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# Low coordinated titanium(III) alkyl – molecular and surface – complexes: detailed structure from advanced EPR spectroscopy

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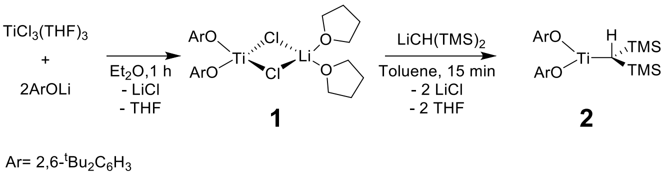
**Abstract:** The structure of paramagnetic surface species is notoriously difficult to determine. For Ti(III) centers related to Ziegler-Natta catalysis, we demonstrate here that detailed structural information can be obtained by advanced EPR spectroscopy and DFT computations, benchmarked on molecular analogues. The hyperfine sublevel correlation (HYSCORE) spectra obtained after reaction with $^{13}$C-labelled ethylene provides information about the coupling for a proton in the first coordination sphere of Ti(III) as well as significant $^{13}$C hyperfine coupling and thereby allows structural assignment of the surface species.

Titanium(III) alkyl species are proposed key intermediates in polymerization and depolymerization processes, from Ziegler-Natta (ZN) catalysis[1] to silica-supported titanium hydrides.[2] However, obtaining unambiguous characterization of these active sites has been a grand challenge in the past sixty years because characterizing paramagnetic titanium(III) species remains a difficult endeavor, in particular for complex multi-site heterogeneous catalysts. With a d$^1$ electronic configuration, EPR spectroscopy appears as an ideal tool to identify Ti(III) species and to probe their coordination environment, especially with the emergence of advanced EPR methods.[3] In fact, recent studies allowed the identification of Ti(III) sites in ZN catalyst activated with $Et_3Al$[4] or even to unravel the local structures of the $Ti^{3+}$ sites immobilized on chlorinated alumina.[5]

Silica-supported metal hydrides prepared by surface organometallic chemistry (SOMC),[6] display unprecedented reactivities such as the low-temperature activation and catalytic conversion of alkanes[2c, 7] as well as ethylene polymerization and depolymerization.[2a, 2b] In the case of titanium, it has been proposed that the surface species are constituted of titanium(IV) hydrides as well as titanium(III) species.[8] While the nature of these Ti(III) species is still not fully elucidated their involvement in ethylene polymerization has been demonstrated,[2a, 2b] suggesting ($\equiv$SiO)$_2$Ti(III)–R as a plausible propagative species. Therefore, isolating and characterizing Ti(III) alkyl species, which are potential analogues of putative active sites in supported catalysts, appears necessary to unambiguously establish the spectroscopic signature of these sites. Only a few examples of titanium(III) alkyl species have been reported due to their intrinsic relative instability.[9] Most of them involve cyclopentadienyl ligands,[10] though there are few exceptions.[11] Nevertheless, there are no reports of titanium(III) alkyl species using alkoxide ligands, that would constitute reasonable models for surface titanium(III) alkyl species. We reason that sterically shielding ligands would avoid the formation of ate or multinuclear complexes and that tri-tert-butoxysiloxy ligands, mimicking the silica surface,[12] or larger aryloxy ligands[13] could afford good models of the surface titanium(III) alkyl sites.

Here, we report the synthesis and characterization of a bis-(aryloxide) titanium(III) alkyl species, (ArO)$_2$Ti[CH(TMS)$_2$] (Ar= 2,6-$^t$Bu$_2$C$_6$H$_3$), and a bis-(siloxide) titanium(III) alkyl species (($^t$BuO)$_3$SiO)$_2$Ti[CH(TMS)$_2$](THF). These complexes constitute good models for silica- or related oxide-supported titanium(III) alkyl species. In particular, we disclose here a method combining pulsed EPR spectroscopy, DFT calculations and X-ray crystallography, allowing to unravel the local environment of Ti(III) centers via the localization of hydrogen in the first coordination sphere of Ti(III). We further apply this method to identify the presence of surface ($\equiv$Si$_2$O)($\equiv$SiO)$_2$Ti(III)–R species involved in the ethylene polymerization activity of the silica-supported titanium hydrides.

