2\ CO \xrightarrow{toluene} TiCp_2(CO)_2 + 2\ NaCl + n\,THF \qquad (3)$$

The THF adduct **1,** on the contrary, reacts smoothly with oxygen containing oxidizing reagents: with 9,10-phenanthrenequinone and dibenzoylperoxide it gives the compounds **2** and **3,** respectively, see eqs. (4) and (5).

$$TiCl_2(THF)_n + 9{,}10\text{-}C_{14}H_8O_2 \xrightarrow{toluene} \underset{\mathbf{2}}{TiCl_2(9{,}10\text{-}C_{14}H_8O_2)} + n\,THF \qquad (4)$$

$$TiCl_2(THF)_n + C_6H_5C(O)OOC(O)C_6H_5 \xrightarrow{toluene} \underset{\mathbf{3}}{TiCl_2(OOCC_6H_5)_2} + n\,THF \qquad (5)$$

The diamagnetic, blue-green quinone derivative **2,** which is not further oxidized by excess quinone, is a microcrystalline solid, soluble in aromatic hydrocarbons and stable in air for short periods of time. The IR spectrum is characterized by a strong absorption at 1454 cm^{-1} attributed [16] to the C–O stretching vibration of the semiquinone ligand, $[C_{14}H_8O_2]^-$. The compound, which is diamagnetic as observed in other semiquinone complexes [16], can be best described as a derivative of d^1 titanium(III) with strong coupling with the unpaired electron on the partially reduced quinone ligand.

The oxidation of **1** by dibenzoylperoxide proceeds in toluene at room temperature affording the diamagnetic, microcrystalline dibenzoato derivative of titanium(IV) (**3**), which shows strong absorptions at 1525 and 1397 cm^{-1} attributed to the asymmetric and symmetric stretching vibrations of the carboxylato ligand, respectively.

The titanium(II) chloro complex, $TiCl_2(THF)_n$, is not soluble in water and does not react with it: addition of diluted sulfuric acid causes slow H_2 evolution up to a H_2/Ti molar ratio of 0.42, titanium(II) being therefore oxidized to titanium(III).

When the reduction of titanium(IV) chloride with sodium was performed in DME, a different reaction pathway was observed: the reduction of $TiCl_4(DME)$ with one equivalent of sodium in DME affords the sodium salt $Na(DME)_n[TiCl_4(DME)]$ (**4**), which was further reduced by treatment with another equivalent of sodium to give a microcrystalline solid identified as $NaTiCl_3(DME)_2$ (**6**). The same titanium(II) derivative can be prepared directly from $TiCl_4(DME)$ by treatment with two equivalents of sodium; see reaction sequence 6.

In CH_2Cl_2 as medium, compound **4** reacts with [PPN]Cl to give the paramagnetic ($\mu_{eff} = 1.51$ BM at 295 K) $PPN[TiCl_4(DME)]$ (**5**), which was characterized analytically and spectroscopically ($\nu_{C-O-C} = 857$, 1030 and 1078 cm^{-1}). The same product was obtained by the reaction of the DME adduct of $TiCl_3$ with [PPN]Cl in dichloromethane.

In order to establish conclusively that **4** contained the still unknown $[TiCl_4(DME)]^-$ anion, a diffractometric study was planned on the easily recrystallized PPN derivative **5**. The diffractometric experiment on a single crystal of **5** has shown that the titanium atom is six-coordinate with four

$$\begin{tikzcd}
TiCl_4(DME) \arrow[r, "Na", "DME"'] \arrow[rr, bend right, "2\ Na"', "DME"'] & \underset{\mathbf{4}}{Na(DME)_n[TiCl_4(DME)]} \arrow[r, "Na", "DME"'] & \underset{\mathbf{6}}{NaTiCl_3(DME)_2}
\end{tikzcd} \qquad (6)$$

chlorine atoms and a bidentate DME molecule. The *cis* geometry of the $[TiCl_4(DME)]^-$ anion is shown in Fig. 3. Selected bond distances and angles are summarized in Table I. The $TiCl_4O_2$ moiety forms a distorted octahedron, the Cl1-Ti-Cl3, Cl_{ax}-Ti-O and Cl_{ax}-Ti-Cl_{eq} angles being 170.19(4)°, 86.2(1)° (mean value) and 93.28(4)° (mean value), respectively. In agreement with the larger covalent radii of chlorine with respect to oxygen, the O1-Ti-O2 angle [75.7(1)°] is smaller than Cl2-Ti-Cl4 [95.08(3)°] . The average Ti-Cl and Ti-O bond lengths are 2.374(1) and 2.172(2) Å and are similar to the values found [17] in NBu_4[*trans*-$TiCl_4(THF)_2$] [2.395(9) and 2.10(1) Å] and in $TiCl_3(THF)_3$ [2.352(3) and 2.118(7) Å] [18]. It is perhaps worth noting that the Ti-Cl(1) bond distance is significantly shorter than the other titanium-chloride bond distances: this might suggest that a Jahn-Teller distortion operates in this $TiCl_4O_2$ chromophore of idealized C_{2v} symmetry, similar to what has been predicted for d^1 complexes of O_h symmetry. The parameters of the coordinated 1,2-dimethoxyethane ligand are close to those observed in other DME complexes such as *cis*-$VI_2(DME)_2$ [9m] , $[Li(DME)_2]I$ [19] and *cis*-$MgCl_2(DME)_2$ [20].

