Supporting Information

Titanium complexes with unsymmetrical imidazolin-2-iminato ligands

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<td>2.5 [Im\textsubscript{AdDipp}NH] (3b) 25</td>
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<td>2.6 [[Im\textsubscript{AdMes}NH]TiCl\textsubscript{3}] (4a) 27</td>
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<td>2.7 [[Im\textsubscript{AdDipp}N]TiCl\textsubscript{3}] CH\textsubscript{2}Cl\textsubscript{2} Solv (4b) 29</td>
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<tr>
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<td>2.9 [Cp(Im\textsubscript{AdDipp}N)TiCl\textsubscript{2}] (5b) 33</td>
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<td>2.10 [[Im\textsubscript{AdMes}N\textsubscript{2}TiCl\textsubscript{2}] 0.5CH\textsubscript{2}Cl\textsubscript{2} (6a) 35</td>
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<tr>
<td>2.11 [[Im\textsubscript{AdDipp}N\textsubscript{2}TiCl\textsubscript{2}] CH\textsubscript{2}Cl\textsubscript{2} (6b) 37</td>
<td></td>
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</tbody>
</table>
1. Spectra

1.1 1-(Adamantyl)-3-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (1a)

$^1$H NMR (500 MHz, C$_6$D$_6$) of 1a:

$^{13}$C NMR (126 MHz, C$_6$D$_6$) of 1a:
1.2 1-(Adamantyl)-3-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (1b)

$^1$H NMR (300 MHz, CD$_6$D$_6$) of 1b:

$^{13}$C NMR (75 MHz, CD$_6$D$_6$) of 1b:
1.3 [Im\textsuperscript{AdMes}NSiMe\textsubscript{3}] (2a)

\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) of 2a:

\textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) of 2a:
1.4 [Im$^{\text{AdDippNSiMe}_3}$] (2b)

$^1$H NMR (400 MHz, $\text{CD}_6$) of 2b:

$^{13}$C NMR (100 MHz, $\text{CD}_6$) of 2b:
1.5 [Im\textsuperscript{AdMesNH}] (3a)

\textsuperscript{1}H NMR (400 MHz, CdD\textsubscript{6}) of 3a:

\textsuperscript{13}C NMR (100 MHz, CdD\textsubscript{6}) of 3a:
1.6 [Im$^{\text{AdDippNH}}$] (3b)

$^1$H NMR (400 MHz, CD$_6$D$_6$) of 3b:

$^{13}$C NMR (100 MHz, CD$_6$D$_6$) of 3b:
1.7 [(Im\textsuperscript{AdMesN})TiCl\textsubscript{3}] (4a)

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) of 4a:

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) of 4a:
1.8 [(Im<sup>AdDippN</sup>)TiCl<sub>3</sub>] (4b)

$^1$H NMR (600 MHz, CDCl<sub>3</sub>) of 4b:

CH<sub>2</sub>Cl<sub>2</sub>

$^{13}$C NMR (151 MHz, CDCl<sub>3</sub>) of 4b:
1.9 [Cp(Im^{AdMes}N)TiCl_2] (5a)

^1H NMR (600 MHz, C_6D_6) of 5a:

^13C NMR (151 MHz, C_6D_6) of 5a:
1.10 \([\text{Cp} (\text{Im}^{\text{AddppN}}) \text{TiCl}_2] \) (5b)

$^1\text{H NMR (500 MHz, CDCl}_3\) of 5b:}

$^{13}\text{C NMR (126 MHz, CDCl}_3\) of 5b:}
1.11 [(Im\textsuperscript{AdMesN})\textsubscript{2}TiCl\textsubscript{2}] (6a)

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) of 6a:

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) of 6a:
1.12 [((ImAdDipp)N)_2TiCl_2] (6b)

^1H NMR (500 MHz, CDCl_3) of 6b:

CH_2Cl_2

^13C NMR (126 MHz, CDCl_3) of 6b:

CH_2Cl_2
$^1$H NMR (400 MHz, CD$_2$Cl$_2$) of 6b at −70 °C:
2. X-Ray Crystal Structure Determinations

For a summary of crystal data, see Tables S4.1 - 4.6. Crystals were mounted on either MiTiGen or Hampton mounts in perfluorinated inert oil. Intensity measurements were performed at 100 K using a Rigaku XtaLAB Synergy S Single Source with mirror-focussed CuKα radiation or a Rigaku XtaLAB Synergy S Single Source with mirror-focussed MoKα radiation. Additional measurements were performed using an Oxford Diffraction Xcalibur Eos diffractometer with MoKα radiation. Data reduction was performed with the CrysAlisPRO software.[A] Absorption corrections were based on multi-scans, analytical methods or face-indexation using a gaussian grid. The structures solved using either direct methods in SHELXS[B] or intrinsic phasing in SHELXT[C] and were refined anisotropically on F2 using the program SHELXL[D] in OLEX2.[E] The hydrogen atoms were, unless otherwise noted, included either as constituents of idealized rigid methyl groups allowed to rotate but not tip, or using a riding model starting from calculated positions. The implementation of BYPASS[F] in OLEX2 had to be used for compound 4b. One figure was created using the program Mercury[G].

CCDC 2174864-2174874 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

References:


2.1 1-(Adamantyl)-3-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (1a)

Identification code: mk31mk

CCDC Number: 2174864

Empirical formula: C_{22}H_{28}N_{2}

Formula weight: 320.46

Temperature: 100(2) K

Wavelength: 0.71073 Å

Instrument (scan mode): XtaLAB Synergy, Single source HyPix (ω scan)

Crystal system: Monoclinic

Space group: P2_1/c

Unit cell dimensions:
- \( a = 13.5173(4) \) Å, \( \alpha = 90^\circ \)
- \( b = 10.3836(2) \) Å, \( \beta = 95.869(2)^\circ \)
- \( c = 12.8450(4) \) Å, \( \gamma = 90^\circ \)

Volume: 1793.45(8) Å³

Z: 4

Density (calculated): 1.187 Mg/m³

Absorption coefficient: 0.069 mm⁻¹

F(000): 696

Crystal habitus: plate (colourless)

Crystal size: 0.279 x 0.211 x 0.143 mm³

Theta range for data collection: 2.478 to 44.855°

Index ranges: -26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -25 ≤ l ≤ 25

Reflections collected: 134137

Independent reflections: 14658 [R(int) = 0.0485]

Completeness to theta = 25.242°: 99.9 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 1.00000 and 0.88245

Refinement method: Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters: 14658 / 0 / 220

Goodness-of-fit on \( F^2 \): 1.066

Final R indices [I>2sigma(I)]: R1 = 0.0441, wR2 = 0.1296

R indices (all data): R1 = 0.0624, wR2 = 0.1381

Largest diff. peak and hole: 0.606 and -0.314 e.Å⁻³

Crystallisation Details:


Measurement and Refinement Details: -
Figure S1: Molecular structure of 1a with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3739(5), C1-N2 1.3651(5), N1-C4 1.4313(5), N2-C13 1.4711(6), N1-C1-N2 102.05(3).
2.2 1-(Adamantyl)-3-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (1b)

