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Cycloaddition reactions of titanium and zirconium imido, oxo and hydrazido complexes supported by tetraaza macrocyclic ligands‡

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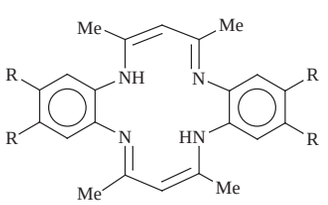
The tetraaza macrocycle-supported titanium and zirconium imido complexes [Ti(NR)(Me_ntaa)] [R = Bu^t, Ph, Tol or 4-$C_6H_4NO_2$; n = 4 or 8 where H_2Me_ntaa = tetra- or octa-methyldibenzotetraaza[14]annulene, respectively] and [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)] react with isocyanates or carbon dioxide to form cycloaddition products generally of the type [M{N(R)C(O)E}(Me_ntaa)] (M = Ti or Zr, R = aryl or *tert*-butyl, E = O, NBu^t or N–aryl). The complex [Zr{$N(C_6H_3Pr^i_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] is also formed by reaction of the bis(arylimide) [Zr($NHC_6H_3Pr^i$-2,6)$_2$(Me_4taa)] with Bu^tNCO. The crystal structures of [Ti{N(Tol)C(O)O}(Me_4taa)] (Tol = *p*-tolyl) and [Zr{$N(C_6H_3Pr^i_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] are described. The *tert*-butyl imido complexes [Ti(NBu^t)(Me_ntaa)] (n = 4 or 8) react with Ph_2NNH_2 to give the corresponding terminal *N,N*-diphenylhydrazido derivatives [Ti($NNPh_2$)(Me_ntaa)] and these yield the cycloaddition products [Ti{$N(NPh_2)C(O)O$}(Me_ntaa)] or [Ti{$N(NPh_2)C(O)N(Tol)$}(Me_4taa)] with CO_2 or TolNCO, respectively. The related titanium oxo complexes [Ti(O)(Me_ntaa)] (n = 4 or 8) react with *p*-tolyl isocyanate to form the *N,O*-carbamate products [Ti{N(Tol)C(O)O}(Me_ntaa)], and with ditolylcarbodiimide to form the *N,N*-ureate derivative [Ti{N(Ph)C(O)N(Ph)}(Me_ntaa)] in which complete rupture of the Ti=O linkage has occurred. Reaction of the *N*-phenyl-*N*-tolyl (asymmetric) ureate [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] with an excess of PhNCO gave quantitative conversion to the N,N-symmetric product [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] and TolNCO. Crossover NMR tube experiments suggest that this reaction occurs *via* an associative mechanism.

Introduction

As part of an ongoing research program in early transition metal imido chemistry,[1–7] we have been exploring the chemistry of tetraaza macrocycle-supported complexes.[8–12] We were especially attracted by the dibenzotetraaza[14]annulene systems Me_ntaa {n = 4 (5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine) or 8 (5,14-dihydro-2,3,6,8, 11,12,15,17-octamethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine); see below}, the coordination chemistry of which has been reviewed.[13,14] These macrocycles are related to the porphyrins but differ in several important respects. For instance, their N_4 coordination cavity 'hole size' is *ca*. 0.1 Å smaller than that of porphyrins and they typically possess non-planar geometries.



Me_4taaH_2, R = H; Me_8taaH_2, R = Me

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‡ *Supplementary data available*: figure depicting the partial structure determination of [Ti{N(Tol)C(O)N(Tol)}(Me_4taa)] **5**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/379/, otherwise available from BLDSC (No. SUP 57465, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

The dibenzotetraaza[14]annulene ligands are well-established supporting environments for both transition metal– and main group metal–ligand mutiple bonds.[13,14] Of particular relevance to the results described herein is the very interesting cycloaddition reaction chemistry that Goedken[15] and Geoffroy and co-workers[16] described for the oxotitanium species [Ti(O)-(Me_ntaa)] (n = 4 or 8) which possesses an unusually reactive Ti=O functional group.[17] We have recently reported the synthesis and imido group exchange reactions of the isoelectronic imido analogues [Ti(NBu^t)(Me_ntaa)] (n = 4 or 8),[8] together with the homologous zirconium imido complex [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)][10] and the bis(amido) species [Zr($NHR)_2$-(Me_4taa)] (R = Bu^t, Ph, $C_6H_3Me_2$-2,6 and $C_6H_3Pr^i_2$-2,6).[9] A number of other Group 4 macrocycle-supported imido derivatives have also recently been described, but no reactivity studies of the metal–imide functional groups were reported.[18–20] In this contribution we describe our studies of the cycloaddition reactions of titanium imido complexes supported by dibenzotetraaza[14]annulene ligands, together with some related chemistry of zirconium and new titanium hydrazido complexes. A part of this work has been communicated.[10]

Experimental

General methods and instrumentation

Manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried over molecular sieves and refluxed over potassium (tetrahydrofuran, hexane), sodium–potassium alloy (pentane) or calcium hydride (dichloromethane) under an atmosphere of dinitrogen and collected by

distillation. Other protio-solvents were used as received. $CDCl_3$ and CD_2Cl_2 were dried over calcium hydride at room temperature (r.t.), and C_6D_6 was dried over potassium at 70 °C. All deuteriated solvents were distilled under reduced pressure and stored under N_2 in Young's ampoules in a dry-box. NMR samples were prepared in a dry-box in Teflon valve (Young's) 5 mm tubes.

^1H and ^{13}C NMR spectra were recorded on either Bruker WM 250, AMX 500 or DPX 300 spectrometers at 298 K unless stated otherwise. The spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional, nOe and spin saturation transfer experiments as appropriate. IR spectra were recorded as Nujol mulls (CsBr plates) or as CH_2Cl_2 solutions (NaCl cell) on either a Perkin-Elmer 2000 or a Nicolet Avatar 360 FTIR spectrometer. Elemental analyses were carried out by the analysis laboratory of this department or by Canadian Microanalytical Services Ltd.

Literature preparations and other starting materials

The complexes [Ti(NR)(Me$_n$taa)] [R = Bu^t, Ph, Tol (*p*-tolyl) or $C_6H_4NO_2$-4; $n = 4$ or 8],[8] [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me$_4$taa)][10] and [Zr($NHC_6H_3Pr^i_2$-2,6)$_2$(Me$_4$taa)][9] were prepared as previously described. *N,N*-Diphenylhydrazine was obtained as follows: to a rapidly stirred aqueous (100 ml) suspension of Ph_2NNH_2·HCl (Sigma-Aldrich, 2.5 g) and $CHCl_3$ (100 ml) was slowly added NaOH pellets until the mixture was strongly basic. The purple organic layer was then separated and the aqueous layer washed with $CHCl_3$ (4 × 20 ml). After combining the organic phases the volatiles were removed on a rotary evaporator to afford a purple oil. This was distilled at 170 °C, 10^{-1} mbar using a Kugelrhor apparatus to afford Ph_2NNH_2 as a light-sensitive, colourless oil which was stored in the dark in a glove-box. Other starting materials were used as received (Sigma-Aldrich) without further purification.

