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Routes to New N-Heterocyclic Carbene Titanium(IV) Imido Complexes

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Mono-N-heterocyclic carbene (NHC) complex TiCl$_2$(NMe$_2$)$_2$(IMes) (**1**) (IMes = 1,3-dimesitylimidazol-2-ylidene) has been prepared through the addition of the free carbene to TiCl$_2$(NMe$_2$)$_2$. This procedure affords **1** in higher yield than the previously reported synthesis of **1** that consists in reacting Ti(NMe$_2$)$_4$ with 2 equiv of the imidazolium IMes·HCl and that in some cases we demonstrated affords **1** with concomitant formation of the titanium(III) bis-NHC complex TiCl$_2$(NMe$_2$)(IMes)$_2$ (**2**). Compound **1** reacts with primary amines to give compounds of the type Ti(=NR)Cl$_2$(NHMe$_2$)(IMes) (**3**). Alternatively, complexes **3** could be prepared from imido precursors Ti(=NR)Cl$_2$(NHMe$_2$)$_2$ and IMes, whereas the pyridine adducts Ti(=NR)Cl$_2$(Py)$_3$ produced Ti(=NR)Cl$_2$(Py)(IMes) (**6**). The reaction between dimeric complexes [Ti(μ-NAr)(NMe$_2$)$_2$]$_2$ (Ar = 2,6-Pr$^i_2$-C$_6$H$_3$ and 2,6-Cl$_2$-C$_6$H$_3$) and the salt IMes·HCl gives incomplete conversions into Ti(=NAr)Cl$_2$(NHMe$_2$)(IMes) with formation of two side products when Ar = 2,6-Cl$_2$-C$_6$H$_3$, formulated as Ti(=NAr)Cl$_2$(IMes)$_2$ (**4**) and Ti(=NAr)Cl(NHAr)(NHMe$_2$)(IMes) (**5**). X-ray studies were carried out for **1**, **2**, **3a**, **3d**, **3e**, **4**, and **5**.

Introduction

In recent years N-heterocyclic carbenes (NHCs) have been the subject of intense investigation.[1] In particular, NHCs emerged as effective ligands in late transition metal chemistry, in which they have found successful applications in homogeneous catalysis such as in olefin metathesis and C–C coupling reactions.[2,3] In contrast, early transition metal NHC complexes have received only very little attention and, most often, were not studied in their highest oxidation state or with simple *monodentate* NHC ligands.[4–14]

The imide functionality is ubiquitous in transition metal chemistry[15,16] and has found practical use in multiple areas of research.[17–21] In the past few years, our group has developed new synthetic routes to early transition metal titanium– and vanadium–imido complexes, including those bearing functional, chiral, and electron-deficient imido groups.[22–27] We then naturally became interested in associating the two ligands—simple monodentate NHC and imide—into the same compounds. Structural data in such compounds would be highly desirable, as it could help in clarifying the nature of the early transition metal–NHC bond. Herein we discuss the different strategies that we employed in order to prepare titanium complexes supported by both imido and 1,3-dimesitylimidazol-2-ylidene (IMes) ligands.

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Table 1. Comparison of Average Interatomic Distances (Å) and Angles (deg) in Complexes 1, 2, 3a, 3d, 3e, 4, and 5

	1[a]	**2**	**3a**	**3d**	**3e**[a]	**4**	**5**
$Ti-N_{imido}$			1.701(3)	1.711(4)	1.677(3)	1.707(2)	1.715(6)
$Ti-C_{IMes}$	2.316(10)	2.293(3) (*C1*) 2.297(3) (*C22*)	2.277(4)	2.263(5)	2.297(3)	2.315(2) (*C1*) 2.307(2) (*C22*)	2.290(6)
$Ti-NMe_2$	1.868(11) (*N3*) 1.858(9) (*N4*)	1.857(3)					
$Ti-Cl$	2.366(3) (*Cl1*) 2.368(3) (*Cl2*)	2.3510(10) (*Cl1*) 2.3876(9) (*Cl2*)	2.3631(14) (*Cl1*) 2.3231(14) (*Cl2*)	2.2946(16) (*Cl1*) 2.3336(16) (*Cl2*)	2.3748(10) (*Cl1*) 2.3895(9) (*Cl2*)	2.3328(7) (*Cl1*) 2.3133(6) (*Cl2*)	2.370(2)
$Ti-N_{NHMe2}$			2.230(3)	2.238(4)	2.197(3)		2.282(6)
$Ti-N_{NHAr}$							1.974(6)
$Ti-N_{imido}-C_{ipso}$			173.2(3)	169.9(4)	173.0(2)	176.80(16)	169.3(6)
$C_{IMes}-Ti-C_{IMes}$		154.23(11)				157.35(8)	
$Cl-Ti-Cl$	164.58(12)	147.93(4)	141.67(5)	136.93(7)	156.09(4)	142.24(3)	
$N_{NMe2}-Ti-N_{NMe2}$	106.1(5)						
$N_{imido}-Ti-N_{NHMe2}$			98.41(15)	93.11(18)	104.30(11)		90.1(3)
$N_{imido}-Ti-C_{IMes}$			103.96(16)	100.5(2)	112.312)	101.94(8) (*C1*) 100.78(8) (*C22*)	96.1(3)
$C_{IMes}-Ti-N_{NHMe2}$			157.05(15)	165.29(17)	142.97(1)		172.0(2)
$C_{carbene}\cdots Cl$	3.057 (C1···Cl1) 3.138 (C1···Cl2)	3.172 (C1···Cl1) 3.232 (C1···Cl2) 3.258 (C22···Cl1) 3.120 (C22···Cl2)	3.190 (C1···Cl1) 3.304 (C1···Cl2)	3.329 (C7···Cl1) 3.175 (C7···Cl2)	3.296 (C1···Cl1) 3.174 (C1···Cl2)	3.247 (C1···Cl1) 3.100 (C1···Cl2) 3.113 (C22···Cl1) 3.222 (C22···Cl2)	3.176 (C1···Cl1)
τ	0.46	0.10	0.26	0.47	0.22	0.25	0.47

[a] Geometric parameters are given for *molecule A*.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded on Bruker ARX250, DPX300, and Avance500 spectrometers, are referenced internally to residual protiosolvent (^1H) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{29}Si NMR (59.6 MHz) spectra were recorded on a Bruker DPX300 spectrometer. Chemical shifts are quoted in δ (ppm). Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). EPR spectra were recorded on a Bruker ELEXYS E500 spectrometer (Xband Super X ER049 microwave bridge). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) or by the Service Central de Microanalyses du CNRS at Vernaison (France).

The $Ti(NMe_2)_4$ used in this study was prepared by a modification of a literature procedure[28] or purchased from commercial sources (Aldrich, Acros). $TiCl_2(NMe_2)_2$ was prepared from reaction of an equimolar amount of $TiCl_4$ and $Ti(NMe_2)_4$. Imido precursors $Ti(=N\text{-}R)Cl_2(NHMe_2)_2$ and $Ti(=N\text{-}R)Cl_2(Py)_3$ were prepared according to our published procedure.[26] Imido-bridged dimers $\{Ti(NR)(NMe_2)_2\}_2$ were prepared by a similar synthesis to the one we used for analoguous vanadium compounds (full details on their synthesis, characterization, and reactivity will be described elsewhere).[22] IMes·HCl was prepared by a literature procedure.[29,30] IMes was obtained by deprotonation of IMes·HCl with NaH in THF using a catalytic amount of $KOBu^t$.

Crystal Structure Determination. The structures of seven compounds were determined. Crystal data collection and processing parameters are given in Table 2. Crystals of **1** (red plates), **2** (dark green parallelepipeds), **3a** (yellow-orange parallelepipeds), **3d** (yellow-orange plates), **3e** (light yellow blocks), **4** (yellow platelets), and **5** (yellow blocks) were obtained. The selected crystals, sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N_2. For all the structures data collection were collected at low temperature ($T = 180$ K) on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems cryostream cooler device or an Oxford Diffraction Kappa CCD Excalibur diffractometer equipped with a cryojet from Oxford Instruments and using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities was observed. Structures have been solved by means of direct methods using the program SIR92[31] and subsequent difference Fourier maps. Models were refined by least-squares procedures on a F^2 by using SHELXL-97[32] integrated in the package WINGX version 1.64,[33] and empirical absorption corrections were applied on the data.[34] For **3a**, it was not possible to solve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON[35] resulted in a smooth refinement. Since a few low-order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for *D*(calc), *F*(000), and the molecular weight are valid only for the ordered part of the structure. Details of the structure solution and refinements are given in the Supporting Information (CIF file). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all structures have been deposited at the Cambridge Crystallographic Data Centre.

$[TiCl_2(NMe_2)_2(IMes)]$ (1). Method 1 (from $Ti(NMe_2)_4$ and IMes·HCl): To a THF solution (5 mL) of 200 mg of $Ti(NMe_2)_4$ (0.89206 mmol) was added by portions 2 equiv of IMes (608 mg, 1.7841 mmol) at room temperature. The resulting orange suspension was stirred for 2 days at RT. A filtration to remove about 330 mg of unreacted IMes·HCl afforded a red solution, from which an orange solid was obtained after pumping off the volatiles. Extraction with 1.5 mL of toluene and layering this filtered solution with 10

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mL of pentane afforded large red crystals of **1**. The crystals were washed with cold pentane (2 × 2 mL) and dried under vacuum to give analytically and spectroscopically pure material. Yield: 65 mg (14%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.73 (s, 4H, $C_6H_2Me_3$), 6.08 (s, 2H, $=CH$), 3.02 (s, 12H, NMe_2), 2.41 (s, 12H, *o-*Me_{Mes}), 2.07 (s, 6H, *p-*Me_{Mes}). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 194.0 (s, $C_{carbene}$), 139.3 (s), 137.5 (s), 136.6 (s), 129.6 (d), 122.0 (d) 48.1 (q, NMe_2), 21.24 (q, Me_{Mes}), 19.57 (q, Me_{Mes}). IR 3164 (w), 3136 (w), 2960 (w), 2813 (m), 2854 (s), 2769 (m), 1607 m), 1536 (w), 1484 (s), 1457 (s), 1411 (m), 1395 (s), 1267 (m), 1247 (m), 1229 (s), 1160 (br), 1104 (m), 941 (vs), 867 (m), 849 (m), 733 (m), 698 (m), 601 (m), 592 (m), 573 (m). Anal. Calcd for $C_{25}H_{36}Cl_2N_4Ti$ (511.35): C, 58.72; H, 7.10; N, 10.96. Found: C, 58.60; H, 7.11; N, 10.84.

