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# Tris(2,6-diisopropylphenolato)titanium(IV) Dihydridodiorganylborates: Synthesis and Structures[‡]

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*Dedicated to Professor Dr. S. G. Shore on the occasion of this 80th birthday*

**Keywords:** Titanium / Boron / Borates / Structure elucidation / Agostic interactions

The reactions of tris(2,6-diisopropylphenolato)titanium(IV) chloride with alkali-metal dihydridodiorganylborates $M(H_2BR_2)$ (M = Li, K; R = Me, $C_6H_{11}$, $CMe_3$; $BR_2 = BC_5H_{10}$, $BC_8H_{14}$) led to the corresponding titanium dihydridodiorganylborates. However, in almost all cases byproducts such as (2,6-diisopropylphenolato)diorganylboranes, triorganylboranes, diorganylboranes, diborane and tetrakis(2,6-diisopropylphenolato)titanium(IV) were also generated. $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3Ti(H_2BR_2)$ compounds also resulted from the interaction of methyltris(2,6-diisopropylphenolato)titanium, for example, with catecholborane. In addition to the formation of tris(2,6-diisopropylphenolato)catecholboratotitanium(IV), *B*-methylcatecholborane was also formed The reaction of potassium dihydro-9-cyclooctylborate with 2,6-bis(2,2-di-*tert*-butyl-2-hydroxyethyl)pyridinetitanium dichloride ($LTiCl_2$) led to the complex $LTi(H_2BC_8H_{14})_2$. This compound showed no agostic C–H···Ti interaction in contrast to $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3$-$TiH_2BC_8H_{14}$ and the corresponding titanium dihydridobis(cyclohexyl)borate.

## Introduction

The existence of titanium tetrakis(tetrahydrido)borate, $Ti(BH_4)_4$, has so far not been proved. Attempts to synthesize it has led to green $Ti(BH_4)_3$,[2] which can be sublimed in vacuo but decomposes above –30 °C. The thermal stability of titanium tetrahydridoborates can be greatly improved by replacing the $BH_4$ groups by other substituents. For instance, the violet $Cp_2Ti(BH_4)$ is stable up to 120 °C.[3] Shore and co-workers have shown that bis(cyclopentadienyl)titanium dihydridodiorganylborates are stable species that are also characterized, depending on their structure, by β-agostic C–H···Ti interactions.[4] The introduction of aryl–O groups at the Ti atom allows not only the synthesis of $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_2Ti(BH_4)_2$ and $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3Ti(BH_4)$, but also the hydride $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3TiH$, which can be isolated as $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3TiH\cdot PMe_3$.[5] Moreover, if 6,6′-di-*tert*-butyl-4,4′-dimethyl-2,2′-methylenebis(phenolate) is used as the ligand L, the titanium(IV) bis(tetrahydrido)borate $LTi(H_3BH)_2$ can be isolated with $\mu_3$-$BH_4$ groups.[6]

In this report we describe several $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3Ti(H_2BR_2)$ compounds and their X-ray structures.

## Results

### Synthesis and Structure of $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3TiMe$

Steric shielding of the titanium centre in tris(phenolato)titanium(IV) compounds can be achieved by introducing bulky organyl groups such as methyl,[7] *tert*-butyl,[8–10] isopropyl[11,12] or phenyl groups[7,13,14] into the 2,6-positions of the phenolato ligand. In this study we chose tris(2,6-diisopropylphenolato)titanium(IV) chloride[5] (**1**), as the starting material, which is readily available, as shown in Equation (1). Compound **1** can be used for the preparation of methyltris(2,6-diisopropylphenolato)titanium(IV) (**2**); see Equation (2), which is a precursor of the methylhydridoborate **4**, as shown in Equation (4), whereas the reaction of **1** with $LiBH_2R_2$ should yield $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_3Ti(H_2BR_2)$ (**3**). So far, only the structures of five alkyltris(organyloxo)titanium compounds are known,[6,8,9] amongst them methyltris(2,6-diphenylphenolato)titanium(IV)[8] and MeTi[N-$(SiMe_3)_2]_3$.[15]

The methyl derivative **2** is susceptible to hydrolysis and photolytic decomposition. It turns black at room temperature within a few hours. NMR signals for the methyl group bonded to the Ti atom are found at $\delta_H$ = 1.92 ppm and $\delta_C$ = 54.5 ppm (Table 1). These atoms are better shielded than those of $(Me_2PCH_2)_2TiMe_4$ ($\delta_H$ = 1.08 ppm, $\delta_C$ = 49.2 ppm).[16]

Single crystals of compound **2** grown from hexane at –30 °C are orthorhombic with the space group *Fdd*2. The molecular structure of **2** is depicted in Figure 1. Although

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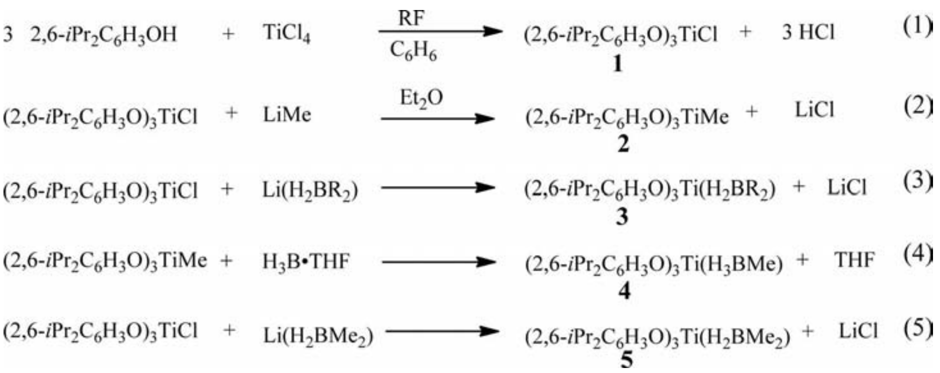


$$3\ 2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH} + \mathrm{TiCl}_4 \xrightarrow[\mathrm{C_6H_6}]{\mathrm{RF}} \underset{\mathbf{1}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCl}} + 3\ \mathrm{HCl} \quad (1)$$

$$(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCl} + \mathrm{LiMe} \xrightarrow{\mathrm{Et_2O}} \underset{\mathbf{2}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiMe}} + \mathrm{LiCl} \quad (2)$$

$$(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCl} + \mathrm{Li(H_2BR_2)} \longrightarrow \underset{\mathbf{3}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti(H_2BR_2)}} + \mathrm{LiCl} \quad (3)$$

$$(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiMe} + \mathrm{H_3B{\bullet}THF} \longrightarrow \underset{\mathbf{4}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti(H_3BMe)}} + \mathrm{THF} \quad (4)$$

$$(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCl} + \mathrm{Li(H_2BMe_2)} \longrightarrow \underset{\mathbf{5}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti(H_2BMe_2)}} + \mathrm{LiCl} \quad (5)$$

Table 1. $^1$H and $^{13}$C NMR signals for compounds **1** and **2** in $C_6D_6$ solution.

| | $\delta$ [ppm] | | | | | |
|---|---|---|---|---|---|---|
| | CH*Me*$_2$ | C*H*Me$_2$ | *m*-H | *p*-H | Ti*Me* | |
| $^1$H NMR (**1**) | 1.13 [d, $^3J(^1H,^1H)$ = 6.8 Hz, 36 H] | 3.43 [sept, $^3J(^1H,^1H)$ = 6.8 Hz, 6 H] | 6.98–7.07 [m, 9 H] | | | |
| $^1$H NMR (**2**)[a] | 1.17 [d, $^3J(^1H,^1H)$ = 6.8 Hz, 36 H] | 3.60 [sept, $^3J(^1H,^1H)$ = 6.8 Hz, 6 H] | 7.08 [d, $^3J(^1H,^1H)$ = 7.4 Hz, 6 H] | 6.95 [t, $^3J(^1H,^1H)$ = 7.2 Hz, 3 H] | 1.92 | |
| | CH*Me*$_2$ | *C*HMe$_2$ | *m*-Ph | *p*-Ph | *o*-Ph | *i*-Ph |
| $^{13}$C NMR (**1**) | 23.06 | 27.52 | 123.01 | 123.76 | 137.4 | 163.06 |
| $^{13}$C NMR (**2**) | 23.31 | 27.88 | 123.16 | 123.38 | 137.4 | 161.08 |

[a] $\delta_C$(MeTi) = 54.54 ppm.

all of the hydrogen atoms could be located in the difference Fourier map, those in the Me groups did not refine well. Therefore they were included in the final refinement with fixed CH bond lengths riding on their C atoms. The coordination sphere of Ti1 is a distorted tetrahedral with a $\psi$-$C_3$ axis through the Ti1 and C37 atoms. The O–Ti–O bond angles range from 113.4(2) to 114.9(2)° and the Ti–O bond lengths from 1.769(3) to 1.785(4) Å. A comparison of the structures of **2** and $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiBH}_4$[5] shows that the Me group needs less space than the $BH_4$ group. For the tetrahydroborate analogue of **2**, the O–Ti–O bond angles are on average 108.1° and the B–Ti–O bond angles are on average 110.8°.[5] Their Ti–O bond lengths are identical to those in the tetrahydroborate. The C–O–Ti bond angles are in the range 171.4(4)–173.1(4)° for **2** and 171.2(5)–175.6(5)° for the tetrahydroborate. This indicates that the oxygen atoms can be considered as sp-hybridized, in accordance with the short C–O bonds and the Ti–O bonds. The Ti–C bond length in **2** is 2.074(7) Å, which is identical to that of the Ti–C bond in $(2,6\text{-}\mathrm{Ph}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiMe}$.[8] However, its Ti–C bond is significantly shorter than the Ti–C bond in $(i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCMe}_3$ [2.095(3) Å][5] or in $[(\mathrm{Me}_3\mathrm{Si})_2\mathrm{N}]_3$-TiMe [2.152(4) Å].[16] Clearly, the aryloxo groups shorten the Ti–C bond lengths due to the electron-withdrawing effect of the O(sp)-hybridized atoms.[17]

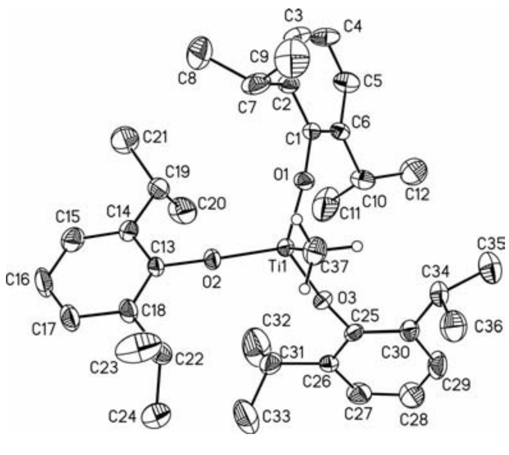


Figure 1. Molecular structure of methyl[tris(diisopropylphenolato)]-titanium(IV) (**2**). Thermal ellipsoids are drawn at the 50% probability level. CH hydrogen atoms have been omitted except for the Me group. Bond lengths [Å] and bond angles [°]: Ti1–O1 1.769(3), Ti1–O2 1.782(4), Ti1–O3 1.785(4), Ti1–C37 2.074(7), O1–C1 1.387(6), O2–C13 1.471(6), O3–C25 1.367(6), Ti1–C37 2.074(7); Ti1···H37B 2.559; O1–Ti1–O2 114.5(2), O1–Ti1–O3 113.4(2), O2–Ti1–O3 114.9(2), O1–Ti1–C37 103.6(2), O2–Ti1–C37 104.4(2), O3–Ti1–C37 104.4(2), C1–O1–Ti1 171.3(4), C13–O2–Ti1 173.1(4), C25–O3–Ti1 171.1(4), O1–C1–C2 117.3(5), O1–C1–C6 118.0(4), C1–C2–C3 115.7(5), C6–C1–C2 124.8(5), C3–C4–C5 120.3(6), C1–C6–C5 115.7(5), C5–C6–C10 123.0(5). Torsion angles [°]: Ti1–O1–C1–C2 96.3, Ti1–O2–C13–C14 –38.8, Ti1–O2–C13–C18 143.0, Ti1–O3–C25–C26 –113.7.