Identification code mk28mk
CCDC Number: 2174865
Empirical formula C_{25}H_{34}N_{2}
Formula weight 362.54
Temperature 100(2) K
Wavelength 1.54184 Å
Instrument (scan mode) XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system Orthorhomic
Space group Pnma
Unit cell dimensions
\[
a = 10.4134(2) \text{ Å} \quad \alpha = 90^\circ \\
b = 12.3697(2) \text{ Å} \quad \beta = 90^\circ \\
c = 16.5809(2) \text{ Å} \quad \gamma = 90^\circ 
\]
Volume 2135.80(6) Å³
Z 4
Density (calculated) 1.127 Mg/m³
Absorption coefficient 0.490 mm⁻¹
F(000) 792
Crystal habitus plate (colourless)
Crystal size 0.347 x 0.100 x 0.089 mm³
Theta range for data collection 4.460 to 77.393°
Index ranges -11<=h<=13, -15<=k<=15, -20<=l<=20
Reflections collected 39788
Independent reflections 2337 [R(int) = 0.0431]
Completeness to theta = 67.684° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.47134
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2337 / 0 / 141
Goodness-of-fit on F² 1.044
Final R indices [I>2sigma(I)] R1 = 0.0398, wR2 = 0.0995
R indices (all data) R1 = 0.0417, wR2 = 0.1013
Largest diff. peak and hole 0.216 and -0.194 e.Å⁻³
Crystallisation Details: toluene/n-hexane -30 °C
Measurement and Refinement Details: -
Figure S2: Molecular structure of 1b with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3709(18), C1-N2 1.3627(18), N1-C4 1.4352(17), N2-C11 1.4765(17), N1-C1-N2 101.48(11).
### 2.3 [(Im\(^{AdMes}\)NSiMe\(_3\))] (2a)

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<td>Empirical formula</td>
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<td>Formula weight</td>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Instrument (scan mode)</td>
<td>Oxford Diffraction Xcalibur, Eos (\omega) scan</td>
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<td>Space group</td>
<td>(P2_1/n)</td>
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<td>Unit cell dimensions</td>
<td>(a = 9.7011(4) \text{ Å} \quad \alpha = 90^\circ)</td>
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<td>(b = 24.1407(8) \text{ Å} \quad \beta = 99.776(4)^\circ)</td>
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<td>(c = 10.2311(4) \text{ Å} \quad \gamma = 90^\circ)</td>
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<td>Volume</td>
<td>2361.24(16) \text{ Å}^3</td>
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<td>Density (calculated)</td>
<td>1.147 \text{ Mg/m}^3</td>
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<td>Absorption coefficient</td>
<td>0.115 \text{ mm}^{-1}</td>
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<td>(F(000))</td>
<td>888</td>
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<td>Crystal habitus</td>
<td>irregular (colourless)</td>
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<td>Crystal size</td>
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<td>Crystallisation Details:</td>
<td>(n)-hexane at -27 °C</td>
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**Solution:** SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

**Refinement:** SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

**Interface:** OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

**Measurement and Refinement Details:** -
Figure S3: Molecular structure of 2a with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.2782(10), N1-Si1 1.6823(7), N2-C1-N3 103.99(6), C1-N1-Si1142.68(7).
### 2.4 [Im^AdMesNH] (3a)

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<td>Unit cell dimensions</td>
<td>a = 16.6873(2) Å, α = 90°</td>
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<td>Density (calculated)</td>
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<td>1456</td>
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<td>fragment of trapezoid (colourless)</td>
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<td>Crystal size</td>
<td>0.108 x 0.101 x 0.099 mm³</td>
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<td>Theta range for data collection</td>
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<td>Max. and min. transmission</td>
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<td>Largest diff. peak and hole</td>
<td>0.280 and -0.283 e.Å⁻³</td>
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<td>Crystallisation Details:</td>
<td>cooling of hot n-hexane solution to room temperature</td>
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<td>Measurement and Refinement Details:</td>
<td>N-H hydrogen was refined freely.</td>
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Figure S4: Molecular structure of 3a with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.2966(14), N2-C1-N3 104.55(9).
2.5 [Im$^\text{AdDippNH}$] (3b)