Salt metathesis of TiCl$_3$(THF)$_3$ with 2 equiv of ArOLi affords the ate–complex [(ArO)$_2$Ti($\mu$-Cl)$_2$Li(THF)$_2$], **1**, as pale green crystals in 84% yield (Scheme 1). Its molecular structure was confirmed by single crystal X-ray diffraction (ESI, Figure S7). Treatment of a toluene solution of **1** with 1 equiv. of [bis-(trimethylsilyl)methyl]lithium yields (ArO)$_2$Ti[CH(TMS)$_2$], **2**, as violet crystals in 66% yield (Scheme 1). Single-crystal X-ray diffraction on **2** reveals a tri-coordinated titanium(III) coordinated to two aryloxides and one alkyl ligand, in an overall distorted trigonal geometry (Figure 1a). The Ti-C$\alpha$ bond length (2.098(3) Å) is unusually short compared to [$\eta^1$-($^t$Bu)-(Ar)N][$\eta^3$-($t$Bu)(Ar)N]Ti[CH(TMS)$_2$] (Ti-C$\alpha$ = 2.137(7) Å),[11c] to [PhC(NSiMe$_3$)$_2$]$_2$TiMe (Ti-C$\alpha$ = 2.120(5) Å)[11a] or LTiMe$_2$ (Ti-C$\alpha$ = 2.123(3) Å and 2.131(3),[11b] LH = (2E,4E)-N2,N4-bis(2,6-diisopropylphenyl)pentane-2,4-diimine). Noteworthy, the hydrogen atom on the C$\alpha$ is found in the difference Fourier map and freely refined (i.e. not calculated). While the complex **2** and [$\eta^1$-($^t$Bu)-(Ar)N][$\eta^3$-($t$Bu)(Ar)N]Ti[CH(TMS)$_2$] have a similar C$\alpha$-H bond lengths (0.93(4) vs. 0.938 Å), the Ti-C$\alpha$-H angles significantly differ (95(2) vs 105(2)°).



**Scheme 1.** Synthesis of molecular complexes **1** and **2**.

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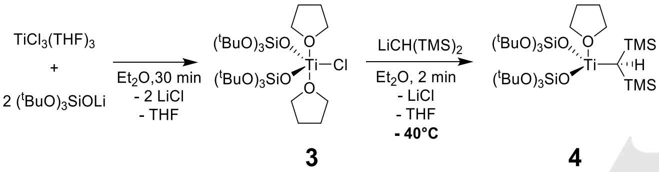
We have also investigated the use of tri-tert-butoxysiloxy ligands, which can provide molecular analogues with ligands closer to the corresponding putative silica-supported titanium(III) alkyl species. Treatment of $TiCl_3(THF)_3$ with 2 equiv. of $(^tBuO)_3SiOLi$ yields the molecular complex $((^tBuO)_3SiO)_2TiCl(THF)_2$, **3**, isolated as violet crystals in 70% yield (Scheme 2). The single crystal X-Ray structure analysis of **3** shows a titanium(III) center with a trigonal bipyramidal coordination with two THF molecules in the apical positions (ESI, Figure S8). The complex $((tBuO)_3SiO)_2Ti[CH(TMS)_2(THF)]$, **4**, is isolated as pale blue crystal in 45% yield by reacting **3** with $LiCH(TMS)_2$ (Scheme 2). **4** is highly reactive and decomposes in solid state and in solution above –15 °C. The single crystal X-ray diffraction structure of **4** shows two crystallographically independent molecules in the unit cell. The analysis of the structure reveals a neutral titanium(III) complex with a trigonal pyramidal geometry with the THF ligand in the apical position (Figure 1b). The Ti-Cα (2.184(6) and 2.147(8) Å) bond length is unusually long compared to molecular complex **2** (ca. 0.1 Å longer).



**Scheme 2.** Synthesis of molecular complexes **3** and **4**.

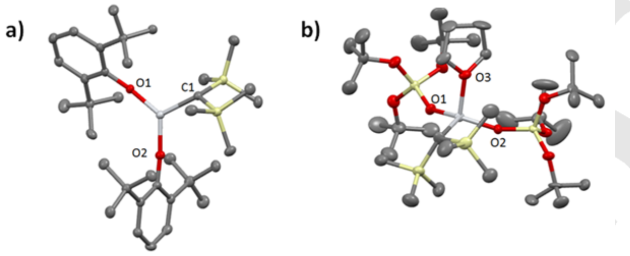


**Figure 1.** Thermal ellipsoid (50% probability) of the crystal structures of a) **2** b) one of the 2 independent molecules in the unit cell of **4**.