## Reactions of Tris(2,6-diisopropylphenolato)titanium Chloride with Alkali Metal Dihydridodiorganylborates

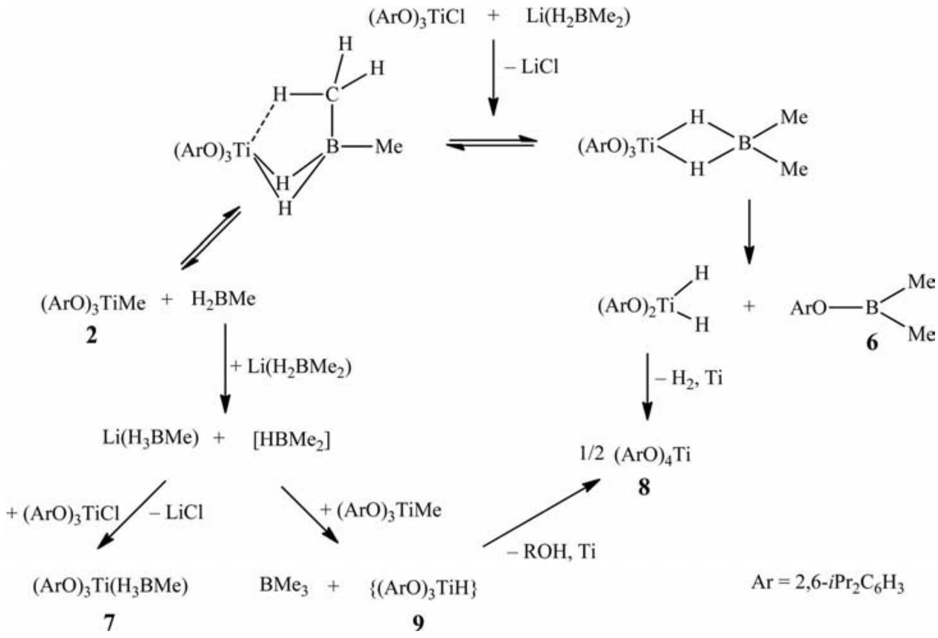
The reaction of **1** with lithium dimethyldihydridoborate in diethyl ether was expected to produce the titanium dihydridodimethylborate **5**; see Equation (5). Although compound **5** was formed, as shown by a triplet in the $^{11}$B NMR spectrum at $\delta$ = 5.6 ppm, $^1J(^1H,^{11}B)$ = 56 Hz, it was only a byproduct with a relative intensity of 4%. The main component in the solution turned out to be (2,6-diisopropylphenolato)dimethyborane (**6**; $\delta_B$ = 56.3 ppm, relative intensity 62%). A quartet at $\delta_B$ = 2.0 ppm [$^1J(^1H,^{11}B)$ = 64 Hz, 16% relative intensity] indicates the formation of $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti}(\mathrm{H}_3\mathrm{BMe})$ (**7**), which results partly from the presence of $\mathrm{LiH}_3\mathrm{BMe}$ as an impurity in the $\mathrm{LiH}_2\mathrm{BMe}_2$ used, but also as a result of ligand exchange according to Equation (6), which is supported by an NMR signal at $\delta_B$ = 86.9 ppm due to $\mathrm{BMe}_3$ (2%).

$$2\mathrm{Li}(\mathrm{H}_2\mathrm{BMe}_2) \rightarrow \mathrm{Li}(\mathrm{H}_3\mathrm{BMe}) + (\mathrm{LiH} + \mathrm{BMe}_3) \qquad (6)$$

The weak $^{11}$B NMR signals at –27.5 (4%) and –17.4 ppm (3%) are unresolved multiplets and could not be reliably assigned. More importantly, single crystals of $(i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_4\mathrm{Ti}$ (**8**) were isolated. This compound was characterized by its unit cell constants.[18] Scheme 1 shows possible reaction pathways.

Unexpected was the heterogeneous reaction of **1** with $\mathrm{K}[\mathrm{H}_2\mathrm{B}(\mathrm{C}_5\mathrm{H}_{10})_2]$[19,20] in pentane ($T$ = –110 to 20 °C). This reaction led to a single $^{11}$B NMR signal at 7.3 ppm, which we assigned to compound **10**; see Equation (7). The signal appears to be a triplet, however, it was not well resolved. Yellow crystals separated from the red filtrate at –30 °C, which proved to be the titaniumtetrakis(phenolate) **8**.[18] This shows that the dihydroborinate **10** disproportionates, most likely according to Equation (8). However, we were unable to isolate **10** by changing the solvent from pentane to THF or diethyl ether, or the temperature from –78 to –30 °C. The IR spectrum of the orange oily residue showed strong IR stretching bands at 2017 and 2181 cm$^{-1}$, which are typical of a dihydridoborinate. This result contrasts the easy preparation and crystal structure determination of bis(cyclopentadienyl)zirconium(IV) dihydridoborinate.[4,19]

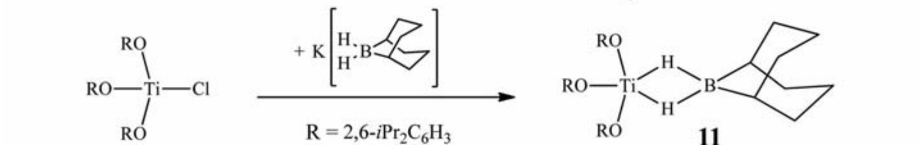
The reaction of **1** with $[\mathrm{K}(\mathrm{H}_2\text{-9-BBN})]$[20] in hexane is much less complicated. Yields of up to 70% of compound **11** ($\delta_B$ = 11.1 ppm) were obtained; see Equation (9). In addition, an $^{11}$B NMR signal at $\delta$ = 29.3 ppm was observed resulting from dimeric 9-borabicyclononane **12**; 17% intensity, see also Equation (10). However, compound **9** could not be isolated. An orange residue was isolated from the filtrate, which on treatment with $\mathrm{CH}_2\mathrm{Cl}_2$ yielded colourless crystals of $\mathbf{11}\cdot\mathrm{CH}_2\mathrm{Cl}_2$. In the supernatant solution only single sets of $^1$H and $^{13}$C NMR signals were observed, which we assigned to the titanium species **11**. This indicates that there is unhindered rotation about the Ti–O and Ti–H–B



Scheme 1.

$$(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiCl} + \mathrm{K}(\mathrm{H}_2\mathrm{BC}_5\mathrm{H}_{10}) \longrightarrow \underset{\mathbf{10}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti}(\mathrm{H}_2\mathrm{BC}_5\mathrm{H}_{10})} + \mathrm{KCl} \qquad (7)$$

$$4\,(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{Ti}(\mathrm{H}_2\mathrm{BC}_5\mathrm{H}_{10}) \longrightarrow 3\,\underset{\mathbf{8}}{(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_4\mathrm{Ti}} + \text{"}\mathrm{Ti}(\mathrm{H}_2\mathrm{BC}_5\mathrm{H}_{10})_4\text{"} \qquad (8)$$



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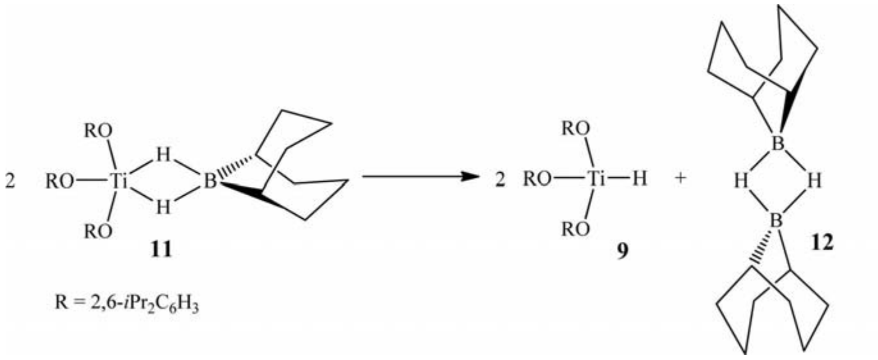

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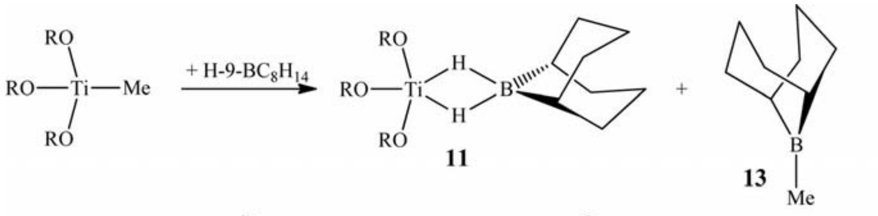

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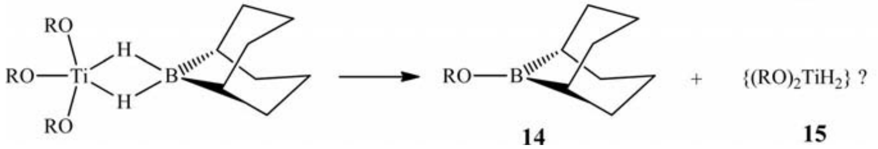


(12)

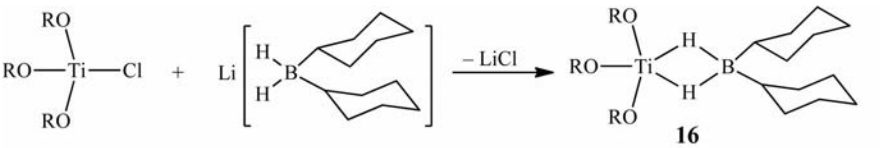
bonds at ambient temperature. A solution of **11** in deuteriotoluene also showed at –80 °C only one set of $^1$H and $^{13}$C NMR signals. Similar NMR spectra were recorded for the analogous [Cp$_2$Zr(9-BBN)] complex.[19] The presence of BH bonds is also manifested by a strong IR band at 2033 cm$^{-1}$. Compound **11**·CH$_2$Cl$_2$ was also characterized by X-ray crystallography.

Compound **11** also resulted from the treatment of compound **2** in diethyl ether with dimeric 9-borabicyclononane [HBC$_8$H$_{14}$]$_2$, (**12**); see Equation (11). This method was quite successful for the preparation of analogous zirconocene–9-BBN complexes.[19] The solution showed after 1 hour, in addition to the $^{11}$B NMR signal for (H-9-BBN)$_2$ at $\delta_B$ = 29.0 ppm, signals at $\delta$ = 88.9 (53% intensity) and 50.8 ppm (29%) for 9-methyl-9-borabicyclcononane (**13**) and 9-(2,6-diisopropylphenolato)-9-borabicyclononane (**14**), respectively; see Equations (11) and (12).[21] The relative intensities of the signals show that the formation of **13** occurs more rapidly than the formation of the ester **14**. Compound **14** provided single crystals for an X-ray structure determination. The expected titanium hydride **15** could not be isolated.

The homogeneous reaction of **1** with lithium bis(cyclohexyl)dihydridoborate[20] in diethyl ether yielded the titanium(IV) bis(cyclohexyl)dihydridoborate **16** within 4 hours almost quantitatively; see Equation (13). $^1$H and $^{13}$C NMR signals for compound **16** and one $^{11}$B NMR signal at $\delta$ = 15.0 ppm were observed both at room temperature and at –80 °C. Therefore there is free rotation of the C–O and Ti–H bonds. Also characteristic is the strong band at 2015 cm$^{-1}$ for a B–H stretching vibration. Although one should expect two bands from BH$_{2,\text{symm}}$ and BH$_{2,\text{asymm}}$, the observation of a single band is not unusual for bidentate bridging BH$_2$ units.[22] A weak band at 2708 cm$^{-1}$ points to the presence of an agostic Ti···H–C bond and this structural unit was identified in its X-ray structure determination.

