Titanium amido- and imido-complexes supported by a tridentate pyrrolyl ligand: syntheses, characterisation and catalytic activities

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The complexes [Ti(NMe$_2$)$_2$(pmpmi)] [H$_2$pmpmi = (2-pyrrolylmethene)-(2-pyrrolylmethyl)imine], [Ti(N^{t}Bu)(pmpmi)(py)$_2$], [Ti(N^{t}Bu)(pmpmi)(dpy)] and [Ti(NPh)(pmpmi)(py)$_2$] have been prepared, characterised and shown to be pre-catalysts for the hydroamination of phenylacetylene with aniline and *p*-chloroaniline. The X-ray structures of [Ti(NMe$_2$)$_2$(pmpmi)], [Ti(N^{t}Bu)(pmpmi)(dpy)] and [Ti(NPh)(pmpmi)(py)$_2$] have been determined.

Keywords: titanium, imines, X-ray structure, hydroamination

Studies of preparation and characterisation of titanium amido- and imido- complexes have largely been driven by investigation of hydroamination reaction, in which an amine is added across an unsaturated C–C bond to form imines, enamines and N-containing heterocycles. Since this process circumvents the formation of byproducts and provides an attractive strategy for the preparation of industrially important N-containing compounds, both inter- and intra-molecular hydroamination have attracted attention for more than 20 years.[1–7] A variety of complexes are known to effect such transformations.[2] Amongst these, titanium complexes have been proved to be some of the most useful catalysts for the hydroamination of alkynes due to their enhanced stability and improved functional group tolerance. Titanium-catalysed hydroamination of alkynes has been extensively studied by many groups around the world.[8–14] This research has indicated that the ligand chelating to the metal centre plays a key role in controlling the regioselectivity of the hydroamination products. In general, anti-Markonikov products are preferentially obtained with titanocene catalysts;[15–18] in contrast, Markovnikov isomers are formed with pyrrolyl ligands.[19–24] As a continuation of our efforts on studying the hydroamination of alkynes catalysed by pyrrolyl ligand-chelated titanium compounds,[25–27] we are exploring the syntheses and catalytic activities of titanium amido- or imido-complexes chelated by H$_2$pmpmi [H$_2$pmpmi = (2-pyrrolylmethene)-(2-pyrrolylmethyl)imine].[28–29] H$_2$pmpmi is a tridentate, dianionic pyrrolyl Schiff base ligand, that potentially forms a bisamido-complex with [Ti(NMe$_2$)$_4$], and provides a straightforward access to titanium imido- complexes.

We now describe the syntheses and structural characterisation of three titanium imido-complexes and one titanium bisamido-complex. The catalytic activities of four complexes towards intermolecular hydroamination of alkynes are also reported.

Experimental

All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified dinitrogen atmosphere. Hexane, toluene and THF were purchased from commercial suppliers and dried over purple sodium benzophenone ketyl. Pyridine and liquid primary amines were pre-dried by CaH_2 and distilled prior to use. [Ti(N^{t}Bu)Cl$_2$(py)$_2$],[30] 2-cyanopyrrole[31] and H$_2$pmpmi were prepared according to the literature procedures. Elemental analyses (C, H, N) were performed with a Carlo-Erba EA 1110 CHNO-S microanalyser. Crystal structure determination was performed with a Bruker SMART APEX II CCDC diffractometer equipped with graphite-monochromatised Mo Kα radiation (λ = 0.71073 Å). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300 or VXR-500 spectrometer. GC/MS spectra were recorded with a GCMS-QP2010.

Crystals grown from concentrated solutions at room temperature were quickly selected and mounted on a glass fibre in wax. The data collections were carried out on a Bruker AXS three-circle goniometer with a CCD detector equipped with graphite-monochromated Mo*K*α radiation by using the ϕ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97.[32,33] The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The structures shown in Figs 1–3 were produced using ORTEP, and ellipsoids are at the 30% probability level.

Preparation of Li$_2$pmpmi

^{n}BuLi (1.25 mL, 1.6 mol L^{-1}, 2 mmol) in hexane (3 mL) was added dropwise to a solution of H$_2$pmpmi (0.1732 g, 1 mmol) in THF (3 mL) cooled to –35 °C. A white precipitate formed immediately. The resulting mixture was allowed to warm to room temperature and stirred for 3 h, then used as the lithiated salt without further purification.