Method 2 (from $TiCl_2(NMe_2)_2$ and IMes): 294 mg of IMes (0.9666 mM) was added to a toluene (4 mL) solution of $TiCl_2(NMe_2)_2$ (200 mg, 0.9666 mM), and the resulting solution was stirred for 12 h at RT. The solution was filtered through a bed of Celite to remove a few impurities and slowly layered with a solution of pentane, affording large red crystals. The crystals were collected and dried under vacuum (320 mg). A second crop (20 mg) could later be obtained from the cold solution (−20 °C). Yield: 340 mg (97%).

[$TiCl_2(NMe_2)(IMes)_2$] (2). This compound was crystallized from a complex mixture of products (containing **1**, **2**, IMes, and IMes•HCl and unknown products) obtained using a procedure similar to the synthesis of **1** but using a reaction time of 3 days at room temperature followed by 14 h at 70 °C. The workup procedure is the same as the one described above for **1**. Green crystals of **2** were selectively obtained by careful layering of a toluene solution of the mixture with small amounts of pentane and collecting the green crystals before red crystals of **1** start to be formed. The yield of **2** is kept very low (20 mg (3%)) in order to get pure **2**, without contamination by **1**. EPR (toluene, 20 °C): $g = 1.9433$. Anal. Calcd for $C_{44}H_{54}Cl_2N_5Ti$ (771.71): C, 68.48; H, 7.05; N, 9.08. Found: C, 68.36; H, 7.03; N, 8.92.

[Ti(=N-2,6-Pr^i_2-C_6H_3)$Cl_2(NHMe_2)$(IMes)] (3a). Method 1 (*Path A* from **1**): A solution of **1** (50 mg, 0.09778 mM) in toluene (1 mL) was stirred overnight with 1 equiv of 2,6-$^iPr_2$-$C_6H_3NH_2$ (17 mg). Volatiles were removed under vacuum, and the cream solid was washed with pentane (2 × 2 mL) and dried under vacuum. Yield: 49 mg (80%).

Method 2 (*Path C* from Ti(=N-2,6-Pr^i_2-C_6H_3)$Cl_2(NHMe_2)_2$): A solution of Ti(=N-2,6-Pr^i_2-C_6H_3)$Cl_2(NHMe_2)_2$ (100 mg, 0.26027 mM) in toluene (2 mL) was treated with 79 mg of IMes and stirred for 12 h. The reaction mixture was filtered, and the resulting pale orange solution was left overnight, during which time crystallization started. Pentane (3 mL) was slowly added to complete the crystallization. The crystals were collected, washed with pentane (3 × 3 mL), and dried under vacuum. Yield: 140 mg (85%).

^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 6.82 (d, $^{3}J = 7.5$ Hz, 2H, $C_6H_3Pr^i_2$), 6.70 (t, $^{3}J = 7.5$ Hz, 1H, $C_6H_3Pr^i_2$), 6.64 (s, 4H, $C_6H_2Me_3$), 6.06 (s, 2H, $=CH$), 4.54 (sept, $^{3}J = 6.7$ Hz, 2H, Pr^i), 3.11 (br m, 1H, $HNMe_2$), 2.34 (s, 12H, o-Me_{Mes}), 2.09 (br d, $^{3}J = 6.0$ Hz, 6H, $HNMe_2$), 1.96 (s, 6H, p-Me_{Mes}), 1.42 (app br t, $^{3}J = 7.9$ Hz, 12H, Pr^i). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 191.1 ($C_{carbene}$), 157.5 (C_6H_3), 145.4 (C_6H_3), 138.3 (*IMes*), 136.0 (*IMes*), 135.6 (*IMes*), 128.8 (*IMes*), 121.9 (C_6H_3), 121.3 ($C=C_{IMes}$), 120.9 (C_6H_3), 39.2 ($HNMe_2$), 27.3 ($CHMe_aMe_b$), 27.0 ($CHMe_2$), 21.9 ($CHMe_aMe_b$), 20.8 (Me_{Mes}), 18.7 (Me_{Mes}). IR: 3291, (w, $NHMe_2$), 3161 (w), 3133 (w), 2960 (w), 2920 (m), 1612 (w), 1539 (w), 1487 (s), 1468 (s), 1421 (m), 1377 (s), 1326 (m), 1247 (m), 1279 (s), 1228 (br), 1098 (m), 987 (s), 897 (s), 853 (s), 750 (vs), 743 (m), 732 (m), 698 (m). Anal. Calcd for $C_{35}H_{48}Cl_2N_4Ti$•(1/2 toluene) (689.62): C, 67.05; H, 7.60; N, 8.12. Found: C, 58.60; H, 7.11; N, 10.84 (this elemental analysis was done on a crystalline sample that was shown by X-ray and ^{1}H NMR to contain 1/2 molecule of toluene).

[Ti(=N-$SiPh_3$)$Cl_2(NHMe_2)$(IMes)] (3b). Complex **3b** was prepared using a slight modification of method 1 described for **3a** (using *in-situ*-prepared **1**). A 50 mg portion of $Ti(NMe_2)_2Cl_2$ (0.24164 mM) and 73.6 mg of IMes (0.24164 mM) were stirred in THF (2 mL) for 5 min. Solid Ph_3SiNH_2 (66 mg) was added to the resulting red solution. After 12 h of stirring at RT, the volatiles were removed under vacuum, affording a cream solid that was washed with pentane (3 × 3 mL). Yield: 130 mg (73%).

^{1}H NMR (300 MHz, C_6D_6): δ 8.07 (dd, $J = 1.8$ and 7.5 Hz, 6H, o-C_6H_5), 7.22 (m, 9H, C_6H_5), 6.38 (s, 4H, $C_6H_2Me_3$), 6.05 (s, 2H, $=CH$), 2.70 (br m, 1H, $HNMe_2$), 2.33 (s, 12H, o-Me_{Mes}), 1.83 (s, 6H, p-Me_{Mes}), 1.60 (d, $^{3}J = 6.0$ Hz, 6H, $HNMe_2$). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 190.8 ($C_{carbene}$), 139.3 (*IMes*), 138.8 (*IMes*), 136.5 (C_6H_5), 136.3 (C_6H_5), 129.8 (*IMes*), 129.3 (C_6H_5), 127.9 (C_6H_5), 121.8 ($C=C_{IMes}$), 38.8 ($HNMe_2$), 21.2 (Me_{Mes}), 18.0 (Me_{Mes}). ^{29}Si NMR (59.63 MHz, C_6D_6): δ −51.1. IR: ν_{NH} not seen, 3043 (w), 2918 (m), 1610 (w), 1538 (w), 1483 (m), 1428 (s), 1231 (m), 1113 (vs), 855 (m), 743 (m), 703 (s), 511 (m). Anal. Calcd for $C_{41}H_{46}Cl_2N_4SiTi$ (741.69): C, 66.39; H, 6.25; N, 7.55. Found: C, 66.41; H, 6.32; N, 7.44.

[Ti(=N-1-adamantyl)$Cl_2(NHMe_2)$(IMes)] (3c). Complex **3c** was obtained as a cream solid in 70% yield using method 1 described for **3a**.

^{1}H NMR (300 MHz, C_6D_6): δ 6.77 (s, 4H, $C_6H_2Me_3$), 6.03 (s, 2H, $=CH$), 2.92 (br m, 1H, $HNMe_2$), 2.40 (s, 12H, o-Me_{Mes}), 2.12 (s, 6H, p-Me_{Mes}), 1.97 (d, $^{3}J = 6.0$ Hz, 6H, $HNMe_2$), 1.85 (br s, 3H, CH_{ada}), 1.48 (br s, 6H, $CH_{2\ ada}$), 1.38 (s, 6H, $CH_{2\ ada}$). IR: ν_{NH} not observed, 3154 (w), 3119 (w), 2909 (s), 2848 (sh), 1607 (m), 1538 (m), 1483 (m), 1456 (m), 1233 (s), 1090 (m), 1035 (m), 896 (m), 852 (m), 734 (m), 570 (m), 466 (m). Anal. Calcd for $C_{33}H_{48}Cl_2N_4Ti$ (619.53): C, 63.98; H, 7.81; N, 9.04. Found: C, 63.90; H, 7.72; N, 8.95.

[Ti(=N-2,6-Cl_2−C_6H_3)$Cl_2(NHMe_2)$(IMes)] (3d). Method 1 (*Path A* from **1**): The reaction of **1** with 2,6-Cl_2-$C_6H_3NH_2$ as descibed for **3a**, method 1, gave mixtures of compounds (see Results and Discussion section).