All the tris(2,6-diisopropylphenolato)titanium dihydrodiorganylborates that we have described so far are prone to the formation of agostic β-Ti···C–H bonds.[23] To avoid such interactions we treated **1** with potassium dihydrido-di-*tert*-butylborate, as shown in Equation (14). In this case no β-Ti···C–H agostic bond was possible. Reaction (14), performed in diethyl ether resulted in a single $^{11}$B NMR signal at $\delta$ = 24.0 ppm for compound **17**. Its $^1$H-coupled NMR spectrum shows significant line-broadening but no sharp triplet. There was a second signal at $\delta_B$ = 81.6 ppm from the borane ($t$Bu)$_2$BH,[21] which results from the decomposition of compound **17**. The $^1$H and $^{13}$C NNR spectra of **17** exhibit only single sets of signals. Its IR spectrum shows two separate stretching frequencies at 2087 cm$^{-1}$ for $\nu$BH$_{2,\text{asym}}$ and at 2021 cm$^{-1}$ for $\nu$BH$_{2,\text{sym}}$. Orange single crystals of **17** were obtained from a concentrated hexane solution.

No reaction was observed on treating **1** with lithium 2-dihydro-2-boratafluorene[20] in diethyl ether as expected for a reaction according to Equation (15). However, when the ether was replaced by THF a $^{11}$B NMR signal at $\delta$ = 7.6 ppm suggested the formation of the corresponding titanium(IV) diorganyldihydridoborate. But this compound could not be isolated because on work-up it decomposed to give (2,6-$i$Pr$_2$C$_6$H$_3$O)$_4$Ti. Similar behaviour was observed for the reaction of **1** with lithium dibenzo-1-oxo-2,2-dihy-



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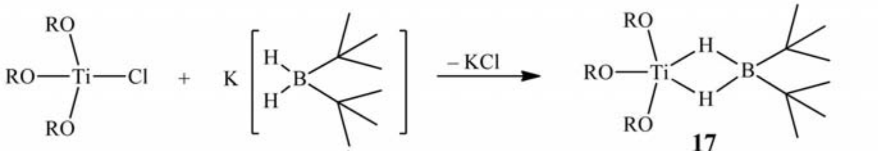


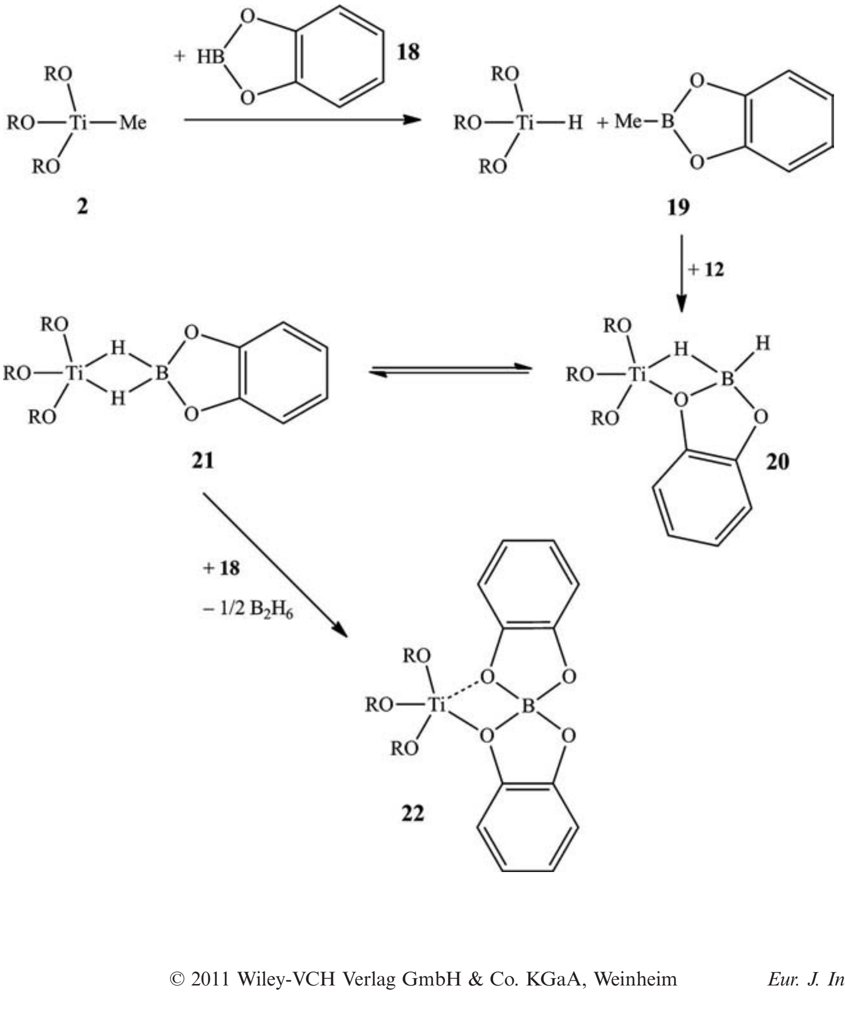
(14)

dridoborate.[20] Two $^{11}$B NMR signals were recorded. A weak signal at $\delta_B$ = –2.5 ppm shows the presence of the lithium compound and the strong signal at $\delta_B$ = 28.3 ppm suggests the presence of the hydridoborate (2,6-$i$Pr$_2$C$_6$H$_3$O)$_3$-Ti[HBOC$_{12}$H$_{10}$] but none of the expected compounds could be isolated.

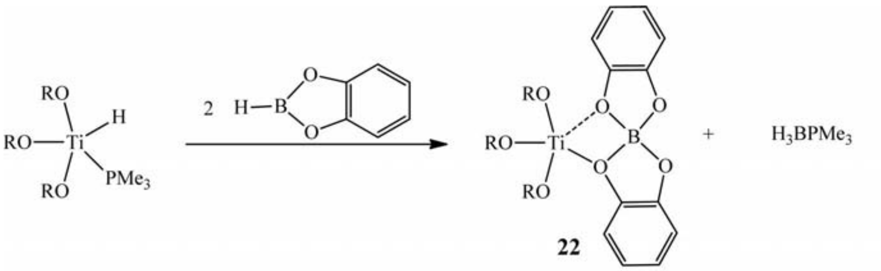
It has been reported that the reaction of Cp$_2$TiMe$_2$ with catecholborane yields methane and titanocene bis(catecholatoborane).[24] Therefore we expected similar behaviour for the reaction of **2** with an excess of catecholborane in pentane. A series of $^{11}$B NMR spectra were recorded by increasing the temperature from –80 to 20 °C in 10 °C inter-

Table 2. Change of composition of the reaction products formed from (2,6-$i$Pr$_2$C$_6$H$_3$O)$_3$TiMe and benzo[1,3,2]dioxaborolane in hexane.

| $T$ [°C] | $\delta_B$ [ppm], intensity [%] | $\delta_B$(B$_2$H$_6$) [ppm], intensity [%] | $\delta_B$(C$_6$H$_4$BO$_2$BH) [ppm], intensity [%] | $\delta_B$(C$_6$H$_4$OBTi) [ppm], intensity [%] | $\delta_B$(C$_6$H$_4$O$_2$BMe) [ppm], intensity [%] |
|---|---|---|---|---|---|
| –80 | 8.7, 10 | 16.8, 8 | 27.2, 82 | – | – |
| –60 | 8.8, 11 | 16.6, 9 | 26.9 [d, $^1J(^{11}B^1H)$ = 148 Hz], 80 | – | – |
| –40 | 9.0, 11 | 16.8 [tt,$^1J(^{11}B,^1H)$ = 130 Hz], 6 | 27.1 [d, $^1J(^{11}B,^1H)$ = 199 Hz], 65 | 22.0 (s), 10 | 33.6, 8 |
| –20 | 8.9, 13 | 16.8 [tt, $^1J(^{11}B,^1H)$ = 120 Hz], 8 | 27.1 [d,$^lJ(^{11}B,^1H)$ = 186 Hz], 62 | 21.5 (s), 10 | 33.8, 8 |
| 0 | 9.3, 8 | 16.8, [tt, $^1J(^{11}B,^1H)$ = 125 Hz], 8 | 27.3 [d,$^1J(^{11}B,^1H)$ = 195 Hz], 60 | 21.8 (s), 13 | 33.9, 10 |
| 20 | – | 17.0 [tt, $^1J(^{11}B,^1H)$ = 125 Hz], 8 | 27.5 [d, $^1J(^{11}B,^1H)$ = 184 Hz], 61 | 21.9 (s), 19 | 33.9, 12 |



Scheme 2.



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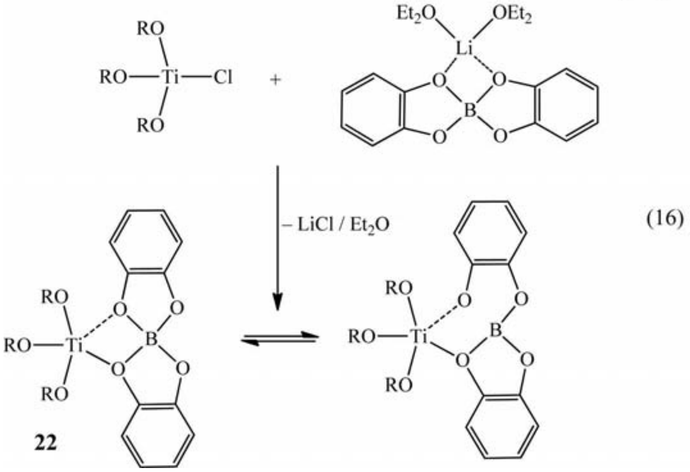
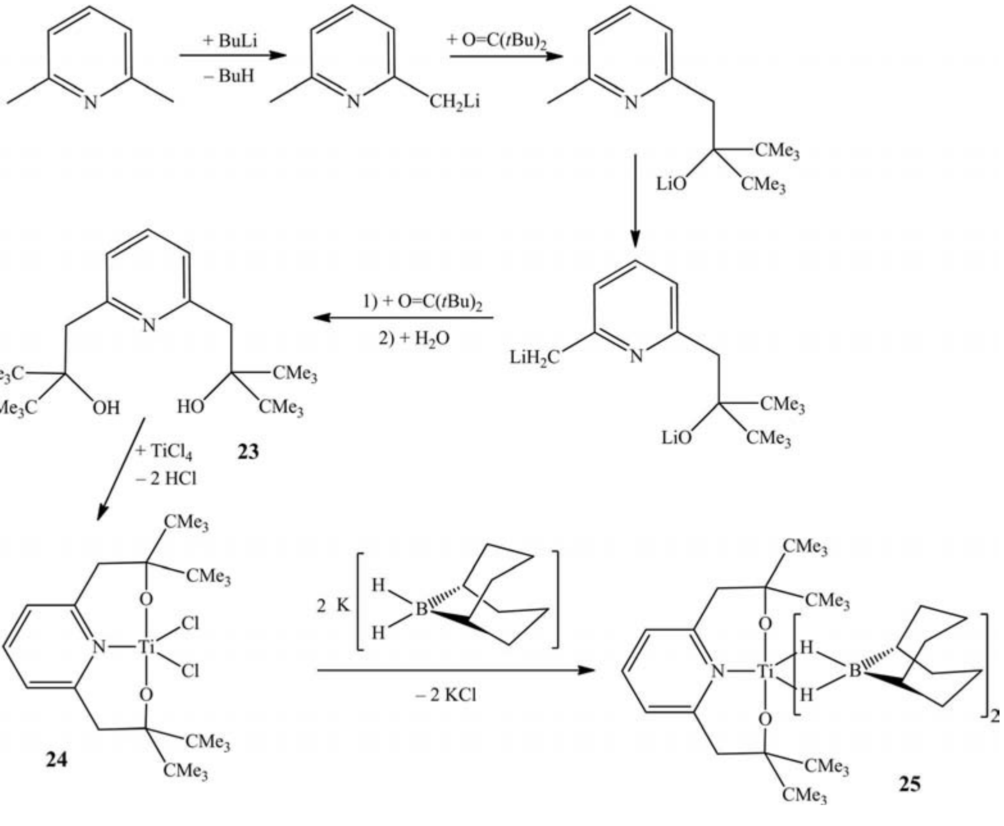


**22**

(16)

vals. The changes in the $^{11}$B NMR spectra are shown in Table 2. At –80 °C signals at 8.8, 16.7 and 27.2 ppm were observed in a ratio of 1:1:8. They showed no BH coupling. The signal at 27.2 ppm results from catecholborane **19** and the signal at 16.7 ppm from $B_2H_6$.[21] Two new species appeared at –50 °C. A resonance at $\delta$ = 21.9 ppm can be assigned to $(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{O})_3\text{Ti}[\text{H}_2\text{BO}_2\text{C}_6\text{H}_4]$ (**21**; 8%) and the signal at $\delta$ = 33.6 ppm to *B*-methylcatecholborane



**23** **24** **25**

Scheme 3.