Preparations

[Ti(NNPh$_2$)(Me$_4$taa)] 1. To a solution of [Ti(NBu^t)(Me$_4$taa)] (0.56 g, 1.20 mmol) in dichloromethane (10 ml) was added *N,N*-diphenylhydrazine (0.23 g, 1.22 mmol). The solution was left at r.t. for 5 days in a closed Young's ampoule with occasional agitation, after which the volatiles were removed under reduced pressure. The resulting powder was washed with hexane to afford **1** as a dark red-brown powder. Yield: 0.44 g (65%).

The following NMR assignments have the N-substituents of the Me$_4$taa ligand in the ring 1- and 2-positions. ^1H NMR ($CDCl_3$, 250.1 MHz, 298 K): δ 7.48, 7.38 (2 × m, 2 × 4 H, C_6H_4 of Me$_4$taa), 6.77 [t, 4 H, $J = 7.7$, *meta*-NN(C_6H_5)$_2$], 6.61 [t, 2 H, $J = 7.8$, *para*-NN(C_6H_5)$_2$], 6.20 [d, 4 H, $J = 7.5$, *ortho*-NN(C_6H_5)$_2$], 5.20 [s, 2 H, NC(Me)C*H*], 2.44 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^1H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 160.4 [N*C*(Me)CH], 145.4 [*ipso*-NN(C_6H_5)$_2$], 139.2 (1- and 2-C_6H_4 of Me$_4$taa), 127.9 [*meta*-NN(C_6H_5)$_2$], 124.9 (4- and 5-C_6H_4 of Me$_4$taa), 123.8 (3- and 6-C_6H_4 of Me$_4$taa), 120.3 [*para*-NN(C_6H_5)$_2$], 116.7 [*ortho*-NN(C_6H_5)$_2$], 104.4 [NC(Me)*C*H], 23.0 [NC(*Me*)CH] [Found (calc. for $C_{34}H_{32}N_6Ti$): C, 71.4 (71.3); H, 5.9 (5.6); N, 14.6 (14.7)%].

[Ti(NNPh$_2$)(Me$_8$taa)] 2. As for **1** but using [Ti(NBu^t)(Me$_8$taa)] (0.25 g, 0.47 mmol) in dichloromethane (10 ml) and *N,N*-diphenylhydrazine (87 mg, 0.47 mmol). Yield of dark red/brown powder **2**: 0.20 g (69%).

The following NMR assignments have the N-substituents of the Me$_8$taa ligand in the ring 1- and 2-positions. ^1H NMR ($CDCl_3$, 250.1 MHz, 298 K): δ 7.28 (s, 4 H, $C_6H_2Me_2$ of Me$_8$taa), 6.72 [t, 4 H, $J = 7.6$, *meta*-NN(C_6H_5)$_2$], 6.61 [t, 2 H, $J = 7.1$, *para*-NN(C_6H_5)$_2$], 6.25 [d, 4 H, $J = 7.6$, *ortho*-NN(C_6H_5)$_2$], 5.15 [s, 2 H, NC(Me)C*H*], 2.44 [s, 12 H, NC(*Me*)CH], 2.42 (s, 12 H, $C_6H_2Me_2$). ^{13}C-{^1H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 159.9 [N*C*(Me)CH], 145.3 [*ipso*-NN(C_6H_5)$_2$], 136.9 [1- and 2-$C_6H_2Me_2$ of Me$_8$taa], 133.3 (4- and 5- $C_6H_2Me_2$ of Me$_8$taa), 127.5 [*meta*-NN(C_6H_5)$_2$], 124.7 (3- and 6- $C_6H_2Me_2$ of Me$_8$taa), 120.0 [*para*-NN(C_6H_5)$_2$], 116.9 [*ortho*-NN(C_6H_5)$_2$], 103.8 [NC(Me)*C*H], 22.3 [NC(*Me*)CH], 20.1 ($C_6H_2Me_2$) [Found (calc. for $C_{38}H_{40}N_6Ti$): C, 71.9 (72.6); H, 7.0 (6.4); N, 12.9 (13.4)%].

Reaction of [Ti(NBu^t)(Me$_4$taa)] with *tert*-butyl isocyanate: NMR scale synthesis of [Ti{N(Bu^t)C(NBu^t)O}(Me$_4$taa)] 3. To a solution of [Ti(NBu^t)(Me$_4$taa)] (25 mg, 0.05 mmol) in $CDCl_3$ (0.7 ml) was added Bu^{t}NCO (10 μl, 0.09 mmol). The mixture was transferred to a 5 mm Young's NMR tube. After 6 days at r.t. all the starting imide complex resonances had been replaced by those assigned to **3**. All attempts to repeat this reaction on a preparative scale were unsuccessful giving mixtures of products including **3**.

The following NMR assignments have the N-substituents of the Me$_4$taa ligand in the ring 1- and 2-positions. ^1H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.8–7.6 (m, 8 H, C_6H_4), 6.11, 5.91 [2 × s, 2 × 1 H, 2 × NC(Me)C*H*], 2.75, 2.69 [2 × s, 2 × 6 H, 2 × NC(*Me*)CH], 0.82 (s, 9 H, TiNBu^t), 0.45 (s, 9 H, C=NBu^t).

[Ti{N(Ph)C(O)N(Ph)}(Me$_4$taa)] 4, [Ti{N(Tol)C(O)N(Tol)}-(Me$_n$taa)] (n = 4, 5 or 8, 6), [Ti{N(Ph)C(O)N(Tol)}(Me$_4$taa)] 8 and [Ti{N($C_6H_4NO_2$-4)C(O)N(R)}(Me$_4$taa)] (R = Bu^t 9 or Ph 10). To a solution of [Ti(NTol)(Me$_4$taa)] (0.18 g, 0.36 mmol) in dichloromethane (30 ml) was added *p*-tolyl isocyanate (48 ml, 0.38 mmol). The solution was stirred at r.t. for 24 h, after which the volume was reduced under reduced pressure and hexane added to afford **5** as a dark green powder. Yield: 0.20 g (88%). Single crystals of **5** were grown at −25 °C from a saturated CH_2Cl_2 solution (3 ml) layered with a CH_2Cl_2–hexane 50 : 50 buffer (2 ml) and then hexane (6 ml). The diffraction data for the best available crystals were unfortunately not of sufficient quality for publication (see SUP 57465). The other compounds were prepared in generally a similar manner as follows. Compound **6** from [Ti(NTol)(Me$_4$taa)] and *p*-tolyl isocyanate in benzene at 10 °C for 30 min. Yield: 89%. Compound **4** from [Ti(NPh)(Me$_4$taa)] and phenyl isocyanate for 24 h. Yield: 71%. Compound **8** from [Ti(NPh)(Me$_4$taa)] and *p*-tolyl isocyanate for 16 h or from [Ti(NTol)(Me$_4$taa)] and phenyl isocyanate for 24 h. Yields: 52% and 62%, respectively. Compounds **9** and **10** from [Ti($NC_6H_4NO_2$-4)(Me$_4$taa)] and *tert*-butyl isocyanate for 3 days or phenyl isocyanate for 24 h. Yields: 84% and 74%, respectively.