Preparation of [Ti(NMe$_2$)$_2$(pmpmi)] (**1**)

H$_2$pmpmi (0.1732 g, 1 mmol) in THF (3 mL) was added dropwise to a solution of [Ti(NMe$_2$)$_4$] (0.2242 g, 1 mmol) in THF (3 mL) cooled to –35 °C. The reaction mixture was allowed to warm to room

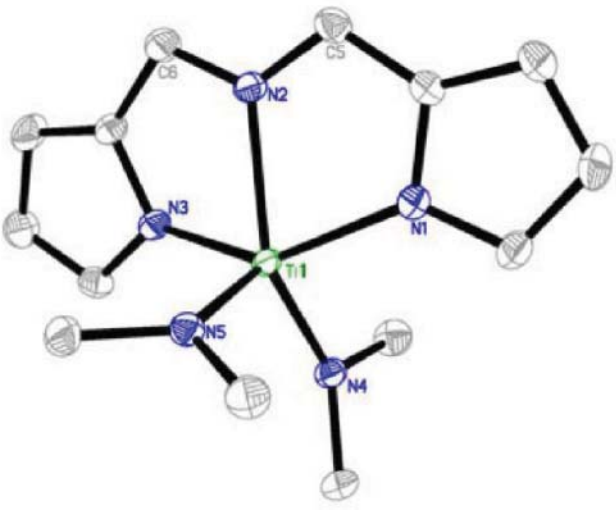

Fig. 1 ORTEP structural drawing of **1**. Ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

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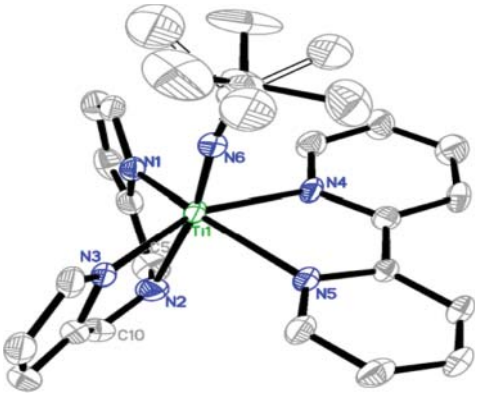


Fig. 2 ORTEP structural drawing of **3**. Ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

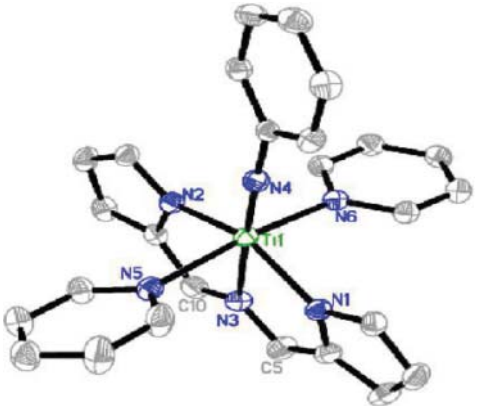


Fig. 3 ORTEP structural drawing of **4**. Ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

temperature and stirred for 16 h, after which time the volatiles were removed under reduced pressure to generate a red solid. Yield: 0.289 g (94%). Red single crystals of **1** were grown from a saturated THF solution left standing at –35 °C in a vibration-free environment. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (1H, s, CH=N), 7.29 (1H, s, 5-C_4H_3N), 6.87 (2H, s, 5-C_4H_3N), 6.64 (1H, d, 3-C_4H_3N), 6.26 (1H, t, 4-C_4H_3N), 6.22 (1H, t, 4-C_4H_3N), 5.98 (1H, s, 3-C_4H_3N), 5.01 (2H, s, CH_2), 3.25 (12H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.1, 142.4, 141.9, 139.1, 127.6, 117.9, 113.9, 111.0, 101.9, 56.7, 46.8 ppm. Anal. Calcd for $C_{14}H_{21}N_5Ti$: C, 54.73; H, 6.89; N, 22.80. Found: C, 54.23; H, 7.01; N, 22.52%.