(8%).[21] An increase to 20% at 20 °C was observed for the bis(catecholato)borate **22**. The amount of diborane remains at 8%, but the amount of catecholborane decreases to 60%. At 20 °C the signal at 8.8 ppm had vanished. Scheme 2 describes the most likely steps in this reaction sequence.

To prove that the titanium hydride $(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{O})_3\text{TiH}$ is an intermediate, we treated $(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{O})_3\text{TiH(PMe}_3)$ with catecholborane and observed analogous behaviour to that of compound **2** [Equation (15)]. The spirocyle **22** showed an $^{11}$B NMR signal at $\delta = 24.5$ ppm. The $^{1}$B NMR signal at $\delta = 35.8$ ppm [dq, $^1J(\text{P,B}) = 58$ Hz, $^1J(^{11}\text{B},^1\text{H}) = 96$ Hz] is due to the phosphanylborane $\text{H}_3\text{BPMe}_3$[21] generated [Equation (15)]. We also checked for the formation of **22** from **1** by treating the latter with lithium bis(catecholato)borate in diethyl ether; see Equation (16). The resulting $^{11}$B NMR spectrum shows a signal at $\delta_\text{B} = 14.1$ ppm for the Li compound and a signal at $\delta = 23.9$ ppm for **22**. The low-field signal indicates that the latter contains a tricoordinated and not tetracoordinated B atom.

Attempts to prepare a dihydridodiorganylborate of bis(tri-*tert*-butylmethanolato)titanium(IV)[20a] from $[(t\text{Bu})_3\text{CO}]_2\text{TiCl}_2$ and $\text{Li[H}_2\text{BC}_8\text{H}_{14}]$ failed. The main product was, as shown by $^{11}$B NMR spectroscopy, bis(9-borabicyclononane) with $\delta_\text{B} = 29.4$ ppm. Therefore a larger ligand L had to be chosen to stabilize a compound of type $\text{LTi(H}_2\text{BC}_8\text{H}_{14})_2$. For this reason we prepared 2,6-[bis(2,2-di-*tert*-butyl-2-hydroxyethyl)]pyridine (**23**) starting from lutidine (Scheme 3). Its reaction with $\text{TiCl}_4$ yielded the pentacoordinate dichlorotitanium complex **24**. Treatment of **24** with $\text{K[H}_2\text{BC}_8\text{H}_{14}]$ in diethyl ether generated **25** (Scheme 3). The $^1$H and $^{13}$C NMR spectra show different sets of signals for the *tert*-butyl groups as well as for the diastereotopic methylene protons. The $^{11}$B NMR signal at $\delta = 20.3$ ppm is broad ($h_{1/2} = 500$ Hz) and the triplet structure is barely visible. However, the presence of $\text{BH}_2$ groups is revealed by two strong IR bands at 2078 and 2027 cm$^{-1}$ with shoulders at 2103 and 2056 cm$^{-1}$, which indicates the bidentate function of the $\text{H}_2\text{BC}_8\text{H}_{14}$ species. This was verified by the determination of the crystal structure of **25**.

## X-ray Structure Determinations

Figure 2 shows the molecular structure of compound **11**. It crystallizes from $\text{CH}_2\text{Cl}_2$ solution at –78 °C to give amber crystals of $\mathbf{11}\cdot\text{CH}_2\text{Cl}_2$ in the triclinic system, space group $P\bar{1}$. The most eye-catching structural feature is the asymmetric coordination of the 9-$\text{H}_2$BBN ligand at the Ti centre. In spite of this, the Ti atom can still be regarded as being tetracoordinated to atoms B1, O1, O2 and O3 because the average deviation from the tetrahedral angles is only 2°. However, the atoms Ti1, H1, H2 and B1 are not arranged in a plane; the interplanar angle H1–Ti1–H2/H1–B1–H2 is 50°. In particular, the bending of the 9-$\text{H}_2$BBN part against the Ti–B–C plane leads to an Ti1–B1–C37 angle of 84.4(1)°, in contrast to the Ti1–B1–C41 angle of 166.8(2)°. This interaction positions H37 in an almost *trans* arrangement with respect to the O1 atom (O1–Ti1–H37 170°) with a Ti···H37 distance of 2.30 Å, which is typical of an agostic Ti···H–C interaction. The Ti1···C37 atom distance is 2.621(3) Å, in contrast to the Ti1···C41 distance of 3.781(3) Å. The B···Ti distance in **11** is 2.212(2) Å and this corresponds to the B···Ti distance of 2.20(2) Å in the corresponding tetrahydroborate[5] in which three Ti–H–B bridge bonds are present. In particular, the reduction of the Ti1–B1–C37 bond angle to 84.4° points to the presence of a β-agostic Ti···H–C interaction in the solid state, which could not be observed in the NMR spectra even at –80 °C.

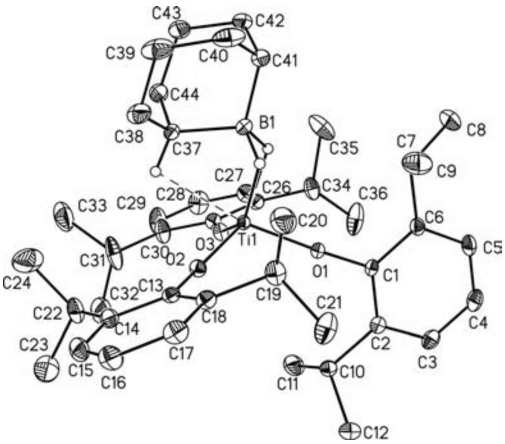


Figure 2. Molecular structure of tris(2,6-diisopropylphenolato)titanium(IV)-dihydrido-9-borabicyclononane ($\mathbf{11}\cdot\text{CH}_2\text{Cl}_2$). Only the Ti complex is depicted. Thermal ellipsoids are drawn at the 25% probability level. CH hydrogen atoms have been omitted except for BH and H37. Bond lengths [Å] and bond angles [°]: Ti1–O1 1.792(1), Ti1–O2 1.806(2), Ti1–O3 1.802(2), Ti1–H1 1.85(2), Ti1–H2 1.86(3), Ti1···H37 2.30(2), Ti1···B1 2.212(2), B1–C37 1.637(2), B1–C41 1.593(2), B1–H1 1.23(1), B1–H2 1.18(1); O1–Ti1–O2 107.01(7), O1–Ti1–O3 106.53(7), O2–Ti1–O3 110.13(7), O1–Ti1–H1 93.3(7), O2–Ti1–H1 146.6(8), O3–Ti1–H1 146.6(8), O1–Ti1–H2 92.2(7), O2–Ti1–H2 93.8(8), O3–Ti1–H2 142.8(8), H1–Ti1–H2 58(1), H1–B1–H2 97(2), H1–B1–C41 117(1), H2–B1–C41 116(1), Ti1–O1–C1 160.2(2), Ti1–O2–C13 161.4(2), Ti1–O3–C25 91.79(8), O1–C1–C2 118.2(2), O1–C1–O6 118.7(2), C1–C1–C6 123.1(2), C1–C6–C5 116.9(2), C1–C2–C3 116.8(2), C2–C3 C4 121.2(2), C3–C4–C5 120.3(2), C4–C5–C6 121.5(2). Torsion angles [°]: Ti1–O1–C1–C2 –89.8, Ti1–O2–C13–C14 152.0; Ti1–O3–C25–C26 44.9.

The 9-BBN ester **14** crystallizes in the orthorhombic space group *Pnma*. Its molecular structure is shown in Figure 3. There is a crystallographically determined mirror plane through atoms B1, O1, C1, C5, C6 and C9. The B1–C bond lengths are 1.563(2) (to C1) and 1.560(2) Å (to C5), and the sum of the bond angles at B1 is 359.9°. The B1–O1 bond length of 1.365 Å is typical of borinic esters $\text{R}_2\text{BOR}$.[21,25] However, the B1–O1–C1 bond angle is fairly open at 127.1(1)° and the C1–B1–C5 plane is perpendicular to the C7–C6–C7A plane of the aromatic ring.

The orange prisms of the bis(cyclohexyl)dihydridoborate (**16**) are triclinic, space group $P\bar{1}$, $Z = 2$. The most striking feature of its molecular structure is that one of the cyclohexyl groups is involved in an agostic β-Ti···H–C interaction (Figure 4). This leads to a Ti···H distance of 2.26(2) Å, whereas the two Ti1–H(B) bonds are, as expected, shorter with 1.86(3) and 1.90(3) Å. A consequence of the Ti1···H–C interaction is that the atoms Ti1, B1, H1 and H2 do not

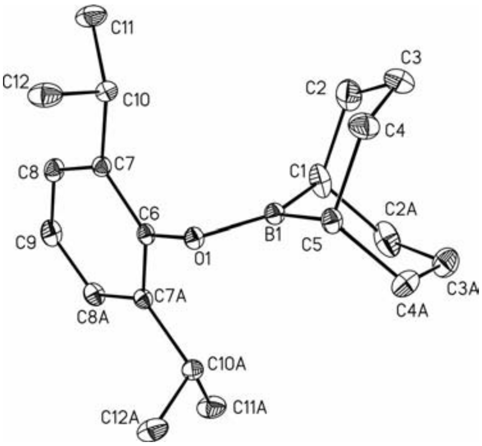


Figure 3. The molecular structure of 9-(2,6-diisopropylphenolato)-9-borabicyclononane (**14**). Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths [Å] and bond angles [°]: B1–O1 1.365(2), O1–C6 1.395(2), B1–C1 1.563(2), B1–C5 1.560(2); O1–B1–C1 127.1(1), O1–B1–C5 119.7(1), C1–B1–C5 113.1(1), B1–O1–C6 124.6(1). Interplanar angles [°]: B1–O1–C6/C7–C6–C7A 90.0, C1–B1–C5/C1–C2–C4–C5 56.9.

lie in a plane, as shown by the interplanar angle between H1–Ti1–H2 and H1–B1–H2 of 50°. Moreover, the difference in angles Ti1–B1–C37 [82.5(1)°] and Ti1–B1–C41 [158.2(3)°] is a consequence of the Ti1···H37–C37 interaction. The B–C bond lengths are about 0.1 Å longer than in **11**. An analysis of the Ti–H and B–H bond lengths indicates that these show the beginnings of B–C bond cleavage (Figure 4).

