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$[HTiCl(THF)_{\sim 0.5}]_x$ – a highly reactive titanium hydride and an active species in the McMurry reaction *

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Abstract

The complex $[TiCl_3(THF)_3]$ reacts with catalytically-prepared solid magnesium hydride (MgH_2^*) or dissolved magnesium hydride (MgH_2') with evolution of hydrogen to give a highly reactive titanium hydride, $[HTiCl(THF)_{\sim 0.5}]_x$ (**1**). The well-known low valent titanium species, obtained by reduction of $TiCl_3$ with $LiAlH_4$, utilized in the McMurry reaction, has been shown to be **1**. An X-ray absorption spectroscopy study (EXAFS) of **1** reveals that the Ti absorber is surrounded by O (from THF) and Cl atoms plus two types of Ti neighbors. Possible structural models for **1** compatible with the EXAFS results are proposed. Complex **1** is an active reagent for the coupling reaction of benzophenone to give tetraphenylethene. During the reaction hydrogen is liberated and the inorganic side product has been shown to be titanium(III) oxychloride; thus the McMurry reaction employing **1** as the reagent can be described by

$$Ph_2CO + \mathbf{1} \xrightarrow[\text{toluene}]{\text{THF or}} 0.5\ Ph_2C{=}CPh_2 + 0.5H_2\uparrow + [TiOCl(THF)_x].$$

On the basis of these results, a new interpretation of the mechanism for the McMurry reaction is presented. Complex **1** also undergoes a number of carbenoid type reactions, which may proceed via a "titanium carbenoid" intermediate **9a–c**.

Key words: Titanium; Hydride; Magnesium; EXAFS

1. Introduction

In recent years, it has been shown that ternary hydrides or binary intermetallics of magnesium [1] can be successfully made by treating catalytically prepared solid [2] or dissolved magnesium hydride [3] (subsequently denoted by MgH_2^* and MgH_2', respectively) with metals, metal hydrides or inorganic and organometallic compounds. The reactions take place under mild, "kinetically controlled" conditions, which in some cases have led to hitherto unknown species of ternary magnesium hydrides and binary intermetallics [1a,b,e–k]. Another feature of this new method is that the resulting hydrides and intermetallics are usually isolated in a finely divided, highly reactive, X-ray-amorphous form. Binary hydrides that do not contain magnesium, *e.g.* SiH_4 [4], can also be prepared by using MgH_2^* or MgH_2' as the hydrogen source.

As possible routes to titanium hydrides, or titanium-magnesium hydrides, we have investigated the reactions of MgH_2^*, MgH_2', or magnesium in the presence of hydrogen, with titanium halides [5]. In the first part of this present paper, we report the preparation and characterization of a reactive titanium hydride $[HTiCl(THF)_{\sim 0.5}]_x$ (**1**) obtained via the reaction of $[TiCl_3(THF)_3]$ with MgH_2^* or MgH_2'. We will also show that the well-known low valent Ti-species (prepared by reducing $TiCl_3$ with $LiAlH_4$ in the molar ratio 1:0.5) used in the McMurry reaction [6,7] is in fact **1**. In the second half of the paper, reactions of **1** are described, especially in relation to the stoichiometry and the mechanism of the McMurry reaction [6–8].

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2. Preparation and characterization of $[HTiCl(THF)_{\sim 0.5}]_x$

2.1. Reaction of $[TiCl_3(THF)_3]$ with MgH_2' in THF and isolation of the product 1

The reaction of $[TiCl_3(THF)_3]$ with MgH_2' [3] in THF between 0 and 25°C occurs with the evolution of hydrogen. It is expected that the reduction of a Ti^{III} compound, such as titanium trichloride, to a Ti^{II}, Ti^{I}, or Ti^{0} species would be accompanied by the evolution of 0.5, 1 or 1.5 mol of H_2 per mol of Ti, respectively. Thus the amount of hydrogen released during the course of a reaction can be used to give information about the formal oxidation state of the resulting titanium species, and therefore was carefully measured throughout all experiments [9*]. It was observed that the quantity of liberated hydrogen varies as a function of the molar ratio, $MgH_2'/TiCl_3$, (Fig. 1 and Table 2, Experimental section) and increases linearly with increasing $MgH_2'/TiCl_3$ reactant molar ratios up to a ratio of 1:1, at which point the amount of hydrogen evolved levels off at a value of 0.5 mol H_2/mol Ti.

These results indicate that in the reactions in which the molar ratios $MgH_2'/TiCl_3$ are greater than one, the resulting Ti species titanium is still found in a +2 oxidation state [10*]. Furthermore, from the amount of hydrogen released in the reactions involving reactant molar ratios $MgH_2'/TiCl_3$ of less than or equal to one, it can be concluded that the two components react in 1:1 molar ratio to generate a Ti^{II} species [11*]. For the reduction of $TiCl_3$ with MgH_2' in a 1:1 molar ratio, the following two reactions can be formulated:

$$[TiCl_3(THF)_3] + MgH_2' \xrightarrow{THF} HTiCl + 0.5H_2\uparrow + MgCl_2 \quad (1)$$

$$[TiCl_3(THF)_3] + MgH_2' \xrightarrow{THF} TiCl_2 + 0.5H_2\uparrow + HMgCl \quad (2)$$

When a reaction was carried out with $[TiCl_3(THF)_3]$ and MgH_2' in a molar ratio of 1:0.5 (0.25 mol H_2/mol Ti released, see Fig. 1), neither HMgCl [12] nor MgH_2' could be detected in the product mixture by IR spectroscopy, which suggests that the reaction does not proceed according to eqn. (2). In experiments involving reactant molar ratios, $TiCl_3/MgH_2'$ of 1:0.5 and 1:1, very fine, black, X-ray amorphous solids separated from the solutions. The black solids, isolated respectively in 35 and 28% yields (with respect to Ti), had the following properties (Table 2, entries 1 and 2): (a) a Ti/Cl ratio of 1 ~ 0.8 and a low Mg content (0.3–1.0 wt %); (b) absorption bands in the IR spectra characteristic of coordinated THF (1030 and 870 cm^{-1}) (from the elemental analyses and IR spectra it could be inferred that *roughly* 0.5 mol of THF are coordinated per mol Ti); and (c) evolution of ~ 1.5 mol H_2/mol Ti upon alcoholysis.

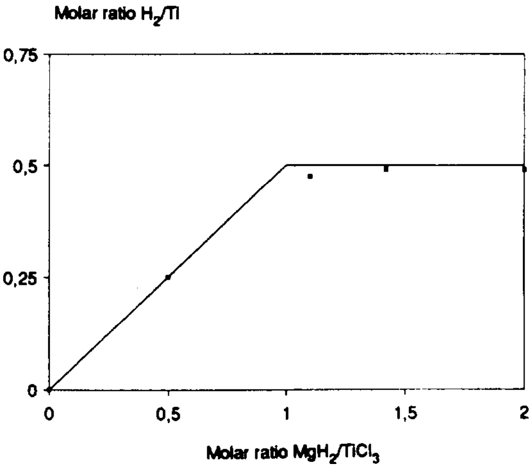

Fig. 1. Hydrogen evolution as a function of the molar ratio of the reactants in the reduction of $[TiCl_3(THF)_3]$ with MgH_2' in THF (0–25°C).

Since low valent titanium is oxidized to Ti^{III} during hydrolysis or alcoholysis [13] and since before hydrolysis titanium is present in the solid as Ti^{II} (as indicated by the amount of H_2 evolved during the synthesis step), the evolution of 1.5 mol H_2/mol Ti upon alcoholysis can be taken as evidence for the existence of a Ti^{II} *mono*hydride. The observed properties of the black solid products detailed above and the amount of H_2 generated during the reduction can be accounted for by formulating the Ti^{II} product as $[HTiCl(THF)_{\sim 0.5}]_x$ (**1**). The synthesis and alcoholysis of **1** can be represented by equations (1) and (3), respectively.

$$\frac{1}{x}\underset{\mathbf{1}}{[HTiCl(THF)_{\sim 0.5}]_x} + 2EtOH \longrightarrow 1.5H_2\uparrow + [TiCl(OEt)_2] \quad (3)$$

At this point it should be noted that a significant proportion of **1** remains in solution even after the reaction between $[TiCl_3(THF)_3]$ and MgH_2' (eqn. (1)) is complete. The yield of the solid **1** can be improved by the addition of pentane or by allowing the solution to age at room temperature (RT) for several weeks. Once isolated, **1** shows only negligible solubility in THF. We assume that the "dissolved form of **1**" is stabilized in THF solution by the presence of $MgCl_2$ and small amounts of quinuclidine, both of which act as solubilizing agents for MgH_2' [3].

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* Reference number with asterisk indicates a note in the list of references.