Preparation of [Ti(N^{t}Bu)(pmpmi)(py)$_2$] (**2**)
Method A: ^{t}BuNH$_2$ (10 mL) was added to a solution of (**1**) (0.3072 g, 1 mmol) in THF. The reaction mixture was heated at 55 °C for 16 h, after which time the volatiles were removed under reduced pressure to produce a red oil. The oil was dissolved in a mixture of THF (3 mL) and pyridine (1.58 g, 20 mmol). The resulting mixture was stirred for 6 h, after which time the volatiles were removed under reduced pressure to provide a red solid. The solid was washed with hexane, and dried under reduced pressure. Yield: 0.399 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (4H, d, 2-C_5H_5N), 7.93 (1H, s, CH=N), 7.80 (1H, s, 5-C_4H_3N), 7.73 (1H, s, 5-C_4H_3N), 7.61 (2H, t, 4-C_5H_5N), 7.17 (4H, t, 3-C_5H_5N), 6.53 (1H, d, 3-C_4H_3N), 6.40 (1H, t, 4-C_4H_3N), 6.37 (1H, t, 4-C_4H_3N), 5.94 (1H, s, 3-C_4H_3N), 4.46 (2H, s, CH_2–N), 0.90 (9H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 152.4, 143.3, 142.5, 139.4, 139.1, 131.6, 126.2, 116.0, 112.9, 110.0, 102.1, 68.2, 53.5, 34.1 ppm. Anal. Calcd for $C_{24}H_{28}N_6Ti$: C, 64.29; H, 6.29; N, 18.74. Found: C, 64.01; H, 6.66; N, 18.53%.

Method B: Li_2pmpmi (1 mmol) solution was added dropwise to a solution of [Ti(N^{t}Bu)Cl_2(py)$_2$] (0.3482 g, 1 mmol) in THF (3 mL) cooled to –35 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h, after which time the volatiles were removed under reduced pressure to produce a red solid. The solid was dissolved in toluene, the precipitate filtered away, and the filtrates were dried under reduced pressure, yielding **2** as a red solid. Yield: 0.368 g (82%).

Preparation of [Ti(N^{t}Bu)(pmpmi)(dpy)] (**3**)
Method A: 2,2′-dipyridyl (0.164 g, 1.05 mmol) and Bu^{t}NH$_2$ (1 mL) was added to a solution of **1** (0.3072 g, 1 mmol) in THF (3 mL). The reaction mixture was stirred for 32 h, after which time the volatiles were removed under reduced pressure to afford a yellow solid. The solid was washed with hexane and dried under reduced pressure. Yield: 0.344 g (77%). ^{1}H NMR (300 MHz, C_6D_6): δ = 8.39 (2H, d, 6-dpy), 7.50 (2H, s, 3-dpy), 7.33 (1H, s, CH=N), 6.94 (1H, t, 5-C_4H_3N), 6.90 (2H, d, 4-dpy), 6.80 (3H, 3,5-C_4H_3N), 6.66 (1H, d, 4-C_4H_3N), 6.47 (2H, t, 5-dpy), 6.28 (1H, s, 4-C_4H_3N), 4.08 (1H, d, CH_2-N), 1.14 (9H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 154.9, 151.8, 142.1, 141.2, 140.2, 139.6, 133.1, 127.8, 122.8, 115.6, 113.4, 110.0, 101.5, 67.9, 58.6, 34.2 ppm. Anal. Calcd for $C_{24}H_{26}N_6Ti$: C, 64.68; H, 5.77; N, 18.83. Found: C, 65.23; H, 6.01; N, 18.00%.

Method B: A solution of 2,2′-dipyridyl (0.164 g, 1.05 mmol) in THF (2 mL) was added dropwise to a solution of [Ti(N^{t}Bu)Cl_2(py)$_2$] (0.3482 g, 1 mmol) in THF (3 mL). A yellow precipitate was formed. The reaction mixture was stirred at room temperature for 8 h, after which time the volatiles were removed under reduced pressure to produce a yellow solid. The solid was dissolved in THF (3 mL) and cooled to –35 °C, then a solution of Li_2pmpmi (1 mmol), cooled to –35 °C, was added. The reaction mixture was allowed to warm to room temperature and stirred for 16 h, after which time the volatiles were removed under reduced pressure to generate a yellow solid. The solid was dissolved in toluene, the white precipitates filtered away, and the filtrate was dried under reduced pressure, yielding **3** as a yellow solid. Yield: 0.388 g (87%).