Figure 5 shows the molecular structure of compound **17**. The orange crystals are triclinic, space group $P\bar{1}$, $Z = 4$. There are two independent molecules in the unit cell that have similar structural data. If we neglect the H atoms bonded to the boron atom then one can describe the coordination sphere at the Ti atoms as distorted tetrahedral. The O–Ti1–O bond angles are 107.5(1), 111.0(1) and 104.2(2)°, and for O–Ti2–O 106.3(1), 108.5(1) and 108.1(1)°. The B1–Ti1–O angles are 105.0(2), 118.9(2) and 110.5(2)°, which compare with 109.7(2), 113.1(2) and 111.0(2)° for B2–Ti2–O. The B–H bond lengths range from 1.13(4) to 1.27(4) Å, whereas the H–B–H bond angles are narrow but equal for both molecules with 82(3)°. This is counterbalanced by the two C–B–C bond angles of 123.9(6) and 125.7(5)°, which differ due to the steric requirements of the *tert*-butyl groups. Compared with compound **16**, we observe significantly longer B–C bonds for **17**. Another consequence is that the shortest distance of the C1 atom to the closest H atom of the *tert*-butyl group is found in molecule B1 (2.88 Å), but in molecule B2 the analogous distance is 3.14 Å. This difference results from the different orientation of the phenoxy groups, which exerts different strains on the *tert*-butyl groups. However, the four-membered rings B1(B2)–H1–H2–Ti1 are planar, in contrast to those in **11** and **16**.

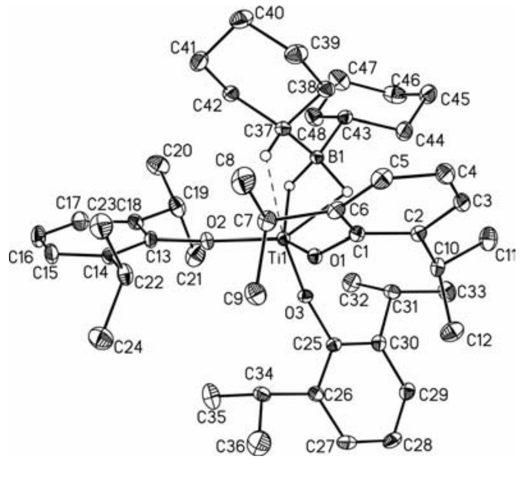


Figure 4. Molecular structure of tris(2,6-diisopropylphenolato)titanium-dihydrido(dicyclohexyl)borate (**16**). Thermal ellipsoids are drawn at the 25% probability level. All hydrogen atoms have been omitted for the sake of clarity except for those at B1 and C37. Bond lengths [Å] and bond angles [°]: Ti1–O1 1.819(92), Ti1–O2 1.796(2), Ti1–O3 1.794(2), C1–O1 1.376(3), C13–O2 1.370(3), C25–O3 1.371(3), Ti1–H1 1.90(3), Ti1–H2 1.86(3), Ti1···H37 2.26(3), Ti1···B1 2.234(4), O1–C1 1.376(3), O2–C13 1.370(3), O3–C25 1.371(3), B1–H1 1.18(3), B1–H2 1.10(3); O1–Ti1–O2 113.00(8), O1–Ti1–O3 103.54(9), O2–Ti1–O3 105.22(9), O1–Ti1–H1 143.9(8), O1–Ti1–H2 139.9(9), O2–Ti1–H1 139.9(9), O2–Ti1–H2 95.0(9), O3–Ti1–H1 96.4(9), O3–Ti1–H2 95.5(9), O1–Ti1–B1 110.7(1), O2–Ti1–B1 112.2(1), O3–Ti1–B1 111.7(1), Ti1–C1–O1 140.6(2), Ti1–O2–C13 170.0(2), Ti1–O3–C25 149.2(2), H1–B1–H2 9.5(2), H2–B1–C43 108(2), H1–B1–C45 114(1), H2–B1–C43 108(2), B1–H1–Ti1 90(2), B1–H2–Ti1 56(2). Interplanar angles [°]: C37–B1–C43/H21–B1–H2 86.4, Ti1–O1–C2/C1 to C6 111, Ti1–O2–C13/C13 to C18 0.6, Ti1–O3–C2–C5/C15 to C30 67.1.

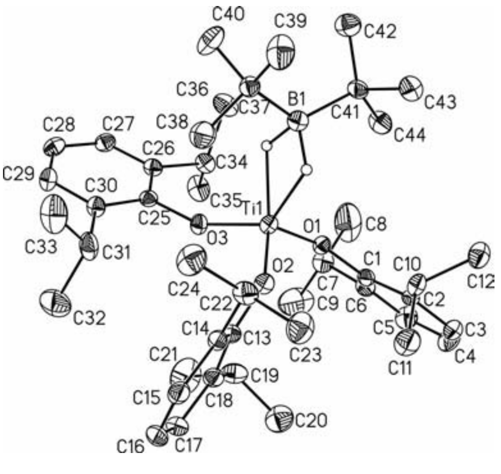


Figure 5. Molecular structure of tris(2,6-diisopropylphenolato)titanium(IV)-dihydrido(di-*tert*-butyl)borate (**17**). Thermal ellipsoids are drawn at the 25% probability level. All hydrogen atoms have been omitted for the sake of clarity except for those at B1. Bond lengths [Å] and bond angles [°]: Ti1–O1 1.776(3), Ti1–O2 1.803(4), Ti1–O3 1.787(3), C1–O1 1.397(5), C13–O2 1.372(6), C25–O3 1.401(5), B1–C37 1.625(8), C37–C38 1.535(8), C37–C39 1.521(7), C37–C40 1.535(7), C41–C42 1.541(7), C41–C43 1.559(7), C41–C44 1.545(7), Ti1···B1 2.498, Ti1–H1 1.75, Ti1–H2 1.82, B1–H1 1.13(1), B1–H2 1.27(1); O1–Ti1–O2 107.5(1), O1–Ti1–O3 111.0(1), O2–Ti1–O3 104.0(2), B1–Ti1–O1 94.6(2), B1–Ti1–O2 95.2(2), B1–Ti1–O3 110.5(2), Ti1–H1–B1 118.9, H2–B1–Ti1 106.7. Interplanar angles [°]: Ti1–O1–C1/C1 to C6 36.1, Ti1–O2–C13/C13 to C18 50.0, Ti1–O3–C25/C25 to C30 102.1.

Compound **25** crystallizes from hexane as amber monoclinic crystals, space group $P2_1/n$, $Z = 4$, after addition of some toluene. The unit cell also shows the presence of toluene and hexane with site occupation factors of 0.7 for toluene and of 0.4 for hexane. Figure 6 shows the molecular structure of compound **25**. The ligand 2,6-[HOC($t$Bu)$_2$CH$_2$]$_2$-C$_5$H$_3$N (**23**) binds to the Ti centre through its two O atoms [Ti–O 1.788 and 1.786(4) Å], whereas the Ti–N bond is rather long at 2.230(4) Å. Together with the two B atoms, these atoms are arranged around the Ti atom in a distorted trigonal bipyramid. N1 and B1 occupy the *trans* positions and the other three atoms are placed in the equatorial plane with bond angles of 123.3(2)° for O1–Ti1–O2, 115.2(2)° for O1–Ti1–B2 and 117.0(2)° for O2–Ti1–B2. The equatorial plane is bent in the direction of the N atom, as shown by the angles of 95.2(2)° for B1–Ti1–O1 and of 101.7(2)° for B1–Ti1–B2. In contrast to compound **11**, the BH$_2$Ti atoms are arranged in a plane and there are no agostic C–H···Ti interactions. On the other hand, the Ti1···B distances are identical, although one would expect a difference for apical and equatorial sites. However, both are significantly longer than in (dmpe)Ti(BH$_4$)$_3$ [2.411(3)],[26] (Me$_3$P)$_2$Ti(BH$_4$)$_3$ [2.40(1)][27] and Cp$_2$TiBH$_4$ [2.37(1) Å].[28] The comparatively large deviations of the Ti1–H bond lengths are astonishing, as shown by Ti1–H1 of 1.83(2) Å, Ti1–H2 of 1.77(2) Å, Ti1–H3 of 1.76(3) Å and Ti1–H4 of 1.93(2) Å. This suggests that the H atoms at B1 form a double bridge with Ti, whereas H4 is only weakly coordinated to the Ti1 atom.

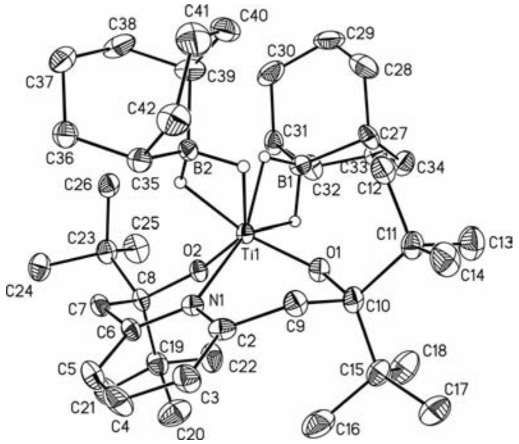


Figure 6. Molecular structure of compound **25**. Thermal ellipsoids are drawn at the 25% probability level. All hydrogen atoms have been omitted for the sake of clarity except for those at B1. Bond lengths [Å] and bond angles [°]: Ti1–O1 1.788(4), Ti1–O2 1.786(4), Ti1–N1 2.230(4), Ti1···B1 2.452(7), Ti1···B2 2.454(7), O1–C10 1.440(7), O2–C8 1.430(6), N1–C2 1.358(7), N1–C6 1.363(7), C1–C2 1.358(7), B1–C27 1.596(9), B1–C31 1.602(9), B2–C35 1.598(9), B2–C39 1.610(9), B1–H1 1.22(6), B1–H2 1.24(6), B2–H3 1.12(6), B2–H4 1.13(6), Ti1–H1 1.83(2), Ti1–H2 1.77(2), TI1–H3 1.76(3), Ti1–H4 1.93(2); O1–Ti1–O2 123.3(2), O1–Ti1–N1 84.0(2), O2–Ti1–N1 83.8(2), O1–Ti1–B1 94.6(2), O2–Ti1–B2 117.0(2), O2–Ti1–B1 95.2(2), N1–Ti1–B1 177.5(2), N1–Ti1–B2 80.7(2), B1–Ti1–B2 101.7(2), C1–N1–C6 119.1(5), C2–N1–Ti1 120.2(4), C2–N1–Ti1 120.2(4), C10–O1–Ti1 144.5(3), C8–O2–Ti1 145.3(3), O1–C10–C9 104.6(4), O1–C10–C11 107.0(4), O2–C8–C19 107.1(4), O2–C8–C7 117.4(5), Ti1–H1–B1 105.1, H2–Ti1–B1 108.3, H3–B2–Ti1 116.0, H4–Ti1–B2 103.4, H1–B1–H2 89.1, H3–B2–H4 89.3, C27–B1–C31 106.4(5), C27–B2–C39 107.1(5). Interplanar angles [°]: C35–B2–C39/C31–B1–C27 90.0, Ti1–N1–O1/C2–C9–C10 63.4, Ti1–N1–O2/C6–C7–C9 60.3.

## Discussion and Conclusion

There are two important points to be considered in discussing the tris(organyloxo)titanium hydroborato complexes: 1) the geometries of the triphenolatotitanium part and 2) the influence of the boranato groups at the Ti(OR)$_3$ fragment. In general, compounds of the type (RO)$_4$Ti are monomeric, for example, (2,6-$i$PrC$_6$H$_3$O)$_4$Ti,[18] (2-$t$Bu-C$_6$H$_4$O)Ti,[9] (2,3,5,6-Me$_4$C$_6$HO)$_4$Ti[9] and [2,6-Me$_2$C$_6$H$_3$O]$_4$-Ti.[29,30] This also holds for several other triorganylphenolatotitanium(IV) compounds, for example, (2,4-$t$Bu$_2$C$_6$H$_3$O)$_3$-TiCl,[10] (3,5-$t$Bu$_2$C$_6$H$_3$O)$_3$TiI,[31] tris(2,4-$t$Bu$_2$C$_6$H$_4$O)$_3$-TiCl,[10] (2-PhC$_6$H$_4$CO)$_3$TiCl·OEt$_2$[10] and (2,6-Ph$_2$C$_6$H$_3$O)$_3$-TiCl.[14] In contrast, ($i$Pr$_2$C$_6$H$_3$O)$_3$TiCl is dimeric,[31] as is (2,4-Me$_2$C$_6$H$_3$O)$_3$TiCl.[10] Amongst these species (2,4-$t$Bu$_2$-C$_6$H$_3$O)TiCl shows the shortest Ti–O bond with 1.575 Å, whereas the longest Ti–O bonds were determined for (3,5-$t$Bu$_2$C$_6$H$_3$O)$_3$TiI.