The following NMR assignments have the N-substituents of the Me$_n$taa (n = 4 or 8) ligand in the ring 1- and 2-positions.

Data for ***4***. ^1H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.08–7.05 (overlapping m, 8 H, C_6H_4 and 4 × *meta*-C_6H_5) 6.83–6.80 (m, 4 H, C_6H_4 of Me$_4$taa), 6.36 (d, 4 H, $J = 8.4$, *ortho*-C_6H_5), 5.78 [s, 2 H, NC(Me)C*H*], 2.49 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^1H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 165.7 (C=O), 159.4 [N*C*(Me)CH], 148.2 (*ipso*-C_6H_5), 135.8 (1- and 2-C_6H_4), 127.1 (*meta*-C_6H_5), 125.9, 123.6 (3- and 6-, and 4- and 5-C_6H_4), 122.8 (*ortho*-C_6H_5), 121.2 (*para*-C_6H_5), 106.5 [NC(Me)*C*H], 23.3 [NC(*Me*)CH]. IR (Nujol): ν(CO) 1628 cm^{-1} [Found (calc. for $C_{35}H_{32}N_6OTi$): C 69.7 (70.0), H 5.8 (5.4), N 13.8 (14.0)%].

Data for ***5***. ^1H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ 7.13 (m, 4 H, C_6H_4 of Me$_4$taa), 6.93 (overlapping 2 × m, 2 × 4 H, *meta*-C_6H_4Me and C_6H_4 of Me$_4$taa), 6.19 (d, 4 H, $J = 8.3$, *ortho*-C_6H_4Me), 5.82 [s, 2 H, NC(Me)C*H*], 2.51 [s, 12 H NC(*Me*)CH], 2.35 (s, 6 H, C_6H_4Me). ^{13}C-{^1H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 167.2 (C=O), 160.1 [N*C*(Me)CH], 146.1 (*ipso*-C_6H_4Me), 136.5 (1- and 2-C_6H_4 of Me$_4$taa), 130.9 (*para*-C_6H_4Me), 127.9

(*meta*-C_6H_4Me), 126.0 (4- and 5-C_6H_4 of Me_4taa), 123.8 (*ortho*-C_6H_4Me), 123.1 (3- and 6-C_6H_4 of Me_4taa), 106.8 [NC(Me)-*C*H], 23.6 [NC(*Me*)CH], 21.0 (C_6H_4Me) [Found (calc. for $C_{37}H_{36}N_6OTi\cdot 2CH_2Cl_2$): C, 58.7 (58.7); H, 5.1 (5.0); N, 10.5 (10.5)%]. IR (CH_2Cl_2): ν(CO) 1630 cm^{-1}.

Data for **6**. ^1H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ 6.92 (d, 4 H, $J = 8.4$, *meta*-C_6H_4Me), 6.62 (s, 4 H, 3- and 4-$C_6H_2Me_2$), 6.12 (d, 4 H, $J = 8.4$, *ortho*-C_6H_4Me), 5.78 [s, 2 H, NC(Me)C*H*], 2.55 [s, 12 H, NC(*Me*)CH], 2.31 (s, 6 H, C_6H_4Me), 2.19 (s, 12 H, $C_6H_2Me_2$). ^{13}C-{^1H} NMR (CD_2Cl_2, 75.5 MHz, 298 K): δ 165.7 (C=O), 158.4, [N*C*(Me)CH], 146.1 (*ipso*-C_6H_4Me), 135.3 (1- and 2-$C_6H_2Me_2$), 132.5 (*para*-C_6H_4Me), 129.6 (4- and 5-$C_6H_2Me_2$), 128.3 (*meta*-C_6H_4Me), 123.5 (3- and 6-$C_6H_2Me_2$), 123.1 (*ortho*-C_6H_4Me), 105.6 [NC(Me)*C*H], 22.9 [NC(*Me*)CH], 20.6 (C_6H_4Me), 19.8, ($C_6H_2Me_2$). IR (CH_2Cl_2): ν(CO) 1628 cm^{-1} [Found (calc. for $C_{41}H_{44}N_6OTi$): C, 71.1 (71.9); H, 6.6 (6.5); N, 11.9 (12.3)%].

Data for **8**. ^1H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.07–7.04 (overlapping m + d, 6 H, C_6H_4 of Me_4taa + *meta*-C_6H_5), 6.90–6.82 (overlapping m + d + t, 7 H, C_6H_4 of Me_4taa + *meta*- and *para*-C_6H_5), 6.36, (d, 2 H, $J = 7.8$, *ortho*-NC_6H_5), 6.25 (d, 2 H, $J = 8.1$, *ortho*-C_6H_4Me), 5.76 [s, 2 H, NC(Me)C*H*], 2.49 [s, 12 H, NC(*Me*)CH], 2.30 (s, 3 H, C_6H_4Me). ^{13}C-{^1H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 160.9 (C=O), 159.4 [N*C*(Me)CH], 148.2 (*ipso*-C_6H_5), 145.7 (*ipso*-C_6H_4Me), 136.1 (1- and 2-C_6H_4 of Me_4taa), 127.6 (*meta*-C_6H_4Me), 127.0 (*meta*-C_6H_5), 125.7 (3- and 6-, or 4- and 5-C_6H_4 of Me_4taa), 123.6 (*ortho*-C_6H_5), 123.4 (*ortho*-C_6H_4Me), 122.7 (4- and 5-, or 3- and 6-C_6H_4 of Me_4taa), 121.1 (*para*-C_6H_5), 106.5 [NC(Me)*C*H], 23.3 [NC(*Me*)CH], 20.9 (C_6H_4Me). IR (Nujol): ν(CO) 1626 cm^{-1} [Found (calc. for $C_{36}H_{34}N_6OTi$): C 70.0 (70.3), H 5.4 (5.6), N 13.3 (13.7)%].

Data for **9**. ^1H NMR ($CDCl_3$, 250 MHz, 298 K): δ 7.92 (d, 2 H, $J = 7.6$, *meta*-$C_6H_4NO_2$), 7.54 (d, 2 H, $J = 6.9$, 6-C_6H_4 of Me_4taa), 7.34, 7.47 (2 × apparent t, 2 × 2 H, apparent $J = 6.9$, 4- and 5-C_6H_4 of Me_4taa), 7.05 (d, 2 H, $J = 6.9$, 3-C_6H_4 of Me_4taa), 6.51 (d, 2 H, $J = 7.6$, *ortho*-$C_6H_4NO_2$), 5.71, 5.65 [2 × s, 2 × 1 H NC(Me)C*H*], 2.52, 2.38 [2 × s, 2 × 6 H NC(*Me*)CH], 0.77 (s, 9 H, Bu^t). ^{13}C-{^1H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 158.7, 158.3 [2 × N*C*(Me)CH], 132.5, 132.4 (1- and 2-C_6H_4 of Me_4taa), 128.1, 127.9 (3- and 6-C_6H_4 of Me_4taa), 124.2 (*meta*-$C_6H_4NO_2$), 123.7, 123.4 (3- and 6-C_6H_4 of Me_4taa), 120.3 (*ortho*-$C_6H_4NO_2$), 105.7, 104.5 [2 × NC(Me)*C*H], 30.0 (N*C*Me_3), 22.9, 22.6 [2 × NC(*Me*)CH]; note: neither N*C*Me_3 nor C=O resonances observed [Found (calc. for $C_{33}H_{35}N_7O_3Ti$): C 63.5 (63.4), H 5.8 (5.6), N 15.3 (15.7)%].