Method 2 (*Path C* from Ti(=N-2,6-Cl_2-C_6H_3)$Cl_2(NHMe_2)_2$): The synthesis was similar to the one described for **3a** using method 2. Compound **3d** was obtained as a pale orange solid in 76% yield (130 mg starting on 100 mg imido-Ti precursor scale). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a saturated toluene solution of **3d**. ^{1}H NMR (300 MHz, C_6D_6): δ 6.81 (d, $^{3}J = 7.8$ Hz, 2H, $C_6H_3Cl_2$), 6.69 (s, 4H, $C_6H_2Me_3$), 6.10 (t, $^{3}J = 7.9$ Hz, 1H, $C_6H_3Cl_2$), 6.09 (s, 2H, $=CH$), 2.67 (br m, 1H, $HNMe_2$), 2.40 (s, 12H, o-Me_{Mes}), 2.02 (d, $^{3}J = 6.0$ Hz, 6H, $HNMe_2$), 1.95 (s, 6H, p-Me_{Mes}). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 191.4 ($C_{carbene}$), 151.1 (C_6H_3), 138.8 (C_6H_3), 137.1 (*IMes*), 136.5 (*IMes*), 133.9 (*IMes*), 129.5 (*IMes*), 127.2 (C_6H_3), 121.9 (C_6H_3), 121.2 ($C=C_{IMes}$), 40.3 ($HNMe_2$), 21.5 (Me_{Mes}), 19.6 (Me_{Mes}). IR: 3295, (w, $NHMe_2$), 3170 (w), 3140 (w), 2916 (w), 1610 (m), 1537 (w), 1487 (s), 1470 (s), 1426 (m), 1325 (m), 1269 (w), 1229 (m), 1071 (m), 1021 (m), 986 (m), 899 (m), 864 (w), 786 (m), 759 (m), 722 (m), 695 (m), 557 (w), 415 (w). Anal. Calcd for $C_{29}H_{34}Cl_4N_4Ti$ (628.29): C, 55.44; H, 5.45; N, 8.92. Found: C, 55.54; H, 5.44; N, 8.82.

[Ti(=N-Bu^t)$Cl_2(NHMe_2)$(IMes)] (3e). Method 2 (*Path C* from Ti(=N-Bu^t)$Cl_2(NHMe_2)_2$): The synthesis was similar to the one described for **3a** using method 2. Compound **3e** was obtained as yellow crystals in 63% yield (120 mg starting on 100 mg imido-Ti precursor scale).

^{1}H NMR (300 MHz, C_6D_6): δ 6.77 (s, 4H, $C_6H_2Me_3$), 6.03 (s, 2H, $=CH$), 2.87 (br m, 1H, $HNMe_2$), 2.39 (s, 12H, o-Me_{Mes}), 2.10 (s, 6H, p-Me_{Mes}), 1.95 (d, $^{3}J = 6.1$ Hz, 6H, $HNMe_2$), 0.85 (s, 9H, Bu^t). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 191.6 ($C_{carbene}$), 139.1

(*IMes*), 137.5 (*IMes*), 137.1 (*IMes*), 129.5 (*IMes*), 122.0 ($C{=}C_{\mathrm{IMes}}$), 39.1 (HNMe_2), 31.3 (Bu^t), 21.3 (Me_{Mes}), 19.5 (Me_{Mes}). IR 3227 (m, $\mathrm{NHMe_2}$), 3119 (w), 3100 (w), 2962 (s), 2916 (s), 1608 (m), 1540 (w), 1486 (s), 1399 (m), 1351 (m), 1267 (w), 1245 (vs), 1015 (s), 904 (m), 851 (s), 744 (m), 507 (s). Anal. Calcd for $\mathrm{C_{27}H_{40}Cl_2N_4Ti}$ (539.41): C, 60.12; H, 7.47; N, 10.39. Found: C, 60.13; H, 7.42; N, 10.22.

[Ti(=N-2,6-$\mathbf{Cl_2{-}C_6H_3)Cl_2(IMes)_2}$] (4). To a THF solution (5 mL) of 100 mg of Ti(=N-2,6-$\mathrm{Cl_2{-}C_6H_3)Cl_2(NHMe_2)_2}$ (0.27105 mmol) was added by portions 2 equiv of IMes (165 mg) at room temperature. The resulting yellow solution was stirred for 24 h at RT. The volatiles were pumped off, and the yellow solid was washed with cold pentane (2 × 5 mL) and dried under vacuum. Yield: 95 mg (40%). Single crystals of **4**, suitable for X-ray diffraction studies, were obtained by slow evaporation of a saturated pentane solution of **4**.

^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 6.62 (s, 8H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 6.61 (d, ^3J = 7.5 Hz, 2H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.01 (t, ^3J = 7.8 Hz, 1H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 5.95 (s, 4H, =C$H$), 2.24 (s, 24H, o-$Me_{Mes}$), 2.12 (s, 12H, p-$Me_{Mes}$). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 192.8 (C_{carbene}), 137.9 ($C_6\mathrm{H_3}$), 137.6 (*IMes*), 136.4 (*IMes*), 129.6 (*IMes*), 126.7 ($C_6\mathrm{H_3}$), 122.2 ($\mathrm{C{=}C_{IMes}}$), 120.0 ($C_6\mathrm{H_3}$), 21.7 (Me_{Mes}), 19.6 (Me_{Mes}) (Note: one missing peak in the aromatic region is obscured by residual protiosolvent). IR: 3168 (w), 3131 (w), 3029 (m), 2917 (m), 2857 (m), 1610 (w), 1540 (w), 1485 (s), 1424 (vs), 1393 (m), 1326 (m), 1263 (m), 1231 (m), 1035 (m), 979 (m), 928 (m), 847 (s), 782 (m), 760 (m), 722 (m), 695 (m), 573 (w), 555 (w). Anal. Calcd for $\mathrm{C_{48}H_{51}Cl_4N_5Ti}$ (887.63): C, 64.95; H, 5.79; N, 7.89. Found: C, 64.96; H, 5.74; N, 7.83.

[Ti(=N-2,6-$\mathbf{Cl_2{-}C_6H_3}$)(NH-2,6-$\mathbf{Cl_2\text{-}C_6H_3}$)Cl($\mathbf{NHMe_2}$)(IMes)] (5). To a THF solution (3 mL) of 100 mg of $\mathrm{Ti(NMe_2)_4}$ (0.44603 mmol) were added 2 equiv of 2,6-$\mathrm{Cl_2\text{-}C_6H_3NH_2}$ (144 mg, 0.89206 mmol) and 1 equiv of IMes·HCl (152 mg, 0.44603 mmol). The solution was stirred for 1 day at RT before removing by filtration a small amount of white insolubles. The volatiles were pumped off, and the orange solid was washed with pentane (2 × 5 mL) and dried under vacuum. Yield: 230 mg (68%).

^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 9.89 (s, 1H, N$H\mathrm{C_6H_2Me_3}$), 6.88 (d, ^3J = 7.2 Hz, 2H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.58 (d, ^3J = 8.0 Hz, 2H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.52 (s, 4H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 6.12 (t, ^3J = 8.0 Hz, 1H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.08 (t, ^3J = 7.9 Hz, 1H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.03 (s, 2H, =C$H$), 2.39 (s, 6H, o-$Me_{Mes}$), 2.23 (s, 6H, o-$Me_{Mes}$), 2.10 (br, 6H, NH$Me_2$), 2.03 (s, 6H, p-$Me_{Mes}$) (Note: the signal for $H\mathrm{NMe_2}$ was not observed). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 191.8 (C_{carbene}), 150.1, 149.6, 137.8, 137.6, 137.5, 136.4, 135.6, 129.1, 128.5, 127.0, 126.0, 122.1, 119.4, 114.5, 41.2 (NHMe_2), 21.1 (*p*-Me_{Mes}), 18.7 (*o*-Me_{Mes}), 18.4 (*o*-Me_{Mes}). IR: 3305 (m, NHAr), 3173 (m, $\mathrm{NHMe_2}$), 3141 (m, $\mathrm{NHMe_2}$), 2917 (m), 1610 (m), 1579 (m), 1447 (s), 1424 (vs), 1329 (m), 1282 (m), 1162 (m), 1070 (m), 972 (m), 893 (m), 865 (m), 849 (m), 778 (m), 726 (m), 717 (m), 658 (m), 658 (m), 456 (m). Anal. Calcd for $\mathrm{C_{35}H_{38}Cl_5N_5Ti}$ (753.84): C, 55.76; H, 5.08; N, 9.29. Found: C, 64.96; H, 5.74; N, 7.83.

[Ti(=N-R)$\mathbf{Cl_2}$(Py)(IMes)] (6). Method 1 (from [Ti(=N-R)$\mathrm{Cl_2(NHMe_2)}$(IMes)] and pyridine): That method was used for R = 2,6-Pr^i_2-$\mathrm{C_6H_3}$, 2,6-$\mathrm{Cl_2{-}C_6H_3}$, and Bu^t. Five equivalents of pyridine was added to a THF or toluene solution (1 mL) of 10 mg of [Ti(=N-R)$\mathrm{Cl_2(NHMe_2)}$(IMes)]. After 30 min at RT, the volatiles were removed under vacuum, giving spectroscopically pure **6**.

6a [R = 2,6-$\mathbf{Pr^i_2\text{-}C_6H_3}$]. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 20 °C): δ 8.72 (d, ^3J = 4.8 Hz, 2H, *Py*), 6.86 (d, ^3J = 7.5 Hz, 2H, $\mathrm{C_6}H_3\mathrm{Pr}^i_2$), 6.72 (t, ^3J = 7.6 Hz, 1H, $\mathrm{C_6}H_3\mathrm{Pr}^i_2$), 6.69 (s, 4H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 6.60 (br, 1H, *Py*), 6.30 (br t, ^3J = 4.7 Hz, 2H, *Py*), 6.14 (s, 2H, =CH), 4.59 (sept, ^3J = 6.6 Hz, 2H, Pr^i), 2.44 (s, 12H, o-Me_{Mes}), 2.09 (br d, ^3J = 6.0 Hz, 6H, HNMe_2), 1.96 (s, 6H, p-Me_{Mes}), 1.41 (app br t, ^3J = 7.8 Hz, 12H, Pr^i). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 192.6 (C_{carbene}), 157.4 ($C_6\mathrm{H_3}$), 150.0 (*Py*), 145.6 ($C_6\mathrm{H_3}$), 138.3 (*IMes*), 136.8 (*Py*), 136.6 (*IMes*), 135.6 (*IMes*), 128.9 (*IMes*), 123.3 (*Py*), 122.3 ($C_6\mathrm{H_3}$), 121.5 ($\mathrm{C{=}C_{IMes}}$), 121.2 ($C_6\mathrm{H_3}$), 27.9 (CHMe_2), 24.1 ($C\mathrm{HMe_2}$), 18.8 (Me_{Mes}), 17.3 (Me_{Mes}).