On the other hand, the Ti–O–C bond angles are largest for (2,6-diphenylphenolato)titanium chloride with an average of 164.7°, which is almost the same angle as found for (2,6-$i$Pr$_2$C$_6$H$_3$O)$_4$Ti (aver. 165.3°).[16] The longest Ti–O bonds are observed for compound **17** (aver. 1.803 Å) and the largest Ti–O–C bond angles for compound **2** (aver. 171.4°). One would expect that short Ti–O and C–O bonds show more sp character, but there is no clear relationship between the Ti1–O–C bond angles and the Ti–O or C–O bond lengths. In fact, the observed C–O bonds correspond to partial C–O double bond character, as also observed for borinic esters.[25]

The Ti···B distances depend significantly on the organyl substituents: the larger the steric requirement of the R groups the longer the Ti···B distance. A comparison of compound **11** with **25** demonstrates that the presence of two H$_2$-9-BBN units also leads to a considerable lengthening of the Ti···B distance. The longest Ti···B distance observed so far was observed for (Me$_2$PCH$_2$CH$_2$PMe$_2$)Ti-(BH$_4$)$_2$ with 2.534 Å.[26] This is of course also a consequence of its +II oxidation state. The introduction of substituents like cyclopentadienyl at the Ti atoms leads to thermal stabilization of, for example, Cp$_2$TiBH$_4$.[4,28] As shown by us in 1995,[5] the introduction of sterically bulky bis- and tris(2,6-diorganylphenolato)titanium(IV) units allows the synthesis of tetrahydridoborate complexes that are stable at ambient temperature.

Studies by Shore and co-workers[4] revealed that Cp$_2$Ti(H$_2$BR$_2$), Cp*Ti(H$_2$BC$_8$H$_{14}$)$_2$ and similar compounds show agostic Ti···H–C interactions. Such interactions have now been proved for compounds **11** and **16**, but not for **10**. Astonishingly, no agostic interaction was observed for **25**. This may be due to the different symmetry because the Ti atom in compound **25** can be considered as pentacoordinated to the 9-BBN groups in an apical and equatorial manner in contrast to the tetracoordination in compounds **11** and **16**.

We also observed that the reactions of $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3$-TiCl with alkali-metal dihydridodiorganylborates often lead not to reasonable amounts of $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_3\mathrm{TiH}_2\mathrm{BR}_2$, but rather to $2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OBR}_2$, $(\mathrm{HBR}_2)_2$, $\mathrm{BR}_3$ and $\mathrm{B}_2\mathrm{H}_6$ as well as $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_4\mathrm{Ti}$. This latter compound is formed most likely via the intermediate $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O}_3)_3$-TiH, which could neither be isolated nor detected by NMR spectroscopy.

Compound **25** crystallizes from hexane after the addition of some toluene as amber monoclinic crystals, space group $P2_1/n$, $Z = 4$. The unit cell also shows the presence of toluene and hexane with site occupation factors of 0.7 for toluene and of 0.4 for hexane. Figure 6 shows its molecular structure.

Our study demonstrates that most tris(2,6-diisopropylphenolato)titanium dihydridodiorganylborates are difficult to isolate and only a few species seem to be more stable than (2,6-dimesitylphenolato)titanium species.

## Experimental Section

**General:** All experiments were performed under anhydrous conditions using Schlenk techniques with either $\mathrm{N}_2$ or Ar as protecting gas. The alkali metal organyl-hydridoborates were prepared according to literature procedures.[20] Anhydrous solvents were prepared by standard methods ($\mathrm{LiAlH}_4$, $\mathrm{CaH}_2$, $\mathrm{P}_4\mathrm{O}_{10}$). NMR: usually $\mathrm{C}_6\mathrm{D}_6$ solvent, $\mathrm{SiMe}_4$ as standard, JEOL GSX 270 and EX 400 spectrometers. IR: Nicolet 520 spectrometer; in Nujol and/or Hostaflon. X-ray diffraction: Siemens P4 diffractometer equipped with a scintillation counter or an area detector, Mo-$K_\alpha$ radiation, LT2 low-temperature device, graphite monochromator.

**Tris(2,6-diisopropylphenolato)titanium Chloride (1):**[5] 2,6-Diisopropylphenol (7.4 mL, 40 mmol) was dissolved in benzene (20 mL). At ambient temperature this solution was added whilst stirring to a solution of $\mathrm{TiCl}_4$ (13 mmol) in benzene (30 mL). A dark-red solution was generated. After the addition the mixture was kept at reflux until the gas evolution (HCl) had ceased. The benzene was then removed by distillation and the remaining dark-orange-brown residue was dried under high vacuum; yield 7.5 g (12.2 mmol, 94%), m.p. 115–120 °C. For NMR spectroscopic data, see Table 1.

**Methyltris(2,6-diisopropylphenolato)titanium (2):** A solution of LiMe (3.21 mL, 1.56 M) diluted with diethyl ether (40 mL) was added to a stirred solution of **1** (5.01 mmol) in diethyl ether (25 mL) at –78 °C within 1 h. The solution was then allowed to reach ambient temperature and stirring was continued for a further 2 h. An olive-green solution formed. The solvent was then removed in vacuo. The solid residue was treated with hexane (60 mL). After filtration the filtrate was reduced in volume in vacuo to about 20 mL. Storing the solution at –30 °C yielded yellow prisms of **2** within a few days; yield 2.12 g (71%), m.p. 110–111 °C. $\mathrm{C}_{37}\mathrm{H}_{54}\mathrm{O}_3\mathrm{Ti}$ (594.71): calcd. C 74.73, H 9.15; found C 74.15, H 9.14. For NMR spectroscopic data, see Table 1.

**Reaction of Tris(2,6-diisopropylphenolato)titanium Chloride with Lithium Dihydridodimethylborate:** A solution of $\mathrm{LiH}_2\mathrm{BMe}_2$ (0.48 M in THF, 12 mL) containing about 10% of $\mathrm{LiH}_3\mathrm{BMe}$ was added to a stirred solution of **1** (3.06 g, 4.97 mmol) in diethyl ether (40 mL). The solution first turned brown and then orange and again turned a brownish colour after the Li compound had been added. The solution was analysed by $^{11}$B NMR spectroscopy 30 min after the addition: $\delta_\mathrm{B}$ = –30.2 [q, $^1J(^1\mathrm{H},^{11}\mathrm{B})$ = 71 Hz, $\mathrm{LiH}_3\mathrm{BMe}$, 5%], –27.5 (br., 4%), –22.0 [t, $^1J(^1\mathrm{H},^{11}\mathrm{B})$ = 72 Hz, $\mathrm{LiH}_2\mathrm{BMe}_2$, 4%], –17.4 (br., 3%), 2.0 [q, $^1J(^1\mathrm{H},^{11}\mathrm{B})$ = 64 Hz, $\mathrm{TiH}_3\mathrm{BMe}$, 16%], 5.6 [t, $^1J(^1\mathrm{H},^{11}\mathrm{B})$ = 56 Hz, $\mathrm{TiH}_2\mathrm{BMe}_2$, 4%], 56.3 (s, $\mathrm{Me}_2\mathrm{BOAryl}$, 62%), 86.9 ($\mathrm{BMe}_3$, 2%). The diethyl ether was removed from the solution by distillation and the orange-brown residue dissolved in pentane (50 mL). Insoluble material was separated by filtration. The brown filtrate was reduced to 20 mL and stored at –30 °C. Orange-yellow prisms separated, which proved to be $(i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_4\mathrm{Ti}$ by the determination of its cell constants[18] as well by its $^1$H and $^{13}$C NMR spectra.

**Reaction of Tris(2,6-diisopropylphenolato)titanium Chloride with Potassium Dihydridoborinate:** $\mathrm{K(H_2BC_5H_{10})}$[20] (630 mg, 1.86 mmol) was dispersed in pentane (15 mL) at –110 °C. A solution of **1** (1.04 g, 1.69 mmol) in pentane (25 mL) was slowly added to the suspension. The mixture was allowed to reach room temperature over 3 h and stirring was continued for another 30 min. The resulting $^{11}$B NMR spectrum showed the following signals: $\delta_\mathrm{B}$ = –19.0 [t, $^1J(^1\mathrm{H},^{11}\mathrm{B})$ = 70 Hz, $\mathrm{KH}_2B\mathrm{C}_5\mathrm{H}_{10}$], 7.3 ppm, (bad resolution of a multiplet, $\mathrm{TiH}_2B\mathrm{C}_5\mathrm{H}_{10}$). IR: $\tilde{\nu}$ = 2017 (br. s, $\nu\mathrm{BH}_2$), 2181 (sh, $\nu\mathrm{BH}_2$) cm$^{-1}$. Insoluble material was removed from the suspension and the solid was washed with pentane (10 mL); yield 440 mg (excess $\mathrm{KH_2BC_5H_{10}{\cdot}3THF}$ and 370 mg KCl). The filtrate was concentrated to about 5 mL and stored at –30 °C. Within 3 weeks, orange-yellow crystals separated, the cell constants of which showed it to be $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_4\mathrm{Ti}$ (**8**).[18] Total removal of the solvent from the filtrate yielded an oil from which no other pure compound could be isolated. Compound **10** could not be isolated.

**Tris(2,6-diisopropylphenolato)titanium Dihydrido-9-boratabicyclononane (11):** A solution of **1** (3.33 g, 5.41 mol) in hexane (40 mL) was added to a suspension of $\mathrm{K(H_2BC_8H_{14})}$[20] (1.01 g, 5.84 mmol) in hexane (40 mL) whilst stirring. After stirring for 2 days, the insoluble product was separated by filtration. The $^{11}$B NMR spectrum of the solution showed two signals, one at $\delta$ = 11.1 ppm (main signal) the other at $\delta$ = 29.3 ppm (dimeric H-9-BBN). The orange filtrate was reduced in volume to a few mL. Storing this solution for several days at –30 °C yielded **11**. Recrystallisation from $\mathrm{CH_2Cl_2}$ produced crystals of **11**·$\mathrm{CH_2Cl_2}$. The $\mathrm{CH_2Cl_2}$ was lost on storing in vacuo. Yield of **11**: 2.68 g (3.81 mmol, 70%), m.p. 130–132 °C. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 1.07–1.15 (m, 2 H, $\mathrm{C_8H_{14}}$), 1.23 [d, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.8 Hz, 36 H, $\mathrm{CH}Me_2$], 1.32–2.01 (m, 12 H, $\mathrm{C}_8H_{14}\mathrm{BH}_2$), 3.87 [sept, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.8 Hz, 6 H, $\mathrm{C}H(\mathrm{CH}_3)_2$], 6.89 [t, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.4 Hz, 3 H, *p*-2,6-*i*Pr], 7.00 [d, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.2 Hz, 6 H, *m*-2,6-*i*Pr$_2$] ppm. $^{13}$C NMR: $\delta$ = 23.79 ($C\mathrm{H}_3$), 24.49 ($C_8\mathrm{H}_{14}$), 27.12 ($C\mathrm{HMe}_2$), 33.36 ($C_8\mathrm{H}_{14}$), 123.61 (*m-C*), 123.65 (*p-C*), 137.62 (*o-C*), 162.68 (*i-C*) ppm. In [D$_8$]toluene at –80 °C only a single set of signals for the aliphatic C atoms were observed. $^{11}$B NMR: $\delta$ = 11.1 (br. m) ppm. $\mathrm{C}_{44}\mathrm{H}_{67}\mathrm{BO}_3\mathrm{Ti}$ (702.7): calcd. C 72.51, H 9.61; found C 72.75, H 9.15.

