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Syntheses and Properties of Cyclopentadienyl-Substituted Imidotitanium Fluorides

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The reaction of 2 equiv of Me_3SnF with $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$ in the presence of at least 2 equiv of pyridine affords $[(\eta^5\text{-}C_5H_4Me)TiF(NPh)]_2$ (**1**) in high yield. $(\eta^5\text{-}C_5H_4SiMe_3)TiCl(N\text{-}t\text{-}Bu)\cdot py$ reacts quantitatively with an equimolar amount of Me_3SnF to yield $[(\eta^5\text{-}C_5H_4SiMe_3)TiF(N\text{-}t\text{-}Bu)]_2$ (**2**). The fluorides $[\eta^5\text{-}Cp'TiF(NSnMe_3)]_2$ ($Cp' = C_5Me_4Et$ (**3**), C_5H_4Me (**4**)) are obtained in high yield by reaction of $N(SnMe_3)_3$ with $(\eta^5\text{-}C_5Me_4Et)TiF_3$ and $(\eta^5\text{-}C_5H_4Me)TiF_3$, respectively. Complex **3** has been characterized by X-ray diffraction. $(MeAlNMes)_4$ (Mes = 2,4,6-trimethylphenyl) reacts as a transamination reagent with 4 equiv of $(\eta^5\text{-}C_5H_4Me)_2TiF_2$ to provide $[(\eta^5\text{-}C_5H_4Me)TiF(NMes)]_2$ (**5**) in low yield.

Introduction

Organoimido complexes of transition metals[1] have received considerable attention in the last years, due to their presumed role in catalytic processes such as propylene ammonoxidation,[2] nitrile reduction,[3] and hydrodinitrogenation catalysis.[4] Complexes of titanium,[5] zirconium,[6] and hafnium with terminal and bridging imidochlorides,[6e,f,7] are well-known but in the case of imidometal(IV) fluoride complexes only one example is described in the literature.[5g] This is due to a lack of suitable synthetic routes for the preparation of these compounds. Recently, we have reported on Me_3SnF as an excellent fluorinating reagent for organometallic chlorides.[8] Furthermore, it was shown that the oxo bridged species $[\eta^5\text{-}Cp^*TiF(O)]_4$ ($Cp^* = C_5Me_5$) can be prepared by treatment of $[\eta^5\text{-}Cp^*TiCl(O)]_3$ with Me_3SnF.[8] This demonstrates that the metathesis reaction is working in the presence of an oxo function at the metal center. $[\eta^5\text{-}Cp^*TiF(O)]_4$ was already accessible from the reaction of $\eta^5\text{-}Cp^*TiF_3$ using $O(n\text{-}Bu_3Sn)_2$.[9]

In order to establish synthetic routes to the isoelectronic imido fluoride complexes of titanium(IV), we report herein an extension of this method and the properties and solid state structure of one of these compounds.

To the best of our knowledge, iminoalanes have not previously been used as transfer reagents for the imino function. These compounds should be particularly effective in their reaction with organometallic fluorides due to the high fluorine affinity toward aluminum.

Results and Discussion

Me_3SnF is particularly suited for the syntheses of organotitanium imido fluorides in high yields. Thus, the imido fluoride **1** can be obtained by treatment of the chloride complex $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$ with an equimolar amount of Me_3SnF in toluene. However, the reaction must be carried out in the presence of pyridine. Otherwise no metathesis reaction takes place. It seems to be necessary to cleave first the imido-bridged dimer $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$ in order to generate *in situ* the mononuclear pyridine adduct $(\eta^5\text{-}C_5H_4Me)TiCl(NPh)\cdot py$. In agreement with this observation, $(\eta^5\text{-}C_5H_4SiMe_3)TiCl(N\text{-}t\text{-}Bu)\cdot py$ can be fluorinated easily with Me_3SnF, and the coordinated pyridine is displaced. Cyclopentadienyltitanium imido fluorides can be obtained alternatively by reaction of cyclopentadienyltitanium trifluorides with tris(trimethylstannyl)-