6d [R = 2,6-$\mathbf{Cl_2\text{-}C_6H_3}$]. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.95 (br s, 2H, *Py*), 6.77 (d, ^3J = 7.8 Hz, 2H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 6.71 (s, 4H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 6.44 (t, ^3J = 5.0 Hz, 1H, Py), 6.35 (br s, 2H, *Py*), 6.15 (s, 2H, =CH), 6.02 (t, ^3J = 7.8 Hz, 1H, $\mathrm{C_6}H_3\mathrm{Cl_2}$), 2.49 (s, 12H, o-$Me_{Mes}$), 1.94 (s, 6H, p-$Me_{Mes}$). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 191.8 (C_{carbene}), 151.8 ($C_6\mathrm{H_3}$), 151.2 (*Py*), 139.0 ($C_6\mathrm{H_3}$), 137.4 (*IMes*), 136.6 (*IMes*), 134.1 (*IMes*), 129.6 (*IMes*), 127.2 ($C_6\mathrm{H_3}$), 124.6 (*Py*), 122.0 ($\mathrm{C{=}C_{IMes}}$), 121.4 ($C_6\mathrm{H_3}$), 21.6 (Me_{Mes}), 19.8 (Me_{Mes}).

6e [R = $\mathbf{Bu^t}$]. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.12 (d, ^3J = 4.8 Hz, 2H, *Py*), 6.78 (s, 4H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 6.67 (app tt, ^3J = 4.8 Hz, 1H, *Py*), 6.41 (app dd, ^3J = 4.7 Hz, 2H, *Py*), 6.08 (s, 2H, =CH), 2.43 (s, 12H, o-Me_{Mes}), 2.08 (s, 6H, p-Me_{Mes}), 0.81 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 191.6 (C_{carbene}), 152.3 (*Py*), 139.1 (*IMes*), 137.6 (*IMes*), 137.3 (*Py*), 130.2 (*IMes*), 128.2 (*IMes*), 123.4 (*Py*), 122.2 ($C{=}C_{\mathrm{IMes}}$), 30.9 (Bu^t), 21.3 (Me_{Mes}), 19.6 (Me_{Mes}).

Method 2 (from [Ti(=N-R)$\mathrm{Cl_2(Py)_3}$] and IMes): That method was used for R = (−)-*cis*-myrtanyl. Solid IMes (30 mg) was added to a suspension of Ti(=N-{(−)-*cis*-myrtanyl})$\mathrm{Cl_2(Py)_3}$ (50 mg, 0.09856 mM) in 1 mL of THF and stirred overnight. Filtration afforded **6f*** as an orange solid, which was washed with pentane and dried under vacuum. Yield: 47 mg (94%).

^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 9.07 (br d, 2H, *Py*), 6.80 (s, 2H, o-$\mathrm{C_6}H^A{}_2\mathrm{Me_3}$), 6.78 (s, 2H, o-$\mathrm{C_6}H^B{}_2\mathrm{Me_3}$), 6.71 (br, 1H, *Py*), 6.44 (t, ^3J = 4.5 Hz, 2H, Py), 6.16 (s, 2H, =CH), 2.48 (s, 6H, o-$Me^A{}_{Mes}$), 2.47 (s, 6H, o-$Me^B{}_{Mes}$), 2.25−2.10 (br, 4H, CH+CH_2N+CH), 2.09 (s, 6H, p-Me_{Mes}), 1.80−1.75 (br, 3H, CH+CH_2), 0.99 (s, 3H, Me_{Myr}), 0.72 (s, 3H, Me_{Myr}). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 191.9 (C_{carbene}), 151.1 (*Py*), 138.1 (*IMes*), 136.6 (*IMes*), 136.3 (*Py*), 129.6 (*Py*), 129.0 (*IMes*), 128.1 (*IMes*), 123.1 (*Py*), 121.4 ($C{=}C_{\mathrm{IMes}}$), 75.9 ($C\mathrm{H_2N}$), 44.6 (CH), 44.0 (CH), 41.6 (CH), 38.3 ($C\mathrm{Me_2}$), 33.7 ($C\mathrm{H_2}$), 28.0 (Me_{Myr}), 26.5 ($C\mathrm{H_2}$), 23.2 (Me_{Myr}), 20.8 (p-Me_{Mes}), 20.3 ($C\mathrm{H_2}$), 18.9 (o-Me_{Mes}). Anal. Calcd for $\mathrm{C_{25}H_{32}Cl_2N_4Ti}$ (507.32): C, 59.19; H, 6.36; N, 11.04. Found: C, 59.04; H, 6.35; N, 10.91.

Results and Discussion

The synthesis and proposed structures of the NHC complexes of titanium are summarized in Figure 1 and Schemes 1–8. Structures of seven complexes are shown in Figures 2 and 4–6 or given in the Supporting Information. Selected metric data are collected in Table 1.

Two main strategies were investigated in order to prepare these titanium(IV) complexes supported by an alkyl-, aryl-, or silyl-imido function and an NHC ligand (IMes was chosen as a typical NHC) and starting from a readily available starting material ($\mathrm{Ti(NMe_2)_4}$). As illustrated in Figure 1, the difference arises from the order of introduction of the two respective ligands. In *Path A* the NHC ligand is introduced before the imide group, while *Paths B and C* consist of introducing the imide group first. Also, the NHC ligand was introduced in two ways: (i) amine elimination from an amido precursor reacted with the salt IMes·HCl (*Paths A* and *B*) or (ii) reaction with free carbene IMes (*Path C*).

1. Investigation of Path A. 1.1. Reaction of $\mathbf{Ti(NMe_2)_4}$ with IMes·HCl and Preparation of $\mathbf{TiCl_2(NMe_2)_2}$(IMes).

While we were initially studying the reaction of imido−titanium compounds with NHC ligands (*vide infra*), Cowley and Abernethy communicated the direct reaction of IMes·HCl with $\mathrm{Ti(NMe_2)_4}$ leading to the NHC complex $\mathrm{TiCl_2(NMe_2)_2}$(IMes) (**1**).[14] This synthetic route presents the advantage of employing directly the imidazolium salt, that way avoiding the preparation of the deprotonated NHC. Inspired by these results, we decided

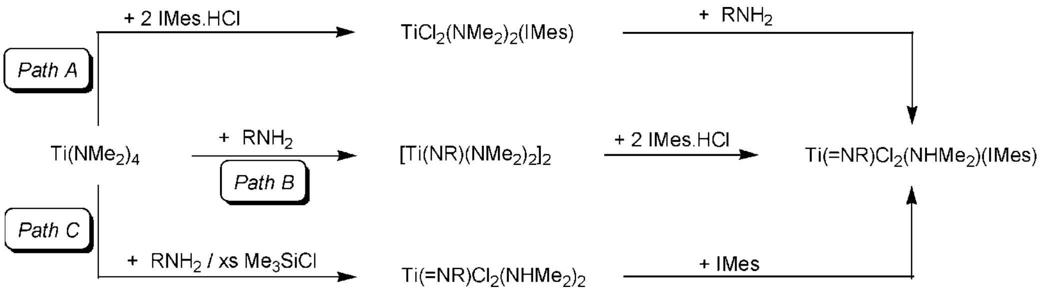


Figure 1. Main strategies employed for the introduction of an imide functionality and a NHC ligand within a titanium compound.

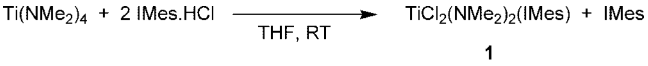
Table 2. Crystallographic Data, Data Collection, and Refinement Parameters for 1, 2, 3a, 3d, 3e, 4, and 5