Compound **6**, which dissolves in DME with a deep brown colour, is paramagnetic (μ_{eff} = 1.86 BM at 290 K) and promptly decomposes in the presence of moisture or dioxygen. The DME ligand shows absorptions at 855, 1033 and 1077 cm^{-1} to be compared with the absorptions at 853, 1119 and 1195 cm^{-1} observed in the free ligand. The magnetic properties of **6** were measured in the range 70–290 K. From a $1/\chi_M^{corr}$ *vs.* T plot, it has been found that **6** obeys the Curie-Weiss law with a Weiss constant $\theta = -16$ K.

Compound **6** is not stable in halogenated solvents such as dichloromethane. In attempts to exchange the sodium cation with PPN^+ in dichloromethane, well formed crystals of **5** were obtained in good yields. Although not investigated in detail, the reaction probably proceeds with reduction of dichloromethane.

We have also examined the interaction of the DME adduct of $TiBr_4$, $TiBr_4(DME)_{0.5}$ [21], with

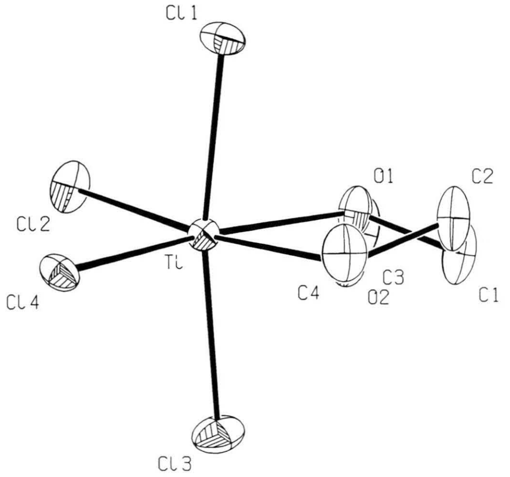


Fig. 3. ORTEP plot of the $[TiCl_4(DME)]^-$ anion in PPN[$TiCl_4$(DME)] (**5**). Thermal ellipsoids are drawn at 30% probability level.

Table I. Selected bond distances (Å) and angles (deg) in PPN[$TiCl_4$(DME)] (**5**). Estimated standard deviations in parentheses refer to the least significant digit.

Ti–Cl1	2.360(1)	Ti–Cl2	2.381(1)
Ti–Cl3	2.374(1)	Ti–Cl4	2.383(1)
Ti–O1	2.174(2)	Ti–O2	2.171(2)
O1–C1	1.446(5)	O1–C3	1.445(4)
O2–C2	1.442(4)	O2–C4	1.427(5)
C1–C2	1.511(6)		
Cl1–Ti–Cl2	91.63(4)	Cl1–Ti–Cl3	170.19(4)
Cl1–Ti–Cl4	93.41(3)	Cl1–Ti–O1	87.4(1)
Ti–O1–C1	113.4(3)	Ti–O1–C3	124.4(2)
Cl1–Ti–O2	85.0(1)	Cl2–Ti–Cl3	95.87(4)
Cl2–Ti–Cl4	95.08(3)	Ti–O2–C2	112.4(2)
Cl2–Ti–O1	94.6(1)	Ti–O2–C4	125.5(2)
Cl2–Ti–O2	169.8(1)	C2–O2–C4	110.7(3)
Cl3–Ti–Cl4	92.22(4)	P1–N–P2	138.1(3)
Cl3–Ti–O1	85.7(1)	O1–C1–C2	106.7(3)
Cl3–Ti–O2	86.6(1)	O2–C2–C1	107.0(2)
Cl4–Ti–O1	170.3(1)	O1–Ti–O2	75.7(1)
Cl4–Ti–O2	94.8(1)		

sodium in DME [22] and we have found that, in agreement with the decreased M-X bond strength on going from X=Cl to X=Br [23], the titanium(IV) derivative is reduced at room temperature with formation of the dark green, crystalline $TiBr_3(DME)_{1.5} \cdot 1.5$ DME (**7**) (reaction 7). The magnetic moment of the crystalline material at 296 K is 1.71 BM, suggesting the presence of magnetically diluted titanium(III) ions of d^1 electronic configuration. In this connection it is worth mentioning that an X-ray crystallographic experiment on $TiBr_3(DME)_{1.5}$ has shown an ionic structure consisting of $[TiBr_2(DME)_2]^+$ cations and $[TiBr_4(DME)]^-$ anions [24].

$$TiBr_4(DME)_{0.5} \xrightarrow[\text{DME}]{\text{Na}} TiBr_3(DME)_{1.5} \cdot 1.5\ \text{DME} \qquad (7)$$