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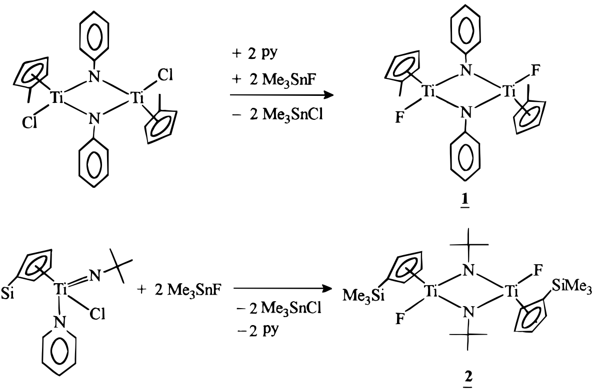
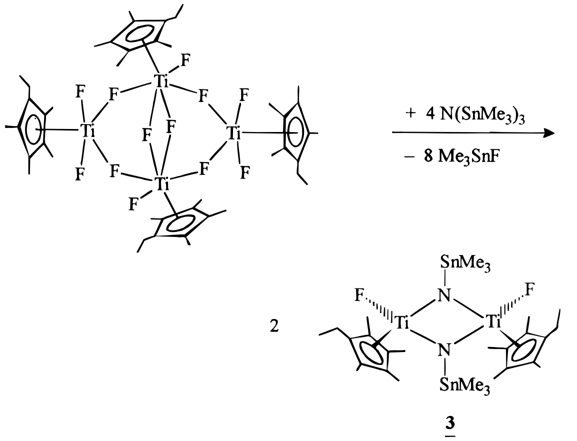
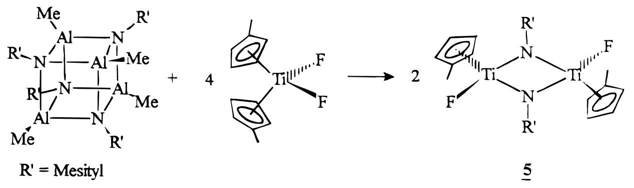
Scheme 1



Scheme 2



Scheme 3



amine. Reaction of $(\eta^5\text{-}C_5Me_4Et)TiF_3$ or $(\eta^5\text{-}C_5H_4Me)TiF_3$, with $N(SnMe_3)_3$ in 1:1 ratio leads to the fluoride complexes $[(\eta^5\text{-}C_5Me_4Et)TiF(NSnMe_3)]_2$ (**3**) and $[(\eta^5\text{-}C_5H_4Me)TiF(NSnMe_3)]_2$ (**4**), respectively. Complex **3** is accessible in refluxing THF while for the synthesis of compound **4** boiling toluene is needed.

Finally, we were interested to determine whether organoiminoalanes are potentially active transfer reagents for the imido function to organotitanium trifluorides. Despite the high fluorine affinity of aluminum the reaction of $\eta^5\text{-}Cp^*TiF_3$ with $(MeAlNMes)_4$[10] takes 12 h at 80 °C in toluene to be completed. Transamination takes place, *vide infra*, but no defined product could be isolated. In contrast to this result $[(\eta^5\text{-}C_5H_4Me)TiF(NMes)]_2$ can be obtained in 20 % yield when $(\eta^5\text{-}C_5H_4Me)_2TiF_2$ is treated with $(MeAlNMes)_4$ under the same conditions. However, it was impossible to characterize a byproduct from this reaction containing the remaining C_5H_4Me group.

The EI mass spectra of complexes **1**, **2**, **3**, **4** and **5** indicate on the basis of their molecular ion peaks that they are also dimers in the gaseous state as formulated in the equations (Schemes 1−3).

The ^{19}F NMR spectra of these cyclopentadienyltitanium imido fluorides gave singlet resonances at low field in the δ range from 82 to 110 ppm. This indicates a relative low electron density at the fluorine nuclei as expected for terminal bonded fluorine. In the ^{19}F NMR spectra of the fluoride complexes $(\eta^5\text{-}Cp^*MF_3)_4$ (M = Zr, Hf) the terminal bonded fluorine atoms resonate at δ 97.5 and 41.8 ppm, respectively, while the bridging ones have chemical shifts of at least 100 ppm to higher field (range from −26.3 to −97.8 ppm).