2.2. Preparation of 1 and deuterated 1 (D-1) by reaction of $[TiCl_3(THF)_3]$ with MgH_2^* or MgD_2^*

When in reactions with $[TiCl_3(THF)_3]$ MgH_2' is replaced by catalytically-prepared, solid magnesium hydride, MgH_2^*, **1** can be obtained in higher yields [5]. The reaction of $[TiCl_3(THF)_3]$ with MgH_2^* in a molar ratio of 1:1 in THF between −10 and 20°C results in evolution of 0.45 mol H_2/mol Ti [9*] and **1** separates as a finely-divided, pyrophoric, black powder in 70–75% yield (eqn. (4); Table 2, entry 3). Similarly, the solid $[DTiCl(THF)_{\sim 0.5}]_x$ (**D-1**) can be isolated in ~60% yield from the reaction between $[TiCl_3(THF)_3]$ and MgD_2^* [1e,2a] (eqn. (5); Table 2, entry 4 and Fig. 7).

$$[TiCl_3(THF)_3] + MgH_2^* \xrightarrow{THF} \mathbf{1}\downarrow + 0.5H_2\uparrow + MgCl_2 \quad (4)$$

$$[TiCl_3(THF)_3] + MgD_2^* \xrightarrow{THF} \underset{\textbf{D-1}}{[DTiCl(THF)_{\sim 0.5}]_x}\downarrow + 0.5D_2\uparrow + MgCl_2 \quad (5)$$

Upon deuterolysis, **1** gives a mixture of HD and D_2 along with a small amount of H_2, $\Sigma(HD + D_2 + H_2)/Ti = 1.52$, $\Sigma H(\text{from HD and } H_2)/Ti = 0.91$ (eqn. (6) and upon iodolysis $\sim 0.5H_2/Ti$ (eqn. (7)). Analogously, hydrolysis of **D-1** yields a mixture of HD and H_2 along with a small amount of D_2, $\Sigma(HD + H_2 + D_2)/Ti = 1.46$, $\Sigma D(\text{from HD and } D_2)/Ti = 0.75$ (eqn. (8)) and upon iodolysis $\sim 0.4D_2/Ti$ (eqn. (9)).

$$\mathbf{1}\begin{array}{l} \nearrow \xrightarrow{D_3O^+} HD + 0.5D_2(+H_2) + Ti^{III} \quad (6) \\ \searrow \xrightarrow{I_2} 0.5H_2 + TiClI_{2-3} \quad (7) \end{array}$$

$$\textbf{D-1}\begin{array}{l} \nearrow \xrightarrow{H_3O^+} HD + 0.5H_2(+D_2) + Ti^{III} \quad (8) \\ \searrow \xrightarrow{I_2} 0.5D_2\uparrow + TiClI_{2-3} \quad (9) \end{array}$$

The appearance of HD as a product during the deuterolysis of **1** and hydrolysis of **D-1** can be taken as evidence for the presence of chemically-bound hydrogen and deuterium in **1** and **D-1**, respectively. Attempts to detect hydride or deuteride ligands by IR, laser-Raman, and solid state NMR spectroscopy were to a large extent unsuccessful. In the IR spectra of **1**, besides the absorption bands associated with complexed-THF, a weak band at 1070 cm^{-1} is consistently observed, but considering data for previously characterized Ti-hydride systems, this band cannot be conclusively assigned to a hydride ligand. (Bands originating from $(\mu\text{-}H)Ti_2$ and $(\mu\text{-}H)_2Ti_2$ entities have been reported between 1140–1250 and at 1450 cm^{-1} [14a–d], and bands attributed to terminal hydride ligands at 1560–1575 and 2000 cm^{-1} [14c,e,f].) An inelastic neutron scattering study is planned in an attempt to identify this band and the hydrogen ligand interaction.

The appearance of a strong band at 335 cm^{-1} with a shoulder at 320 cm^{-1} in the far IR spectrum of **1** does provide conclusive evidence for a Ti–Cl bond. In order to obtain more information about the structural environment about Ti, an EXAFS study of **1** and several model compounds was undertaken, as described in Section 2.5.

2.3. Preparation of titanium hydrides by reduction of $[TiCl_3(THF)_3]$ with magnesium in the presence of hydrogen

In connection with their studies on nitrogen fixation, Yamamoto *et al.* [15] have reported that in the presence of $[TiCl_3(THF)_3]$, an excess of magnesium in THF reacts slowly with hydrogen with the formation of magnesium hydride. They assume that a transiently-formed titanium hydride species acts as the catalyst for the hydrogenation of magnesium. We have found that by reduction of $[TiCl_3(THF)_3]$ with *stoichiometric* amounts of magnesium in the presence of hydrogen it is possible to prepare titanium hydrides.

The amount of hydrogen absorbed in the course of the reduction of $[TiCl_3(THF)_3]$ by Mg powder under a hydrogen atmosphere (1 bar, RT) varies as a function of the applied reactant molar ratio $Mg/TiCl_3$, as depicted in Fig. 2. The number of moles of H_2 absorbed per mole titanium (Fig. 2) increases linearly with increase in the molar ratio of the reactants and reaches a value of 0.5 for a 1:1 $Mg/TiCl_3$ ratio. In the case of $Mg/TiCl_3$ molar ratios of 1.5:1 and 2:1, approximately 1 mol H_2/mol Ti is absorbed.

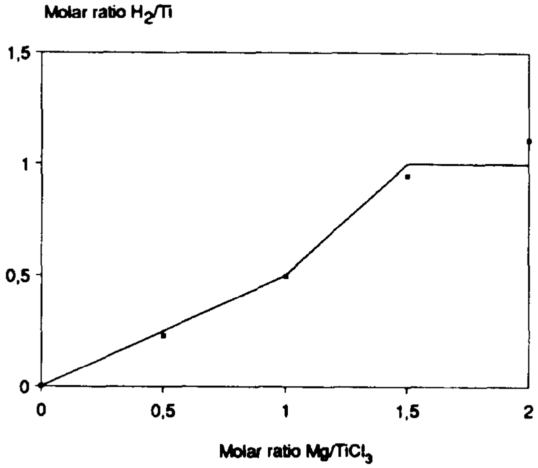


Fig. 2. Hydrogen absorption as a function of the molar ratio of the reactants in the reaction between $[TiCl_3(THF)_3]$ and Mg powder under a hydrogen atmosphere (1 bar, RT).

Since magnesium hydride could not be detected by IR spectroscopy in the products of the reactions involving 1:1 and 1.5:1 $Mg/TiCl_3$ ratios, the observed uptake of 0.5 and ~1 mol of H_2/mol Ti during the course of the reactions points to the formation of a mono- and di-hydride of titanium, respectively. In the former case, **1** was isolated in 46% yield from the reaction mixture by filtration (eqn. (10), Table 2, entry 5). In the latter case, a "titanium dihydride" was obtained in form of a black pyrophoric powder, probably contaminated with **1**, since it contained 9.4% Cl and yielded only 0.7 H_2/Ti upon iodolysis [5]. This novel and highly reactive "TiH_2" merits further investigation [16].

$$[TiCl_3(THF)_3] + Mg + 0.5H_2 \xrightarrow{THF} \mathbf{1}\downarrow + MgCl_2 \quad (10)$$

2.4. *Isolation of 1 from the reaction involving the McMurry reagent* $\{[TiCl_3(THF)_3] + 0.5LiAlH_4\}$

Low valent titanium species obtained by reduction of $TiCl_3$ or $TiCl_4$ with metals (Mg, Li, K, Zn, ZnCu), metal hydrides ($LiAlH_4$, LiH) or K-graphite have found widespread application in organic syntheses, especially as reagents for the McMurry and related reactions [6–8]. Recently we showed that one of the products generated during the reduction of $TiCl_3$ with Mg in THF is a novel inorganic Grignard complex $[Ti(MgCl)_2 \cdot THF]_x$ [17].

In 1974, McMurry and Fleming reported the preparation of a low valent titanium species capable of inducing a carbonyl coupling reaction [6a]. This reagent [6,7] was obtained from the reaction of two equivalents of $TiCl_3$ with one equivalent of $LiAlH_4$ in THF; the reduction was reported to proceed rapidly with evolution of heat and gas and a colour change to black [6]. Geise *et al.* suggest that the reduced Ti species consists of metallic titanium particles with THF and HCl chemisorbed on the surface, and that the titanium atoms present on the surface of the particles show a higher oxidation state corresponding to their particular interaction with H or Cl, and the overall average valency would correspond to the formal Ti^I state [18].

For the induced coupling of ketones, Geise *et al.* [18] observed an optimal ratio of 1:0.5 for the $TiCl_3/LiAlH_4$/THF system and *ca.* 1:0.8 for the $TiCl_4/LiAlH_4$/THF system. They suggest that some of the reducing agent is lost due to the presence of impurities and thus the reactions (11) and (12) occur, a Ti^I species being formed along with Al^0 in the presence of HCl. An average bulk valency of +1 for titanium has also been assumed for the $TiCl_4/LiAlH_4$/THF system used for the reduction of nitro compounds and deoxygenation of N-oxides [19].

$$5TiCl_3 + 2LiAlH_4 \longrightarrow 5''Ti^ICl'' + 2Al^0 + 2LiCl + 8HCl \ [18b] \quad (11)$$

$$5TiCl_4 + 3LiAlH_4 \longrightarrow 5''Ti^ICl'' + 3Al^0 + 3LiCl + 12HCl \ [18c] \quad (12)$$

The recognition that **1** is the product of the reaction between $[TiCl_3(THF)_3]$ and magnesium hydride in a 1:1 molar ratio (eqns. (1) and (4)) prompted us to reinvestigate the reaction between $TiCl_3$ and $0.5LiAlH_4$/THF used to prepare the so-called McMurry reagent [6,7]. As in the previous reactions with MgH_2' or MgH_2^* the evolution of hydrogen was continuously monitored during the experiments [9*]. The investigation of the reaction between α-$TiCl_3$ and $LiAlH_4$ in THF turned out to be complicated because of the simultaneous catalytic decomposition of $LiAlH_4$ in the presence of α-$TiCl_3$, which resulted in the formation of metallic aluminum [5,18,20]. Thus an undeterminable quantity of $LiAlH_4$ intended for the reduction of $TiCl_3$ is lost.