Preparation of [Ti(NPh)(pmpmi)(py)$_2$] (**4**)
Method A: Aniline (0.0931 g, 1 mmol) in THF (3 mL) was added dropwise to a solution of **1** (0.3072 g, 1 mmol) in THF (3 mL), cooled to –35 °C,. The reaction mixture was allowed to warm to room temperature and stirred for 12 h, after which time the volatiles were removed under reduced pressure to afford a brown solid. The solid was dissolved in the mixture of THF (3 mL) and pyridine (1 mL). The resulting mixture was stirred for 6 h, after which time the volatiles were removed under reduced pressure to provide a red solid. The solid was washed with hexane and dried under reduced pressure. Yield: 0.422 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (4H, d, 2-C_5H_5N), 7.97 (1H, s, CH=N), 7.89 (1H, s, 5-C_4H_3N), 7.84 (1H, s, 5-C_4H_3N), 7.59 (2H, t, 4-C_5H_5N), 7.16 (4H, t, 3-C_5H_5N), 7.04 (2H, t, 3-C_6H_5N), 6.84 (2H, d, 2-C_6H_5N), 6.70 (1H, t, 4-C_6H_5N), 6.60 (1H, s, 3-C_4H_3N), 6.40 (1H, t, 4-C_4H_3N), 6.36 (1H, t, 4-C_4H_3N), 5.98 (1H, s, 3-C_4H_3N), 4.65 (1H, s, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 152.1, 143.1, 142.4, 139.9, 139.1, 130.8, 130.4, 126.7, 126.5, 126.0, 122.1, 116.8, 113.4, 110.5, 102.4, 53.8 ppm. Anal. Calcd for $C_{26}H_{24}N_4Ti$: C, 66.67; H, 5.16; N, 17.94. Found: C, 66.31; H, 5.01; N, 17.73%.

Method B: A solution of aniline (0.0931 g, 1 mmol) in THF (2 mL) was added dropwise to a solution of [Ti(N^{t}Bu)Cl_2(py)$_2$] (0.3482 g, 1 mmol) in THF (3 mL) cooled to –35 °C. The reaction mixture was stirred at room temperature for 16 h, after which time volatiles were removed under reduced pressure to provide a brown solid. The solid was dissolved in THF (3 mL) and cooled to –35 °C, then a solution of Li_2pmpmi (1 mmol), cooled to –35 °C, was added. The resulting reaction mixture was allowed to warm to room temperature and stirred for 16 h, after which time the volatiles were removed under reduced pressure to generate a brown solid. The solid was dissolved in toluene, the white precipitates filtered away, and the filtrate was dried under reduced pressure, yielding **4** as a red solid. Yield: 0.197 g (42%).

Catalytic reactions; general procedure
The pre-catalyst (0.3 mmol), amine (4.5 mmol), alkyne (3 mmol) and toluene (5 mL) was added to a 50 mL pressure tube in a drybox. The pressure tube was sealed with a teflon screw cap, taken out of the drybox and heated at 100 °C for 16 h. Then at 0 °C the reaction solution was carefully added to a suspension of $LiAlH_4$ in toluene and the mixture was refluxed for 3 h. After cooling the solution to 0 °C, the excess amount of $LiAlH_4$ was hydrolysed with aqueous NaOH

(3 mol L^{-1}). The mixture was then extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. Column chromatography of the residue on silica gel afforded the pure amine derivatives.

N-Phenylphenethylamine (**7a**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.79 (8H, Ph), 6.89–7.00 (2H, *p*–Ph), 4.12 (1H, NH), 3.79 (2H, $PhCH_2$), 3.29–3.37 (2H, $NHCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 138.0, 128.1, 127.8, 127.7, 125.5, 120.8, 113.0, 44.0, 34.3 ppm. MS (GC/MS of $PhN{=}CHCH_2Ph$, determined before being reduced to $PhNHCH_2CH_2Ph$): *m/z* (%) = 195 (50) [M^+], 104 (100) [$C_6H_5N{=}CH^+$], 91 (25) [$C_6H_5CH_2^+$], 77 (62) [$C_6H_5^+$].