Identification code  mk15mk
CCDC Number:  2174868
Empirical formula  C$_{25}$H$_{35}$N$_3$
Formula weight  377.56
Temperature  100(2) K
Wavelength  1.54184 Å
Instrument (scan mode)  XtaLAB Synergy, Single source, HyPix ($\omega$ scan)
Crystal system  Monoclinic
Space group  $P2_1/c$
Unit cell dimensions  
\begin{align*}
    a &= 13.8605(1) \text{ Å} & \alpha &= 90^\circ \\
    b &= 6.5130(1) \text{ Å} & \beta &= 98.599(1)\circ \\
    c &= 24.0076(2) \text{ Å} & \gamma &= 90^\circ 
\end{align*}
Volume  2142.89(4) Å$^3$
$Z$  4
Density (calculated)  1.170 Mg/m$^3$
Absorption coefficient  0.521 mm$^{-1}$
$F(000)$  824
Crystal habitus  lath (colourless)
Crystal size  0.352 x 0.067 x 0.039 mm$^3$
Theta range for data collection  3.225 to 77.449$^\circ$
Index ranges  
\begin{align*}
    -17 \leq h \leq 17, \\
    -6 \leq k \leq 8, \\
    -30 \leq l \leq 30
\end{align*}
Reflections collected  47042
Independent reflections  4470 [R(int) = 0.0319]
Completeness to theta = 67.684$^\circ$  100.0 %
Absorption correction  Gaussian
Max. and min. transmission  1.000 and 0.784
Refinement method  Full-matrix least-squares on $F^2$
Data / restraints / parameters  4470 / 0 / 261
Goodness-of-fit on $F^2$  1.038
Final R indices [I>2sigma(I)]  
\begin{align*}
    R1 &= 0.0378, wR2 = 0.0967 \\
    R & = 0.0401, wR2 = 0.0998
\end{align*}
Largest diff. peak and hole  0.265 and -0.212 e.Å$^{-3}$
Crystallisation Details:  n-hexane -40 °C
Measurement and Refinement Details:  N-H hydrogen was refined freely.
Figure S5: Molecular structure of 3b with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.289(13), N2-C1-N3 104.7(8).
### 2.6 [(ImAdMesNH)TiCl$_3$] (4a)

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<td>CCDC Number:</td>
<td>2174869</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{22}$H$</em>{28}$Cl$_3$N$_3$Ti</td>
</tr>
<tr>
<td>Formula weight</td>
<td>488.72</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Instrument (scan mode)</td>
<td>XtaLAB Synergy, Single source, HyPix ($\omega$ scan)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.6555(2) Å, $\alpha$ = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 23.9142(3) Å, $\beta$ = 98.744(2)°</td>
</tr>
<tr>
<td></td>
<td>c = 10.2854(2) Å, $\gamma$ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2347.33(7) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.383 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.720 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1016</td>
</tr>
<tr>
<td>Crystal habitus</td>
<td>irregular (orange)</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.370 x 0.269 x 0.100 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.731 to 41.154°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17&lt;=$h&lt;=$17, -44&lt;=$k&lt;=$44, -19&lt;=$l&lt;=$19</td>
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<td>Reflections collected</td>
<td>209853</td>
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<tr>
<td>Independent reflections</td>
<td>15591 [R(int) = 0.0354]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.000 and 0.272</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>15591 / 0 / 265</td>
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<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.051</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0268, wR2 = 0.0751</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0329, wR2 = 0.0774</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.626 and -0.215 e.Å$^3$</td>
</tr>
<tr>
<td>Crystallisation Details:</td>
<td>DCM/n-hexane</td>
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</table>