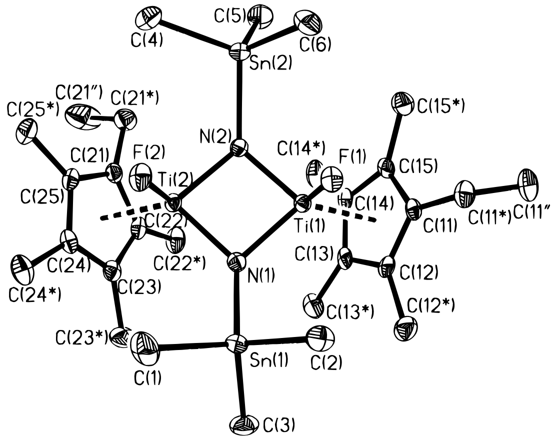


Figure 1. Structure of $[(\eta^5\text{-}C_5Me_4Et)TiF(NSnMe_3)]_2$ (**3**). Selected bond distances (Å) and bond angles (°). With hydrogen atoms omitted for clarity: Ti(1)−F(1) 1.836(2), Ti(1)−N(2) 1.903(3), Ti(1)−N(1) 1.911(3), Sn(1)−N(1) 2.067(3), Ti(1)−Cp(1) 2.101(2); F(1)−Ti(1)−N(1) 106.36(11), Ti(1)−N(2)−Ti(2) 94.35(13), Ti(1)−N(1)−Ti(2) 93.97(13), Ti(2)−N(2)−Sn(2) 126.45(14), Ti(1)−N(1)−Sn(1) 126.1(2), Ti(1)−N(2)−Sn(2) 126.62(14), Ti(2)−N(1)−Sn(1) 129.12(14), N(2)−Ti(1)−N(1) 85.61(12), F(1)−Ti(1)−N(2) 106.02(11), N(2)−Ti(2)−N(1) 85.44(12).

The crystal structure of **3** has been determined by single-crystal X-ray diffraction at low temperatures. The molecular structure of **3** is shown in Figure 1, along with selected bond distances and angles. In agreement with the result of the ^{19}F NMR in C_6D_6 solution, **3** is an imido N-bridged dimer in the solid state as well.

The Ti_2N_2 four-membered ring core deviates from planarity (mean deviation from the best least-squares plane of the four atoms involved 0.05 Å). **3** displays a cis geometry of the ligands with respect to the Ti_2N_2 ring. The $SnMe_3$ groups are slightly bent out of the Ti_2N_2 plane toward the same side where the fluoride ligands are oriented (distance between the least-squares Ti_2N_2 plane and: Sn(1) = 0.73 Å; Sn(2) = 0.81 Å). This minimizes the steric repulsion between the bulky C_5Me_4Et and the $SnMe_3$ groups. The structure is similar to the comparable imido chloride complex $[\eta^5\text{-}Cp^*TiCl(NSnMe_3)]_2$ (**6**).[6e]

The Ti−N bond lengths in **3** (1.903(3)−1.912(3) Å) are equivalent and only slightly longer than the corresponding ones of the chloride complex **6** (mean 1.890 Å). The Ti−F bond distances in complex **3** (mean 1.839 Å) are comparable with those in $[\eta^5\text{-}Cp^*TiF(O)]_4$ (1.845 Å) or in $(\eta^5\text{-}C_5Me_4Et)TiF_3$ (mean 1.830 Å).

Conclusions

It has been shown that Me_3SnF is a suitable fluorinating reagent for organometallic chlorides even when an imido function is present. This method as well as the reaction of cyclopentadienyltitanium trifluorides with tris(trimethylstannyl)amine are convenient synthetic routes for preparing cyclopentadienyltitanium imido fluorides in high yields. Their solid state structures are comparable to those of the analogous chloride complexes. They are imido N-bridged dimers possessing a Ti_2N_2 four-membered ring. From the stronger electronic back donation of fluorine rather than chlorine to the titanium center

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[10] Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

results a stronger basicity of the nitrogen atoms and the complexes become more stable against bases like pyridine.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere by standard Schlenk techniques. Solvents (including NMR solvents) were distilled under N_2 prior to use from an appropriate drying agent. Abbreviations: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, *t*-Bu = $C(CH_3)_3$, Mes = 2,4,6-$(CH_3)_3C_6H_2$.