Subsequently we found that the catalytic decomposition of $LiAlH_4$ can be virtually avoided if $[TiCl_3(THF)_3]$ is used instead of α-$TiCl_3$ and the reaction is carried out at low temperatures [5]. Accordingly, $LiAlH_4$ was added to a suspension of $[TiCl_3(THF)_3]$ (molar ratio 0.5:1) in THF at −78°C, and the mixture was then slowly raised to room temperature. Under these conditions hydrogen evolution began at *ca.* −50°C and continued until a total amount corresponding to 0.5 mol H_2/mol Ti was collected (at RT). Addition of pentane precipitated **1** from the black product mixture in THF and allowed its isolation in 46% yield; the properties of **1** thus obtained (Table 2, entry 6) were almost identical to those of the species isolated in reactions with MgH_2^* or MgH_2', and, indeed as detailed below, **1** is an active species for the McMurry reaction. Thus the reported optimal $TiCl_3/LiAlH_4$ molar ratio of 1:0.5 for the McMurry reagent is correct for the reduction of $TiCl_3$ with $LiAlH_4$, and the reaction can now be better represented as in eqn. (13).

$$[TiCl_3(THF)_3] + 0.5LiAlH_4 \xrightarrow[Pe]{THF} \mathbf{1}\downarrow + 0.5H_2\uparrow + 0.5LiCl + 0.5AlCl_3 \quad (13)$$

2.5. *X-ray absorption spectroscopic study and structural characterization of 1*

X-ray absorption spectra were recorded at the titanium K-edge (4965 eV) on the EXAFS 3 spectrometer at the French synchrotron facility, DCI at LURE, operated at 1.85 GeV and approximately 300 mA. The

X-ray beam was monochromatized with a double Si[111] crystal slightly detuned for harmonic rejection. The spectrometer was calibrated by assigning the first maximum in the absorption edge of a 5-μm titanium foil as 4965 eV. Measurements were performed in transmission mode and spectra generally recorded from 100 eV before the edge to 900 eV after it (stepsize 2 eV). Helium-filled ionization chambers were used to measure the incident and transmitted X-ray flux.

Species **1**, and the reference compounds α-$TiCl_3$ and $TiCl_3(THF)_3$, were examined. Since all of these solids are air/moisture sensitive and/or pyrophoric, sampling was carried out in each case under argon immediately prior to recording of the EXAFS spectrum. Mulls of the solid in paraffin oil were made, stored over molecular sieves, and then loaded and pressed between the Parafilm window of stainless steel sample holders to form homogeneous films free from pinholes or cracks. In each case at least five spectra were recorded at 77 K.

Reduction and analysis of all data was carried out using the programs developed by Michalowicz, *EXAFS pour le MAC* [21]. The X-ray absorption spectra were subjected to background removal and normalization by standard techniques (linear pre-edge function, removal of the background curvature using a high (5th–6th) order polynomial or a spline polynomial with division of the absorption spectrum into manually selected zones) and the resulting EXAFS spectra were selectively summed to give the best signal-to-noise ratio and minimum mean standard deviation. Fourier transformation was carried out over a range typically 2.5–15 $Å^{-1}$ using a Hamming window and k^3 weighting. Quantitative analysis using curve-fitting procedures was performed on Fourier-filtered spectra, back-transformed to reciprocal space, by systematically varying the coordination number N_i (this was however fixed at crystallographic values for the reference compounds, the Debye–Waller factor σ_i, and R_i, the distance of the ith shell of atoms from the absorber.

For the model compounds Ti, α-$TiCl_3$ and $TiCl_3(THF)_3$, the phase and amplitude functions utilized were the *ab initio* values of McKale calculated using spherical wave approximation [22]. These gave satisfactory agreement with the known structures when allowance was made for changes in the energy origin E_0 and for variations in the γ parameter (used to compute the photoelectron mean free path, $\lambda = k/\gamma$) for each type of atom shell Ti–Ti, Ti–O, Ti–Cl (see Table 1). The values of the latter parameter so determined were used in least squares refinement cycles of **1**.

As mentioned in Section 2.4 Geise *et al.* [18] have suggested that the low valent Ti system formed in the reaction between $TiCl_3$ and $LiAlH_4$, in other words **1**, consists of Ti particles with HCl and THF chemisorbed on to the surface. Comparison of the EXAFS (Fig. 3) and Fourier transformed EXAFS (FT, Fig. 4) spectra of **1** with those of titanium foil clearly indicates that there are substantial differences in the local environments around Ti in these two materials. In particular, the first atom shell in **1** lies at a significantly shorter distance out than that of the first titanium coordination shell in metallic titanium, (around 2 Å before phase correction, compared with *ca.* 2.5 Å in titanium foil) and the existence of metallic titanium – even nanoparticulate, where a slight contraction of metal-metal distances would be expected – can therefore be excluded.

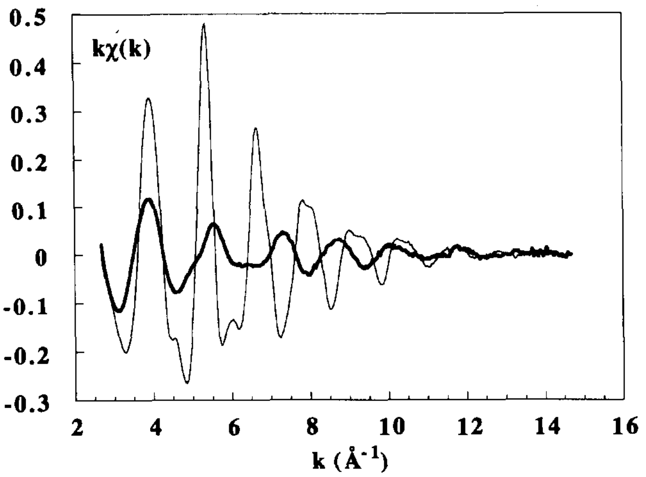


Fig. 3. Background-subtracted and normalized EXAFS data for 1 (▬) and Ti metal (———).

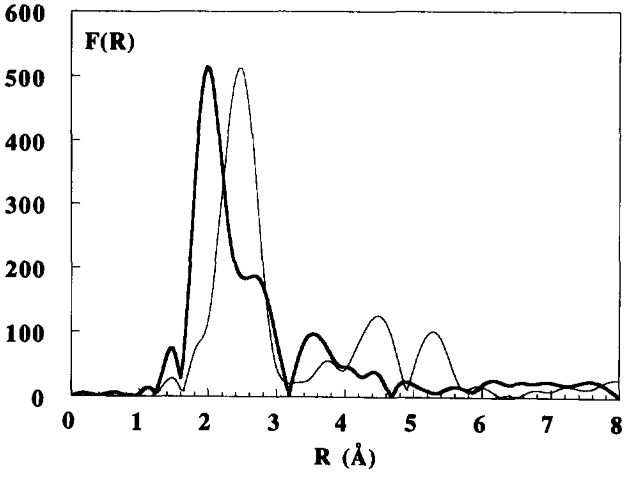


Fig. 4. Fourier transformed EXAFS spectrum (FT) of 1 (▬) and Ti metal (———), phase shift not corrected. The intensity of the FT for 1 is in fact approximately 1/3 of that for Ti metal and was normalized here to aid in the visual comparison.

The amplitude of the EXAFS signal of **1** is low, largely due its amorphous character and, in Fig. 4, the intensity of the FT of **1** has been normalized against that of titanium metal over the first shell of atoms to facilitate visual comparison.

Closer examination of the FT of **1** in Fig. 4 reveals the presence of 2 massifs, the first including two maxima (at 2.0 and 2.7 Å prior to phase correction) and the second, weaker, of discernible maximum at 3.5 Å. Inclusion of phase functions (either experimental, derived from model compounds $TiCl_3$ or Ti metal, or McKale functions) into the calculation of the FT allowed identification of these signals as arising from backscattering from chlorine, and from two titanium shells respectively. Quantitative analysis was initially performed on Fourier-filtered, back-transformed EXAFS spectrum, filtered to include the first two maxima (1.4 to 3.2 Å). In a second stage, a broader filter envelope allowed a global refinement of the structural parameters of all shells out to 4 Å, from which the local environment around titanium in **1** can be described as containing a first coordination sphere composed of oxygen (from THF ligands, 0.4 atoms at 2.13 Å) and chlorine (1.5 atoms at 2.44 Å) and a second and third spheres occupied by titanium atoms at 3.10 (1.3 atoms) and 4.04 Å (1.9 atoms). Figure 5 shows the agreement between the experimental EXAFS and that calculated using the structural data of Table 1 and the single scattering EXAFS equation.

The presence of a strong contribution to the EXAFS oscillations of chlorine backscatters precludes also any description of **1** as a titanium hydride, of which three crystallographically distinct phases are known, corresponding to different x values in TiH_x [23]. The interatomic distances are 2.935 and 4.151 Å in the hexagonal phase formed when $x \sim 0.46$; 3.113 and 4.403 Å in the face centered cubic structure formed when $x \sim 1.22$; and 3.144, 4.279 and 4.528 Å in the face-centered tetragonal cell of TiH_2, none of which agrees satisfactorily with the EXAFS-determined Ti–Ti distances in **1**.