N-4-Chlorophenylphenethylamine (**7b**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.96 (8H, Ph), 7.37 (1H, *p*-Ph), 4.27 (1H, NH), 4.03 (2H, $PhCH_2$), 3.54 (2H, $NHCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 138.3, 128.3, 127.8, 127.6, 125.4, 116.5, 112.0, 44.0, 34.4 ppm. MS (GC/MS of *p*-$ClPhN{=}CHCH_2Ph$, determined before being reduced to *p*-$ClPhNHCH_2CH_2Ph$): *m/z* (%) = 229 (52) [M^+], 138 (100) [$ClC_6H_4N{=}CH^+$], 111 (42) [$ClC_6H_4^+$], 91 (24) [$C_6H_5CH_2^+$].

Results and discussion

Treatment of a [$Ti(NMe_2)_4$] solution with 1 equiv. of H_2pmpmi leads to near quantitative transamination generating [$Ti(NMe_2)_2$ (pmpmi)] (**1**) with loss of 2 equiv. of $HNMe_2$ (Scheme 1). The compound is readily isolated as a red solid and red single crystals of **1** were grown at –35 °C.

Single-crystal X-ray diffraction studies reveal that complex **1** crystallises in the triclinic crystal system of the *P*-1 space group. The overall structure of **1** is remarkably close to a distorted square pyramid (Fig. 1), with one amide nitrogen atom axial and the other four equatorial. The angles between the equatorial nitrogen atoms add up to 343.13°. The three nitrogen atoms of the pmpmi^{2-} ligand are nearly coplanar. As expected, the donor amine exhibits the longest Ti1–N2 bond (2.184(3) Å). The averaged Ti–N(pyrrolyl) bond distance is found to be 0.195 Å longer than the averaged Ti–N(dimethylamide) bond length. An analysis of the known and crystallographically determined Ti–N(NMe_2) bond lengths reveals that the Ti–N(NMe_2) bond distances in **1** are relatively short, averaging 1.870(3) Å.

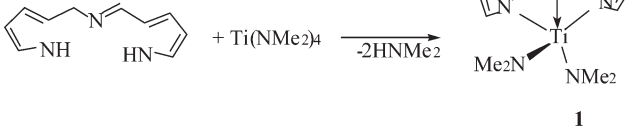
In the presence of pyridine and using ^{t}BuNH$_2$ as the solvent, **1** was completely converted to **2** after heating at 55 °C for 16 h. Complex **2** was also synthesised by adding Li_2pmpmi to 1 equiv. of [$Ti(N^tBu)Cl_2(py)_2$] (Scheme 2). Unfortunately, a single-crystal of **2** was not successfully cultivated. The ^{1}H NMR spectrum of **2** shows signals for a N^{t}Bu group and two pyridine molecules. The signals of the pmpmi^{2-} ligand can be also observed. The solution ^{1}H NMR, ^{13}C NMR spectra and elemental analysis data are fully consistent with the structure of **2**.

Addition of 2,2′-dipyridyl and ^{t}BuNH$_2$ to a solution of **1** in THF yielded **3**. Complex **3** was also synthesised by adding Li_2pmpmi to the mixture of [$Ti(N^tBu)Cl_2(py)_2$] and 2,2′-dipyridyl (Scheme 3).