With two equivalents of sodium, the titanium(II) derivative, $Na[TiBr_3(DME)_{1.2}]$, **8,** was obtained in *ca.* 50 % yield, reaction (8), characterized analytically and spectroscopically (ν_{C-O-C} = 859, 1029 and 1082 cm^{-1}). The magnetic properties of **8** were measured in the temperature range 70–290 K. As observed for the other compounds reported in this paper, **8** shows a magnetic moment (2.11 BM at 290 K) which is reduced with respect to the value expected for magnetically diluted titanium(II) of d^2 electronic configuration, the Curie-Weiss law being obeyed with a Weiss constant $\theta = -28$ K. This and the low number of DME ligands *per* titanium suggest an oligonuclear bromide-bridged structure for the anion in this compound, with part of the analytically detected DME coordinated around the sodium cation.

$$TiBr_4(DME)_{0.5} \xrightarrow[\text{DME}]{\text{2 Na}} NaTiBr_3(DME)_{1.2} \qquad (8)$$

Some of us have recently used [9m, 25] bis(mesitylene)vanadium(0), $Vmes_2$, obtained in high yields from $VCl_3/Al/AlCl_3$ in mesitylene, as a starting material for the preparation of inorganic and coordination compounds of vanadium(II) and vanadium(III) in non-aqueous media by reaction with protic acids or oxidizing agents.

We have now found that $Vmes_2$ is promptly oxidized to $VCl_2(DME)_n$ by CPh_3Cl in DME solution, according to eq. (9).

$$Vmes_2 \xrightarrow[\text{CPh}_3\text{Cl}]{\text{DME}} VCl_2(DME)_n + 2\ \text{mes} \qquad (9)$$

The DME-adduct of vanadium(II) chloride was isolated in high yields directly from the reaction mixture due to its low solubility in DME. It is interesting to note that the compound is pale-green in the presence of DME, gives bright green THF solutions (λ_{max}= 655 nm; ε = 8.3 M^{-1} cm^{-1}) and turns gray during the drying procedure *in vacuo* at room temperature, thus suggesting progressive loss of DME; accordingly, the DME content varies depending on the drying conditions.

It is noteworth that the analogous compounds of vanadium(II) with the heavier halides give mononuclear 1:2 DME adducts of formula $VX_2(DME)_2$, X = Br, I [9m], the different behaviour being clearly related to the size of the halide. Presumably the smaller chloride bridge favours the formation of an ionic or a polynuclear structure, the latter with all-bridging chlorides.

Conclusions

This work has shown that the course of the reduction of titanium(IV) halides with sodium depends both on the solvent and the halide. While the reduction of $TiCl_4$ in THF with one or two equivalents of sodium affords the neutral species $TiCl_3(THF)_3$ and $TiCl_2(THF)_2$, respectively, the reaction in DME affords products containing a Cl/Ti molar ratio higher than 2, namely, the titanium(III) derivative $Na[TiCl_4(DME)]$ and the titanium(II) complex $NaTiCl_3(DME)_2$. This is presumably due to the chelate effect of DME on titanium, which disfavours sodium solvation by the same ether. In DME the products of the sodium reduction depend on the halide, and $TiBr_4(DME)_{0.5}$ affords both neutral $TiBr_3(DME)_{1.5} \cdot 1{,}5$ DME or ionic $NaTiBr_3(DME)_{1.2}$.

Moreover, this work reports new simple procedures for the synthesis of the THF-soluble titanium(II) and vanadium(II) chlorides, namely $TiCl_2(THF)_n$ and $VCl_2(DME)_n$. The titanium(II) compound is characterized by a rather low reactivity toward substitution; on the other hand, it promptly reacts with oxygen-containing oxidizing agents (9,10-phenanthrenequinone or dibenzoylperoxide) to the corresponding complexes of oxidized titanium.

Experimental Section

All operations were carried out in a conventional vacuum line using standard Schlenk-tube techniques, under an atmosphere of prepurified argon. The reaction vessels were oven dried prior to use.

Infrared spectra were recorded with a Perkin Elmer mod. FT 1725X instrument on solutions or nujol or polychlorotrifluoroethylene (PCTFE) mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. NMR spectra {^{1}H: 200 MHz, reference TMS} were recorded with a Varian Gemini 200 BB spectrometer.

Magnetic susceptibility measurements were performed in the temperature range 290–70 K with a Faraday balance using $CuSO_4.5\ H_2O$ as standard. For the diamagnetic correction, Pascal contributions [26] were used.

Titanium analyses were performed by ICP-AES using a Perkin Elmer Elan 4000 instrument. The same technique was used for sodium analyses.

The THF or DME adducts of $TiCl_4$, $TiCl_3$, and $TiBr_4$ were prepared according to literature with variable amounts of ether solvents according to the drying procedure [27]. [PPN]Cl [28] and NaCp·0.5 THF [29] were prepared according to literature. Commercial (Fluka) 9,10-phenanthrenequinone was sublimed at 160 °C/0.05 mmHg. Benzoyl peroxide (C. Erba) was recrystallized from ethyl alcohol, dried *in vacuo* at room temperature and stored at *ca.* 4 °C.