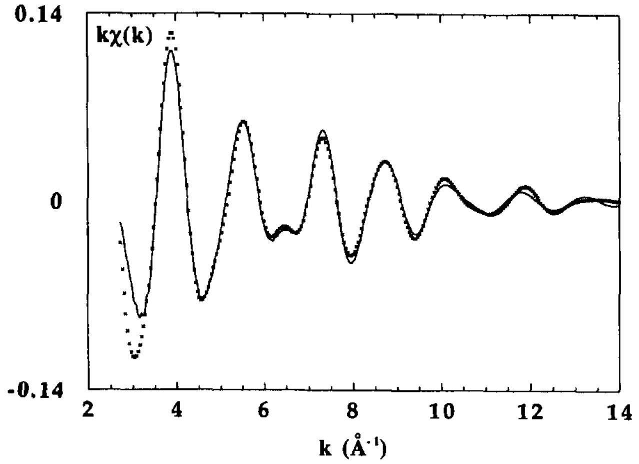


Fig. 5. Fit of the backtransform of all shells in the FT (filtered from 1.4 to 4.2 Å) of **1**. ×, experimental; ———, calculated.

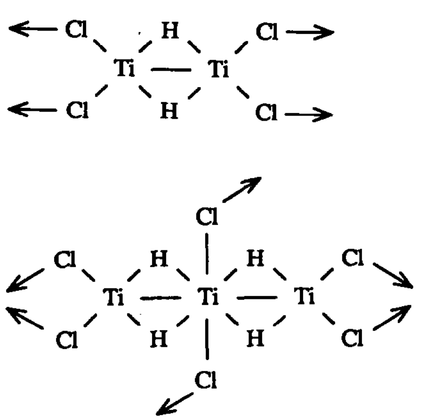
The Ti–Cl distance in **1** determined from EXAFS, 2.44 Å, can be attributed either to a bridging interaction (generally in the range 2.41 to 2.61 Å) or to an averaged value corresponding in reality to both bridging and terminal bonds (generally in the range 2.27 and 2.41 Å). Such a situation is encountered in $CsTi_2Cl_7$ [24], where the average Ti–Cl distance is 2.43 Å. This compound also serves to provide typical Ti · · · Ti interatomic distances when doubly bridged through chlorine, namely 3.57 and 3.78 Å. Other examples found in the literature either for doubly-chloride or hydride-bridged titanium atoms are less appropriate, since they contain organic ligands, but from an appraisal of a number of titanium-containing complexes [25,26], doubly H-bridged and doubly-Cl-bridged intermetal distances fall under 3 Å and between 3.4 and 4 Å,

TABLE 1. Structural parameters derived from EXAFS spectroscopy for Ti foil, α-$TiCl_3$, $TiCl_3(THF)_3$, and $[HTiCl(THF)_{\sim 0.5}]_x$ (**1**) [a]

	Shell	N	σ, Å	γ	R_{exp}, Å	R_{th}, Å [b]	ΔE_o, eV	Res, %
Ti	Ti	12	0.10(1)	0.60(10)	2.93(1)	2.926	−6	1
α-$TiCl_3$	Cl	6	0.06(1)	0.60(10)	2.40(1)	2.460	−3	2
$TiCl_3(THF)_3$	O	3	0.06(2)	0.76(10)	2.10(2)	2.126	−4	
	Cl	3	0.06(1)	0.60(10)	2.39(2)	2.346	3	5
$[HTiCl(THF)_{\sim 0.5}]_x$	O	0.4(4)	0.08(4)	0.76	2.13(12)		9	
	Cl	1.5(7)	0.05(4)	0.6	2.44(4)		5	
	Ti	1.3(10)	0.02(5)	0.6	3.10(5)		2	
	Ti	1.9(7)	0.05(3)	0.6	4.04(5)		6	5.5

[a] N: number of atoms in the shell; σ: Debye–Waller factor; γ: parameter for photoelectron mean free path; R: distance from the Ti absorber; ΔE_o: shift in the energy origin; and $\text{Res} = \Sigma_k(k[\chi_{exp}(k)] - k[\chi_{th}(k)])^2 k^3 / \Sigma_k(k[\chi_{exp}(k)]^2)k^3$.

[b] Mean distance from the Ti absorber as calculated from single crystal diffraction data.



Scheme 1.

respectively. Using this as a basis, the Ti ··· Ti interactions determined by EXAFS for **1** are tentatively assigned as arising from doubly H-bridged (3.10 Å) and doubly Cl-bridged (4.04 Å) titanium atoms.

The insoluble nature of the precipitated solid **1** suggests that the material may possess a chain-like structure, possibly arising from the polymerization of a soluble titanium species in solution. A fundamental repeat unit may then consist of dimeric or trimeric Ti groups bridged through hydrogen (such a unit would be compatible with the observed coordination number of 1.3), with such fragments then further linked through chlorine atoms. A highly schematic representation of such arrangements, which respect the stoichiometry of the sample, [$H_{1-1.3}TiCl_{0.8-1}(THF)_{\sim 0.5}$], is shown in Scheme 1.

While much caution is necessary in interpreting the coordination numbers derived from EXAFS, it seems that this model suffers from providing an insufficient number of longer Ti ··· Ti distances at 4.04 Å. This could be accounted for simply by invoking the possibility of interchain Ti ··· Ti interactions, or may be an indication that the structure can be better described in terms of clustering of titanium atoms. For example, the binary titanium chloride Ti_7Cl_{16} [27] contains trigonal planar clusters of titanium (Ti ··· Ti length 2.954 Å) linked by a second type of titanium at > 3.80 Å. These interatomic distances are close to those determined for **1** in the present study. A tetranuclear cluster structure can be projected for **1** in which a trigonal planar group of titanium atoms (with Ti–Ti distances of 3.10 Å) is capped by titanium at a distance of 4.04 Å. Alternatively, a trigonal bipyramid can be drawn, in which the Ti ··· Ti distances are 3.10 and 4.04 Å. In either case, chlorine and hydrogen would then bridge over the edges and/or faces, as shown in Scheme 2.

3. The McMurry and other reactions induced by [HTiCl(THF)$_{\sim 0.5}$]$_x$ or [DTiCl(THF)$_{\sim 0.5}$]$_x$

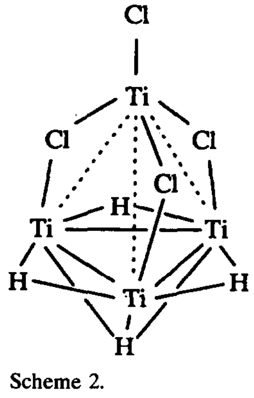
3.1. The reductive coupling of benzophenone

Reductive coupling of benzophenone to tetraphenylethene (**2**) through the application of the reagent obtained from the reaction {$TiCl_3 + 0.5LiAlH_4$} was initially performed by McMurry *et al.* [6] and subsequently investigated by Geise *et al.* [18a]. After careful optimization of the reaction conditions (*i.e.* reactant molar ratio $TiCl_3:LiAlH_4$:benzophenone, 1:0.5:1; solvent, THF; reaction temperature, RT) tetraphenylethene yields of > 95% were achieved [18a]. We have selected the reductive coupling of benzophenone to serve as a reference system in our study of the McMurry reaction involving **1** and **D-1** (solids isolated from the reaction solution) or "dissolved" **D-1′** (Section 2.1. and 2.2.) as reagents.

The reaction of benzophenone with **1** in a molar ratio of 1:1 in THF at RT occurs with the evolution of 0.4 mol H_2/mol Ti and gives a 70% yield of the coupling product **2**. When the same reaction was carried out in toluene a titanium(III) oxychloride was isolated and identified as the inorganic side-product (see Experimental Section). Thus the coupling (or McMurry) reaction of benzophenone in the presence of **1** can be formulated, as shown in eqn. (14).

$$Ph_2CO + \mathbf{1} \xrightarrow[\text{toluene}]{\text{THF or}} \underset{\mathbf{2}}{0.5Ph_2C{=}CPh_2} + 0.5H_2\uparrow + [TiOCl(THF)_x] \quad (14)$$

The course of this coupling reaction was studied by using **D-1** as the reagent and a 1/1 molar ratio of reactants. At defined intervals, samples were taken from the reaction mixture, immediately hydrolyzed, and the products quantitatively analyzed by gas chromatography (GC) for compound **2** and any intermediate products. The amount of D_2 liberated during the



Scheme 2.

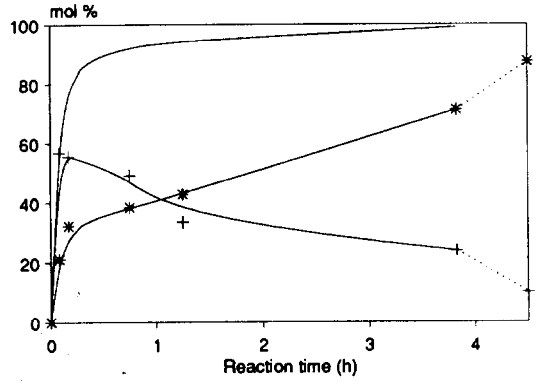


Fig. 6. The progression of the coupling reaction of benzophenone at RT in THF utilizing $[DTiCl(THF)_{\sim 0.5}]_x$ (D-1) as the reagent (molar ratio 1:1). * ——— *, mol% of tetraphenylethene (2); + ——— +, mol% of pinakol (4) (hydrolysis product of Ti-pinakolate); ———, evolution of D_2. After 240 min, the reaction mixture was heated at reflux for 40 min, whereby the yield of 2 (* ··· *) increases and the pinakolate drops (+ ··· +).

reaction was also carefully measured [9*]. The results are presented graphically in Fig. 6. Even 5 min after the addition of benzophenone to the suspension of D-1 in THF, 60 mol% of D_2 (based on the mass of D-1 weighed in) had been liberated. At the same time, only 20 mol% of the benzophenone had been converted into **2**, while the formation of an intermediate pinacolate (**3**), (benzpinacol (**4**) as detected by GC is the hydrolysis product of this intermediate) reached its maximum at almost 60 mol%. As the reaction proceeded, the concentration of **3** decreased while that of the coupling product **2** increased. After 5h at RT, 71 mol% of **2** had been generated. When the reaction mixture was kept for 40 min under reflux, the yield of **2** was increased to 87 mol%, with concomittant reduction of the pinacolate content.