We further characterize **2** and **4** by continuous wave (CW) and pulsed EPR spectroscopy (details in ESI, part B). The CW EPR spectra show an $S = 1/2$ system with rhombic g-tensors, $g_x = 1.8555$, $g_y = 1.9388$, $g_z = 2.0018$ and $g_x = 1.9193$, $g_y = 1.9429$, $g_z = 1.9826$, for **2** and **4**, respectively (Figure 2). The compound **2** features a significantly larger *g*-anisotropy, *g*-distribution and isotropic $Ti^{3+}$ hyperfine coupling (see Tables. 1, S1 & S3), indicative of a weaker ligand field with a high s-orbital contribution to the spin density centered on Ti. While not resolved in the CW EPR spectra, weakly coupled $^1H$ are observed for both **2** and **4** in HYSCORE (Figures 2 & S1). The most intense feature in the spectra are the ridges perpendicular to the diagonal at the proton Zeeman frequency of 15.2 MHz. Simulation of the ridges reveals isotropic hyperfine couplings of –1.0 ± 0.5 MHz and 5.5 ± 0.5 MHz for **2** and **4**, respectively, with anisotropies of (–6.0, –6.0, 12.0) MHz and (–4.5, –4.5, 9.0) MHz (see Table 1). Using the point-dipole approximation allows us to estimate $Ti^{3+}\ldots H$ distances of 2.33 ± 0.15 Å and 2.59 ± 0.10 Å for **2** and **4**, respectively. For complex **2**, the closest proton from the aryloxide ligands has a distance of 2.7497(6) Å to the Ti center while the distance to the H on Cα is 2.36(4) Å. This indicates that the latter proton is observed, assuming that molecular complexes display similar geometry both in solid-state and in solution. This is even more pronounced with complex **4**, as the closest proton to the Ti(III) center is the one on the Cα of the alkyl ligand (calculated at 2.5439(11) and 2.6348(11) Å for the two independent molecules) while the second closest is the one from the Cα of the THF (3.1313(11) Å).

In order to corroborate this assignment, we also computed the hyperfine coupling of the proton on Cα by DFT. The isotropic couplings of the optimized structures are 0.1 and 3.2 MHz for **2** and **4**, respectively, in agreement with the experimental values observed in frozen solution (–1.0 ± 0.5 and 5.5 ± 0.5 MHz for **2** and **4**, respectively). DFT computed spin-dipole contributions {(–2.8, –6.0, 8.8 MHz) and (–4.1, –5.2, 9.2 MHz) for **2** and **4**, respectively} are also consistent with the experimental ones and lead to HYSCORE simulations almost as good as the best fit (Figure S2, Table S2). As the Ti-H distances can vary in appreciable amounts (Table 1), we also calculated the corresponding isotropic coupling and spin dipole contribution directly from the geometry of the X-ray structure. In short, the isotropic coupling is mostly governed by the location of the hydrogen atoms with respect to the SOMO; it is small and varies only little for compound **2** because the hydrogen atom lies in the nodal plane of the SOMO. However, it varies greatly for **4** because the hydrogen atom lies in or out of the nodal plane, depending on the conformation of the alkyl chain (ESI – Figure S4 and Table S5). The better agreement between the isotropic hyperfine coupling calculated from the DFT-optimized structure and the experimentally observed coupling suggests that the DFT-optimized structure is closer than the X-ray structure to the structure experimentally observed in the frozen solution. However, this has to be taken with care, since previous pioneering work on $Ti(III)(OH_2)_6^{3+}$ has shown that the difference in hyperfine parameters and energy can be very subtle.[14] Overall, as a result of their different coordination number, complex **2** displays a shorter Ti-Cα bond than found in complex **4** (2.098(3) Å vs 2.184(6) and 2.147(8) Å), inducing different $Ti(III)\ldots H$ distances as evidenced by X-ray crystallography (2.36(4) Å vs. 2.5439(11) and 2.6348(11) Å for **2** and **4**, respectively) and confirmed by HYSCORE ($Ti^{3+}\ldots H$ distances of 2.33 ± 0.15 Å and 2.59 ± 0.10 Å for **2** and **4**, respectively). In these systems, HYSCORE, combined with DFT calculations, can hence allow for the determination of interatomic distances otherwise available only from single crystal XRD studies, which are not applicable to metal-oxide supported species. This makes HYSCORE ~~is~~ a powerful tool for localization of the hydrogen atom in the first coordination sphere of Ti(III) alkyl species and for probing the influence of the local geometry/coordination of the Ti(III) center on the Ti(III)-Alkyl bonds.