Synthesis of $TiCl_2(THF)_n$ (**1**)

a) By reduction with sodium: A solution of $TiCl_4(THF)_2$ (6.27 g, 18.78 mmol) in THF (120 ml) was treated with finely divided sodium (0.87 g, 38.0 mmol). The colour of the solution changed gradually from yellow to green and finally to black. After 48 h stirring at room temperature, the solution was filtered, the volume reduced to 40 ml *in vacuo* and heptane (100 ml) was added. The black solid which formed was filtered off and dried *in vacuo*. It was analytically and spectroscopically identified as $TiCl_2(THF)_2.0.25$ THF (2.41 g, 46% yield).

Analysis for $C_9H_{18}Cl_2O_{2.25}Ti$

Calcd	Cl 25.2	Ti 17.0%,
Found	Cl 24.8	Ti 17.1%.

IR spectrum (nujol mull): 1347vw, 1040w, 1009m-s, 855s, 728w, 682w, 639w, 589w, 464w and 451m cm^{-1}. The compound is extremely sensitive to oxygen and moisture and is soluble in inert organic solvents, such as THF and aromatic hydrocarbons. The ^{1}H-NMR spectra in C_6D_6 show broad signals at 5.40, 3.75, 3.33, and 1.66 ppm; by treatment with D_2O in the presence of air, decomposition of the compound was observed and the ^{1}H-NMR spectrum of the resulting yellow-orange solution showed two sharp signals at 3.57 and 1.42 ppm attributed to THF.

The magnetic moment at 290 K was found to be 1.33 B.M. ($\chi_M^{corr} = 696\times10^{-6}$ cgsu, diam. corr. = -171×10^{-6} cgsu). The values of χ_M^{corr} and of the magnetic moment as a function of temperature are listed in Table II.

b) By reduction with sodium amalgam: $TiCl_4(THF)_2$ (4.62 g, 13.84 mmol) was treated at room temperature with 2% sodium amalgam obtained from mercury (31.5 g) and sodium metal (0.63 g, 27.40 mmol) in THF (100 ml). After 24 h stirring, the reaction mixture was filtered on glass wool, the volume of the solution reduced *in vacuo* to about 40 ml and heptane (100 ml) added. The solid which formed was filtered off and dried *in vacuo* (0.68 g, 22% yield of $TiCl_2(THF)_{1.5}$).

Analysis for $C_6H_{12}Cl_2O_{1.5}Ti$

Calcd	Cl 31.2	Ti 21.1%,
Found	Cl 32.6	Ti 20.9%.

Reactions of $TiCl_2(THF)_2$

A) Substitution reactions

a) DME: $TiCl_2(THF)_2$ (0.273 g, 1.04 mmol) was treated with DME (12 ml) to form a dark brown suspension. After 48 h stirring at room temperature the light brown solid was filtered off and dried *in vacuo* (0.14 g, 52% yield). The solid was analytically identified as $TiCl_2(DME)_{1.4}$.

Analysis for $C_{5.6}H_{14}Cl_2O_{2.8}Ti$

Calcd	Cl 28.9	Ti 19.5%,
Found	Cl 30.5	Ti 18.9%.

IR spectrum (nujol mull): 1277vw, 1241vw, 1194w, 1153w, 1088m, 1039s, 973vw, 900s, 851vs, 641w, 599w, 448m and 403s cm^{-1}. By treatment with D_2O in the presence of air, decomposition of the compound was observed and the ^{1}H NMR spectrum of the resulting yellow-orange solution showed two sharp resonances at 1.88 and 1.64 ppm due to DME.

The preparation was repeated several times, the DME content of the isolated product depending on the time of the drying procedure *in vacuo* at room temperature.

b) Sodium cyclopentadienide/CO: A suspension of NaCp·0.5 THF (0.42 g, 3.4 mmol) and $TiCl_2(THF)_2$ (0.44 g, 1.7 mmol) in toluene (50 ml), was stirred for 24 h at room temperature under an

Table II. Magnetic data for $TiCl_2(THF)_n$ (**1**), $NaTiCl_3(DME)_2$ (**6**), and $NaTiBr_3(DME)_{1.2}$ (**8**), in the range 290–70 K.