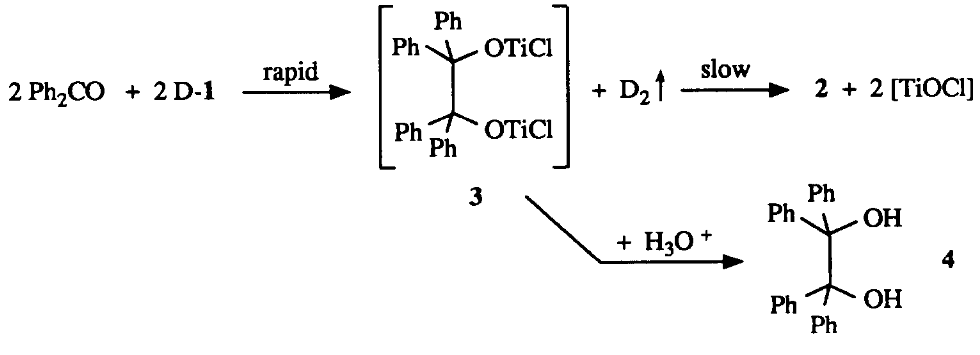
Based on these results a reaction sequence illustrated in Scheme 3 can be suggested for the reductive coupling reaction of benzophenone induced by D-1.

The formation of the titanium(II) pinacolate intermediate (**3**) is the rapid step of the reaction sequence and the elimination of [TiOCl] from **3** the slow step [28*]. The liberation of deuterium occurs simultaneously with the formation of the intermediate pinacolate (Scheme 3). Since the gas released during this McMurry reaction with D-1 is deuterium, this is further proof that deuterium (and hydrogen) is chemically bound to D-1 (and **1**). During the course of the reaction the titanium is oxidized from a formal valence state of +2 (in the reagent and intermediate **3**) to +3 (in TiOCl). However, as a result of the homolytic dissociation of the deuterium (or hydrogen) ligand, an additional electron is left over for the reaction. Hence D-1 (or **1**) behaves as a (strong) *two*-electron reducing agent.

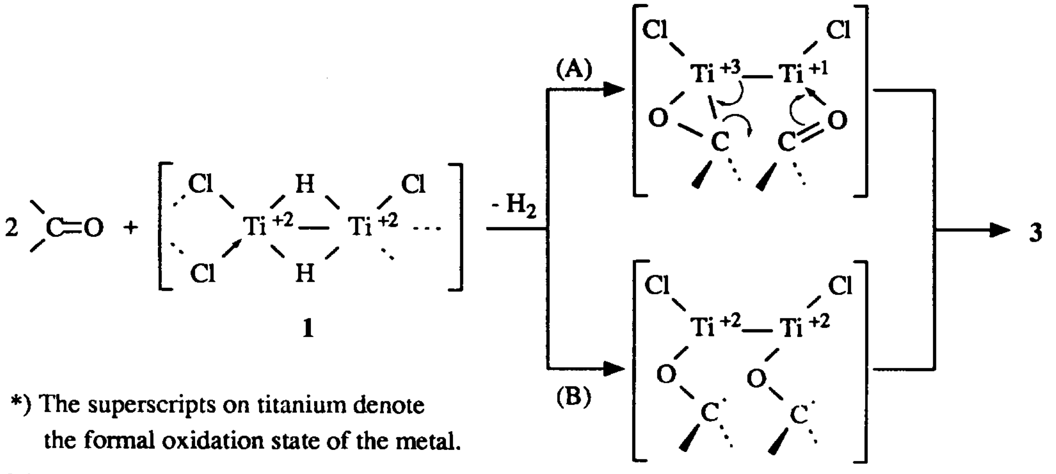
Since the reductive coupling of benzophenone with **1** or D-1 affords tetraphenylethene (**2**) in nearly the same yield under comparable conditions as that from use of the genuine McMurry reagent [6,18a], and further since **1** can be isolated from the reaction of $TiCl_3$ and $LiAlH_4$ (molar ratio 1:0.5) in THF (Section 2.4.), it is evident that **1**, not finely-divided metallic titanium or a "Ti^1Cl" complex [8g,18], is the active species in the well-known McMurry reagent system $\{TiCl_3 + 0.5LiAlH_4\}$.

The mechanism of the formation of the pinacolate (**3**) from benzophenone and **1** (or D-1) is still uncertain. However in the light of the structural models suggested for **1** in Section 2.5., the possible mechanism depicted in Scheme 4 can be suggested.

Since hydrogen is liberated almost immediately during the reaction, it appears that the hydride ligands in **1** are only weakly bound to titanium. Furthermore the basicity of the hydride ligands is apparently too low to cause hydrogenation of the carbonyl C atom during the carbonyl addition in the first step. As a hydride ligand is lost, thus vacating a coordination site on Ti, the ketone is reduced and becomes coordinated to tita-



Scheme 3.



*) The superscripts on titanium denote the formal oxidation state of the metal.

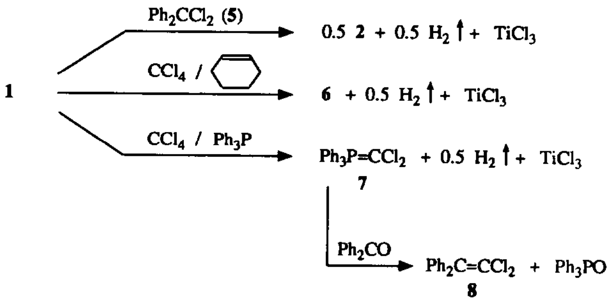
Scheme 4.

nium either as a ketyl radical or via a side-on carbonyl group. As previously discussed [8d,g,30–32], subsequent C–C bond formation occurs either by dimerization of the ketyl radicals (pathway B) or by nucleophilic attack on the carbonyl group of a second ketone by the reduced, complexed, aromatic carbonyl entity (pathway A). In pathway A, since the Ti–C bond is broken the complexed aromatic carbonyl group can be considered to be a dianion. In order to explain experimentally observed cross coupling reactions among aromatic ketones, McMurry *et al.* [30,31] have proposed that dimerization occurs by a dianion pathway. Recently, Fürstner and Jumbaum [32] have presented a number of arguments in favor of a dianion mechanism rather than a ketyl radical path for the cyclization of aromatic acyloxy- and acyl-amido-carbonyl compounds in the titanium/graphite-induced synthesis of heterocycles. The existence of such dianions of aromatic ketones has been conclusively proven by the X-ray crystal structure determinations of dilithium benzophenone [33] and ytterbium benzophenone [34]. In both cases, the carbonyl group of the benzophenone ligand is complexed "side-on" to the metal. "Side-on" coordinated aldehyde complexes of Zr and Hf have been shown to be intermediates in C–C coupling reactions, as described by Roddick and Bercaw [35a]. These coupling reactions are, however, in contrast to the situation in our systems, brought about by monometallic complexes.

This study, together with our previous investigation [17] on the nature of the low valent Ti species, definitively confirms the recently expressed view [8h] that structurally various McMurry reagents may exist and be active, differing according to the method of their preparation. As has been shown here (section 2.1. and ref. [10*]), the reaction of $TiCl_3$ with MgH_2' in THF yields either 1 or a highly reactive "TiH_2" depending on the molar ratio of the reactants. In the case of the reduction of $TiCl_3$ with Mg in THF [17], which of two complexes, $[TiMgCl_2 \cdot x THF]$ and $[Ti(MgCl)_2 \cdot x THF]$ is formed is dependent simply on the reaction time. It is expected that each of these species will display a unique chemical reactivity, and so their identification may be fruitful in improving the selectivity and reproducibility in their application as reagents, or even lead to discovery of new reactions.

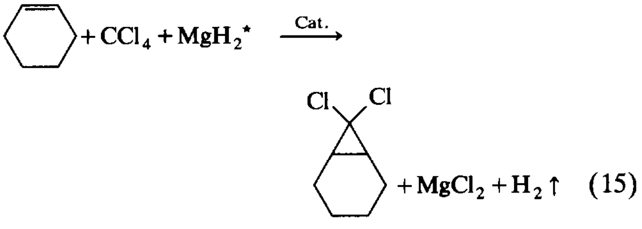
3.2. *Carbenoid reactions of 1*

Olah *et al.* [36] have reported the synthesis of **2** in a 96% yield through the reductive dimerization of diphenylmethylene chloride (**5**) induced by the McMurry reagent. We have also been able to carry out this dimerization reaction (84% yield of **2**) in a hexane/THF mixture by use of application of **1** as the reagent (Scheme 5).