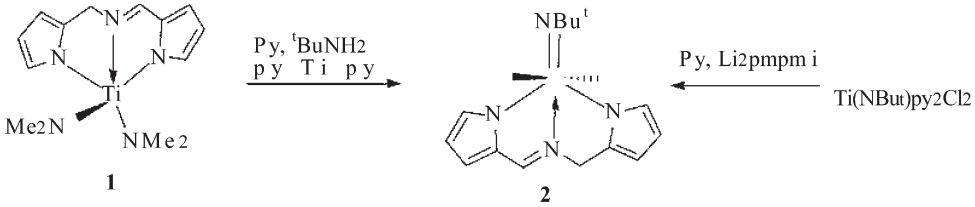
Complex **3** was structurally characterised by single-crystal X-ray diffraction (Fig. 2). The titanium atom was coordinated by one nitrogen atom of a N^{t}Bu group by a double bond, two nitrogen atoms from 2,2′-dipyridyl, and three nitrogen atoms from one pmpmi^{2-} ligand. The six nitrogen atoms around the titanium atom display a pseudo-octahedral geometry. The three nitrogen atoms of the pmpmi^{2-} ligand are not coplanar. The Ti1=N6 bond distance is the shortest [1.696(3) Å]. Similar to **1**, the donor amine of the pmpmi^{2-} ligand exhibits the longest Ti1–N2 bond (2.267(3) Å). The two Ti–N (dipyridyl) bond lengths are slightly shorter than that of the donor amine Ti–N bond of the pmpmi^{2-} ligand. The averaged Ti–N(pyrrolyl) bond length is 2.102(3) Å.

Addition of 1 equiv. of $PhNH_2$ to **1** followed by adding an excess of pyridine yielded **4** in 90% isolated yield. Alternatively, treatment of Li_2pmpmi with a mixture of [$Ti(N^tBu)Cl_2(py)_2$] and aniline, produced **4** in good yield (Scheme 4).

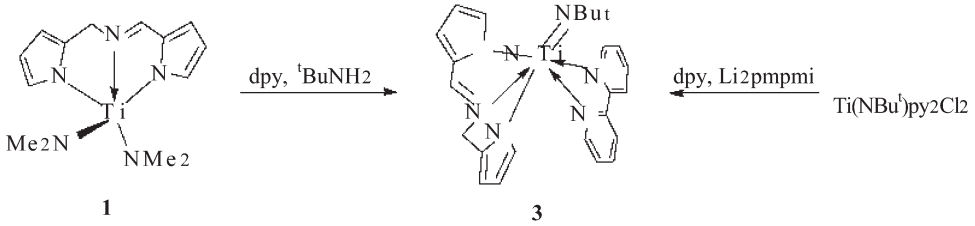
An ORTEP structural representation derived from single-crystal X-ray diffraction on **4** (Fig. 3) showed that the complex is pseudo-octahedral, with the three coplanar nitrogen atoms of the pmpmi^{2-} ligand facially occupying three sites. The angle of N1–Ti1–N2 is 148.46(9). The opposite position of the pmpmi^{2-} ligand is occupied by a NPh group, and the angle of N3–Ti1–N4 is 177.07(10), which indicates that the nitrogen atom of the NPh group and the three nitrogen atoms of the pmpmi^{2-} ligand are nearly coplanar too. The two axial positions of the distorted octahedron were occupied by two pyridine nitrogen atoms. As expected, the Ti–N(pyrrolyl), Ti–N(pyrrolylmethene), Ti–N(phenyl) and Ti–N(pyridine) bond distances in **4** are similar with those of in complex **3**.



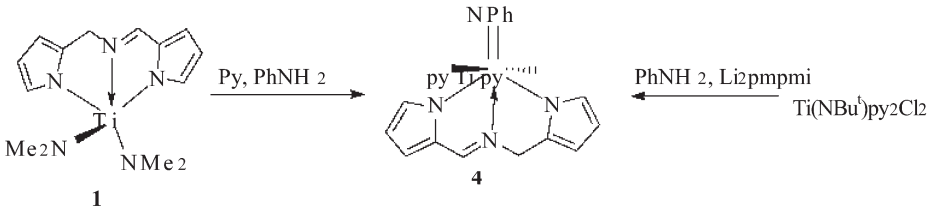
Scheme 1 Synthesis of **1**.



Scheme 2 Synthesis of **2**.



Scheme 3 Synthesis of **3**.



Scheme 4 Synthesis of **4**.