Starting Materials. Me_3SnF,[11] $N(SnMe_3)_3$,[12] $(MeAlNMes)_4$,[10] $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$,[13] $(\eta^5\text{-}C_5H_4SiMe_3)TiCl(N\text{-}t\text{-}Bu)\cdot py$,[5f] $(\eta^5\text{-}C_5Me_4Et)TiF_3$,[8] $(\eta^5\text{-}C_5H_4Me)TiF_3$,[8] and $(\eta^5\text{-}C_5H_4Me)_2TiF_2$[8] were prepared from the literature procedures.

Physical Measurements. ^1H NMR spectra were recorded on a Bruker WP 80 SY instrument, and ^{19}F, ^{13}C and ^{119}Sn NMR spectra, on a Bruker MSL 400 instrument, using $SiMe_4$, $CFCl_3$, and $SnMe_4$, respectively, as external standards. In all cases C_6D_6 was used as a solvent. The infrared spectra were obtained using a Bio-Rad FTS-7 spectrophotometer. Mass spectra were recorded on a Varian MAT CH5 and Finnigan MAT 8230 system. Melting points (uncorrected) were measured by using a Büchi 510 apparatus. Elemental analyses were performed by the Analytical Laboratory of the Inorganic Institute at the Universität Göttingen.

Preparations. $[(\eta^5\text{-}C_5H_4Me)TiF(NPh)]_2$ (1). A mixture of $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$ (1.50 g, 2.96 mmol) and Me_3SnF (1.08 g, 5.92 mmol) in toluene (50 mL) was stirred with pyridine (0.5 mL) for 8 h at 60 °C. All volatile contents were removed carefully *in vacuo*, yielding an orange solid. The solid was washed once with cold hexane (20 mL). Recrystallization from toluene (20 mL) at −24 °C affords **1** as yellow-orange crystals which were filtered off and dried *in vacuo*, yield 1.26 g (2.66 mmol, 90%). Mp: 153 °C. ^1H NMR (C_6D_6): δ 7.10−6.79 (m, 5 H, N*Ph*), 6.14 (t, J_{HH} = 2.7 Hz, 2 H, C_5H_4Me), 5.65 (t, J_{HH} = 2.7 Hz, 2 H, C_5H_4Me), 1.96 (s, 3 H, C_5H_4Me). ^{19}F NMR (C_6D_6): δ 95.9 (s). Mass spectrum (EI): *m/z* 474 (M, 60), 395 (M − C_5H_4Me, 100%). Anal. Calcd for $C_{24}H_{24}F_2N_2Ti_2$: C, 60.79; H, 5.10; F, 8.01; N, 5.91. Found: C, 60.7; H, 5.0; F, 8.0; N, 5.9.

$[(\eta^5\text{-}C_5H_4SiMe_3)TiF(N\text{-}t\text{-}Bu)]_2$ (2). A mixture of $(\eta^5\text{-}C_5H_4SiMe_3)TiCl(N\text{-}t\text{-}Bu)\cdot py$ (1.04 g, 2.80 mmol) and Me_3SnF (0.51 g, 2.80 mmol) in toluene (40 mL) was stirred at 100 °C for 1 h. The solution was allowed to cool to room temperature and all reaction volatiles were removed *in vacuo*. Recrystallization from toluene (15 mL) at −24 °C afforded light-red crystals of **2**, which were filtered off and dried *in vacuo*, yield 0.72 g (1.31 mmol, 94 %). Mp: 218 °C. ^1H NMR (C_6D_6): δ 6.99 (t, J_{HH} = 2.4 Hz, 4 H, $C_5H_4SiMe_3$), 5.95 (t, $^3J_{HH}$ = 2.4 Hz, 4 H, $C_5H_4SiMe_3$), 1.05 (s, 18 H, C*Me*$_3$), 0.31 (s, 18 H, Si*Me*$_3$). ^{13}C NMR (C_6D_6): δ 117.5 (s, $C_5H_4SiMe_3$), 113.9 (s, $C_5H_4SiMe_3$), 74.9 (s, CMe_3), 33.1 (s, C*Me*$_3$), −0.9 (s, Si*Me*$_3$). ^{19}F NMR (C_6D_6): δ 109.5 (s). Mass spectrum (EI): *m/z* 550 (M, 20), 479 (M − N-*t*-Bu, 100%). IR (CsI): ν 1180 st, 1046 st, 1012 st, 840 st, 822 st, 801 st, 643 st, 623 st, 595 st, 408 st, cm^{-1}. Anal. Calcd for $C_{24}H_{44}F_2N_2Si_2Ti_2$: C, 53.36; H, 8.06; F, 6.90; N, 5.09. Found: C, 53.3; H, 7.8; F, 7.0; N, 5.3.