	1	2	3a	3d	3e	4	5[a]
chemical formula	$C_{25}H_{36}Cl_2N_4Ti$	$C_{44}H_{54}Cl_2N_5Ti$	$C_{35}H_{48}Cl_2N_4Ti$	$C_{29}H_{34}Cl_4N_4Ti$	$C_{27}H_{40}Cl_2N_4Ti$	$C_{48}H_{51}Cl_4N_5Ti$	$C_{35}H_{38}Cl_5N_5Ti$
fw	511.38	771.72	643.57	628.30	539.40	887.64	753.85
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	*Pcab*	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1$
a, Å	18.8864(19)	15.1103(5)	13.2517(5)	9.2583(7)	16.2363(6)	13.2498(9)	a = 12.1170(8)
b, Å	16.5995(13)	11.5282(4)	42.872(2)	40.714(4)	17.0367(7)	14.9309(14)	10.8360(7)
c, Å	17.9096(16)	24.8172(9)	13.2474(5)	8.6018(7)	43.7810(17)	23.7215(16)	14.5802(9)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	105.273(9)	93.401(3)	90.0	108.365(7)	90.0	89.522(8)	111.287(6)
γ, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0
V, Å^3	5416.4(8)	4315.4(3)	7526.2(5)	3077.3(5)	12110.4(8)	4692.7(6)	1783.8(2)
Z	4	4	8	4	16	4	2
D_{calc}, g cm^{-3}	1.254	1.188	1.136	1.356	1.183	1.256	1.404
μ (Mo Kα), mm^{-1}	0.532	0.357	0.396	0.651	0.480	0.448	0.647
F(000)	2160	1636	2736	1304	4576	1856	780
θ range (deg)	2.55 to 25.35	2.70 to 26.37	3.08 to 25.35	2.69 to 24.71	1.56 to 25.68	2.19 to 26.15	2.61 to 25.35
no. of measd reflns	38 100	33 133	50 967	20 562	95 537	45 892	12 910
no. of unique reflns/ R_{int}	9891/0.1451	8827/0.0646	6865/0.1266	5224/0.0889	11491/0.0437	9054/0.0852	6510/0.0553
no. of params/ restraints	57/0	483/0	391/0	321/0	631/0	535/0	423/19
final *R* indices [$I > \sigma 2(I)$]	R1 = 0.1088 wR2 = 0.2897	R1 = 0.0439 wR2 = 0.1043	R1 = 0.0566 wR2 = 0.1313	R1 = 0.0676 wR2 = 0.1370	R1 = 0.0546 wR2 = 0.1201	R1 = 0.0381 wR2 = 0.0811	R1 = 0.0736 wR2 = 0.1895
final *R* indices all data	R1 = 0.2467 wR2 = 0.3608	R1 = 0.1054 wR2 = 0.1544	R1 = 0.1223 wR2 = 0.1625	R1 = 0.1300 wR2 = 0.1642	R1 = 0.0763 wR2 = 0.1301	R1 = 0.0742 wR2 = 0.0919	R1 = 0.1011 wR2 = 0.2093
goodness of fit	0.967	0.998	1.001	1.020	1.088	0.903	1.016
$\Delta\rho_{max}$, $\Delta\rho_{min}$	1.269 and −0.749	0.357 and −0.342	0.507 and −0.332	0.959 and −0.763	0.616 and −0.566	0.324 and −0.308	2.125 and −0.729

[a] Absolute structure parameter: 0.04(6).

to further evaluate this route leading to **1** that could represent a good precursor to imido−NHC complexes (*Path A*).

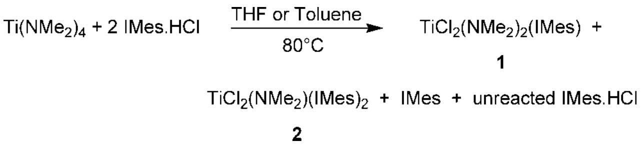
Scheme 1. Synthesis of NHC Complex 1



According to Cowley and Abernethy, **1** was obtained by treatment of $Ti(NMe_2)_4$ with 2 equiv of IMes•HCl in THF. As summarized in Scheme 1, the reaction proceeds through amine elimination (deprotonation of the imidazolium salt by the dimethylamide ligand), with concomitant formation of 1 equiv of IMes. Although the authors reported a 45% yield, in our hands the reaction proved difficult to go to completion. Indeed, we noticed that about half of the IMes•HCl introduced is recovered by filtration of the reaction mixture at the end of the reaction. As a consequence, compound **1** was obtained in only very modest yield (14−25%) after a necessary recrystallization step (to separate **1** from free IMes). Our attempts to improve the conversion of $Ti(NMe_2)_4$ to **1** by varying the experimental conditions (solvent, stoichiometry of reactants, longer reaction time) met with little success, and large amounts of IMes•HCl were invariably recovered during workup.

By contrast,heating the previous red suspension (composed of $Ti(NMe_2)_4$, **1**, IMes•HCl, and IMes) to 80 °C for 14 h led to a color change (to brown-green) (Scheme 2). Filtration to remove unreacted IMes•HCl and crystallization of the filtrate by layering with a solution of pentane afforded a mixture of red crystals of complex **1** (as confirmed by ^{1}H NMR) and dark green crystals of the paramagnetic complex **2**.[36] Noteworthy, selective crystallization by progressively adding small portions of pentane to a toluene solution and by separating the green crystals (before the red crystals begin to grow) afforded a pure sample of complex **2**.

Scheme 2. Synthesis of NHC Complex 1 with Concomitant Formation of 2



It is unclear how **2** is formed, but preliminary studies suggest that the presence of large amounts of unreacted IMes•HCl could be involved in its formation from reaction with **1**. Further studies will be necessary to clarify this point.

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[36] We were unable to determine the ratio **1**:**2** by NMR spectroscopy due to the strong paramagnetism of **2**. A visual determination under microscope showed this ratio to be approximately 1.

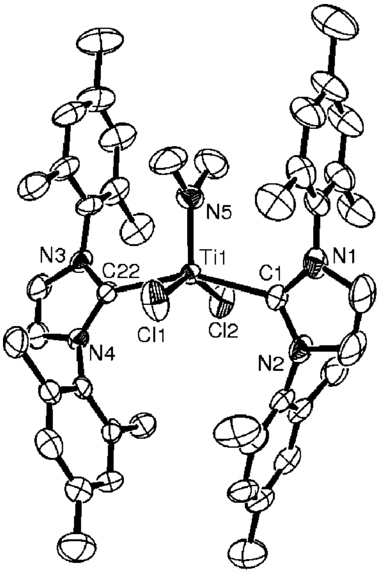

Figure 2. Molecular structure of **2**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Ti(1)−C(1) 2.293(3), Ti(1)−C(22) 2.297(3), Ti(1)−N(5) 1.857(3), Ti(1)−Cl(1) 2.3510(10), Ti(1)−Cl(2) 2.3876(9), C(1)−Ti(1)−C(22) 154.23(11), N(5)−Ti(1)−Cl(1) 101.69(10), N(5)−Ti(1)−Cl(2) 110.379(10), Cl(1)−Ti(1)−Cl(2) 147.93(4), C(1)−Ti(1)−N(5) 103.20(12), C(1)−Ti(1)−Cl(1) 86.14(8), C(1)−Ti(1)−Cl(2) 87.29(8), C(22)−Ti(1)−N(5) 102.57(11), C(22)−Ti(1)−Cl(1) 89.00(8), C(22)−Ti(1)−Cl(2) 83.49(8).

The green crystals of **2** were suitable for an X-ray structure determination. A thermal ellipsoid plot of the molecular structure of **2** is presented in Figure 2 along with selected bond lengths and angles, and in Table 1 for a comparison of its structural parameters. The X-ray structure analysis confirmed that **2** is a paramagnetic Ti(III) complex formulated as $TiCl_2(NMe_2)(IMes)_2$.

The coordination geometry of the pentacoordinated metal center is distorted square pyramidal ($\tau = 0.10$),[37] with the two respectively *trans* carbon atoms of the IMes ligands and the two *trans* chloride atoms forming the base of the pyramid. The Ti atom is 0.582(1) Å out of the mean plane through C(1)Cl(1)C(22)Cl(2) [mean deviation 0.07(1) Å]. The dimethylamide group is stuck between two mesityl substituents of each carbene ligand. Titanium−carbene bond distances are slightly shorter than in **1** (*vide infra*, av 2.32 Å) with Ti−C(1) = 2.293(3) and Ti−C(22) = 2.297(3) Å. The other bond distances are unremarkable ($Ti-NMe_2$ = 1.857(3) Å, Ti−Cl ca. 2.37 (av)). The short distances between the carbene carbon atoms and chlorine atoms (ranging from 3.120 to 3.256 Å), within the sum of van der Waals radii for C and Cl (3.45 Å),[38] support the presence of $C_{carbene}\cdots Cl$ intramolecular interactions. This observation was already made in other early transition metal−NHC complexes and interpreted as electron density from a lone pair of chloride donated into formally vacant molecular orbitals situated on the carbenic carbon.[7,14] These $C_{carbene}\cdots Cl$ interactions can be considered as a form of back-donation in which the electron density comes from the chlorine ligands rather than the metal center.[39]

1.2. Reaction of $TiCl_2(NMe_2)_2$ with IMes: Quantitative Preparation of $TiCl_2(NMe_2)_2(IMes)$. In order to get compound **1** in higher yield for further use (i.e., generation of the imido complex), we then decided to use $TiCl_2(NMe_2)_2$ as starting material.[40] The reaction of $TiCl_2(NMe_2)_2$ with 1 equiv of IMes proceeded smoothly in toluene and afforded directly red crystals of **1** in almost quantitative yield (Scheme 3). Spectroscopic studies (IR, NMR), elemental analysis, and X-ray studies confirmed these red crystals to be complex **1**. Although the solid state structure of **1** has previously been reported,[14] we crystallized **1** in a different diamorph with two independent molecules in the monoclinic cell. The molecular structure of **1** will not be discussed (full details are given as Supporting Information), but selected bond distances and angles are reported in Table 1 for comparison purposes.

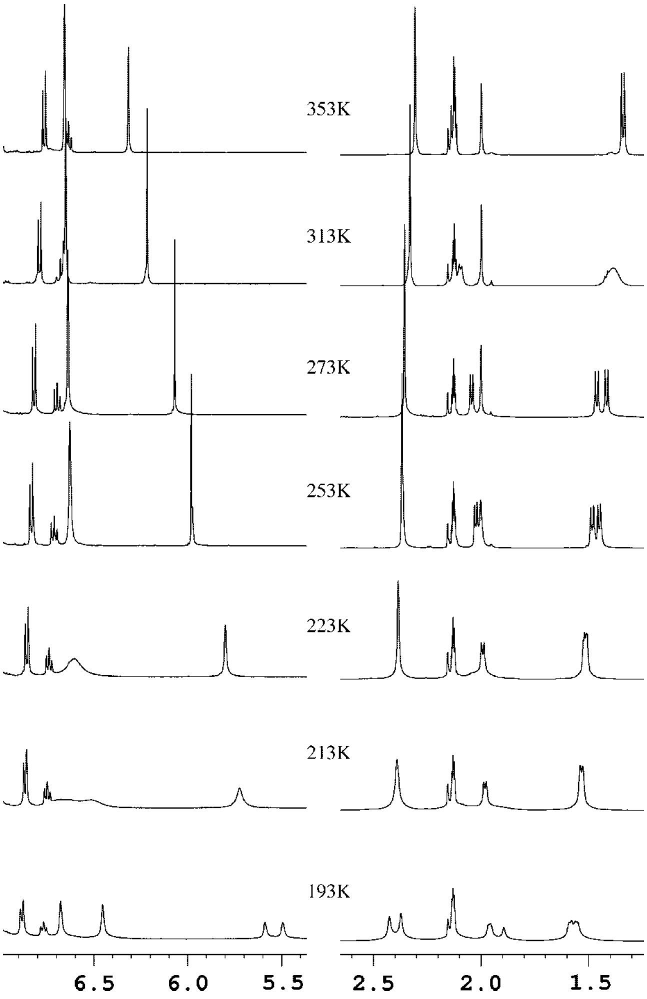

Figure 3. Variable-temperature ^1H NMR (500 MHz) study on **3a** in toluene-d_8, in the δ 7.0−5.4 and 2.6−1.3 region (the chemical shift scale is in ppm).