Data for ***10***. ^1H NMR ($CDCl_3$, 250.1 MHz, 298 K): δ 7.96 (d, 2 H, $J = 9.2$, *meta*-$C_6H_4NO_2$), 7.21–6.88 (overlapping m, 11 H, C_6H_4 of Me_4taa, *para*- and *meta*-NC_6H_5), 6.49 (d, 2 H, $J = 9.2$, *ortho*-$C_6H_4NO_2$), 6.25 (d, 2 H, $J = 7.3$, *ortho*-C_6H_5), 5.85, 5.83 [2 × s, 2 × 1 H, 2 × NC(Me)C*H*], 2.53, 2.47 [2 × s, 2 × 6 H, 2 × NC(*Me*)CH]. ^{13}C-{^1H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 159.3 [N*C*(Me)CH], 158.9 (C=O), 133.4 (1- and 2-C_6H_4 of Me_4taa), 127.4–121.1 (3- to 6-C_6H_4 of Me_4taa, C_6H_5, $C_6H_4NO_2$), 106.5, 106.0 [2 × NC(Me)*C*H], 22.9 [NC(*Me*)CH]. IR (Nujol): ν(CO) 1643 cm^{-1}.

[Zr{N($C_6H_3Pr^i_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] 7. *Method (a): from [Zr(NC$_6H_3Pr^i_2$-2,6)(py)(Me_4taa)] and tert-butyl isocyanate.* To a solution of [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)] (0.482 g, 0.701 mmol) in toluene (30 ml) was added *tert*-butyl isocyanate (0.10 ml, 0.876 mmol) to give an immediate colour change to yellow-brown. After 2 h the solution was concentrated to *ca.* 10 ml and crystals of **7**·C_7H_8 suitable for X-ray study diffraction formed overnight at r.t. (0.254 g). The solution was decanted off and the crystals were washed with a minimal quantity of hexanes. The combined washings and mother-liquor yielded a further crop of **7**·C_7H_8 (0.050 g). Total yield: 0.304 g, (54%).

Method (b): from [Zr(NHC$_6H_3Pr^i_2$-2,6)$_2$(Me_4taa)] and tert-butyl isocyanate. To a solution of [Zr($NHC_6H_3Pr^i_2$-2,6)$_2$(Me_4taa)] (0.175 g, 0.223 mmol) in toluene (10 ml) was added *tert*-butyl isocyanate (0.50 ml, 0.444 mmol) to yield **7**·C_7H_8 after standing at r.t. overnight. Yield: 0.060 g, (38%).

The following NMR assignments have the N-substituents of the Me_4taa ligand in the ring 1- and 2-positions. The compound was insufficiently soluble for reliable ^{13}C NMR characterisation. ^1H NMR (C_6D_6, 250.1 MHz, 298 K): δ 7.23–6.98 (overlapping m, 11 H, 3- and 4-$C_6H_3Pr^i_2$ and C_6H_4 of Me_4taa), 4.99 [br s, 2 H, NC(Me)C*H*], 2.50 (sept, 2 H, $J = 6.7$, C*H*Me_2), 1.84 [s, 12 H, NC(*Me*)CH], 1.36 (s, 9 H, Bu^t), 1.31, 1.22 (2 × d, 2 × 6 H, $J = 6.7$, CH*Me*$_2$) Found (calc. for $C_{39}H_{48}N_6OZr\cdot C_7H_8$): C, 68.8 (69.0); H, 7.3 (7.1); N, 10.5 (10.5)%. IR (Nujol): ν(CO) 1641 cm^{-1}

Reaction of [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] 4 with pinacol. To a $CDCl_3$ solution of **4** in a 5 mm Young's valve NMR tube was added pinacol (1 equivalent). After 2 h the colour had changed from brown to red and the resulting ^1H NMR spectrum showed quantitative formation of [Ti{$OC(Me)_2CH_2CH_2$-$C(Me_2)O$}(Me_4taa)] and *N,N*-diphenylurea by comparison with authentic samples described previously[8] or purchased from Sigma-Aldrich.

[Ti{N(NPh_2)C(O)N(Tol)}(Me_4taa)] 11. To a solution of [Ti($NNPh_2$)(Me_4taa)] (0.14 g, 0.24 mmol) in dichloromethane (10 ml) was added *p*-tolyl isocyanate (50 ml, 0.40 mmol). The reaction was stirred at r.t. for 3 days, after which the volume was reduced and hexane added to afford **11** as a dark green powder, which was dried *in vacuo*. Yield: 0.12 g (70%).

The following NMR assignments have the N-substituents of the $Me_n taa$ ($n = 4$ or 8) ligand in the ring 1- and 2-positions. ^1H NMR (CD_2Cl_2, 300.0 MHz, 298 K): δ 7.36–7.06 (m, 8 H, C_6H_4 of Me_4taa), 6.97 [t, 4 H, $J = 7.8$, *meta*-$NN(C_6H_5)_2$], 6.88 (d, 2 H, $J = 8.2$, *meta*-C_6H_4Me), 6.73 [t, 2 H, $J = 7.3$, *para*-$NN(C_6H_5)_2$], 6.44 [d, 4 H, $J = 7.8$, *ortho*-$NN(C_6H_5)_2$], 6.34 (d, 2 H, $J = 8.2$, *ortho*-C_6H_4Me), 5.80, 5.03 [2 × br s, 2 × 1 H, 2 × NC(Me)C*H*: $\nu_{1/2}$ = *ca.* 6 Hz], 2.56 [s, 6 H, NC(*Me*)CH], 2.23 [s, 9 H, overlapping NC(*Me*)CH and C_6H_4Me]. ^{13}C-{^1H} NMR (CD_2Cl_2, 75.5 MHz, 298 K): δ 169.5 (C=O), 160.6, 159.7 [2 × N*C*(Me)CH], 147.0 [*ipso*-$NN(C_6H_5)_2$], 146.2 (*ipso*-C_6H_4Me), 138.4, 137.7 (1- and 2-C_6H_4 of Me_4taa), 131.2 (*para*-C_6H_4Me), 128.3 [*meta*-$NN(C_6H_5)_2$], 127.8 (*meta*-C_6H_4Me), 125.3, 126.6, 123.0 (three of 3- to 6-C_6H_4 of Me_4taa), 123.4 (overlapping one of 3- to 6-C_6H_4 of Me_4taa and *ortho*-C_6H_4Me), 123.4 (*ortho*-NC_6H_4-Me-4), 120.2 [*para*-$NN(C_6H_5)_2$], 118.3 [*ortho*-$NN(C_6H_5)_2$], 107.6, 107.4 [2 × NC(Me)*C*H], 24.1, 23.9 [2 × NC(*Me*)CH], 21.0 (C_6H_4Me). IR (CH_2Cl_2): ν(CO) 1656 cm^{-1} [Found (calc. for $C_{42}H_{39}N_7OTi\cdot 0.5CH_2Cl_2$): C, 68.6 (68.2); H, 5.4 (5.4); N, 13.0 (13.1)%].