	$TiCl_2(THF)_2$ (**1**)		$NaTiCl_3(DME)_2$ (**6**)		$NaTiBr_3(DME)_{1.2}$ (**8**)	
T (K)	$\chi_M$corr (10^6 cgsu)	μ_{eff} (B.M.)	$\chi_M$corr (10^6 cgsu)	μ_{eff} (B.M.)	$\chi_M$corr (10^6 cgsu)	μ_{eff} (B.M.)
68	2909.7	1.26				
70			4557.7	1.60	5331.0	1.73
75	2851.6	1.31				
80	2840.1	1.35	4362.7	1.68	5216.9	1.83
90	2706.4	1.40	4400.5	1.79	5324.2	1.96
100	2331.2	1.37	3837.9	1.76	4700.2	1.95
110	2142.7	1.38	3689.6	1.81	4537.0	2.01
120			3404.7	1.81	4227.4	2.02
125	1936.9	1.40				
130			3192.6	1.83	3928.2	2.03
140			3031.3	1.85	3754.2	2.03
150	1585.9	1.39				
160			2680.5	1.86	3367.5	2.08
180	1298.6	1.37	2381.1	1.86	3006.6	2.09
200			2115.4	1.85	2674.5	2.08
210	1077.6	1.35				
220			1931.3	1.85	2455.4	2.09
230	948.7	1.33				
240	860.8	1.29	1779.9	1.86	2261.7	2.09
250	877.1	1.33				
260	827.5	1.32	1602.3	1.83	2043.7	2.07
270	793.3	1.31				
280	804.8	1.35	1490.2	1.83	1951.4	2.10
290	695.9	1.34	1481.5	1.86	1904.7	2.11

atmosphere of argon without any apparent change. After this period, the suspension was placed in a glass autoclave (Büchi, Uster, CH) and stirred at room temperature for 48 h under CO at a pressure of 7 atm. An IR spectrum of the solution in the carbonyl stretching region showed the absorptions typical of $Cp_2Ti(CO)_2$ [30] (1968 and 1885 cm^{-1}); a conversion of about 64% was calculated from the intensity of the 1885 cm^{-1} band (ε = 2200 M^{-1} cm^{-1}). After heating at 70 °C for 7 h, the IR spectrum was found to be unchanged.

B) Redox reactions

a) 9,10-Phenanthrenequinone: $TiCl_2(THF)_2$ (0.15 g, 0.57 mmol) was added to a solution of 9,10-phenanthrenequinone (0.12 g, 0.57 mmol) in toluene (30 ml). An immediate reaction took place with formation of a blue-green solid in a blue solution. The solid was filtered off and dried *in vacuo* and analyzed as $TiCl_2(C_{14}H_8O_2)$ (**2**), (0.17 g, 91% yield).

Analysis for $C_{14}H_8Cl_2O_2Ti$

Calcd	C 50.9	H 2.9%,
Found	C 51.4	H 2.5%.

IR spectrum (nujol and polychlorotri-fluoroethylene mull): 2958m-w, 2929m, 2856vw, 1595s, 1559m, 1514m-s, 1494s, 1454vs, 1391s, 1347m-s, 1292m-s, 1259s, 1224m, 1165w, 942w, 787w, 759m-s, 1126w, 718m, 688m, 587m-w, 544m and 443w cm^{-1}.

b) Benzoyl peroxide: The THF adduct $TiCl_2(THF)_2$ (0.56 g, 2.13 mmol) was added to a solution of benzoyl peroxide (0.52 g, 2.15 mmol) in toluene (50 ml). An immediate colour change took place. After 48 h stirring at room temperature, the pale yellow solid was filtered off, washed with toluene (5 ml) and dried *in vacuo*. The solid was identified as $TiCl_2(OOCC_6H_5)_2$, **3**, (0.43 g, 56 % yield).

Analysis for $C_{14}H_{10}Cl_2O_4Ti$

Calcd	Cl 19.6	Ti 13.3%,
Found	Cl 20.5	Ti 13.8%.

IR spectrum (polychlorotrifluoroethylene mull): 3392bw, 2955w, 2928w, 2857vw, 1597m, 1525s, 1493m, 1447m, 1397vs cm^{-1}.

The same reaction performed in heptane afforded the same product (IR) but contaminated by some starting material.

c) Diluted sulfuric acid: In a gas-volumetric apparatus, $TiCl_2(THF)_2$ (0.285 g, 1.1 mmol) was treated with water at 24.3 °C. No gas evolution was observed. After treatment with 10 mmol of diluted H_2SO_4 (10% v/v), dihydrogen (0.46 mmol) was slowly evolved up to a H_2/Ti molar ratio of 0.42 (after 24 h).

Reduction of $TiCl_4(DME)$ with sodium in DME

A) With one equivalent: Synthesis of $Na(DME)_n[TiCl_4(DME)]$ (**4**)

A solution of $TiCl_4(DME)$ (4.48 g, 16.0 mmol) in DME (100 ml) was stirred with finely divided sodium (0.33 g, 14.3 mmol) for 24 h at room temperature. The green reaction mixture was heated at 50 °C and filtered while still hot. Slow cooling of the solution afforded a bright green crystalline solid. A second crop of crystals was obtained by adding heptane (3.87 g, 55% yield).

Analysis for $Na(DME)_{1.5}[TiCl_4(DME)]$,
$C_{10}H_{25}Cl_4NaO_5Ti$
Calcd Cl 31.7 Ti 10,9%,
Found Cl 31.2 Ti 10.9%.