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**Table 1.** Hyperfine tensor parameters obtained by fits of the HYSCORE spectra and DFT calculations, Ti – H distances obtained from HYSCORE spectra, by XRD (for molecular complexes) and by DFT optimization. Extended table can be found in the ESI (Table S1).

| | Compound **2** | Compound **4** | $(\equiv SiO)_2TiR$ |
|---|---|---|---|
| *A* tensor ($^1H$), spectral fit[a] (MHz) | $A_{iso}$ = -1.0<br>$A_{dip}$ = [-6.0; -6.0; 12.0] | $A_{iso}$ = 5.5<br>$A_{dip}$ = [-4.5; -4.5; 9.0] | $A_{iso}$ = 5.5<br>$A_{dip}$ = [-4.0; -4.0; 8.0] |
| *A* tensor ($^1H$), DFT (MHz) | $A_{iso}$ = 0.1<br>$A_{dip}$ = [-2.8; -6.0; 8.8] | $A_{iso}$ = 3.2<br>$A_{dip}$ = [-4.1 -5.2 9.2] | $A_{iso}$ = 5.7<br>$A_{dip}$ = [-4.6; -2.2; 6.8] |
| *r*(Ti–H)[b], HYSCORE (Å) | 2.33±0.15 | 2.59±0.10 | 2.69±0.21 |
| *r* (Ti–H), X-ray (Å) | 2.36±0.04 | 2.5439±0.0011<br>2.6348±0.0011 | |
| *r*(Ti–H), DFT (Å) | 2.449 | 2.523 | 2.658 |

[a] The uncertainty of the spectral fit is ±0.5 MHz.

[b] The uncertainty given is the variance of the errors resulting from [a] and from the non-axiality of the dipolar hyperfine coupling observed in DFT

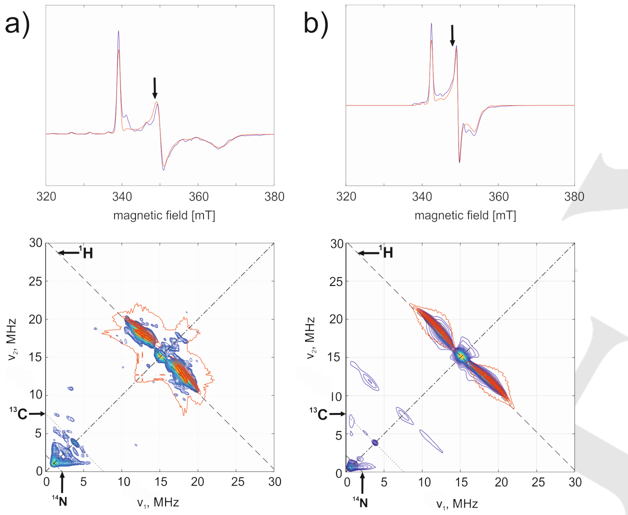

**Figure 2.** EPR spectroscopic characterization of compounds a) **2** and b) **4**. Top: CW EPR spectrum (blue) and simulation (red). Bottom: HYSCORE spectra (blue to yellow) with simulation (red), the (-,+) quadrants are shown in Figure S5. Simulation parameters (see text) are summarized in Table S1. HYSCORE experiments were performed at τ = 128 ns at magnetic field positions indicated with an arrow in the EPR spectra (top). Antidiagonal lines in the HYSCORE spectra indicate Zeeman frequencies of $^1H$ (dashed), $^{13}C$ (dotted) and $^{14}N$ (dashed dotted). The weak antidiagonal ridge centred at 7.5 MHz is an aliased artefact from imperfect phase cycling.

We thus investigate the silica-supported titanium hydrides, $TiH@SiO_2$,[2c, 8c] a complex system with multiple species, e.g. surface Ti(IV) and Ti(III) hydride species, which have been proposed to promote ethylene polymerization.[2a, 2b] In order to probe the structure of Ti(III) species, we apply the same methodology as described above for molecular complexes to these Ti(III) sites contacted with $^{13}C$-dilabeled ethylene. Weakly coupled $^1H$ is again observed by HYSCORE. Simulation of the HYSCORE spectra reveals an isotropic coupling of 5.5 ± 0.5 MHz (Figure 3b, right), which is the same (within experimental error) as the one found for the molecular complex **4**. Furthermore, the anisotropic part is (–4.0, –4.0, 8.0 MHz) and provides a $Ti^{3+}\ldots H$ distance of ca. 2.69 ± 0.21 Å. Similar data are also obtained using DFT calculations on a small cluster model,[15] where the Ti(III) is in a tetrahedral geometry with two siloxide ligands and a coordinated siloxane bridge (Figure 3b) with $Ti^{3+}\ldots HC\alpha$ of 2.66 Å and a calculated isotropic coupling of 5.69 MHz for one of the two protons. According to DFT calculations the barrier to rotation of the alkyl group is ca. 2.3 kcal mol$^{-1}$, hence this movement should be frozen out under measurement conditions (10 K). According to DFT calculations, the experimentally observed hyperfine coupling is not consistent with an OH-group, coordinated to the Ti(III) center (calculated isotropic coupling of 17.9 MHz, Figure S3 and Table S4). Note that also calculations for a model without a coordinated siloxane bridge to Ti(III) lead to a significantly different isotropic coupling of –3.6 MHz, supporting the presence of a siloxane bridge coordinated to Ti(III) in the observed alkyl species. In fact, according to DFT calculations, the isotropic hyperfine coupling to the proton in the α-position is remarkably sensitive to the Ti…O distance (i.e. the distance between the Ti center and the oxygen atom from the siloxane bridge) and decreases rather smoothly as this distance is elongated (Table S6). Together with the $^{13}C$ hyperfine coupling observed by HYSCORE (Figure 3c, right), all these data point towards the presence of $(\equiv Si_2O)(\equiv SiO)_2Ti(III){-}R$ as (one of) the propagative species of the silica-supported titanium hydrides.