[Ti{N(R)C(O)O}($Me_n taa$)] (R = Bu^t, $n = 4$ 12 or 8 13; R = Tol, $n = 4$ 14 or 8 15). A CH_2Cl_2 solution (10 ml) of [Ti(NBu^t)(Me_4taa)] (0.20 g, 0.43 mmol) in a Young's valve ampoule was freeze–pump–thaw degassed twice, finally leaving the solution to warm up under the vapour pressure of the solvent. Carbon dioxide (*ca.* 1.1 atm) was then added to the ampoule *via* a Schlenk line. The solution was stirred for 30 min at r.t., after which the mixture was transferred to a Schlenk tube and the volatiles were removed under reduced pressure to afford **12** as an analytically pure, red-brown powder. Yield: 0.19 g (88%). The compounds **13**–**15** were prepared in a similar manner from the corresponding titanium imido complexes [Ti(NR)($Me_n taa$)]. Yields: 85–88%. Diffraction quality crystals of **14** were grown at −25 °C from a saturated CH_2Cl_2 solution (3 ml) of **14** layered with a CH_2Cl_2–hexane 50 : 50 buffer (2 ml) and then hexane (6 ml). The other compounds can be recrystallised in a similar manner.

The following NMR assignments have the N-substituents of the Me_ntaa ($n = 4$ or 8) ligand in the ring 1- and 2-positions.

Data for ***12***. ^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.58–7.38 (m, 8 H, C_6H_4), 5.76, 5.57 [2 × s, 2 × 1 H, 2 × NC(Me)C*H*], 2.59, 2.54 [2 × s, 2 × 6 H, 2 × NC(*Me*)CH], 0.64 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 165.3 (C=O), 158.6, 157.3 [2 × N*C*(Me)CH], 134.2, 132.7 (1- and 2-C_6H_4), 128.1, 126.5 (4- and 5-C_6H_4), 124.0, 123.7 (3- and 6-C_6H_4), 105.7, 105.6 [2 × NC(Me)C*H*], 56.2 (N*C*Me$_3$), 29.6 (NC*Me*$_3$), 23.2, 23.0 [2 × NC(*Me*)CH]. IR (CH_2Cl_2): ν(CO) 1636 cm^{-1} [Found (calc. for $C_{27}H_{31}N_5O_2Ti\cdot0.5CH_2Cl_2$): C, 60.6 (60.3); H, 6.2 (5.9); N, 12.6 (12.8)%].

Data for ***13***. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.31, 7.24 (2 × s, 2 × 4 H, 2 × $C_6H_2Me_2$), 5.68, 5.50 [2 × s, 2 × 1 H, NC(Me)C*H*], 2.54, 2.50 [2 × s, 2 × 6 H, NC(*Me*)CH], 2.34, 2.29 (2 × s, 2 × 6 H, 2 × $C_6H_2Me_2$), 0.62 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 166.1 (C=O), 157.6, 156.3 [2 × N*C*(Me)CH], 137.5, 136.2 (1- and 2-$C_6H_2Me_2$), 131.6, 129.9 (4- and 5-$C_6H_2Me_2$), 124.4, 124.2 (3- and 6-$C_6H_2Me_2$), 105.2, 105.1 [2 × NC(Me)C*H*], 55.6 (N*C*Me$_3$), 29.7 (NC*Me*$_3$), 22.9 [overlapping 2 × NC(*Me*)CH], 20.1, 20.5 (2 × $C_6H_2Me_2$). IR (Nujol): ν(CO) 1642 cm^{-1} [Found (calc. for $C_{31}H_{39}N_5O_2Ti\cdot0.5CH_2Cl_2$): C, 62.1 (62.6); H, 6.8 (6.7); N, 11.7 (11.6)%].

Data for ***14***. ^{1}H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ 7.30 (apparent s, 8 H, C_6H_4 of Me_4taa), 6.83 (d, 2 H, $J = 8.0$, *meta*-C_6H_4Me), 6.12 (d, 2 H, $J = 8.2$, *ortho*-C_6H_4Me), 5.81 [s, 2 H, NC(Me)C*H*], 2.57 [s, 12 H, NC(*Me*)CH], 2.25 (s, 3 H, C_6H_4Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 159.2 [N*C*(Me)CH], 144.8 (*ipso*-C_6H_4Me), 134.8 (1- and 2-C_6H_4 of Me_4taa), 130.2 (*para*-C_6H_4Me), 127.7 (*meta*-C_6H_4Me), 126.9 (4- and 5-C_6H_4 of Me_4taa), 123.4 (3- and 6-C_6H_4 of Me_4taa), 121.6 (*ortho*-C_6H_4Me), 106.6 [NC(Me)C*H*], 23.1 [NC(*Me*)CH], 20.1 (C_6H_4Me). The C=O resonance was not observed. Variable temperature ^{1}H NMR spectra to −90 °C in CD_2Cl_2 showed that resonances at δ 2.57, 5.81 and 7.30 in the ^{1}H NMR spectrum broadened but did not decoalesce; line widths for the other resonances were temperature-independent. Similarly, the ^{13}C-{^{1}H} NMR spectrum at −90 °C did not show any splitting of the resonances. IR: ν(CO) 1676 (Nujol) or 1663 cm^{-1} (CH_2Cl_2).

Data for ***15***. ^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.00 (apparent s, 4 H, $C_6H_2Me_2$), 6.83 (d, 2 H, $J = 8.3$, *meta*-C_6H_4Me), 6.18 (d, 2 H, $J = 8.3$, *ortho*-C_6H_4Me), 5.71 [s, 2 H, NC(Me)C*H*], 2.70 [s, 12 H, NC(*Me*)CH], 2.56, 2.55 (overlapping 2 × s, 15 H, $C_6H_2Me_2$ and C_6H_4Me). ^{13}C-{^{1}H} NMR data ($CDCl_3$, 75.5 MHz, 298 K): δ 164.6 (C=O, confirmed by labelling experiment with $^{13}CO_2$), 157.9 [N*C*(Me)CH], 145.6 (*ipso*-C_6H_4Me), 136.7 (1- and 2-$C_6H_2Me_2$), 134.6 (*para*-C_6H_4Me), 131.4 (4- and 5-$C_6H_2Me_2$), 127.6 (*meta*-C_6H_4Me), 124.1 (3- and 6-$C_6H_2Me_2$), 121.5 (*ortho*-C_6H_4Me), 106.1 [NC(Me)C*H*], 23.5 [NC(*Me*)CH], 21.2 (C_6H_4Me), 20.5 ($C_6H_2Me_2$). IR (CH_2Cl_2): ν(CO) 1657 cm^{-1} [Found (calc. for $C_{34}H_{37}N_5O_2Ti\cdot xCH_2Cl_2$): C, 67.5 (67.8); H, 6.0 (6.2); N, 11.3 (11.6)%].