Scheme 5.

By reacting CCl_4 with cyclohexene in the presence of a 1:1 mixture of $TiCl_4$ and $LiAlH_4$ in THF, Mukaiyama *et al.* [37] prepared 7,7-dichlornorcarane (**6**) in 79% yield. When CCl_4 is treated with **1** in THF in the presence of cyclohexene, H_2 (0.6 mol H_2/mol Ti) along with **6** (*ca.* 70% yield) are generated (Scheme 5). If the same reaction mixture is quenched with ethanol before the reaction is complete, chloroform can be detected among the volatile products [5]. The production of chloroform during protolysis may be an indication that an intermediate trichloromethyltitanium dichloride (**9**: R = Cl) is formed during the reaction. The synthesis of **6** can also be effected by using MgH_2^* and catalytic amounts of $[TiCl_3(THF)_3]$ (5 mol%) (eqn. (15)). It is assumed that in the catalytic cycle, $[TiCl_3(THF)_3]$ reacts with MgH_2^* to form **1** (eqn. (4)), which subsequently participates in the production of **6**. As **6** is formed according to Scheme 5, $[TiCl_3(THF)_3]$ is regenerated, and the catalytic cycle can be repeated. Thus **1** functions as a catalytic intermediate in the cyclopropanation of cyclohexene. It should also be mentioned here that **1** is an active catalyst for the hydrogenation of lithium under mild conditions to produce a highly reactive lithium hydride (eqn. (16)) [5]. Catalytic syntheses of lithium hydride from the elements from **1**, **6**, **6a**, λ^4-trithiapentalene-$FeCl_3$ or related systems have been previously reported [38].



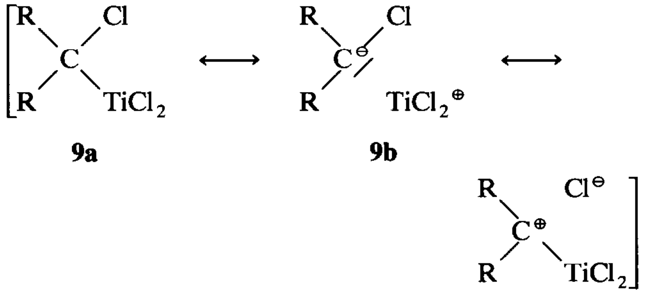
6

Cat. = 5 mol% $[TiCl_3(THF)_3]$

$$Li + 0.5H_2 \xrightarrow[\text{RT, 1 bar}]{\text{THF/5 mol\% 1}} LiH \qquad (16)$$

Reaction of CCl_4 with **1** in the presence of triphenylphosphine also takes place with the evolution of hydrogen, to give triphenylphosphine-dichloromethylene (**7**) [39]. The formation of **7** was confirmed by subjecting it to the Wittig reaction, 1,1-dichloro-2,2-diphenylethene (**8**) and triphenylphosphine oxide being obtained.

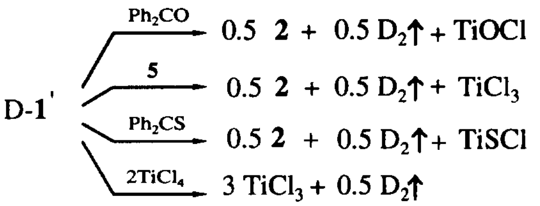
The reactions shown in Scheme 5 can be designated as "carbenoid-type" reactions [40]. During course of such a reaction (**1** with either Ph_2CCl_2 or CCl_4), it is expected that a titanium-carbenoid species is formed as an intermediate; this species can be represented by canonical structures **9a–c**, R = Ph, Cl.



9a **9b** **9c**

3.3. Reactions of the "dissolved D-1" (D-1′)

The dissolved form of the reagents **1** or D-**1** (see Sections 2.1. and 2.2.) can be also be effectively used in a number of reactions, as summarized in Scheme 6. All the reactions were conducted at 0°C in THF. Benzophenone and diphenylmethylene chloride (**5**) react with D-**1**′ to give tetraphenylethene (**2**) in approximately the same yield as reactions starting from solid **1** or D-**1**. The inorganic products of these reactions, $[TiOCl(THF)_x]$ and $[TiCl_3(THF)_3]$, respectively, could be isolated. With $TiCl_4$, D-**1**′ undergoes a redox reaction with the evolution of D_2 and formation of $[TiCl_3(THF)_3]$.



Scheme 6.

4. Experimental details

IR: Nicolet 7000. MS: Varian MAT CH 5, CH 7 or Finnegan MAT 8230. GC/MS: combination of an F 22 Perkin-Elmer gas chromatograph with a Varian CH 7A spectrometer. GC: glass capillary columns with various stationary phases, commercial instruments, H_2 as carrier gas, FID detection. Elemental analyses: Dornis & Kolbe, Mülheim/Ruhr. Vacuum definition: vacuum = 0.1 mbar: high vacuum = 10^{-3} mbar.

Starting materials: α-$TiCl_3$ (99%, Aldrich,) was heated in vacuum at 50°C for 10 h in order to remove $TiCl_4$. α-$TiCl_3$ was converted into $[TiCl_3(THF)_3]$ by heating it in THF under reflux for 15–20 h [41]. Mg powder: Eckart Werke PK-31, 270 mesh. THF was heated under reflux over magnesium anthracene · 3THF [42] and distilled.

All reactions and operations with air-sensitive materials were performed under argon in air- and water-free solvents.

4.1. Preparation of 1 from $[TiCl_3(THF)_3]$ and MgH_2' (molar ratio 1 : 1)

3.92 M solution of MgH_2' in THF (5.5 ml, 21.6 mmol; prepared using 1 mol% of a $FeCl_2$ catalyst, 4 mol% of $MgCl_2$ and 5 mol% of quinuclidine [3a]) was added dropwise to a stirred suspension of 21.3 mmol of $[TiCl_3(THF)_3]$ in 100 ml of THF maintained at −78°C. $[TiCl_3(THF)_3]$ was prepared *in situ* from 3.28 g of α-$TiCl_3$ (see under Starting materials above) and the stirred reaction mixture was allowed to gradually warm up from −78°C to room temperature during 20 h. The H_2 evolution began at a reaction temperature of nearly 0°C, and reaction proceeded exothermically to give a final volume of 221 ml of H_2 (verified by MS), which corresponds to 9.1 mmol or 0.43 mol H_2/mol Ti [9*]. The black suspension was filtered (D4 glass frit). The solid isolated was washed several times with THF followed by pentane, and finally dried under high vacuum. Yield of **1**: 0.71 g (28%). Elemental analysis (EA) (%): C 17.03, H 3.19, Cl 25.45, Ti 41.05, Mg 0.96. Upon hydrolysis with 4 N H_2SO_4, 173.2 mg of **1** yielded 58 ml of H_2. Data concerning **1**, thus prepared, are listed in Table 2, entry 1.

Pentane (100 ml) was added to the filtrate (280 ml) and the mixture was stirred for 4 h at room temperature. The solid was filtered off, washed and dried, to give an additional 1.10 g (35%) of **1**, contaminated with $MgCl_2$. Hydrolysis: 1.58 mol H_2/mol Ti; EA (%): Ti 38.2, Cl 29.5, Mg 3.0 [43*].

4.2. Preparation of 1 from $[TiCl_3(THF)_3]$ and MgH_2' (molar ratio 1 : 0.5)

The procedure as described above was repeated but with 24.9 mmol of $[TiCl_3(THF)_3]$ (prepared *in situ* from 3.84 g of α-$TiCl_3$ in 50 ml of THF) and 2.0 ml of a 5.5 M solution of MgH_2' in THF (11.0 mmol; prepared as above); 146 ml of H_2 (6.0 mmol; 0.24 mol H_2/mol Ti) were collected during the reaction [9*]: Yield of **1**: 1.17 g (35%). EA (%): C 24.00, H 4.36, Cl 26.65, Ti 35.73, Mg 0.27 [43*]. Data for **1** prepared in this way are listed in Table 2, entry 2.

4.3. Preparation of 1 from $[TiCl_3(THF)_3]$ and MgH_2^* (The preferred route to 1)

The procedure was as in the first experiment above but starting from 118 mmol of MgH_2^* suspended in 20 ml of THF (prepared *in situ* using 1 mol% of $CrCl_3$ and 4 mol% of $MgCl_2$ at 25°C [2d]) and 117.5 mmol $[TiCl_3(THF)_3]$ (prepared *in situ* from 18.14 g of α-$TiCl_3$ in 200 ml of THF); 1270 ml of H_2 (52.3 mmol; 0.45 mol H_2/mol Ti) were collected [9*]: The solid **1** was filtered off, washed 8 times with 50 ml aliquots of THF (to remove all traces of $MgCl_2$) and 4 times with pentane, then dried for 6 h in high vacuum. 11.78 g (73.6% yield) of **1** was isolated as a very pyrophoric black powder, amorphous to X-rays, virtually insoluble in THF. At temperatures above 60°C (under argon) **1** decomposes, but the solid can be stored without decomposition under argon at room temperature. (EA (%): C 22.98, H 4.01, Cl 27.38, Ti 35.13, Mg 0.25, Cr 0.007.) During protolysis with EtOH, 445.5 mg of **1** gave 127 ml of gas with the composition (as determined by MS analysis): 97.5% H_2 (5.1 mmol; 1.56 mol H_2/mol Ti), 1.9% EtOH, and 0.7% THF. Upon deuterolysis with D_2O, 391.8 mg of **1** gave 106 ml of gas with the composition (MS analysis): 43.6% HD, 48.3% D_2 and 8.2% H_2. Iodolysis (with iodine in toluene) of a 411.5 mg sample of **1** produced 36 ml of gas having the composition (MS analysis): 98.4% H_2 (1.46 mmol; 0.48 mol H_2/mol Ti) and 1.6% THF. Protolysis of the filtrate led to 1140 ml of gas with the composition (MS analysis): 98.9% H_2 (1.59 mol H_2/mol Ti) and 1.1% THF. Analysis of the aqueous solution originating from the hydrolysis of the filtrate yielded 29.5 mmol of Ti, 270 mmol of Cl and 119.5 mmol of Mg [43*]. Further information about **1** made in this way is given in Table 2, entry 3. A sample of **1** prepared by this method was used for the EXAFS study.