$[(\eta^5\text{-}C_5Me_4Et)TiF(NSnMe_3)]_2$ (3). A mixture of $(\eta^5\text{-}C_5Me_4Et)TiF_3$ (1.27 g, 5.0 mmol) and $N(SnMe_3)_3$ (2.53 g, 5.0 mmol) in THF (50 mL) was refluxed for 8 h. When the reaction was cooled to room temperature, THF was removed from the suspension *in vacuo*. The residue was extracted with hexane (70 mL) and filtered. **3** precipitated as light-red crystals after reducing the volume of the filtrate to 20 mL. The product was filtered off and dried *in vacuo*, yield 1.75 g (2.22 mmol, 89%). Mp: 163.5 °C. ^1H NMR (C_6D_6): δ 2.58 (q, $^3J_{HH}$ = 7.5 Hz, 4 H, $C_5Me_4(CH_2CH_3)$), 2.12 (s, 12 H, C$_5$*Me*$_4$Et), 2.05 (s, 12 H, C$_5$*Me*$_4$Et), 1.00 (t, $^3J_{HH}$ = 7.4 Hz, 6 H, $C_5Me_4(CH_2CH_3)$), 0.40 (s, $^2J_{SnH}$ = 55 Hz, 18 H, Sn*Me*$_3$). ^{13}C NMR (C_6D_6): δ 126.1 (s, C_5Me_4Et), 120.7 (s, C_5Me_4Et), 119.9 (s, C_5Me_4Et), 20.8 (s, $C_5Me_4(CH_2CH_3)$), 15.2 (s, $C_5Me_4(CH_2CH_3)$), 12.5 (s, C$_5$*Me*$_4$Et), 12.2 (s, C$_5$*Me*$_4$Et), −0.3 (s, Sn*Me*$_3$). ^{19}F NMR (C_6D_6): δ 87.9 (s). ^{119}Sn NMR (C_6D_6, $SnMe_4$): δ 29.9 (s). Mass spectrum (EI): *m/z* 788 (M, 30), 639 (M − C_5Me_4Et, 100%). IR (KBr): ν 726 st, 658 st, 611 st, 583 st, 527 st, 505 st, 376 st cm^{-1}. Anal. Calcd for $C_{28}H_{52}F_2N_2Sn_2Ti_2$: C, 42.36; H, 6.65; F, 4.82; N, 3.56. Found: C, 42.5; H, 6.6; F, 5.0; N, 3.5.

Table 1. Crystallographic Data for **3**

compd	**3**
empirical formula	$C_{28}H_{52}F_2N_2Sn_2Ti_2$
fw	787.90
data collcn at T/°C	−123(2)
cryst dimens/mm	0.5 × 0.4 × 0.4
cryst syst	monoclinic
space group	$P2_1/c$
a/Å	8.160(2)
b/Å	18.749(4)
c/Å	21.828(4)
β/deg	99.48(3)
cell vol V/Å^3	3293.9(12)
formula units per cell, Z	4
calcd density, ρ/Mg m^{-3}	1.589
Abs. coeff, μ/mm^{-1}	1.996
F(000)	1584
measured 2θ-range/deg	7−45
no. of data measured; no. of unique data	4309, 4289 (R_{int} = 0.04)
R,[a] wR2[b] ($I > 2\sigma I$)	0.025, 0.063
R, wR2 (all data)	0.029, 0.075
goodness of fit S[c]	1.117
weight factors a, b[d]	0.03, 5.31
refined params	341
restraints	0
largest diff peak, largest hole/e Å^{-3}	+0.644, −0.833