[Ti{N(NPh$_2$)C(O)O}(Me$_4$taa)] 16. A CH_2Cl_2 solution (10 ml) of [Ti(NNPh$_2$)(Me$_4$taa)] **1** (0.14 g, 0.24 mmol) in a Young's valve ampoule was freeze–pump–thaw degassed twice, finally allowing the solution to warm up under the vapour pressure of the solvent. Carbon dioxide (*ca.* 1.1 atm) was then admitted to the ampoule *via* a Schlenk line. The solution was stirred for 30 min at r.t., after which the mixture was transferred to a Schlenk tube and the volatiles were removed under reduced pressure. The resulting dark powder was recrystallised at −25 °C from a saturated CH_2Cl_2 solution layered with hexane to afford **16** as a dark red powder. Yield: 0.12 g (80%).

The following NMR assignments have the N-substituents of the Me_4taa ligand in the ring 1- and 2-positions. ^{1}H NMR ($CDCl_3$, 250 MHz, 298 K): δ 7.36 (m, 8 H, C_6H_4), 6.98 [t, 4H, $J = 7.2$, *meta*-NN(C$_6$H$_5$)$_2$], 6.76 [t, 2 H, $J = 7.2$, *para*-NN(C$_6$H$_5$)$_2$], 6.31 [d, 4 H, $J = 7.6$, *ortho*-NN(C$_6$H$_5$)$_2$], 5.47 [s, 2 H, NC(Me)C*H*], 2.47 [s, 12 H, C(*Me*)CH]. ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 167.3 (C=O), 159.0 [N*C*(Me)CH], 146.3 [*ipso*-NN(C$_6$H$_5$)$_2$], 136.5 (1- and 2-C_6H_4), 128.0 [*meta*-NN(C$_6$H$_5$)$_2$], 126.9, 123.7 (3- and 6-, and 4- and 5- of C_6H_4), 120.3 [*para*-NN(C$_6$H$_5$)$_2$], 118.5 [*ortho*-NN(C$_6$H$_5$)$_2$], 107.5 [NC(Me)C*H*], 23.7 [NC(*Me*)CH]. IR (CH_2Cl_2): ν(CO) 1685 cm^{-1}. Satisfactory analysis could not be obtained.

[Ti{N(NPh$_2$)C(O)O}(Me$_8$taa)] 17. As for **16** but using [Ti(NNPh$_2$)(Me$_8$taa)] (0.08 g, 0.13 mmol) in CH_2Cl_2 (10 ml). Yield of dark red **17**: 0.07 g (80%).

The following NMR assignments have the N-substituents of the Me_8taa ligand in the ring 1- and 2-positions. ^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.15 (s, 4 H, 3- and 6- $C_6H_2Me_2$), 6.99 [t, 4 H, $J = 7.8$, *meta*-NN(C$_6$H$_5$)$_2$], 6.79 [t, 2 H, $J = 7.7$, *para*- NN(C$_6$H$_5$)$_2$], 6.34 [d, 4 H, $J = 7.6$, *ortho*-NN(C$_6$H$_5$)$_2$], 5.44 [s, 2 H, NC(Me)C*H*], 2.47 [s, 12 H, NC(*Me*)CH], 2.30 (s, 12 H, $C_6H_2Me_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 166.5 (C=O), 158.1 [N*C*(Me)CH], 146.2 [*ipso*-NN(C$_6$H$_5$)$_2$], 136.2 (1- and 2-$C_6H_2Me_2$), 133.8 (4- and 5-$C_6H_2Me_2$), 127.8 [*meta*-NN(C$_6$H$_5$)$_2$], 124.3 (3- and 6-$C_6H_2Me_2$), 120.1 [*para*-NN(C$_6$H$_5$)$_2$], 118.6 [*ortho*-NN(C$_6$H$_5$)$_2$], 107.4 [NC(Me)C*H*], 23.7 [NC(*Me*)CH], 20.3 ($C_6H_2Me_2$). IR (CH_2Cl_2): ν(CO) 1681 cm^{-1} [Found (calc. for $C_{39}H_{40}N_6O_2Ti\cdot0.5CH_2Cl_2$): C, 66.9 (66.4); H, 6.4 (5.8); N, 11.6 (11.7)%].

[Ti{N(Tol)C(NTol)N(Tol)}(Me$_4$taa)] 18. To a solution of [Ti(NTol)(Me$_4$taa)] (0.20 g, 3.8×10^{-4} mol) in CH_2Cl_2 (30 ml) was added di-*p*-tolylcarbodimide (0.090 g, 0.38 mmol) in CH_2Cl_2 (20 ml) at room temperature. After 24 h the volume of CH_2Cl_2 was reduced, hexane added and the solution cooled to −30 °C for 24 h to yield **18** as a red-brown powder. Yield: 0.17 g (64%). Although a satisfactory elemental analysis could not be obtained, the product was >95% pure by ^{1}H NMR spectroscopy.

The following NMR assignments have the N-substituents of the Me_ntaa ($n = 4$ or 8) ligand in the ring 1- and 2-positions. ^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.23–7.20, 6.91–6.88 (2 × m, 2 × 4 H. 2 × C_6H_4 of Me_4taa), 6.71 (overlapping 2 × d, 4 H, 2 × $J = 8.0$, 2 × *meta*-C_6H_4Me), 6.43 (d, 2 H, $J = 7.9$, *meta*-C_6H_4Me), 6.0–5.66 (overlapping 3 × d, 6 H, 2 × *ortho*-C_6H_4Me), 5.75 [s, 2 H, NC(Me)C*H*], 2.45 [s, 12 H, NC(*Me*)CH], 2.22 (s, 6 H, C_6H_4Me), 1.96 (s, 3 H, C_6H_4Me).

[Ti{N(Tol)C(O)O}(Me$_4$taa)] 14 from [Ti(O)(Me$_4$taa)] and *p*-tolyl isocyanate. To a solution of [Ti(O)(Me$_4$taa)] (0.11 g, 0.26 mmol) in CH_2Cl_2 (10 ml) was added *p*-tolyl isocyanate (35 ml, 0.28 mmol). The reaction was stirred at r.t. for 30 min, after which the volatiles were removed under reduced pressure to afford **14** as a spectroscopically pure, dark red powder. Yield: 0.10 g (75%).