IR spectrum (nujol mull): 2096w, 2027w, 1932w, 1279m-s, 1243m-s, 1191s, 1156m, 1125vs, 1078vs, 1030vs, 857vs, 825m, 773w, 650vw, 600vw, 572vw and 418vs cm^{-1}. The magnetic moment at 295 K was found to be 1.55 B.M. ($\chi_M^{corr} = 1006\times10^{-6}$ cgsu, diam. corr. = -274.5×10^{-6} cgsu).

When the preparation was repeated several times, the DME content of the isolated product clearly depended on the drying procedure *in vacuo* at room temperature.

Synthesis of $PPN[TiCl_4(DME)]$ (**5**)

To a suspension of $Na(DME)_{1.5}[TiCl_4(DME)]$ (0.58 g, 1.32 mmol) in CH_2Cl_2 (15 ml) was added PPNCl (0.77 g, 1.35 mmol). After 10 min stirring, a green solution with a colourless precipitate was obtained. After filtration, Et_2O (15 ml) was added to the resulting solution, and a bright green crystalline solid was thus obtained (0.70 g, 62% yield).

Analysis for $PPN[TiCl_4(DME)]$,
$C_{40}H_{40}Cl_4NO_2P_2Ti$
Calcd C 58.7 H 4.9 N 1.7 Ti 5.9%,
Found C 57.3 H 4.6 N 1.7 Ti 5.5%.

IR (nujol mull): 1587w, 1300m, 1281m, 1249s, 1183m, 1162m, 1113s, 1086s, 1053s, 998m, 973m, 902w, 861s, 826w, 791w, 766m, 754m, 746s, 616m, 548s, 536s, 503s, 470m, 448m and 404w cm^{-1}. The magnetic moment at 295 K was found to be 1.51 B.M. ($\chi_M^{corr} = 955.7\times10^{-6}$ cgsu, diam. corr. = -508.3×10^{-6} cgsu). Crystals suitable for the subsequent X-ray diffractometric study were obtained from a CH_2Cl_2 solution layered with Et_2O.

Table III. Lattice constants and parameters of the structure determination of $PPN[TiCl_4(DME)]$ (**5**).

Compound	$PPN[TiCl_4(DME)]$
Formula	$C_{40}H_{40}Cl_4NO_2P_2Ti$
Molecular weight	818.4
Crystal dimensions (mm)	0.65×0.65×0.65
Temperature (K)	253
Space group	$Pna2_1$ (No. 33)
Cell constants (Å)	
a	14.445(4)
b	15.690(4)
c	17.544(6)
Volume (Å^3)	3976(2)
Z	4
D_{calc} ($g\,cm^{-3}$)	1.366
μ (cm^{-1})	5.96
F(000)	1692
Data collection range (θ, deg)	3–27
Scan type	ω
Measured reflections	9301
Absorption correction	none
Indep. refls. in refinement	7403 [$I > \sigma(I)$]
Refined parameters	450
Resd. electron dens. (e/Å^3)	0.56
R^a	0.041
$R_w{}^b$	0.042
GOF	1.153

[a] $\Sigma|\Delta F|/\Sigma|F_o|$; [b] $[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2|F_o|$.

The same compound was obtained by addition of PPNCl to preformed $TiCl_3(DME)_{1.5}\cdot1.5$ DME.

X-ray structure determination of $PPN[TiCl_4(DME)]$ (**5**): The structure was determined at 253 K with an ENRAF Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å, graphite-monochromator). Crystal data, data collection parameters and refinement results are collected in Table III. The structure was refined with the local version of the SDP program system [31].

The compound crystallizes in the orthorhombic space group $Pna2_1$ with four cations and four anions in the unit cell. The positional parameters of the central titanium and the four chlorine ligands in the anion as well as those of the P–N–P moiety and parts of the phenyl rings were obtained from direct methods [32]. The structure model was completed by subsequent difference Fourier maps. Hydrogen atoms in calculated standard geometry (C–H = 0.98 Å) were included in structure factor calculations with isotropic temperature factors $B_H = 1.3\cdot B_C$. The fractional coordinates of the non-hydrogen atoms are listed in Table IV.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, on quoting the depository number CSD 59177.

Table IV. Table of positional parameters of PPN[$TiCl_4$(DME)] (**5**). Estimated standard deviations in parentheses refer to the least significant digit.