Scheme 3. High-Yield Synthesis of NHC Complex 1

$$TiCl_2(NMe_2)_2 + IMes \xrightarrow[THF,\ RT]{} \underset{\mathbf{1}}{TiCl_2(NMe_2)_2(IMes)}$$

1.3. Imido−titanium Complexes Generated from $TiCl_2(NMe_2)_2(IMes)$. As shown in Scheme 4, treatment of a toluene solution of **1** with 1 equiv of the aniline 2,6-Pr^i-C_6H_3-NH_2 produced the desired imido compound [Ti(=N-2,6-Pr^i-C_6H_3)Cl_2($NHMe_2$)(IMes)] (**3a**) as a cream solid in 80% yields. This

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[37] τ is the angular parameter commonly used to describe the geometry around the metal center in pentacoordinate complexes and defined as $\tau = (\alpha-\beta)/60$ (α and β are the two largest L−M−L bond angles, with $\alpha \geq \beta$). Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

[38] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

[39] Diez-Gonzalez, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874−883.

[40] Although we used isolated $TiCl_2(NMe_2)_2$ in most of the syntheses reported in this article, we have checked that *in-situ*-prepared $TiCl_2(NMe_2)_2$ (from equimolar amounts of $TiCl_4$ and $Ti(NMe_2)_4$) or $TiCl_2(NMe_2)_2(THF)_2$ (from equimolar amounts of $TiCl_4$ and $Ti(NMe_2)_4$ in THF) can be used as well for convenience.

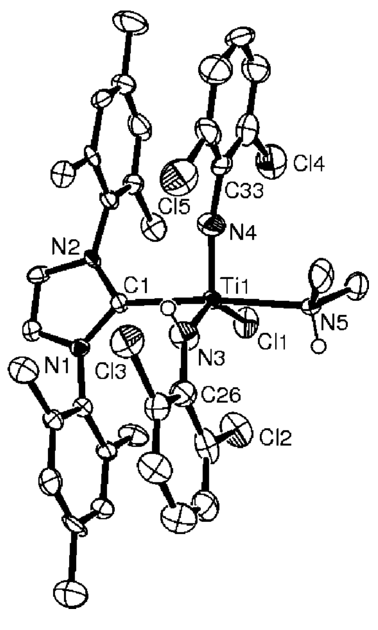

Figure 4. Molecular structure of **5**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Ti(1)−C(1) 2.290(6), Ti(1)−N(4) 1.715(6), Ti(1)−N(3) 1.974(6), Ti(1)−N(5) 2.282(6),), Ti(1)−Cl(1) 2.370(2), Ti(1)−N(4)−C(33) 169.3(6), C(1)−Ti(1)−N(5) 172.0(2), C(1)−Ti(1)−N(4) 96.1(3), C(1)−Ti(1)−N(4) 93.3(3), C(1)−Ti(1)−Cl(1) 85.95(17), N(4)−Ti(1)−N(5) 90.1(3), N(4)−Ti(1)−Cl(1) 114.9(3), N(4)−Ti(1)−N(3) 100.9(3), N(5)−Ti(1)−Cl(1) 86.94(15), N(5)−Ti(1)−N(3) 90.3(2), N(5)−Ti(1)−Cl(1) 144.0(2).

Scheme 4. Synthesis of Ti(=NR)Cl$_2$(NHMe$_2$)(IMes) from 1

$$\mathbf{1} + RNH_2 \xrightarrow[\text{THF, RT}]{} Ti(=NR)Cl_2(NHMe_2)(IMes)$$

3a : R = 2,6-Pr$^i_2$-C$_6$H$_3$
3b : R = SiPh$_3$
3c : R = 1-adamantyl

formulation for **3a** follows from NMR spectroscopic studies, IR, and microanalysis and has been confirmed unequivocally through a crystal structure determination (*vide infra*).

The room-temperature ^{1}H NMR spectrum of **3a** in C$_6$D$_6$ shows one set of broad resonances for the isopropyl groups, indicating fluxional behavior of the complex. To clarify this point, a temperature-dependent ^{1}H NMR experiment was carried out in toluene-*d*$_8$. At 273 K in toluene-*d*$_8$, the signal for the isopropyl groups of the spectrum sharpens to two doublets and one septet, corresponding to the methyl (**a**, **b**) and the methine resonances of the isopropyl group, respectively (Figure 3). Upon heating **3a** at 353 K, one doublet and one septet are observed for the isopropyl methyl and methine resonances, respectively. In toluene-*d*$_8$, the temperature of coalescence is observed at 313 K. This first dynamic process suggests that the steric hindrance of the isopropyl groups does not allow rotation of the imido ligand around the N−C axis, and therefore the methyl groups are in different chemical environments (the two methyl groups in each isopropyl are not equivalent (−CHMe^{A}Me^B)). Below 273 K, a second dynamic process is observed. This is reflected in the methyl signals of the isopropyl groups (that merge into one broad doublet at 213 K and split into two broad doublets below 193 K), as well as in the signals attributable to the IMes ligand (each were singlets at room temperature) that broadened until they split into two singlets at 193 K. This second dynamic process probably involves hindered rotation of the IMes ligand around the Ti−C axis and is consistent with the structure of **3a** observed in the solid state (see below).

Other NHC complexes with different types of imido groups could be prepared in good yields using this method (*Path A*), namely, the triphenylsilyl-imido complex [Ti(=N-SiPh$_3$)Cl$_2$(NHMe$_2$)(IMes)] (**3b**) and the 1-adamantyl-imido complex [Ti(=N-1-Ad)Cl$_2$(NHMe$_2$)(IMes)] (**3c**) (Ad = 1-adamantyl).

2. Investigation of *Path B*: Reaction of [Ti(μ-NAr)(NMe$_2$)$_2$]$_2$ with IMes·HCl. Turning now to *Path B*, we studied the reaction between the imido-bridge dimers [Ti(μ-NAr)(NMe$_2$)$_2$]$_2$ (Ar = 2,6-Pr$^i_2$-C$_6$H$_3$ and 2,6-Cl$_2$-C$_6$H$_3$) and the salt IMes·HCl (2 equiv per Ti). Ideally, we expect the reaction to proceed via amine elimination of the two −NMe$_2$ bonds. Dimer complexes [M(μ-NR)(NMe$_2$)$_2$]$_2$ (M = Ti, V) are easily prepared from M(NMe$_2$)$_4$ precursors and a primary amine, as previously reported by us[22,24,27] and others.[41,42]

The ^{1}H NMR spectrum of the crude reaction mixture obtained by treating a THF solution of [Ti(N-2,6-Pr$^i_2$-C$_6$H$_3$)(NMe$_2$)$_2$]$_2$ with 2 equiv (per Ti) of IMes·HCl revealed the presence of the desired NHC complex [Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)(IMes)] (**3a**) together with large amounts of unreacted starting materials (ca. 50%).

Interestingly, the reaction between [Ti(N-2,6-Cl$_2$-C$_6$H$_3$)(NMe$_2$)$_2$]$_2$ and IMes·HCl in THF solution gave less clear-cut observations, since a complex mixture of four compounds arose as observed in the ^{1}H NMR spectrum (after separating from unreacted IMes·HCl) (see Scheme 5). Although we were unable to selectively separate all these compounds, we were able to clearly identify (with the help of the ^{1}H NMR spectroscopic data and X-ray diffraction analyses) unreacted [Ti(N-2,6-Cl$_2$-C$_6$H$_3$)(NMe$_2$)$_2$]$_2$ as well as three new species: the *desired* complex [Ti(=N-2,6-Cl$_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)(IMes)] (**3d**), the *bis-NHC* imido complex [Ti(=N-2,6-Cl$_2$-C$_6$H$_3$)Cl$_2$(IMes)$_2$] (**4**), and the *amido* complex [Ti(=N-2,6-Cl$_2$−C$_6$H$_3$)(NH-2,6-Cl$_2$-C$_6$H$_3$)Cl(NHMe$_2$)(IMes)] (**5**).

Complexes **4** and **5** were later prepared by more direct and selective syntheses (see Section 3 for the direct synthesis of **4**). The *amido* complex [Ti(=N-2,6-Cl$_2$−C$_6$H$_3$)(NH-2,6-Cl$_2$-C$_6$H$_3$)Cl(NHMe$_2$)(IMes)] (**5**) was synthesized in good yield by sequential addition of 2 equiv of the aniline 2,6-Cl$_2$-C$_6$H$_3$NH$_2$ and 1 equiv of IMes·HCl to a THF solution of Ti(NMe$_2$)$_4$. This complex is obtained as yellow crystals after suitable workup. Compound **5** was characterized by single-crystal X-ray diffraction study. Thermal ellipsoid plots are presented in Figure 4 along with selected bond lengths and angles, and in Table 1 for a comparison of their structural parameters. Overall, the molecular structure, which is in between square pyramid and trigonal bipyramid (τ = 0.47), resembles that of **3d** (*vide infra*), except that one chlorine atom has been replaced by one anilido ligand. Indeed the geometry around that amido N atom is trigonal planar, with a Ti−N$_{\text{amido}}$ bond length of 1.974(6) Å, which is in between that observed for the imido [1.715(6) Å] and the amino bond distances [2.282(6) Å]. The Ti−C bond distance of 2.290(6) Å is close to that found in the other NHC complexes reported in this article. The distance C$_{\text{carbene}}$···Cl of 3.176 Å suggests again the existence of intramolecular interactions.