**Tris(2,6-diisopropylphenolato)titanium(IV) Dicyclohexyldihydridoborate (16):** A solution of $\mathrm{LiBH_2(C_6H_{11})_2{\cdot}THF}$[20] (1.95 g, 6.63 mmol) in diethyl ether (50 mL) was slowly added to a stirred solution of **1** (3.68 g, 5.98 mmol) in diethyl ether (35 mL) at ambient temperature. LiCl precipitated. The solution turned orange. After 4 h, the solvent was removed in vacuo and after filtration the residue was treated with hexane (80 mL). Insoluble material was removed by filtration. Then hexane (ca. 60 mL) was removed from the clear orange filtrate in vacuo. The remaining solution was cooled to –30 °C. Within 2 days single crystals of **16** separated; yield 3.73 g (4.91 mmol, 82%), m.p. 137–140 °C. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 1.15–1.73 (m, 22 H, $\mathrm{C}_{12}H_{22}$), 1.25 [d, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.8 Hz, 36 H,

$CH(CH_3)_2$], 3.88 [sept, $^3J(^1H,^1H)$ = 6.4 Hz, 6 H, $CH(CH_3)_2$], 6.88 [t, $^3J(^1H,^1H)$ = 7.2 Hz, 3 H, *p-H*], 6.98 [d, $^3J(^1H,^1H)$ = 7.4 Hz, 6 H, *m-H*] ppm. $^{13}C$ NMR: $\delta$ = 23.94 [$CH(CH_3)_2$], 26.92 (*p*-$C_6H_{11}$), 27.13 [$CH(CH_3)_2$], 28.66 (*m*-$C_6H_{11}$), 32.06 (*i*-$C_6H_{11}$), 33.86 (*o*-$C_6H_{11}$), 123.37 (*m-C*) 123.53, (*p-C*), 137.42 (*o-C*), 162.11 (*i-C*) ppm. Even at –80 °C only single sets of signals for the aliphatic C atoms of the borate ligand as well as for the aryloxy ligands were observed. $^{11}B$ NMR: $\delta$ = 15.0 [t, $^1J(^1H,^{11}B)$ = 65 Hz; only observed by line-sharpening] ppm. IR (Hostaflon): $\tilde{\nu}$ = 2784 (w), 2733 (w), 2708 (w), 2143 (m), 2015 (st, $BH_2$), 1971 (m), 1916 (w), 1852 (vw) $cm^{-1}$. $C_{48}H_{75}BO_3Ti$ (758.91): calcd. C 75.97, H 9.96; found C 76.01, H 9.54.

**Tris(2,6-diisopropylphenolato)titanium(IV) Di-*tert*-butyldihydridoborate (17):** A solution of **1** (3.42 g, 5.53 mmol) in diethyl ether (40 mL) was dropped into a stirred solution of $K(H_2BtBu_2)$[20] (1.43 g, 8.6 mmol) in diethyl ether (30 mL). After stirring the orange-brown solution for 20 h the ether was removed from the suspension in vacuo (1 Torr) and the solid residue suspended in hexane (60 mL). After filtration the filtrate was reduced in volume to about 20 mL. Orange prisms separated from the solution at –30 °C within 3 d. Yield of **17**: 3.42 g (68 %), m.p. 132–134 °C (dec). $^1H$ NMR ($C_6D_6$): $\delta$ = 1.23 [d, $^3J(^1H,^1H)$ = 6.8 Hz, 36 H, $CH(CH_3)_2$], 1.49 [br. s., 18 H, $C(CH_3)_3$], 3.72 [sept, $^3J(^1H,^1H)$ = 6.8 Hz, 6 H, $CHMe_2$], 6.86 [t, $^3J(^1H,^1H)$ = 7.2 Hz, 3 H, *p*-$C_6H_3$], 7.00 [d, $^3J(^1H,^1H)$ = 7.4 Hz, 6 H, *m*-$C_6H_3$] ppm. $^{13}C$ NMR: $\delta$ = 23.82 [$CH(Me_3)_2$], 27.31 [$CH(Me_3)_2$], 34.84 ($CMe_3$), 123.39 (*m*-C), 123.61 (*p*-C), 137.49 (*o*-C), 162.32 (*i*-C) ppm. $^{11}B$ NMR: $\delta$ = 24.0 (multiplet not resolved), 81.6 (br., low intensity, $Bu_2BH$) ppm. IR (Hostaflon): $\tilde{\nu}$ = 2087 (st, $BH_2$), 2021 (st, $BH_2$), 2180 (st, $^{10}BH_2$) $cm^{-1}$ and others. $C_{44}H_{71}BO_3Ti$ (706.73): calcd. C 74.78, H 10.63; found C 73.83, H 10.80.

**2,6-Bis(2,2-di-*tert*-butyl-2-hydroxyethyl)pyridinetitanium(IV) Dichloride (24):** A solution of 2,6-bis(2,2-di-*tert*-butyl-2-hydroxyethyl)pyridine (**23**; 4.84 g, 12.3 mmol) in toluene (100 mL) was added to a stirred solution of $TiCl_4$ (2.33 g, 12.3 mmol) in toluene (40 mL). This resulted in the formation of an orange suspension. HCl was released on heating the suspension at reflux. The now clear yellow solution was set aside for 18 h. Then it was heated at reflux for another 4 h. The volume of the solution was reduced to about 20 mL in vacuo. Crystals of **24** separated at –30 °C, which were isolated and dried in vacuo. From the filtrate another batch of colourless crystals separated within 2 days. Total yield of **24**: 3.9 g (69 %), m.p. 265 °C (dec.). $^1H$ NMR ($CDCl_3$): $\delta$ = 1.11 (s, $CMe_3$), 3.34 (s, $CH_2$), 6.53 [d, $^3J(^1H,^1H)$ = 7.81 Hz, 3-H, py], 7.93 [t, $^3J(^1H,^1H)$ = 7.81 Hz, 4-H, py] ppm.

**2,6-Bis(2,2-di-*tert*-butyl-2-hydroxyethyl)pyridinetitanium(IV) Bis-(9,9-dihydro-9-borabicyclononane) (25):** A diethyl ether solution (30 mL) of $Li(H_2BC_8H_{14})$[19] (0.86 g, 4.64 mmol) was added to a diethyl ether solution (26 mL) of compound **24** (1.06 g, 2.08 mmol) within 10 min. A white suspension formed that slowly turned blue-green. The ether was removed in vacuo and the residue was treated with hexane (30 mL). After filtration a few drops of toluene were added and the solution turned dark blue. Storing the solution at –30 °C the filtrate turned amber and single crystals separated within 4 d; yield only about 12 well-shaped single crystals were isolated besides microcrystalline **25** (700 mg), m.p. 132 °C (dec., black colour). $^1H$ NMR ($C_6D_6$): $\delta$ = 0.89–1.97 (m, 9-BBN), 0.89 (s, $CMe_3$), 2.11 (s), 2.18 [d, $^2J(^1H,^1H)$ = 16.0 Hz], 3.96 [d, $^2J(^1H,^1H)$

Table 3. Crystallographic data and data related to structure solution and refinement.

| Compound | **2** | **10** | **11** | **16** | **17** | **25** |
|---|---|---|---|---|---|---|
| Formula | $C_{37}H_{54}O_3Ti$ | $C_{20}H_{31}BO$ | $C_{45}H_{66}BCl_2H_3O_3Ti$ | $C_{48}H_{75}BO_3Ti$ | $C_{44}H_{71}BO_3Ti$ | $C_{44}H_{10}B_2N_2O_4Ti$ |
| $M_r$ | 594.70 | 298.26 | 787.61 | 758.79 | 706.72 | 738.12 |
| Crystal size [mm] | 0.2 × 0.2 × 0.3 | 0.4 × 0.5 × 0.6 | 0.2 × 0.5 × 0.6 | 0.2 × 0.2 × 0.25 | 0.3 × 0.3 × 0.4 | 0.2 × 0.3 × 0.4 |
| Crystal system | orthorhombic | orthorhombic | triclinic | triclinic | triclinic | monoclinic |
| Space group | *Fdd*2 | *Pnma* | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| $a$ [Å] | 36.8369(6) | 12.841(3) | 11.406(3) | 10.947(4) | 11.2670(2) | 11.669(9) |
| $b$ [Å] | 39.9611(2) | 16.025(5) | 12.898(3) | 11.591(4) | 21.7485(5) | 18.707(13) |
| $c$ [Å] | 10.6105(2) | 8.782(2) | 16.977(4) | 19.308(7) | 21.8012(5) | 22.282(16) |
| $\alpha$ [°] | 90 | 90. | 86.570(6) | 85.07(1) | 60.985(1) | 90 |
| $\beta$ [°] | 90 | 90 | 87.590(1) | 76.81(1) | 75.42(1) | 100.37(2) |
| $\gamma$ [°] | 90 | 90 | 66.496(3) | 68.44(2) | 75.35(1) | 90 |
| $V$ [Å$^3$] | 15619.1(4) | 1807.1(9) | 2285.9(9) | 2218(1) | 4466.8(2) | 4784(6) |
| $Z$ | 16 | 4 | 2 | 2 | 4 | 8 |
| $\rho_{calcd.}$ [$Mg\,m^{-3}$] | 1.012 | 1.096 | 1.144 | 1.136 | 1.051 | 1.011 |
| $\mu$ [$mm^{-1}$] | 0.248 | 0.064 | 0.340 | 0.231 | 0.225 | 0.210 |
| $F(000)$ | 5152 | 656 | 848 | 828 | 1544 | 1603 |
| Index range | $-45 \le h \le 46$ | $-15 \le h \le 15$ | $-14 \le h \le 14$ | $-13 \le h \le 13$ | $-8 \le h \le 8$ | $-15 \le h \le 15$ |
|  | $-50 \le k \le 46$ | $-20 \le k \le 20$ | $-14 \le k \le 16$ | $-14 \le k \le 13$ | $-27 \le k \le 27$ | $-23 \le k \le 19$ |
|  | $-13 \le l \le 13$ | $-11 \le l \le 11$ | $-21 \le l \le 21$ | $-24 \le l \le 24$ | $-27 \le l \le 27$ | $-28 \le l \le 28$ |
| $2\theta$ [°] | 58.26 | 54.88 | 58.26 | 58.84 | 52.70 | 58.12 |
| $T$ [K] | 183(2) | 183(2) | 193(2) | 183(2) | 203(2) | 213(2) |
| Reflections collected | 22290 | 8776 | 12939 | 12897 | 22509 | 23283 |
| Reflections unique | 7916 | 1953 | 6950 | 7097 | 12076 | 9894 |
| Refl. observed (4$\sigma$) | 4321 | 1793 | 5870 | 5859 | 6450 | 4524 |
| $R_{int.}$ | 0.0848 | 0.0418 | 0.0375 | 0.0342 | 0.0894 | 0.0883 |
| Number of variables | 383 | 174 | 493 | 502 | 931 | 500 |
| Weighting scheme[a] $x/y$ | 0.0867/47.78 | 0.0562/0.594 | 0.0498/1.9403 | 0.0000/2.5934 | 0.0000/6.9493 | 0.0822/21.5574 |
| GOF | 1.129 | 1.055 | 1.059 | 1.204 | 1.188 | 1.184 |
| Final $R$ (4$\sigma$) | 0.0662 | 0.0434 | 0.0462 | 0.0544 | 0.0680 | 0.0992 |
| Final $wR_2$ | 0.1603 | 0.1112 | 0.1144 | 0.1056 | 0.1233 | 0.2523 |
| Largest residual peak [$e\,Å^{-3}$] | 0.491 | 0.278 | 0.676 | 0.284 | 0.355 | 1.185 |

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

= 15.4 Hz, C$H_2$], 6.39 [d, $^3J(^1H,^1H)$ = 7.85 Hz, 3-H, py], 6.79 [t, $^3J(^1H^1H)$ = 7.75 Hz, 4-H, py] ppm. $^{13}$C NMR: $\delta$ = 30.23 (C$Me_3$), 33.45 (C$Me_3$), 24.12, 25.60, 31.20 ($C_8H_{14}$), 43.05, 44.81, 45.01 ($C$Me$_3$, $CH_2$), 97.57 ($C$O), 124.09 (C-3, py), 139.33 (C-4, py), 160.61 (C-2, py) ppm. $^{11}$B NMR: $\delta$ = 20.3 (br.) ppm. $C_{41}H_{75}BNO_2Ti$ (683.55): calcd. C 72.0, H 11.05, N 2.05; found C 69.12, H 10.51, N 1.89.