Measurement and Refinement Details: -
Figure S6: Molecular structure of 4a with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3265(7), N1-Ti1 1.7347(5), N2-C1-N3 107.41(4), C1-N1-Ti1 162.58(5), Cl1-Ti1-Cl2 111.50(2), N1-C1-N2 124.07(5), N1-C1-N3 128.50(5).
Identification code: mk26mk
CCDC Number: 2174870
Empirical formula: C_{26}H_{36}Cl_{5}N_{3}Ti
Formula weight: 615.73
Temperature: 100(2) K
Wavelength: 0.71073 Å
Instrument (scan mode): XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system: Triclinic
Space group: P1̅
Unit cell dimensions:
- a = 9.8202(4) Å, α = 63.091(5)°
- b = 13.2868(6) Å, β = 81.445(4)°
- c = 14.4204(7) Å, γ = 76.358(4)°
Volume: 1628.59(15) Å³
Z: 2
Density (calculated): 1.256 Mg/m³
Absorption coefficient: 0.691 mm⁻¹
F(000): 640
Crystal habitus: fragment of block (orange)
Crystal size: 0.18 x 0.10 x 0.05 mm³
Theta range for data collection: 2.137 to 32.385°
Index ranges: -14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -21 ≤ l ≤ 20
Reflections collected: 43682
Independent reflections: 9833 [R(int) = 0.0215]
Completeness to theta = 25.242°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.88732
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 9833 / 0 / 320
Goodness-of-fit on F²: 1.030
Final R indices [I>2sigma(I)]: R1 = 0.0581, wR2 = 0.1560
R indices (all data): R1 = 0.0667, wR2 = 0.1618
Largest diff. peak and hole: 2.297 and -1.603 e.Å⁻³
Crystallisation Details: dichloromethane/n-hexane -30 °C

Measurement and Refinement Details: A solvent mask was calculated and 66 electrons were found in a volume of 231 Å³ in 1 void per unit cell. This is consistent with the presence of 0.5[CH₂Cl₂], 0.25[C₆H₁₄] per Asymmetric Unit which account for 67 electrons per unit cell. A reason why the molecules could not be refined satisfactorily might be their disorder along a canal. Additionally modulation could be a reason, as ‘smeared’ reflexes were observed along the c* axis.
Figure S7: Molecular structure of 4b·CH₂Cl₂·Solv. with thermal displacement parameters drawn at 50% probability. All hydrogens, one molecule of CH₂Cl₂ and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.330(3), N1-Ti 1.7316(17), N2-C1-N3 106.89(17), C1-N1-Ti1 173.04(16), Cl1-Ti1-Cl2 109.17(3), N1-C1-N2 124.33(17), 128.75(18).

Figure S8: Depiction of the solvent accessible voids in the structure of 4b in Mercury.
Identification code: mk22mk
CCDC Number: 2174871
Empirical formula: C_{27}H_{33}Cl_{2}N_{3}Ti
Formula weight: 518.36
Temperature: 100(2) K
Wavelength: 1.54184 Å
Instrument (scan mode): XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system: Orthorhombic
Space group: P2_12_12_1
Unit cell dimensions:
- a = 9.97590(10) Å, α = 90°
- b = 11.30190(10) Å, β = 90°
- c = 22.11580(10) Å, γ = 90°
Volume: 2493.48(4) Å³
Z: 4
Density (calculated): 1.381 Mg/m³
Absorption coefficient: 5.029 mm⁻¹
F(000): 1088
Crystal habitus: trapezoid (orange)
Crystal size: 0.228 x 0.126 x 0.072 mm³
Theta range for data collection: 3.998 to 77.473°
Index ranges:
- -12 ≤ h ≤ 10,
- -14 ≤ k ≤ 14,
- -27 ≤ l ≤ 28
Reflections collected: 53498
Independent reflections: 5264 [R(int) = 0.0323]
Completeness to theta = 67.684°: 100.0 %
Absorption correction: Gaussian
Max. and min. transmission: 1.000 and 0.670
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 5264 / 0 / 302
Goodness-of-fit on F²: 1.033
Final R indices [I > 2σ(I)]:
- R1 = 0.0218, wR2 = 0.0504
R indices (all data):
- R1 = 0.0227, wR2 = 0.0513
Absolute structure parameter: 0.434(5)
Largest diff. peak and hole:
- 0.242 and -0.226 e.Å⁻³
Crystallisation Details:
- toluene/n-hexane room temperature