3. Investigation of *Path C*: Reaction of [Ti(=NR)Cl$_2$(L)$_n$] Precursors with Free NHC. *Path C* consists of introducing the terminal imide group first and then reacting this imido precursor with free carbene IMes. Our experience in handling imido compounds led us naturally to employ [Ti(=NR)Cl$_2$(NHMe$_2$)$_2$] synthons. The dimethylamine ligands in these titanium and

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(41) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357–363.

(42) Nugent, W. A.; Harlow, R. L *Inorg. Chem.* **1979**, *18*, 2030–2032.

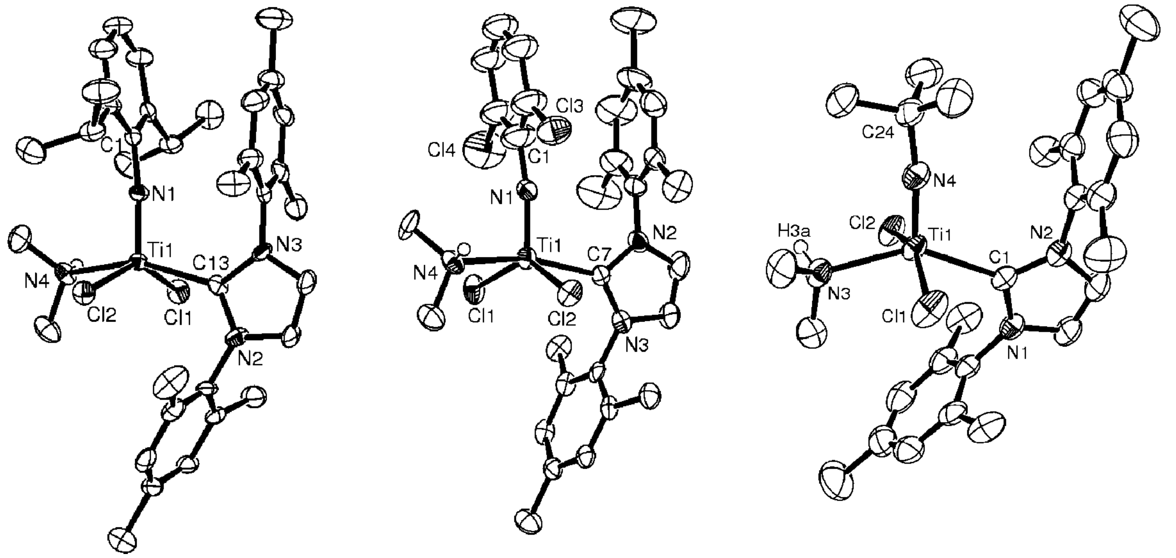
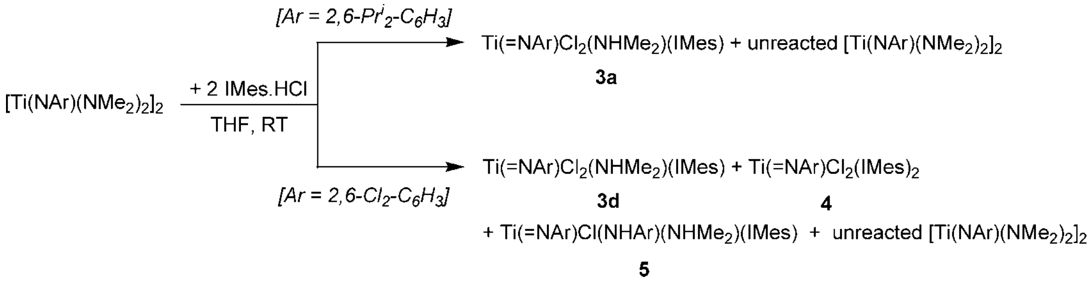


Figure 5. Molecular structure of **3a** (left), **3d** (middle), and **3e** (right), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. For **3a**: Ti(1)−C(13) 2.277(4), Ti(1)−N(1) 1.701(3), Ti(1)−N(4) 2.230(3), Ti(1)−Cl(1) 2.3631(14), Ti(1)−Cl(2) 2.3231(14), Ti(1)−N(1)−C(1) 173.2(3), C(13)−Ti(1)−N(4) 157.05(15), Cl(1)−Ti(1)−Cl(2) 141.67(5), N(1)−Ti(1)−Cl(1) 108.89(12), N(1)−Ti(1)−Cl(2) 108.58(13), N(1)−Ti(1)−C(13) 103.96(16), N(1)−Ti(1)−N(4) 98.41(15), C(13)−Ti(1)−Cl(1) 86.84(11), C(13)−Ti(1)−Cl(2) 91.81(11), Cl(1)−Ti(1)−N(4) 81.08(10), Cl(2)−Ti(1)−N(4) 85.84(10). For **3d**: Ti(1)−C(7) 2.263(5), Ti(1)−N(1) 1.711(4), Ti(1)−N(4) 2.238(4), Ti(1)−Cl(1) 2.2946(16), Ti(1)−Cl(2) 2.3336(16), Ti(1)−N(1)−C(1) 169.9(4), C(7)−Ti(1)−N(1) 100.5(2), Cl(1)−Ti(1)−Cl(2) 136.93(7), N(1)−Ti(1)−Cl(1) 110.49(15), N(1)−Ti(1)−Cl(2) 111.58(15), N(1)−Ti(1)−N(4) 93.11(18), C(7)−Ti(1)−Cl(1) 93.84(13), C(7)−Ti(1)−Cl(2) 87.37(12), Cl(1)−Ti(1)−N(4) 86.59(11), Cl(2)−Ti(1)−N(4) 82.38(12). For **3e**: Ti(1)−C(1) 2.297(3), Ti(1)−N(4) 1.677(3), Ti(1)−N(3) 2.197(3), Ti(1)−Cl(1) 2.3748(10), Ti(1)−Cl(2) 2.3895(9), Ti(1)−N(4)−C(24) 173.0(2), C(1)−Ti(1)−N(3) 142.97(10), Cl(1)−Ti(1)−Cl(2) 156.09(4), N(4)−Ti(1)−Cl(1) 103.35(10), N(4)−Ti(1)−Cl(2) 100.17(10), N(4)−Ti(1)−C(1) 112.31(12), N(4)−Ti(1)−N(3) 104.30(11), C(1)−Ti(1)−Cl(1) 89.67(7), C(1)−Ti(1)−Cl(2) 85.31(7), Cl(1)−Ti(1)−N(3) 87.10(7), Cl(2)−Ti(1)−N(3) 83.01(7).

Scheme 5. Reaction between [Ti(NAr)(NMe$_2$)$_2$]$_2$ and IMes·HCl



related vanadium complexes have been shown to be easily replaced by several neutral N-, O- or P-donor ligands.[22,23,26,43]

The reaction between [Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)$_2$] and 1 equiv of free IMes in toluene at 20 °C produces pale orange crystals of [Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)(IMes)] (**3a**) in 85% yield. IMes also reacts with other imido−titanium [Ti(=NR)Cl$_2$(NHMe$_2$)$_2$] synthons in toluene, and NHC complexes [Ti(=N-2,6-Cl$_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)$_2$] (**3d**) and [Ti(=N-Bu^t)Cl$_2$(NHMe$_2$)$_2$] (**3e**) are obtained as orange and yellow crystals, respectively, in good yields (Scheme 6). The proton NMR spectra of **3d** and **3e** in C$_6$D$_6$ at 20 °C show sharp resonances for all signals, in contrast with the fluxional behavior previously discussed for **3a**.

X-ray quality crystals were obtained for the three complexes **3a**, **3d**, and **3e** and were studied by diffraction analysis.[44] These studies showed **3a**, **3d**, and **3e** to have a structure analogous to that of their parent precursors, i.e., a distorted square pyramid ($\tau = 0.25$ (**3a**), 0.47 (**3d**), and av 0.20 (**3e**)) containing an imido ligand in the apical position with short Ti−N$_{\text{imido}}$ bond distances [Ti−N$_{\text{imido}}$ = 1.701(3) Å (**3a**), 1.711(4) Å (**3d**), av 1.678 Å (**3e**)], two *trans* chloride ligands, and one IMes ligand [Ti−C$_{\text{IMes}}$ = 2.277(4) Å (**3a**), 2.263(5) Å (**3d**), av 2.29 Å (**3c**)] *trans* to the remaining NHMe$_2$ ligand (Figure 5). Other bond distances and angles are unexceptional, and as for complexes **1**, **2**, and **5**, the crystallographic data for **3a**, **3d**, and **3e** suggest C$_{\text{carbene}}\cdots$Cl intramolecular interactions (Table 1).

The dimethylamine ligand in complexes **3** is easily substituted by a pyridine ligand from reaction with 1 equiv of pyridine in THF, affording quantitatively complexes [Ti(=N-R)Cl$_2$(Py)(IMes)] with R = 2,6-Pr$^i_2$-C$_6$H$_3$ (**6a**), 2,6-Cl$_2$-C$_6$H$_3$ (**6d**), and Bu^t (**6e**) (Scheme 7). Moreover, first indications show that the coordinated IMes is not showing any lability in the presence of good donors such as an excess of pyridine.