**Reaction of Tris(2,6-diisopropylphenolato)titanium(IV) Chloride with Lithium(H,H-9-borafluorenyl)·3THF:** A suspension of $Li(H_2BC_{13}H_9)\cdot 3THF$[20] (1.17 g, 3.02 mmol) in diethyl ether (50 mL) was added to a solution of **1** (1.68 g, 2.73 mmol) in diethyl ether (15 mL) at 0 °C. After stirring for 10 min, the residue in the dropping funnel was added to the suspension by adding THF (10 mL). This caused a change in colour from orange to orange-red. The solution showed then an $^{11}$B NMR signal at –20.4 ppm [t, $^1J(^{11}B,^1H)$ = 78 Hz, rel. intensity: 73%, $C_{12}H_8BH_2Li$] and 7.6 ppm [broad signal of $C_{12}H_8BH_2Ti(OAr)_3$, 27%)]. After stirring the solution for 18 h at ambient temperature the solvent was removed in vacuo. The solid residue was treated with hexane (60 mL) and the insoluble material removed by filtration. After 50% of the hexane had been evaporated, the filtrate was cooled to –30 °C. Yellow crystals separated which proved to be tetrakis(2,6-diisopropylphenolato)titanium by determining its cell constants.[18]

**Reaction of Methyltris(2,6-diisopropylphenolato)titanium(IV) with Catecholborane:** Compound **2** (30 mg) was dissolved in hexane (2 mL) in an NMR tube. After cooling with liquid nitrogen, 10 drops of catecholborane were added. The NMR tube was then sealed in vacuo. $^{11}$B NMR spectra were recorded at various temperatures beginning at –80 °C. The observed data are summarized in Table 2. It can be seen that the main product is the *B*-methylcatecholborane (**19**; increase from 8 to 20% at higher temperature) as well as $(2,6\text{-}i\text{Pr}_2C_6H_3O)_3Ti[H_2B(O_2C_6H_4)]$, **20**–**22**.

**X-ray Structure Analysis:** The air- and moisture-sensitive crystals were covered with a perfluoroether oil, cooled with cold $N_2$ to about –30 °C and a suitable crystal selected under the microscope. It was fixed on a glass fibre, which was mounted in a small copper tube and then transferred to the goniometer head cooled to about –80 °C by the flow of $N_2$. Reflections of five sets of 15 frames were collected at different $\omega$ and $\phi$ angles for the determination of the cell constants with the program SAINT.[32] Data collection was performed in the hemisphere mode and reduced with the program SMART.[32] SHELX93 or SHELXTL[32] was used for data reduction, structure solution and refinement. The positions of the BH atoms were isotropically refined, all other H atoms bonded to C atoms were placed at calculated positions and refined as riding on the respective C atoms. Table 3 contains relevant crystallographic data.

CCDC-778514 (for **2**), -778515 (for **14**), -778516 (for **11**), -778517 (for **16**), -778518 (for **25**) and -77519 (for **17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] St. Leiner, P. Mayer, H. Nöth, *Z. Naturforsch., Teil B* **2009**, *64*, 793–799.

[2] a) H. R. Hoekstra, J. J. Katz, *J. Am. Chem. Soc.* **1949**, *71*, 2488–2492; b) B. D. James, M. G. H. Wallbridge, *J. Inorg. Nucl. Chem.* **1966**, *28*, 2456–2457; c) H. Nöth, *Angew. Chem.* **1961**, *73*, 371–383; d) V. V. Volkov, K. G. Myakishev, *Sibirskii Khim. Zh.* **1992**, *5*, 105–108; e) V. Volkov, K. G. Myakishev, *Isvest. Akad. Nauk SSSR, Seriya Khimichesk.* **1987**, *6*, 1429–1431; f) J. Z. Fang, H. M. Chen, *Appl. Phys. Lett.* **2009**, *94*, 044104/1–3; g) C. J. Dain, J. Anthony, M. J. Goode, D. G. Evans, K. T. Nicholls, D. W. H. Rankin, H. E. Robertson, *J. Chem. Soc., Dalton Trans.* **1991**, 967–977.

[3] a) H. Nöth, R. Hartwimmer, *Chem. Ber.* **1960**, *93*, 2238–2245; b) H. Nöth, R. Hartwimmer, *Chem. Ber.* **1960**, *93*, 2246–2251.

[4] a) E. Ding, B. Du, F. C. Liu, S. Liu, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **2005**, *44*, 4871–4878; b) E. J. M. Hamilton, J. S. Park, X. Chen, S. Liu, M. R. Sturgeon, E. A. Meyers, S. G. Shore, *Organometallics* **2009**, *28*, 3973–3980; c) S. G. Shore, J. S. Park, Y. Chen, S. Liu, *Nat. Meet. Am. Chem. Soc.*, San Francisco, **2006**, *INOR*–370; d) F. Lacroix, C. E. Plesnik, S. Liu, E. A. Meyers, S. G. Shore, *J. Organomet. Chem.* **2003**, *687*, 69–77; e) N. N. Ho, R. Bau, S. Liu, J. Liu, E. A. Meyers, S. G. Shore, *J. Organomet. Chem.* **2002**, *654*, 216–220; f) C. Plesnik, F. Liu, S. Liu, J. Liu, E. A. Meyers, S. G. Shore, *Organometallics* **2001**, *20*, 3599–3606.

[5] H. Nöth, M. Schmidt, *Organometallics* **1995**, *14*, 4601–4610.

[6] F. Corraza, C. Floriani, A. Chiesi-Villa, C. Gutamini, *Inorg. Chem.* **1991**, *30*, 145–148.

[7] a) M. G. Thorn, J. E. Hill, S. A. Waratuka, E. S. Johnson, P. E. Fanwick, I. P. Rothwell, *J. Am. Chem. Soc.* **1997**, *119*, 8630–8641; b) M. G. Thorn, Z. E. Etheridge, P. E. Fanwick, I. P. Rothwell, *J. Organomet. Chem.* **1999**, *591*, 148–152.

[8] R. T. Toth, D. W. Stephan, *Can. J. Chem.* **1998**, *69*, 172–178.

[9] A. J. Nelson, Ch. Shen, J. M. Waters, *Polyhedron* **2006**, *25*, 2039–2054.

[10] F. Akagi, T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 11936–11937.

[11] A. Shah, A. Sing, R. F. C. Mehrotra, *Ind. J. Chem., Sect. A* **1993**, *32*, 632–635.

[12] R. N. Chesnut, L. D. Durfee, D. Loren, P. E. Fanwick, I. P. Rothwell, K. Folting, J. D. Hoffman, *Polyhedron* **1987**, *6*, 2013–2026.

[13] A. Sato, A. Hattori, K. Ishima, S. Saito, H. Yamamoto, *Chem. Lett.* **2003**, *32*, 1002–1007.

[14] K. Waterpaugh, C. N. Caughlan, *Inorg. Chem.* **1966**, *5*, 1782–1786.

[15] K. H. Thiele, H. Windisch, H. Schumann, G. Kociol-Köhn, *Z. Anorg. Allg. Chem.* **1994**, *620*, 523–526.

[16] D. C. Bradley, H. Cutynska, J. D. J. Backer-Dirks, M. B. Hursthouse, A. A. Ibrahim, M. Montecalli, *Polyhedron* **1990**, *9*, 1423–1427.

[17] M. Schmidt-Amelunxen, Ph. D. Thesis, University of Munich, **1995**.

[18] L. D. Durfee, S. L. Latesky, I. P. Rothwell, J. C. Huffman, K. Fölting, *Inorg. Chem.* **1985**, *24*, 4569–4573.

[19] a) G. T. Jordan, S. G. Shore, *Inorg. Chem.* **1996**, *35*, 1089–1090; b) G. T. Jordan, F. C. Liu, S. G. Shore, *Inorg. Chem.* **1997**, *36*, 5597–5602.

[20] a) J. Knizek, Diploma Thesis, University of Munich, **1996**; b) J. Knizek, Ph. D. Thesis, University of Munich, **1999**; c) J. Knizek, H. Nöth, *J. Organomet. Chem.* **2000**, *614*/*615*, 168–187.

[21] H. Nöth, B. Wrackmeyer, *NMR-Basic Principles and Progress*, vol. 14 (“Nuclear Magnetic Resonance Spectroscopy of Boron Compounds”) (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, Heidelberg, New York, **1978**.

[22] T. J. Marks, J. R. Kolb, *Chem. Rev.* **1977**, *77*, 263–293.

[23] a) A. Haaland, W. Scherer, K. Ruud, G. S. McGrady, A. J. Downs, O. Swang, *J. Am. Chem. Soc.* **1998**, *120*, 3762–3772; b) W. Scherer, T. Priemeier, A. Haaland, H. V. Volden, G. S. Mc Grady, A. J. Downs, R. Boese, *Organometallics* **1998**, *17*, 4406–4412; c) Z. Dawoosi, M. L. H. Green, V. S. B. Mtetwa, K. Prout, A. J. Schultz, J. Williams, T. F. Koetzle, *J. Chem.*

*Soc., Dalton Trans.* **1986**, 1629–1637; d) G. S. Grady, A. J. Downs, A. Haaland, W. Scherer, D. C. McKean, *Chem. Commun.* **1997**, 1547–1548.

[24] J. F. Hartwig, C. N. Muhoro, C. He, O. Eisenstein, R. Bosque, F. Maseras, *J. Am. Chem. Soc.* **1996**, *118*, 10936–10937.

[25] a) P. Willerhausen, A. Hofmann, M. Pilz, W. Massa, A. Berndt, *Z. Naturforsch., Teil B* **1992**, *47*, 983–991; b) G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685–1691; c) M. Drouin, H. G. Michel, Y. Gundon, W. Ogilvie, *Acta Crystallogr., Sect. C* **1993**, *49*, 75–79; d) I. Ghesner, W. E. Piers, M. Parvez, R. McDonald, *Can. J. Chem.* **2006**, *84*, 81–92; e) S. J. Rettig, J. Trotter, *Can. J. Chem.* **1983**, *61*, 2334–2340; M. T. Ahsby, W. A. Sheshtawa, *Organometallics* **1994**, *13*, 236–243; f) B. Wrackmeyer, W. Milius, *Chem. Ber.* **1995**, *120*, 679–687.

[26] J. A. Jensen, G. S. Girolami, *Inorg. Chem.* **1989**, *28*, 2107–2113.

[27] a) J. A. Jensen, J. E. Gozum, D. M. Pollina, G. S. Girolami, *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644; b) J. A. Jensen, G. S. Girolami, *J. Chem. Soc., Chem. Commun.* **1986**, 1160–1163.

[28] K. M. Melmed, D. Coucouvanis, S. J. Lippard, *Inorg. Chem.* **1973**, *12*, 232–236.

[29] S. D. Bunge, T. J. Boyle, H. D. Pratt, T. M. Afam, M. A. Rodriguez, *Inorg. Chem.* **2004**, *43*, 6035–6041.

[30] S. L. Latesky, J. Keddington, A. K. McMullen, J. P. Rothwell, J. C. Huffman, *Inorg. Chem.* **1985**, *24*, 995–1001.

[31] T. J. Boyle, L. A. Ottley, M. A. Rodriguez, R. M. Sewell, T. A. Alam, S. K. McIntyre, *Inorg. Chem.* **2008**, *47*, 1008–1017.

[32] Programs used for the determination of unit cells, data reduction and structure solution: *SAINT*, *SMART*, and *SHELXTL*, Bruker Analytical Instruments, Madison, version 5.1 and *SHELX93*, S. G. Sheldrick, University of Göttingen.

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