Measurement and Refinement Details:
- Refined as a 2-component inversion twin.
Figure S9: Molecular structure of 5a with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.319(2), N1-Ti1 1.7758(16), Ti1-Cl1 2.3135(5), Ti1-Cl2 2.3156(5), Ti1-C5 centroid 2.0562(9), N2-C1-N3 105.99(15), C1-N1-Ti1 170.26(14), Cl1-Ti1-Cl2 101.87(2), N1-C1-N2 125.66(16), N1-C1-N3 128.31(16).
2.9 [Cp(ImAdDippN)TiCl₂] (5b)

Identification code: mk27mk
CCDC Number: 2174872
Empirical formula: C₃₀H₃₉Cl₂N₃Ti
Formula weight: 560.44
Temperature: 100(2) K
Wavelength: 0.71073 Å
Instrument (scan mode): XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system: Monoclinic
Space group: P2₁/n
Unit cell dimensions:

\[ a = 10.3898(2) \text{ Å} \]
\[ b = 19.4721(2) \text{ Å} \]
\[ c = 13.9922(2) \text{ Å} \]
\[ \alpha = 90° \]
\[ \beta = 101.575(2)° \]
\[ \gamma = 90° \]

Volume: 2773.21(7) Å³
Z: 4
Density (calculated): 1.342 Mg/m³
Absorption coefficient: 0.526 mm⁻¹
F(000): 1184
Crystal habitus: fragment of trapezoid (orange)
Crystal size: 0.221 x 0.207 x 0.148 mm³
Theta range for data collection: 2.240 to 38.315°
Index ranges: -17≤h≤17, -33≤k≤33, -24≤l≤24
Reflections collected: 193977
Independent reflections: 14793 [R(int) = 0.0306]
Completeness to theta = 25.242°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.89211
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 14793 / 0 / 329
Goodness-of-fit on F²: 1.070
Final R indices [I>2sigma(I)]: R1 = 0.0307, wR2 = 0.0836
R indices (all data): R1 = 0.0358, wR2 = 0.0856
Largest diff. peak and hole: 0.842 and -0.715 e Å⁻³
Crystallisation Details: dichloromethane/n-hexane room temperature

Measurement and Refinement Details: -
Figure S10: Molecular structure of 5b with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3189(8), N1-Ti1 1.7760(5), Ti1-Cl1 2.3074(3), Ti1-Cl2 2.3117(2), Ti1-C5 Centroid 2.0689(4), N2-C1-N3 106.13(5), C1-N1-Ti1 170.86(5), Cl1-Ti1-Cl2 102.873(11), N1-C1-N2 125.75(6), N1-C1-N3 128.10(6).
Identification code: mk19mk
CCDC Number: 2174873
Empirical formula: C_{44.5}H_{57}Cl_{3}N_{6}Ti
Formula weight: 830.21
Temperature: 100(2) K
Wavelength: 1.54184 Å
Instrument (scan mode): XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system: Monoclinic
Space group: P2_1/n
Unit cell dimensions:
\[
a = 13.24640(4) \text{ Å} \quad \alpha = 90^\circ \\
b = 13.47847(4) \text{ Å} \quad \beta = 101.0795(3)^\circ \\
c = 24.79338(8) \text{ Å} \quad \gamma = 90^\circ
\]
Volume: 4344.13(2) Å³
Z: 4
Density (calculated): 1.269 Mg/m³
Absorption coefficient: 3.655 mm⁻¹
F(000): 1756
Crystal habitus: irregular (orange)
Crystal size: 0.253 x 0.110 x 0.098 mm³
Theta range for data collection: 3.534 to 77.822°
Index ranges: -16≤h≤16, -17≤k≤17, -31≤l≤28
Reflections collected: 94547
Independent reflections: 9180 [R(int) = 0.0312]
Completeness to theta = 67.684°: 100.0 %
Absorption correction: Gaussian
Max. and min. transmission: 1.000 and 0.531
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 9180 / 6 / 596
Goodness-of-fit on F²: 1.069
Final R indices [I>2σ(I)]: R1 = 0.0450, wR2 = 0.1290
R indices (all data): R1 = 0.0462, wR2 = 0.1308
Largest diff. peak and hole: 1.180 and -0.885 e.Å⁻³
Crystallisation Details: CH₂Cl₂/n-hexane at room temperature
Measurement and Refinement Details: The CH₂Cl₂ fragment is disordered over an inversion center and occupies a special position. Therefore, its occupancy was set at 0.5 and refined accordingly. Additionally the mesityl group on one ligand is disordered and was refined accordingly resulting in a 60/40 occupancy.
Figure S11: Molecular structure of the main component of 6a·0.5CH₂Cl₂ with thermal displacement parameters drawn at 50% probability. All hydrogens, 0.5 molecules of CH₂Cl₂ and the minor component of the disordered mesityl group at N5 are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.304(2), C23-N4 1.302(2), N1-Ti1 1.7951(15), N4-Ti1 1.7867(16), Ti1-Cl1 2.2938(5), Ti1-Cl2 2.3160(5), N2-C1-N3 105.89(14), N5-C23-N6 105.69(15), C1-N1-Ti1 166.51(13), C23-N4-Ti1 166.94(13), Cl1-Ti1-Cl2 109.49(2), N1-Ti1-N4 113.57(8).
2.11 [(ImAdDippN)₂TiCl₂]·CH₂Cl₂ (6b)