4.4. Preparation of D-1 from $[TiCl_3(THF)_3]$ and MgD_2^*

The procedure was as described above but starting from 115 mmol of $[TiCl_3(THF)_3]$ (prepared *in situ* from 17.80 g of α-$TiCl_3$ in 300 ml of THF) and 115 mmol of MgD_2^* suspended in 20 ml of THF (prepared *in situ* using 1 mol% of $CrCl_3$ and 4 mol% of $MgCl_2$ at 25°C [1e,2d]); 1180 ml of D_2 (0.42 mol D_2/mol Ti; verified through MS analysis) were collected during the reaction (see Fig. 7) [9*]: 8.16 g of D-**1** was obtained (61.6% yield). EA (%): C 20.02, H 3.39, Cl 31.20, Ti

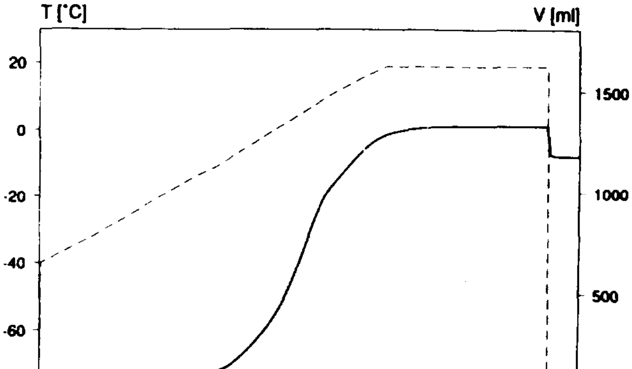


Fig. 7. The development of D_2 gas during the course of the reaction between $[TiCl_3(THF)_3]$ with MgD_2^* in THF (molar ratio 1 : 1). ———, D_2 evolution; - - - - - -, temperature of the reaction mixture.

41.51, Mg 0.54. Protolysis of a 402.4 mg sample of D-1 delivered 126 ml of gas of the composition (MS analysis): 42.9% HD, 51.6% H_2, 3.7% D_2 and 1.9% EtOH. The results of protolysis and iodolysis are shown in Table 2 along with IR spectroscopic data (entry 4). The filtrate obtained from the filtration step was used in the reactions described in Section 3.3 [43*].

4.5. Preparation of 1 from $[TiCl_3(THF)_3]$, Mg and H_2

A suspension of 129 mmol $[TiCl_3(THF)_3]$ in 400 ml THF, prepared *in situ* from 19.84 g of α-$TiCl_3$ was transferred under argon to a reaction flask. The flask was then evacuated, filled to atmospheric pressure with H_2, and connected to a 2 l automatic gas burette [9*] which also contained H_2. To the stirred suspension of $[TiCl_3(THF)_3]$/THF, 3.12 g (128 mmol) of Mg powder were added during 15 min. Absorption of H_2 began after *ca.* 1 h of stirring. After 4 h stirring no further H_2 uptake was noted; 1645 ml of H_2 were absorbed (67.7 mmol; 0.53 mol H_2/mol Ti). The resulting product mixture was worked up as previously described for the preparation of **1** using MgH_2' and 7.78 g of **1** were isolated (46% yield). EA (%): C 16.69, H 3.52, Cl 29.36, Ti 36.5, Mg 0.29. A sample of **1** weighing 525.1 mg when treated with D_2O, gave 167 ml of gas with the composition (MS analysis): 47.2% HD, 25.9% D_2, 25.0% H_2. The iodolysis results, together with other data for **1** prepared in this way are given in Table 2, entry 5 [43*].

4.6. Preparation of 1 from $[TiCl_3(THF)_3]$ and $LiAlH_4$

1.96 g (51.6 mmol) of $LiAlH_4$ were gradually added to a stirred suspension of 98.6 mmol of $[TiCl_3(THF)_3]$ (prepared *in situ* from 15.2 g of α-$TiCl_3$) in 200 ml of THF at −78°C. The stirred mixture was allowed to warm slowly during 10 h from −78°C to room temperature. The H_2 evolution began at *ca.* −50°C, yielding a final H_2 volume of 995 ml (MS analysis: 41.0 mmol H_2; 0.42 mol H_2/mol Ti) [9*]. The reaction mixture was filtered and 100 ml of pentane were added to the filtrate. The filtrate was stirred for 6 h at room temperature and then filtered. The solid isolated was washed with THF and pentane, and dried under high vacuum. Yield of **1**: 5.52 g (46%). EA (%): C 19.74, H 3.33, Cl 25.34, Ti 39.64, Al 0.67, Li 0.20. Other data for **1** prepared in this way are given in Table 2, entry 6 [43*].

TABLE 2. Preparation of $[HTiCl(THF)_{\sim 0.5}]_x$ (1) and $[DTiCl(THF)_{\sim 0.5}]_x$ (D-1)

Entry	Preparation method of **1** (D-1)	$\frac{H_2(D_2)}{Ti}$ [a]	Composition of **1** based on el. anal. [b]	Yield of **1** (D-1) (%) [c]	Protolysis $[H_2/Ti]$	Iodolysis $[H_2/Ti]$	IR [d] $[cm^{-1}]$	Far-IR [e] $[cm^{-1}]$	μ_{eff} [B.M.]	BET $[m^2/g]$
1	$TiCl_3 \cdot 3THF + MgH_2'$	0.43	$TiCl_{0.8}C_{1.7}H_{3.7}$	28	1.60	–	1030 s 870 vs	–	–	–
2	$TiCl_3 \cdot 3THF + 0.5MgH_2'$	0.24	$TiCl_{0.8}C_{2.7}H_{5.8}$	35	1.44	–	1020 s 915 w 865	–	–	–
3	$TiCl_3 \cdot 3THF + MgH_2^*$	0.45	$TiCl_{1.1}C_{2.6}H_{5.5}$	73.6	1.56	0.48	1027 s 915 w 870 vs	335 vs	1.19	30.2
4	$TiCl_3 \cdot 3THF + MgD_2^*$	0.42	$TiClC_{1.9}H_{3.9}$	61.6		0.51 [f]	1030 s 920 w 870 vs	–	1.07	49.0
5	$TiCl_3 \cdot 3THF + Mg + H_2$	0.53 [g]	$TiCl_{1.1}C_{1.8}H_{4.6}$	46	1.74	0.7	1025 s 915 w 860 vs	330	–	86.8
6	$TiCl_3 \cdot 3THF + 0.5LiAlH_4$	0.42	$TiCl_{0.9}C_2H_4$	46	1.68	–	1020 s 915 w 865 vs	335 vs	1.37	49.7

[a] $H_2(D_2)$ evolution during the reaction.

[b] The %-composition of all analyzed elements is given in the text of the experimental section.

[c] Based on Ti.

[d] Measured in nujol suspension; the observed characteristic absorption bands of coordinated THF are given.

[e] Measured in a polyethylene matrix; the observed Ti–Cl stretching vibration modes.

[f] Mol gas/Ti (D_2 61.6, HD 33.5, H_2 4.7%), 0.79 D/Ti.

[g] H_2 absorption.

4.7. Preparation of 2 from Ph_2CO and 1 in THF

A solution of 0.547 g (3.0 mmol) of Ph_2CO and 0.205 g of n-$C_{19}H_{40}$ (internal standard for GC) in 10 ml of THF was introduced from a gas-tight syringe into a stirred suspension of 0.460 g (3.4 mmol) of **1** (Table 2, entry 3) in 10 ml of THF. The suspension was stirred at room temperature for 7 h, during which evolution of 31.8 ml H_2 (1.3 mmol; 0.38 mol H_2/mol Ti) was recorded [9*]. The mixture was treated with 2 M HCl and the aqueous layer extracted with ether. The extract was analyzed by GC which revealed that 0.354 g of **2** (71% yield) and 18 mg (3%) of Ph_2CO had been formed.

4.8. Preparation of 2 from Ph_2CO and 1 in toluene

The reaction was carried out and the products analyzed in the same way as for the reaction in THF above. A solution of 0.750 g (4.1 mmol) of Ph_2CO in 10 ml of toluene and one of 0.53 g (3.9 mmol) of **1** (Table 2, entry 3) in 10 ml of toluene were mixed. The reaction time was 4 days, during which 24.6 ml of H_2 were liberated (0.24 mol H_2/mol Ti). The mixture was filtered and the isolated solid washed with toluene and dried under high vacuum to give 0.59 g of TiOCl (91%). EA (%): C 23.41, H 2.30, Cl 19.87, Ti 28.92 (Ti : Cl = 1 : 0.93). During hydrolysis of the solid, no gas was evolved, showing that the oxidation state of titanium is not less than +3 [13]. IR spectrum (Nujol): ν = 1015s and 860s (metal coordinated THF), broad absorption in the range of 400–800 cm^{-1} (Ti–O bonds?). From these results, it is judged that the solid is [TiOCl(THF)$_x$]. The filtrate was hydrolyzed and worked up as described above for the reaction in THF. The ether extract was analyzed by GC and found to contain 0.306 g (45% yield) of **2** and 9 mg of Ph_2CO.