Atom	x	y	z	B_{eq} (Å^2)
Ti	0.79491(4)	0.18314(3)	0.6837	1.876(9)
Cl1	0.85608(6)	0.04369(5)	0.68612(5)	2.97(1)
Cl2	0.70641(6)	0.15732(6)	0.79582(5)	3.19(2)
Cl3	0.75932(7)	0.33051(5)	0.67506(6)	4.02(2)
Cl4	0.67389(5)	0.14602(5)	0.59755(5)	2.60(1)
P1	0.71695(5)	0.20741(4)	1.08348(4)	1.47(1)
P2	0.69330(5)	0.18925(5)	1.25072(4)	1.56(1)
O1	0.9181(2)	0.2236(2)	0.7451(1)	3.04(5)
O2	0.8967(2)	0.2060(2)	0.5950(1)	2.82(4)
N	0.7087(2)	0.2342(1)	1.1705(1)	1.75(4)
C1	0.9879(3)	0.2609(3)	0.6964(2)	4.23(8)
C2	0.9900(3)	0.2082(3)	0.6243(2)	4.30(9)
C3	0.9171(3)	0.2655(3)	0.8184(2)	5.2(1)
C4	0.8949(3)	0.1701(3)	0.5203(2)	4.10(9)
C11	0.7128(2)	0.3031(2)	1.0273(2)	1.68(5)
C12	0.7034(2)	0.2974(2)	0.9481(2)	2.37(6)
C13	0.7102(3)	0.3704(2)	0.9041(2)	2.98(7)
C14	0.7263(2)	0.4486(2)	0.9382(2)	2.36(6)
C15	0.7360(2)	0.4545(2)	1.0169(2)	2.22(6)
C16	0.7291(2)	0.3819(2)	1.0613(2)	1.69(5)
C21	0.6886(2)	0.2714(2)	1.3222(2)	1.75(5)
C22	0.6768(2)	0.2484(2)	1.3984(2)	2.45(6)
C23	0.6811(3)	0.3100(2)	1.4546(2)	3.17(7)
C24	0.6957(3)	0.3938(2)	1.4352(2)	3.26(7)
C25	0.7044(3)	0.4179(2)	1.3597(2)	3.03(7)
C26	0.7014(2)	0.3560(2)	1.3027(2)	2.35(6)
C31	0.6282(2)	0.1356(2)	1.0505(2)	1.92(5)
C32	0.5462(2)	0.1655(2)	1.0190(2)	2.31(6)
C33	0.4763(2)	0.1092(2)	1.0020(2)	3.24(7)
C34	0.4859(3)	0.0233(3)	1.0166(2)	4.01(9)
C35	0.5679(3)	−0.0075(2)	1.0476(2)	3.61(8)
C36	0.6391(2)	0.0481(2)	1.0641(2)	2.50(6)
C41	0.7895(2)	0.1225(2)	1.2772(2)	1.75(5)
C42	0.7985(2)	0.0405(2)	1.2471(2)	2.04(5)
C43	0.8806(2)	−0.0036(2)	1.2562(2)	2.61(6)
C44	0.9537(2)	0.0322(2)	1.2946(2)	2.87(7)
C45	0.9460(2)	0.1134(2)	1.3248(2)	2.67(7)
C46	0.8634(2)	0.1586(2)	1.3165(2)	2.23(6)
C51	0.8260(2)	0.1572(2)	1.0607(2)	1.80(5)
C52	0.8978(2)	0.1577(2)	1.1123(2)	2.28(6)
C53	0.9818(2)	0.1193(2)	1.0934(2)	3.22(7)
C54	0.9933(2)	0.0835(3)	1.0227(3)	3.71(8)
C55	0.9222(3)	0.0857(3)	0.9701(2)	4.09(8)
C56	0.8378(2)	0.1215(2)	0.9889(2)	3.05(7)
C61	0.5879(2)	0.1284(2)	1.2546(2)	1.83(5)
C62	0.5779(2)	0.0531(2)	1.2962(2)	3.13(7)
C63	0.4936(3)	0.0104(2)	1.2943(3)	3.85(8)
C64	0.4212(2)	0.0404(2)	1.2520(3)	3.78(8)
C65	0.4305(2)	0.1166(3)	1.2123(2)	3.72(8)
C66	0.5133(2)	0.1595(2)	1.2131(2)	2.68(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\cdot[a^2\cdot \mathrm{beta}(1,1) + b^2\cdot \mathrm{beta}(2,2) + c^2\cdot \mathrm{beta}(3,3)$.

B) With two equivalents: Synthesis of $NaTiCl_3(DME)_2$ (**6**)

a) From $TiCl_4(DME)$*:* A solution of $TiCl_4$(DME) (6.69 g, 23.9 mmol) in DME (150 ml) was treated with finely divided sodium (1.09 g, 47.4 mmol). After 24 h stirring, the reaction mixture was filtered; the resulting solid was extracted with boiling DME for 7 h. The volume of the extract was reduced *in vacuo* and the resulting black solid was filtered off, washed with heptane and dried in vacuo (4.50 g, 55% yield).

Analysis for $NaTiCl_3(DME)_2$, $C_8H_{20}Cl_3NaO_4Ti$

Calcd	Cl 29.7	Ti 13.4%,
Found	Cl 30.3	Ti 13.9%.

IR spectrum (nujol mull): 1278w, 1240m, 1186m, 1155w, 1077vs, 1033vs, 1000s, 855vs, 829s and 416s cm^{-1}.