[a] $R = [\sum||F_o| - |F_c||]/[\sum|F_o||]$. [b] $wR2 = [[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]]^{1/2}$. [c] $S = [[\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]]^{1/2}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

$[(\eta^5\text{-}C_5H_4Me)TiF(NSnMe_3)]_2$ (4). $(\eta^5\text{-}C_5H_4Me)TiF_3$ (1.50 g, 8.15 mmol) and $N(SnMe_3)_3$ (4.12 g, 8.15 mmol) in THF (50 mL) were treated as described for the preparation of compound **3**. The extraction procedure was carried out with toluene (20 mL) to yield 2.27 g (3.50 mmol, 86%) of yellow-orange **4**. Mp: 155 °C. ^1H NMR (C_6D_6): δ 6.41 (t, J_{HH} = 2.6 Hz, 4 H, C$_5$*H*$_4$Me), 5.58 (t, J_{HH} = 2.7 Hz, J_{HH} = 0.6 Hz, 4 H, C$_5$*H*$_4$Me), 2.13 (t, J_{HH} = 0.6 Hz, 6 H, C$_5$H$_4$*Me*). ^{19}F NMR (C_6D_6): δ 82.6 (s). Mass spectrum (EI): *m/z* 648 (M, 20), 165 ($SnMe_3$, 100%). Anal. Calcd for $C_{18}H_{32}F_2N_2Sn_2Ti_2$: C, 33.38; H, 4.98; F, 5.87; N, 4.33. Found: C, 33.1; H, 4.9; F, 5.9; N, 4.3.

$[(\eta^5\text{-}C_5H_4Me)TiF(NMes)]_2$ (5). A solution of $(MeAlNMes)_4$ (2.01 g, 2.9 mmol) in toluene (30 mL) was added dropwise under stirring to a solution of $(\eta^5\text{-}C_5H_4Me)_2TiF_2$ (2.79 g, 11.4 mmol) in toluene (30 mL) at room temperature. The reaction mixture was heated for 10 h at 80 °C. Afterward the volume of the solution was reduced to 20 mL *in vacuo* and the mixture was kept at −24 °C. The product crystallized as red crystals, which were filtered off and dried *in vacuo*, yield 0.96 g (1.72 mmol, 30%). Mp: 194 °C dec. ^1H NMR (C_6D_6): δ 6.75 (s, 4 H, Mes−*H*), 5.49 (m, 8 H, C$_5$*H*$_5$Me), 2.75 (s, 12 H, *o*-Me−*H*), 2.13 (s, 6 H, *p*-Me−*H*), 1.66 (s, 6 H, C$_5$H$_4$Me−*H*). ^{19}F NMR (C_6D_6): δ 100.1 (s). Mass spectrum (EI): *m/z* 559 (M, 35), 426 (M − NMes, 100%). IR (KBr): ν 1606 m, 1492 m, 1462 vst, 1378 vst, 1213 st, 1154 st, 1052 m, 853 vst, 731 st, 590 st, 535 st cm^{-1}. Anal. Calcd for $C_{30}H_{36}F_2N_2Ti_2$: C, 64.53; H, 6.50; F, 6.80; N, 5.02. Found: C, 64.3; H, 6.4; F, 6.8; N, 4.8.

X-ray Data Collection, Structure Solution, and Refinement of 3. Orange crystals, suitable for X-ray diffraction were grown from THF at room temperature. A crystal was mounted on a glass fiber in a rapidly cooled perfluoropolyether.[14] Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument at 150(2) K, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), ω−2θ scans (7° < 2θ < 45°), on-line profile fitting,[15] and constant scan speed. The structure was solved by the Patterson method SHELXS-90[16] and

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(13) $[(\eta^5\text{-}C_5H_4Me)TiCl(NPh)]_2$ was made analogously to the preparations described in ref 5g.

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refined against F^2 on all data by full-matrix least-squares methods with SHELXL-93.[17] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on two methyl groups were refined disordered in two alternative sites. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Details of the crystal structure refinement are summarized in Table 1. Further details of the crystal structure investigation are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, England, on quoting the full journal citation.

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Supporting Information Available: Listings of crystal data, atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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