4.9. Preparation of 2 from Ph_2CO and D-1 in THF

A solution of 0.912 g (5.0 mmol) of Ph_2CO and 0.955 g of n-$C_{19}H_{40}$ (internal standard for GC) in 10 ml of THF was added dropwise from a gas-tight syringe (through a septum) to a stirred suspension of 0.715 g (6.1 mmol) of D-**1** (Table 2, entry 4) in 50 ml of THF. The gas evolution during the reaction was monitored with an automatic gas burette [9*] connected directly to the reaction flask. At specific times, 2.0 ml samples were taken from the stirred suspension with a syringe and hydrolyzed with a saturated Na_2CO_3 solution. The amount of **2** in ether extracts was quantitatively determined by GC by use of the n-$C_{19}H_{40}$ as internal standard. Subsequently **2** served as the internal standard for the quantitative analysis of Ph_2CO, **4**, Ph_2CHOH and Ph_2CH_2 by HPLC. The data for the variation in the concentration of **4** and **2** through the reaction are presented graphically in Fig. 6. In all the samples only a small amount of Ph_2CHOH and Ph_2CH_2 (4–5%) could be detected. In the first sample, even after a reaction time of 5 min, only 4.7% of the initial amount of Ph_2CO was present. After a reaction time of 4 h at room temperature, 70 ml of gas (Fig. 6) had been evolved with the composition (MS analysis): 63.7% D_2, and 36.3% HD. Subsequently, the reaction mixture was heated for 40 min under reflux, during which the conversion to **2** increased from 74 to 87%.

4.10. Preparation of 2 from 5 and 1 in an n-hexane / THF mixture

The reaction was conducted and the product mixture analyzed as described for the reaction with Ph_2CO in THF, starting from 0.66 g (5.0 mmol) of **1** (Table 2, entry 3) in 10 ml of n-hexane and 0.8 ml (1.01 g; 4.3 mmol) of **5**. After reaction for 48 h 43.1 ml of H_2 were evolved, and the conversion to **2** reached 57 mol% as determined by GC. At this point 5 ml of THF were added and the mixture was stirred for a further 50 min at room temperature. An additional 23.4 ml of H_2 was liberated (total amount of H_2 evolved: 0.55 mol H_2/mol Ti). Hydrolysis of the reaction mixture and subsequent work-up afforded 0.62 g (84% yield) of **2** with a purity of 97.9% (GC analysis).

4.11. Preparation of 6 from cyclohexene, CCl_4 and 1 in THF

A solution of 0.30 ml (0.50 g; 3.1 mmol) of CCl_4 in 5 ml of THF was added dropwise from a syringe (through a septum) to a stirred suspension of 0.69 g (5.0 mmol) of **1** (Table 2, entry 3) in a mixture of 5.0 ml (49 mmol) of cyclohexene and 10 ml of THF. The gas evolution [9*] stopped after 40 min and corresponded to 0.61 mol H_2/mol CCl_4 (GC/MS analysis). After 3 h of stirring at RT, the volatile components of the reaction mixture were removed by distillation under vacuum and condensation in a cold trap. The distillate was analyzed by GC and GC/MS, and 0.348 g (68%) of **6** were found. The residue from the distillation gave, after hydrolysis and subsequent work-up, an additional 26 mg (5%) of **6**.

4.12. Preparation of 6 from cyclohexene, CCl_4, MgH_2^* and a catalytic amount of $TiCl_3(THF)_3$

A solution of 0.50 ml (5.0 mmol) of CCl_4 in 5 ml of THF was added dropwise from a syringe (through a septum) to a stirred suspension of 5.4 mmol of MgH_2^* [2a] in a mixture of 0.25 mmol of [$TiCl_3(THF)_3$] [41], 5.0 ml (49 mmol) of cyclohexene, and 25 ml of THF. The gas evolution [9*] stopped after 10 h, and corresponded to 0.85 mol H_2/mol CCl_4. The volatile components of the reaction mixture were then removed by distillation under vacuum condensed into a cold trap. The distillate was analyzed by GC, and 442 mg (54%) of **6** were found.

4.13. Catalytic synthesis of LiH with 1 as a catalyst

The reaction flask containing a suspension of 0.14 g (20 mmol) of Li powder in 20 ml of THF was evacuated, filled to atmospheric pressure with H_2, and connected to a 0.5 l automatic gas burette [9*] that also contained H_2. To the stirred suspension was added 0.15 g (1.1 mmol) of **1** (Table 2, entry 5); the H_2 absorption began immediately after the addition of the catalyst and stopped after 15 h and uptake of 236 ml of H_2 (0.49 mol H_2/mol Li). The solid was filtered off, washed with THF and dried in vacuum to give 0.24 g of a grey pyrophoric powder. IR (Nujol): 1100–500 cm^{-1} (br., LiH); 0.21 g of the LiH on protolysis with EtOH gave 436 ml of gas containing 99.2% H_2 (MS).

4.14. Preparation of 7 from Ph_3P, CCl_4 and 1; 8 from 7 and Ph_2CO

A solution of 0.50 ml (0.84 g; 5.5 mmol) of CCl_4 in 5 ml of toluene was added dropwise to a stirred suspension of 0.73 g (5.5 mmol) of **1** (Table 2, entry 3) and 1.49 g (5.7 mmol) of Ph_3P in 5 ml of toluene. The exothermic reaction was accompanied by evolution of 46 ml of gas. After 30 min of stirring, a solution consisting of 0.91 g (5.0 mmol) Ph_2CO in 5 ml of toluene was added to the brown reaction mixture, whereupon a black suspension was formed. After 8 h of stirring, the mixture was hydrolyzed and the aqueous layer extracted with ether. After removal of the solvents by distillation under vacuum, the residual yellow oil was dissolved in 50 ml of toluene. This toluene solution was analyzed by GC (with n-$C_{19}H_{40}$ as an internal standard) and GC/MS and shown to contain 10.1 mg (1.5 mmol) of **2** and 36 mg (1.5 mmol) of **8**. MS (70 eV), m/z: 182 [Ph_2CO], 248 [**8**], 332 [**2**], 278 [Ph_3PO]. ^{31}PNMR ($CDCl_3$): $\delta = 29.01$.

TABLE 3. Tetraphenylethene (**2**) obtained from the reaction of D-1 (D-1′) in solution with either Ph_2CO, Ph_2CCl_2 or Ph_2CS in THF at 0°C

D-1′ (mmol)	Reaction partner (mmol)	D_2/Ti	**2** (%)	Ti component
6.7	Ph_2CO (7.1)	0.27	47	TiOCl [a]
6.7	Ph_2CCl_2 (7.0)	0.37	74	not analyzed
6.7	Ph_2CS (7.0)	0.36	61	TiSCl [b]

[a] 0.128 g of TiOCl were isolated by centrifuging the reaction mixture. EA (%): Ti 36.64, Cl 27.16, C 20.13, H 3.89 IR: 1020 and 870 cm^{-1} (coordinated THF).

[b] 0.551 g of TiSCl were isolated by filtering the reaction mixture. EA (%): Ti 27.15, Cl 14.45, S 21.36 C 23.23, H 3.90. IR: 1010 and 850 cm^{-1} (coordinated THF).

4.15. Preparation of 2 from D-1′ and Ph_2CO, Ph_2CCl_2 or Ph_2CS in THF at 0°C (general procedure)

A solution of 7.0 mmol each of Ph_2CO, Ph_2CCl_2 and Ph_2CS in 10 ml of THF was added from a gas-tight syringe to a stirred solution of **D-1′** containing 6.7 mmol of Ti 5.4 mmol of D, 22.0 mmol of Mg and 45.9 mmol of Cl in 100 ml of THF (see preparation of **D-1**) maintained at 0°C. After the D_2 evolution stopped [9*], the resulting product mixture was analyzed as described for the reaction of **1** with Ph_2CO in THF. The results of the experiments are listed in Table 3.

4.16. Preparation of $[TiCl_3(THF)_3]$ from D-1′ and $[TiCl_4(THF)_2]$

A solution of 5.03 g (15 mmol) $[TiCl_4(THF)_2]$ in 50 ml of THF was added dropwise with stirring during 30 min to a stirred solution of 100 ml of the D-1′ solution in THF described above (containing 6.7 mmol of Ti, *etc.*). The D_2 evolution [9*] began immediately after the addition of the reagent, and after 4 h gave a final volume of 62.4 ml gas, containing 88.9% of D_2 (0.37 mol D_2/mol **D-1**; verified by MS). Upon concentration of the reaction mixture to 50 ml, a pale-blue precipitate separated out. The precipitate (5.3 g) was isolated and identified as $[TiCl_3(THF)_3]$ on the basis of the elemental analysis (Ti 12.34, Cl 27.41, C 37.46, H 6.42%) and the IR spectrum (1010 and 850 cm^{-1}, coordinated THF).

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