The same product was obtained by treating a solution of $Na(DME)_{1.5}[TiCl_4(DME)]$ (0.89 g, 2.03 mmol) in DME (60 ml) with finely divided sodium (0.05 g, 2.17 mmol). After 12 h stirring the reaction mixture was filtered off and the solvent evaporated to dryness affording a 92% yield of $NaTiCl_3(DME)_2$ (IR and Ti, Cl analysis). The magnetic moment at 290 K was found to be 1.86 B.M. (χ_M^{corr} = 1481×10^{-6} cgsu, diam. corr. = −217×10^{-6} cgsu). The values of χ_M^{corr} and of the magnetic moment as a function of temperature are reported in Table II.

Reduction of $TiBr_4(DME)_{0.5}$ *with sodium*

a) Sodium to titanium molar ratio = 1; synthesis of $TiBr_3(DME)_{1.5}\cdot 1.5$ *DME* (**7**): A solution of $TiBr_4(DME)_{0.5}$ (1.16 g, 2.80 mmol) in DME (40 ml) was treated with finely divided sodium (0.065 g, 2.83 mmol). After 12 h stirring the dark green reaction mixture was filtered. The volume of the solution was reduced to 15 ml *in vacuo*. After 12 h at −30 °C, a green crystalline solid was obtained, and identified analytically as $TiBr_3(DME)_{1.5}\cdot 1.5$ DME (0.47 g, 30% yield).

Analysis for $C_{12}H_{30}Br_3O_6Ti$

Calcd	Br 43,0	Ti 8.6%,
Found	Br 43.2	Ti 8.6%.

IR spectrum (nujol mull): 1279w, 1261vw, 1244w, 1192m, 1125s, 1082s, 1029s, 980w, 888w, 859s, 639w, 595w, 444m and 417m cm^{-1}. The magnetic moment at 296 K was found to be 1.72 B.M. (χ_M^{corr} = 1242×10^{-6} cgsu, diam. corr. = −211×10^{-6} cgsu). The preparation was repeated several times, and it was observed that the DME content of the isolated product depended on the drying procedure in vacuo at room temperature.

b) Sodium to titanium molar ratio = 2: synthesis of $NaTiBr_3(DME)_{1.2}$ (**8**): A solution of $TiBr_4(DME)_{0.5}$ (1.26 g, 3.05 mmol) in DME (50 ml) was treated with two equivalents of finely divided sodium (0.14 g, 6.08 mmol). After 72 h stirring the brown reaction mixture was filtered and the solid was washed with DME (10 ml); the volume of the solution was then reduced to 15 ml in vacuo. Treatment with heptane (25 ml) gave a dark liquid phase, from which a light brown solid was obtained after two successive washings with heptane. The solid was analytically and spectroscopically identified as $NaTiBr_3(DME)_{1.2}$ (0.60 g, 47% yield).

Analysis for $C_{4.8}H_{12}Br_3NaO_{2.4}Ti$
Calcd Br 57.2 Ti 11.2%,
Found Br 57.4 Ti 10.5%.

IR spectrum (nujol mull): 1280vw, 1262vw, 1244vw, 1193w, 1126w-m, 1082m, 1029s, 975w, 859m-s, 800m and 423w cm^{-1}. The magnetic moment at 290 K was found to be 2.11 B.M. (χ_M^{corr} = 1904.7×10^{-6} cgsu, diam. corr. = -191.0×10^{-6} cgsu). The values of χ_M^{corr} and of the magnetic moment as a function of temperature are reported in Table II. The preparation was repeated several times, the DME content of the product depending on the drying procedure *in vacuo* at room temperature.

Reaction of $Vmes_2$ *with* CPh_3Cl. *Synthesis of* $VCl_2(DME)_n$: A solution of $Vmes_2$ (0.729 g, 2.50 mmol) in DME (50 ml) was treated dropwise with a solution of CPh_3Cl in DME. After addition of 20 ml of the solution of the chloride (2.5 mmol), a mixture of a brown and a green solid in a deep red solution was observed. The addition of the second equivalent (20 ml of solution) caused the decoloration of the solution and the formation of a pale green solid. After 15 h stirring at room temperature, the pale green solid was collected by filtration, washed with DME (2×10 ml) and dried *in vacuo* at room temperature. The drying procedure caused the colour of the solid to change from pale green to grey-green. The analytical data correspond to the formula $VCl_2(DME)_{1.1}$ (0.335 g, 62% yield).

Analysis for $C_{4.4}H_{11}Cl_2O_{2.2}V$
Calcd Cl 32.1 V 23.1%,
Found Cl 31.7 V 23.7%.

IR spectrum (nujol mull): 1282w, 1261w, 1243w, 1196w, 1096m-s, 1064vs, 975w, 867s, 802w, 723w, 604w and 594m cm^{-1}.

The compound dissolves in THF with a bright green colour.

Note added in proof

F. A. Cotton et al. have reported [M. A. Ataya, F. A. Cotton, I. H. Matonic, C. A. Murillo, Inorg. Chem. **34,** 5424 (1995)] that THF solutions of titanium(II) chloride are obtained by reduction of $TiCl_3$ with KC_8.

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