Catalytic intermolecular hydroamination of alkynes with amines

The successful preparation of the titanium bisamido-complex **1** and imido-complexes **2**–**4** prompted us to explore the catalytic activity of **1–4** in the hydroamination of alkynes (**5**) by amines (**6**). Initially, we investigated the reaction of aniline with three alkynes (phenylacetylene, 3-hexyne and diphenylacetylene) catalysed by 10 mol % of **1**. For comparison purpose, the catalytic reactions were carried out at 100 °C in toluene for 24 h with a 1:1.5 molar ratio of alkyne and aniline. Because the resulting imines were not stable to column chromatography, the hydroamination products were directly reduced to amines by $LiAlH_4$. The results are shown in Table 3. As can be seen in Table 3, complex **1** could promote the hydroamination of phenylacetylene and afforded the desired amines (**7** and **8**) with good yield (62%; Table 3, entry 1). No hydroamination products were determined for 3-hexyne and diphenylacetylene (Table 3, entries 2, 3). The anti-Markovnikov product is the exclusive product of hydroamination of phenylacetylene with aniline.

Then we probed the hydroamination of phenylacetylene by two aromatic amines (aniline and *p*-chloroaniline) catalysed by **1**–**4** (Table 3, entries 4, 6–11). All of the catalysts could mediate the hydroamination of phenylacetylene and provided **7a** and **7b** with good yields. In all cases, the anti-Markovnikov product was favoured, often in excess of 94:6, over the Markovnikov product.

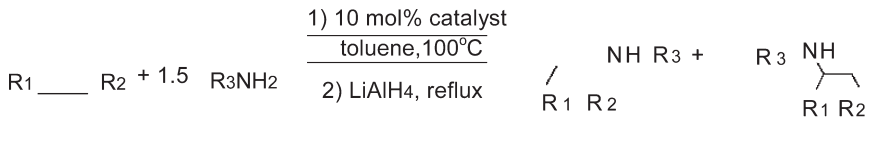
Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**, **3** and **4** · Tol

1			
Ti(1)–N(1)	2.081(3)	Ti(1)–N(2)	2.184(3)
Ti(1)–N(3)	2.048(3)	Ti(1)–N(4)	1.883(3)
N(2)–C(5)	1.332(4)	Ti(1)–N(5)	1.857(2)
N(2)–C(6)	1.396(4)		
N(5)–Ti(1)–N(4)	104.88(11)	N(4)–Ti(1)–N(2)	145.21(10)
N(5)–Ti(1)–N(2)	109.76(11)		
3			
Ti(1)–N(1)	2.093(3)	Ti(1)–N(2)	2.267(3)
Ti(1)–N(3)	2.110(3)	Ti(1)–N(4)	2.252(3)
Ti(1)–N(5)	2.247(3)	Ti(1)–N(6)	1.696(3)
N(2)–C(5)	1.444(5)	N(2)–C(10)	1.284(4)
N(6)–Ti(1)–N(1)	104.30(12)	N(6)–Ti(1)–N(4)	93.79(11)
N(6)–Ti(1)–N(3)	101.25(12)	N(6)–Ti(1)–N(5)	96.60(12)
N(1)–Ti(1)–N(2)	71.29(11)	N(3)–Ti(1)–N(2)	73.68(11)
N(4)–Ti(1)–N(2)	93.48(10)		
4 · Tol			
Ti(1)–N(1)	2.089(2)	Ti(1)–N(2)	2.074(2)
Ti(1)–N(3)	2.216(2)	Ti(1)–N(4)	1.728(2)
Ti(1)–N(5)	2.245(2)	Ti(1)–N(6)	2.252(2)
N(3)–C(5)	1.348(3)	N(3)–C(10)	1.388(4)
N(1)–Ti(1)–N(3)	74.47(9)	N(2)–Ti(1)–N(3)	74.04(9)
N(3)–Ti(1)–N(5)	87.62(9)	N(3)–Ti(1)–N(6)	82.88(8)
N(4)–Ti(1)–N(1)	105.67(10)	N(4)–Ti(1)–N(2)	105.87(10)
N(4)–Ti(1)–N(5)	95.30(10)	N(4)–Ti(1)–N(6)	94.20(9)

Table 1 Crystallographic data and structure refinement for complexes **1**, **3** and **4** · Tol