[Ti{N(Tol)C(O)O}(Me$_8$taa)] 15 from [Ti(O)(Me$_8$taa)] and *p*-tolyl isocyanate. To a solution of [Ti(O)(Me$_8$taa)] (0.05 g, 0.11 mmol) in dichloromethane (10 ml) was added *p*-tolyl isocyanate (15 ml, 0.12 mmol). The solution was stirred at r.t. for 30 min, after which the volatiles were removed under reduced pressure to afford **15** as a spectroscopically pure, dark red powder. Yield: 0.05 g (75%).

NMR tube scale reaction of [Ti(O)(Me$_8$taa)] and *tert*-butyl isocyanate. [Ti(O)(Me$_8$taa)] (30 mg, 0.06 mmol) and Bu^{t}NCO (10 μl, 0.09 mmol) were dissolved in $CDCl_3$ (0.7 ml) in a 5 mm Young's NMR tube. Samples were stored in the dark in order to avoid the light-induced back reaction (see Results and discussion) After 11 and 17 days there was 45 and 70% conversion, respectively of [Ti(O)(Me$_8$taa)] to [Ti{N(Bu^t)C(O)O}(Me$_8$taa)] **13**.

Table 1 Data collection and processing parameters for [Ti{N(Tol)-C(O)O}(Me_4taa)] **14**

Formula	$C_{30}H_{28}O_2N_5Ti$
M	538.49
Crystal system, space group	Triclinic, $P\bar{1}$
a/Å	8.920(2)
b/Å	12.903(3)
c/Å	13.55(1)
α/°	67.19(4)
β/°	76.02(4)
γ/°	73.68(2)
U/Å^3	1365(2)
Z	2
D_c/g cm^{-1}	1.31
μ/mm^{-1}	2.94
Crystal size/mm	0.08 × 0.08 × 0.10
T/K	173
Absorption correction	DIFABS[22]
T_{min}, T_{max}	0.40, 0.75
θ range for data collection/°	0.00 to 75.00
Reflections collected: total, independent, R_{int}	5433, 5233, 0.03
Data, restraints, parameters	3045 [$I > 2\sigma(I)$], 0, 343
Final R,[a] R_w[b]	0.0670, 0.0736
Largest peak, hole/e Å^{-3}	0.46, −0.47

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{\frac{1}{2}}$.

[Ti{N(Tol)C(O)N(Tol)}(Me_8taa)] 6 from [Ti(O)(Me_8taa)] and di-*p*-tolylcarbodiimide. To a CH_2Cl_2 (5 ml) solution of di-*p*-tolylcarbodiimide (28 mg, 0.13 mmol) was added an orange CH_2Cl_2 (5 ml) solution of [Ti(O)(Me_8taa)] (55 mg, 0.12 mmol). The solution was stirred at r.t. for 24 h, after which the colour had changed to dark green. The volatiles were removed under reduced pressure to afford an oily green powder, which was recrystallised from CH_2Cl_2 and hexane to afford spectroscopically pure **6** by ^{1}H and ^{13}C NMR and IR spectroscopy. Yield: 45 mg (60%).

Crystal structure determination of [Ti{N(Tol)C(O)O}(Me_4taa)] 14

Crystal data and collection and processing parameters are given in Table 1. A plate-like crystal of **14** was mounted in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius CAD4 diffractometer. Data were collected using ω–2θ scans with Cu-Kα radiation (λ = 1.54180 Å). We attribute the relatively large standard uncertainty for lattice c parameter to poor crystal morphology. Note that the given standard uncertainty of 0.01 Å gives an error of *ca.* ±0.001 Å on derived bond lengths (if parallel to this axis) and so is not significant at the molecular level in this case. Equivalent reflections were merged and the structure was solved by direct methods (SIR92[21]). Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined in a riding model with fixed isotropic displacement parameters 1.3 times the equivalent isotropic displacement parameter of their supporting atom. Subsequent Fourier difference syntheses were consistent with hydrogen atoms being placed in appropriate locations. Face-indexing could not be reliably carried out because of severe icing and so a DIFABS[22] absorption correction was applied based on a converged isotropic model. Non-hydrogen atoms were subsequently refined anisotropically and a Chebychev weighting scheme[23] was applied towards to end of the refinement. Examination of the refined secondary extinction parameter[24] and an agreement analysis suggested that no extinction correction was required.

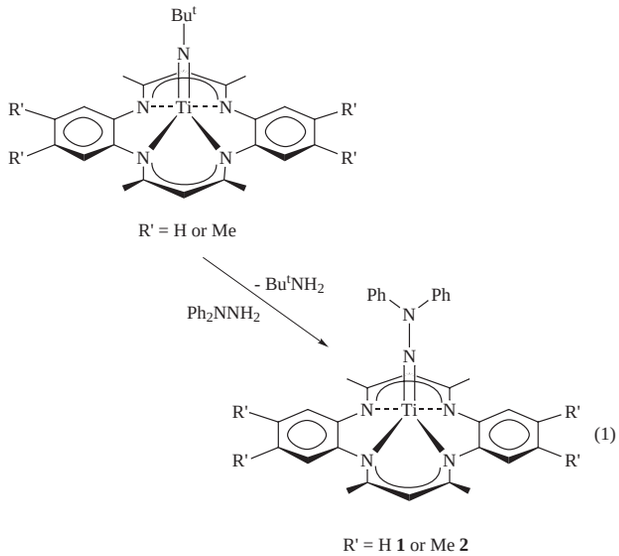
All crystallographic calculations were performed using SIR92[21] and CRYSTALS-PC.[25]

CCDC reference number 186/1267.

See http://www.rsc.org/suppdata/dt/1999/379/ for crystallographic files in .cif format.

Results and discussion[26]

The macrocycle-supported imido complexes selected for study were [Ti(NR)(Me_ntaa)] (R = Bu^t, Ph, Tol, or $C_6H_4NO_2$-4; n = 4 or 8) and [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)], the syntheses of which we have recently described.[8,10] For the purposes of comparison we also prepared the titanium hydrazido complexes [Ti($NNPh_2$)(Me_ntaa)] (n = 4 **1** or 8 **2**) as shown in eqn. (1). Thus



(1)