Identification code: mk24mk2
CCDC Number: 2174874
Empirical formula: C₅₁H₇₀Cl₄N₆Ti
Formula weight: 956.83
Temperature: 100(2) K
Wavelength: 1.54184 Å
Instrument (scan mode): XtaLAB Synergy, Single source, HyPix (ω scan)
Crystal system: Monoclinic
Space group: P2₁/c
Unit cell dimensions:
\[a = 16.9882(3) \, \text{Å} \quad \alpha = 90^\circ\]
\[b = 18.0462(2) \, \text{Å} \quad \beta = 116.512(2)^\circ\]
\[c = 18.3671(3) \, \text{Å} \quad \gamma = 90^\circ\]
Volume: 5038.71(15) Å³
Z: 4
Density (calculated): 1.261 Mg/m³
Absorption coefficient: 3.694 mm⁻¹
F(000): 2032
Crystal habitus: needle (orange)
Crystal size: 0.135 x 0.080 x 0.051 mm³
Theta range for data collection: 2.907 to 77.812°
Index ranges:
\[-21 \leq h \leq 21, \quad -19 \leq k \leq 22, \quad -23 \leq l \leq 23\]
Reflections collected: 122767
Independent reflections: 10633 [R(int) = 0.0647]
Completeness to theta = 67.684°: 100.0 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.58339
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 10633 / 6 / 567
Goodness-of-fit on F²: 1.076
Final R indices [I>2sigma(I)]: R1 = 0.0561, wR2 = 0.1599
R indices (all data): R1 = 0.0606, wR2 = 0.1649
Largest diff. peak and hole: 0.813 and -1.177 e.Å⁻³
Crystallisation Details: dichloromethane/n-hexane room temperature

Measurement and Refinement Details: Data had to be cut due to sample decay.
Figure S12: Molecular structure of the main component of 6b-CH$_2$Cl$_2$ with thermal displacement parameters drawn at 50% probability. All hydrogens and one molecule of CH$_2$Cl$_2$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.304(3), C26-N4 1.302(3), N1-Ti1 1.7994(18), N4-Ti1 1.8067(18), Ti1-Cl1 2.2836(6), Ti1-Cl2 2.3042(6), N2-C1-N3 105.69(18), N5-C26-N6 105.24(18), C1-N1-Ti1 167.14(17), C26-N4-Ti1 167.64(17), Cl1-Ti1-Cl2 105.19(3), N1-Ti1-N4 116.99(9).