	1	**3**	**4** · Tol
Formula	$C_{14}H_{21}N_5Ti$	$C_{24}H_{26}N_6Ti$	$C_{33}H_{32}N_6Ti$
Fw	307.23	446.41	560.52
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	P b c a	*P* 2/*c*
a (Å)	8.9025(18)	17.583(4)	13.582(3)
b (Å)	9.6471(19)	15.334(3)	10.688(2)
c (Å)	10.725(2)	20.516(4)	21.733(7)
α (°)	107.22(3)	90.00	90.00
β (°)	94.11(3)	90.00	112.69(2)
γ (°)	116.35(3)	90.00	90.00
V (Å^3)	765.9(3)	5531.4(19)	2910.7(13)
Z	2	8	4
D_{calcd} (g cm^{-3})	1.332	1.072	1.279
F(000)	324	1872	1176
Crystal size(mm^3)	0.36 x 0.28 x 0.12	0.40 x 0.17 x 0.09	0.30 x 0.22 x 0.13
μ/mm^{-1}	0.557	0.328	0.327
Theta range for data collection	2.05 to 25.70	1.99 to 25.00	2.03 to 26.23
Limiting indices	$-10 \le h \le 10$	$-20 \le h \le 20$	$-15 \le h \le 16$
	$-11 \le k \le 11$	$-18 \le k \le 18$	$-10 \le k \le 13$
	$-13 \le l \le 13$	$-24 \le l \le 22$	$-26 \le l \le 26$
Data/restraints/parameters	2896/0/185	4859/0/297	5854/21/356
GOF	1.082	0.898	1.046
No. of total Reflns	10458	23786	21527
No. of unique Reflns (*R*int)	2896 [0.0432]	4859 [0.0684]	5854 [0.0482]
R^1, WR^2 [$I>2a(I)$]	0.0473, 0.1362	0.0599, 0.1512	0.0519, 0.1234
R^1, WR^2 [all data]	0.0641, 0.1477	0.1039, 0.1704	0.0923, 0.1421
Largest diff. peak and hole(e Å^{-3})	0.679 and –0.499	0.307 and –0.261	0.650 and –0.436

Table 3 The hydroamination of alkynes with amines catalysed by **1–4**[a]



Entry	Alkyne	R_3NH_2	Catalyst	Products	Isolated yield, reduction product of (**7**) /%	Ratio (**7**)/(**8**)[b]
1	Phenylacetylene	Aniline	**1**	**7a, 8**	62	98/2
2	3-Hexyne	Aniline	**1**	–	nr	–
3	Diphenylacetylene	Aniline	**1**	–	nr	–
4	Phenylacetylene	*p*-Chloroaniline	**1**	**7b, 8**	54	88/12
5	Phenylacetylene	*tert*-Butylamine	**1**	**7c**	trace	100/0
6	Phenylacetylene	Aniline	**2**	**7a, 8**	57	98/2
7	Phenylacetylene	*p*-Chloroaniline	**2**	**7b, 8**	59	97/3
8	Phenylacetylene	Aniline	**3**	**7a, 8**	65	97/3
9	Phenylacetylene	*p*-Chloroaniline	**3**	**7b, 8**	63	98/2
10	Phenylacetylene	Aniline	**4**	**7a, 8**	64	97/3
11	Phenylacetylene	*p*-Chloroaniline	**4**	**7b, 8**	54	94/6

[a] Isolated yields of the corresponding amines. Reaction conditions: (1) alkyne (3.0 mmol), amine (4.5 mmol), 10 mol% catalyst, toluene (5 mL), 100 °C, 20 h; (2) Reduced by $LiAlH_4$, followed by column chromatography.
[b] Determined by GC–MS analyses prior to the reduction.

Complex **1** catalysed hydroamination of phenylacetylene with tert-butylamine was examined and trace amount of hydroamination product (**7c**) was detected (Table 3, entry 5).

Conclusions

Four titanium complexes incorporating a tridentate, dianionic pyrrolyl ligand have been synthesised and characterised. The catalytic activities of **1**–**4** towards the hydroamination of alkynes have been studied. Complexes **1–4** were active pre-catalysts for the hydroamination reactions of phenylacetylene with aniline and *p*-chloroaniline.

CCDC-763963 (**1**), 792053 (**3**) and 763962 (**4**·Tol) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336-033; or deposit@ccdc.cam.ac.uk).

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