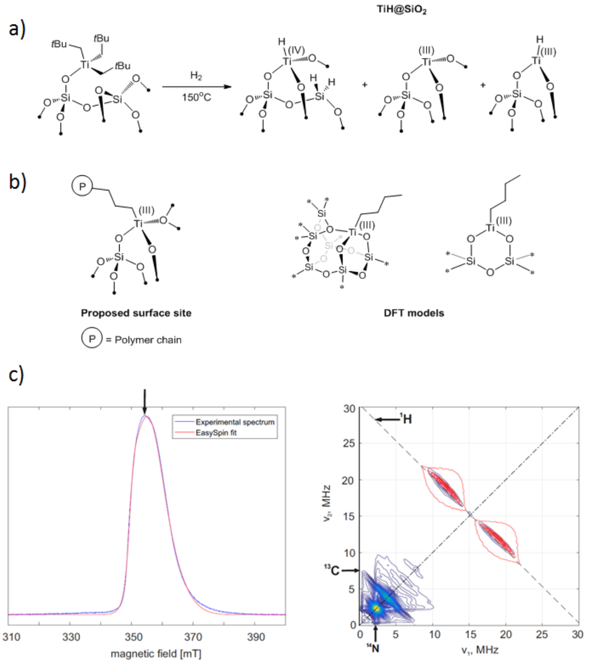

**Figure 3.** a) Synthesis of the silica-supported titanium hydrides b) Identified Ti(III)-alkyl species formed upon contacting $TiH@SiO_2$ with $^{13}C$-dilabeled ethylene and DFT models of the surface species, where OH groups were replaced by asterisks in the figure for sake of clarity. c) Echo-detected EPR spectrum (blue) and simulation (red, parameters in Tab. S1) (left); HYSCORE spectrum (blue to yellow) and simulation (red, parameters in Tab. S1) (right). HYSCORE measurement was performed at τ = 128 ns at field position, indicated by an arrow in the EPR spectrum. Antidiagonal lines indicate Zeeman frequencies of $^1H$ (dashed), $^{13}C$ (dotted) and $^{14}N$ (dashed dotted).

In conclusion, we have reported the synthesis of two low coordinated bis(alkoxide) titanium(III) alkyl molecular complexes, fully characterized by X-ray crystal structure analysis and EPR spectroscopy. Combining X-ray crystallographic data, HYSCORE spectroscopy, and DFT calculations has allowed us to establish a methodology to characterize and to track fine changes in the location of the $\alpha$-hydrogen atom of alkyl chains bound to Ti(III) sites. This methodology applied to the silica-supported titanium hydride polymerization catalyst provides evidence on the presence of tetra-coordinated $(\equiv Si_2O)(\equiv SiO)_2Ti(III)$–Alkyl surface species, as a key intermediate in olefin polymerization. We are currently investigating this approach to characterize a broad range of supported catalysts with paramagnetic centers.

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**Keywords:** EPR • HYSCORE • molecular models • surface chemistry • titanium(III) alkyl

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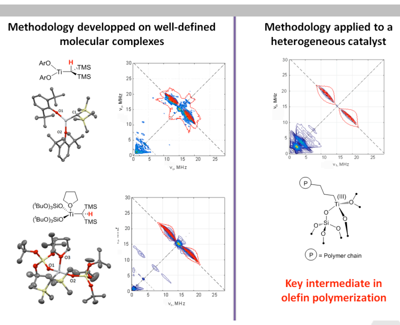
# COMMUNICATION

**HIGH SCORE.** 2D HYSCORE EPR augmented with DFT calculations allows detecting and characterizing Ti(III) alkyl species, in particular in silica-supported ethylene polymerization catalysts.



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**Low coordinated titanium(III) alkyl – molecular and surface – complexes: detailed structure from advanced EPR spectroscopy**