Analogous pyridine adduct [Ti(=N-Myr*)Cl$_2$(Py)(IMes)] (**6f***) [Myr* = (−)-*cis*-myrtanyl] could also be prepared by displacement of pyridines in the chiral tris-pyridyne precursor [Ti(=N-Myr*)Cl$_2$(Py)$_3$] (Scheme 8).

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(43) Adams, N.; Bigmore, H. R.; Blundell, T. L.; Boyd, C. L.; Dubberley, S. R.; Sealey, A. J.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 2882–2894.

(44) For simplicity, discussion has been limited to only one of the two independent units of **3e** in the unit cell. There are no significant differences in the bond parameters between these two species.

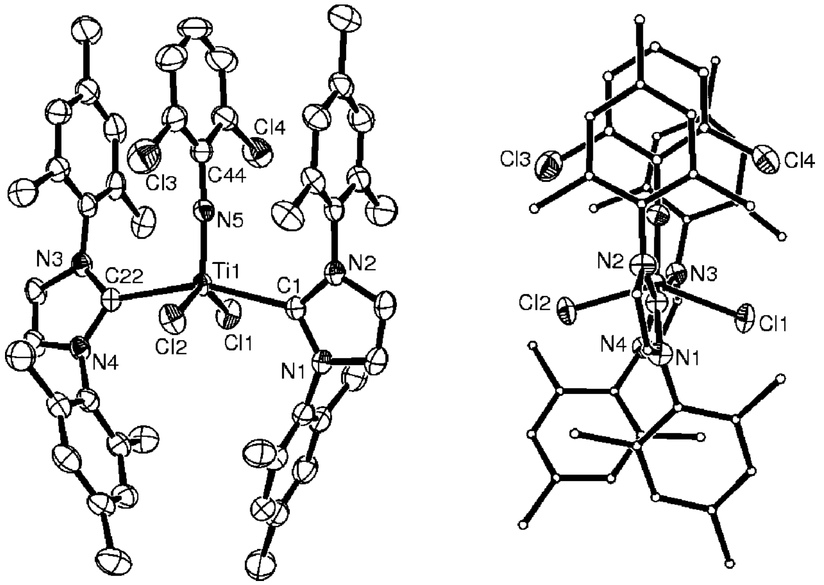


Figure 6. Molecular structure of **4**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Ti(1)−C(1) 2.315(2), Ti(1)−C(22) 2.307(2), Ti(1)−N(5) 1.707(2), Ti(1)−Cl(1) 2.3328(7), Ti(1)−Cl(2) 2.3133(6), Ti(1)−N(5)−C(44) 176.80(16), C(1)−Ti(1)−C(22) 157.35(8), N(5)−Ti(1)−Cl(1) 110.15(7), N(5)−Ti(1)−Cl(2) 107.61(7), Cl(1)−Ti(1)−Cl(2) 142.24(3), C(1)−Ti(1)−N(5) 101.94(8), C(22)−Ti(1)−N(5) 100.70(8), C(1)−Ti(1)−Cl(1) 88.63(6), C(1)−Ti(1)−Cl(2) 84.09(6), C(22)−Ti(1)−Cl(1) 84.26(5), C(22)−Ti(1)−Cl(2) 88.43(5).

Scheme 6. Synthesis of Ti(=NR)Cl$_2$(NHMe$_2$)(IMes) from Ti(=NR)Cl$_2$(NHMe$_2$)

$$\mathrm{Ti({=}NR)Cl_2(NHMe_2)_2} + \mathrm{IMes} \xrightarrow[\text{- HNMe}_2]{\text{THF, RT}} \mathrm{Ti({=}NR)Cl_2(NHMe_2)(IMes)}$$

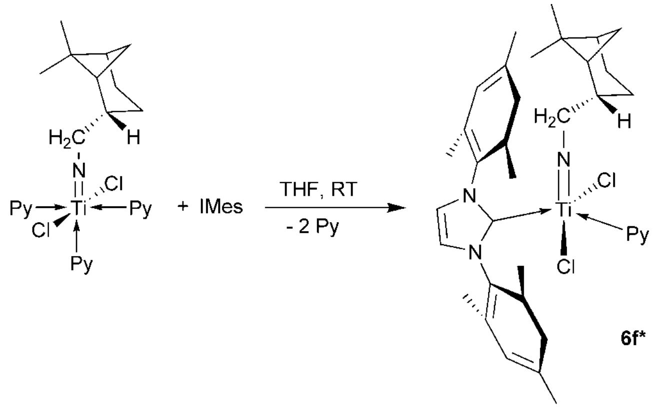
3a : R = 2,6-Pr$^i_2$-C$_6$H$_3$
3d : R = 2,6-Cl$_2$-C$_6$H$_3$
3e : R = Bu^t

Scheme 7. Synthesis of Ti(=NR)Cl$_2$(Py)(IMes)

$$\underset{\mathbf{3}}{\mathrm{Ti({=}NR)Cl_2(NHMe_2)(IMes)}} + \mathrm{Py} \xrightarrow[\text{- HNMe}_2]{\text{THF, RT}} \mathrm{Ti({=}NR)Cl_2(Py)(IMes)}$$

6a : R = 2,6-Pr$^i_2$-C$_6$H$_3$
6d : R = 2,6-Cl$_2$-C$_6$H$_3$
6e : R = Bu^t

Scheme 8. Synthesis of Ti(=N-Myr)Cl$_2$(Py)(IMes)



6f*

Noteworthy, except **3d**, which could react further with a second equivalent of free IMes (see below), the bulky imido group in the other complexes [Ti(=N-R)Cl$_2$(NHMe$_2$)(IMes)] (**3a**−**c**, **3e**) apparently prevents coordination of a second molecule of carbene by displacement of the dimethylamine ligand.

By contrast, the *bis-NHC* imido complex [Ti(=N-2,6-Cl$_2$-C$_6$H$_3$)Cl$_2$(IMes)$_2$] (**4**) was synthesized by addition of 2 equiv of IMes to compound **3d**, at RT in THF. The high solubility of **4** in hydrocarbon solvents leads to a purified yield of approximately 40%. It has been fully characterized by NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The ^{1}H NMR spectrum of complex **4** clearly shows a ratio of 2:1 for the two IMes ligands versus the imido group. The molecular structure (Figure 6) confirms this proposal and clearly shows that coordination of the two NHC ligands is possible due to the planar nature of the imido group. The compound crystallized in the monoclinic $P2_1/c$ space group. The coordination geometry of titanium is distorted square pyramidal ($\tau = 0.25$), and the Ti atom is 0.603(1) Å out of the mean plane through C(1)C(22)Cl(1)Cl(2) [mean deviation 0.15(1) Å]. The Ti center is surrounded by two chlorine atoms located in *trans* position, two *trans*-IMes ligands, and one nitrogen atom of the imido in the apical position. The distances and angles associated with the titanium center and the ligands are comparable to those found in other M(=NR)Cl$_2$(NHMe$_2$)$_2$ complexes (M = Ti,[26,43] V[22,27]). Compound **4** exhibits a short Ti−N$_{\mathrm{imido}}$ distance of 1.707(2) Å with an almost linear imido linkage [Ti−N$_{\mathrm{imido}}$−C$_{\mathrm{ipso}}$ angle = 176.80(16)°]. The two *trans*-NHC ligands have mean Ti−C bonds of ca. 2.31 Å. The two chlorine atoms have mean Ti−Cl bond distances of 2.32 Å and form a Cl(1)−Ti−Cl(2) angle of 142.24(3)°. The structure of **4** is further characterized by an almost eclipsed geometric arrangement of the two IMes and the aromatic ring of the imido ligand along the $C_{carbene}-C_{carbene}$ vector. The negative influence by the (weak) steric hindrance is apparently compensated by some positive arene $\pi-\pi$ interaction between the coplanar aromatic rings of Mes and $C_6H_3Cl_2$ pairs.[45]

Conclusions

We have demonstrated that use of the amine elimination method in the reaction of the imidazolium salt IMes·HCl and amido complexes $Ti(NMe_2)_4$ and $[Ti(NAr)(NMe_2)_2]_2$ gives only incomplete conversions for the production of NHC complexes $TiCl_2(NMe_2)_2(IMes)$ (**1**) and $Ti(=NAr)Cl_2(NHMe_2)(IMes)$, respectively. Several side products were also isolated from these reactions. Therefore, the direct addition of IMes to $TiCl_2(NMe_2)_2$ proved to be a preferable synthetic route for high-yield preparation of **1**. We reported that members of the new class of imido−NHC complexes $Ti(=NR)Cl_2(L)(IMes)$ ($L = NHMe_2$, Py) could be prepared from amine elimination reaction between **1** and a primary amine or from imido precursors $Ti(=NR)Cl_2(L)_n$. Although the direct comparison of the metal−carbon bond lengths measured in these d^0 and d^1 complexes does not help clarifying the nature of the early metal−NHC bond, the structural data for these compounds revealed the presence of $C_{carbene}\cdots Cl$ interactions. This is an indication of a form of back-donation, which will have to be confirmed by a theoretical analysis of the specific bonding features in these complexes. In future studies, we look forward to preparing other early transition metal−NHC species and to comparing their reactivity to related non-NHC complexes, including in catalytic processes.

Acknowledgment. We are grateful to the CNRS for financial support.

Supporting Information Available: CIF files and tables of atomic coordinates and bond distances and angles for the X-ray crystal structures of complexes **1**, **2**, **3a**, **3d**, **3e**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) The parameters for the offset π-stacked geometry measured are the following: $\pi-\pi$ distances between centroid rings of Mes groups and $C_6H_4Cl_2$ are 3.735 and 3.626 Å; $\pi-\pi$ distances between planes (of Mes and $C_6H_4Cl_2$ rings) are 3.545 and 3.410 Å; offset angle between the ring normal of the aryl-imido and the centroid of the vector are 18.5° and 21.1° (for a review on $\pi-\pi$ stacking, see: Janiak, C. *Dalton Trans.* **2000**, 3885−3896).