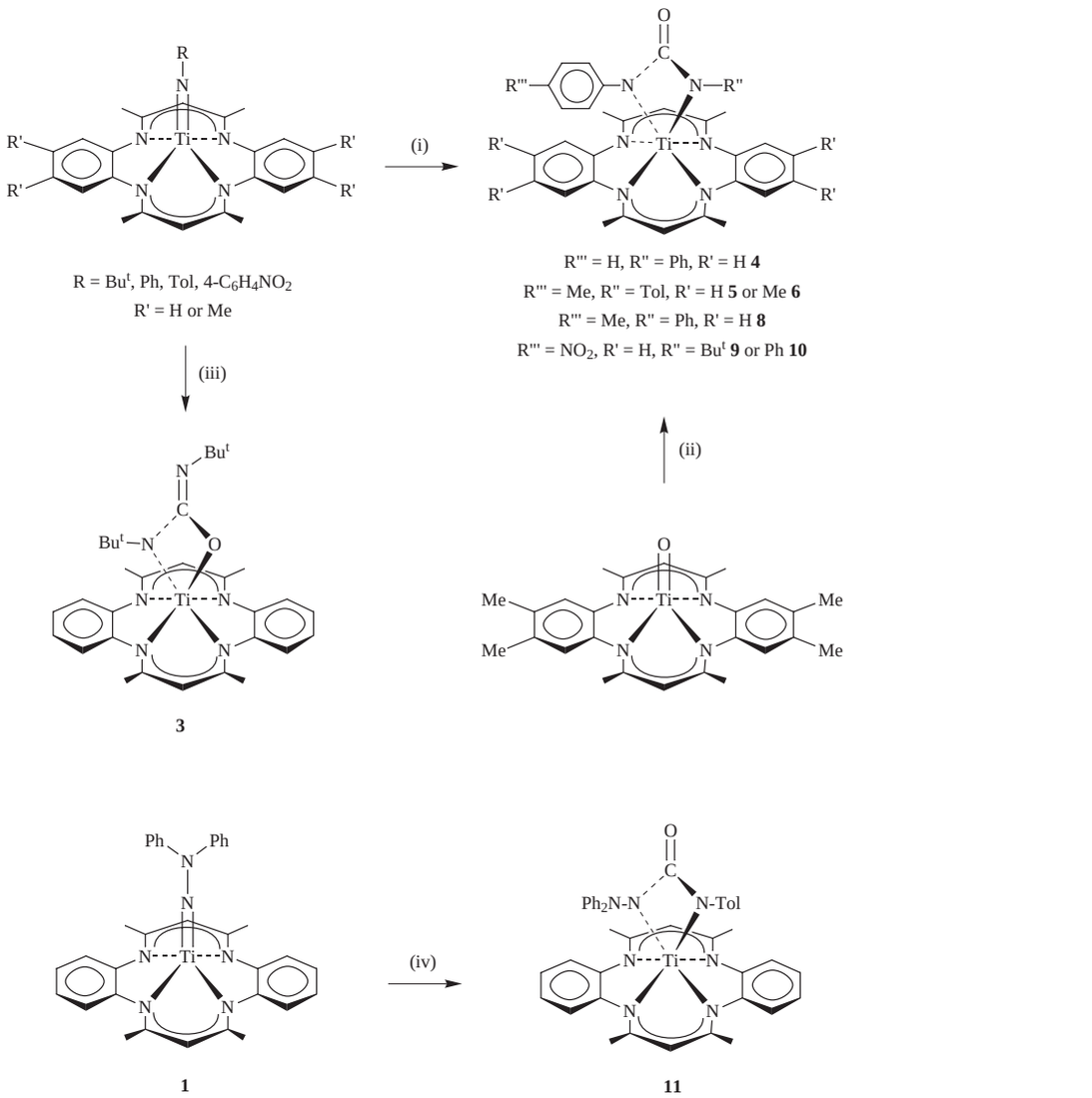
reaction of [Ti(NBu^t)(Me_ntaa)] (n = 4 or 8) with one equivalent of *N,N*-diphenylhydrazine in dichloromethane for 5 days gave **1** or **2** in 65–69% yield. This imido exchange synthetic method is analogous to that used for the synthesis of [Ti(NR)(Me_ntaa)] (R = phenyl or substituted phenyl) from RNH_2 and [Ti(NBu^t)-(Me_ntaa)][8] and which has been applied to a number of other systems.[27–34] We are not aware, however, of its use previously for the synthesis of hydrazido complexes.

Repeated attempts to obtain diffraction quality crystals of **1** and **2** were unsuccessful. Nevertheless, these compounds are proposed to possess the monomeric, η^1-hydrazido geometries illustrated in eqn. (1) based on spectroscopic data and by analogy with [Ti(NR)(Me_ntaa)] (R = Bu^t or aryl),[8] [Ti(E)-(Me_ntaa)] (E = O, S, Se and Te)[15,16,35] and [Zr(η-C_5H_5)$_2$(NN-Ph_2)(py′)] (py′ = 4-dimethylaminopyridine) which possesses a near-linear Zr=N–NPh_2 linkage.[36] Although well-established for Groups 5 to 8 transition metals, terminal hydrazido complexes of Group 4 are rare,[37,38] with the only structurally characterised example being the aforementioned zirconocene complex.[36]

Reactions of Group 4 imido and hydrazido complexes with isocyanates

The reactions of [Ti(NR)(Me_ntaa)] (R = Bu^t, Ph, Tol or $C_6H_4NO_2$-4; n = 4 or 8), [Ti($NNPh_2$)(Me_ntaa)] (n = 4 **1** or 8 **2**) and [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)] with organic isocyanates are summarised in Schemes 1 and 3. Reactions of Groups 5 to 9 transition metal imido complexes with isocyanates have previously been described,[32,34,39–47] giving rise to ureato cycloaddition products either as isolable derivatives or postulated intermediates. In contrast, there has been only one such report for a Group 4 metal derivative, namely [Zr(η^5-C_5H_5)$_2$(NBu^t)-(THF)].[48] Reaction of this complex with Bu^{t}NCO is thought to give an N,O-bound ureato intermediate [Zr(η^5-C_5H_5)$_2${N(Bu^t)-C(NBu^t)O}] (not observed) which then undergoes a retrocyclisation reaction to afford oligomeric [Zr(η^5-C_5H_5)$_2$(O)]$_n$ and the carbodiimide Bu^{t}NCNBu^t.

(a) Isocyanate cycloaddition reactions of titanium imido complexes. Our initial studies focused on the *tert*-butylimido com-



Scheme 1 Reactions of titanium imido and hydrazido complexes with isocyanates and some comparitive studies for [Ti(O)(Me_8taa)]. Reagents and conditions: (i) R″NCO, CH_2Cl_2 or benzene, 10 °C or r.t., 30 min–3 d, 52–89%; (ii) (for **6**) TolNCNTol, CH_2Cl_2, r.t., 24 h, 60%; (iii) Bu^tNCO, $CDCl_3$, r.t., 6 days, >95%; (iv) TolNCO, CH_2Cl_2, r.t., 3 days, 70%.

plex [Ti(NBu^t)(Me_4taa)]. However, reactions of this complex with phenyl isocyanate gave only mixtures of unidentified products. NMR tube reactions with an excess of *tert*-butyl isocyanate in $CDCl_3$ strongly supported the formation of the N,O-bound ureato product [Ti{N(Bu^t)C(NBu^t)O}(Me_4taa)] **3** after 6 days. The N,O-coordination is inferred from (i) two different Bu^t group resonances (integral ratio 1 : 1), only one of which (that at δ 0.45) gives rise to a detectable nOe enhancement of proximal Me_4taa ligand resonances, and (ii) a reduction of effective symmetry to C_s for the Me_4taa ligand as compared to C_{2v} symmetry for [Ti(NBu^t)(Me_4taa)] itself. Unfortunately, repeated attempts to isolate the compound **3** on a preparative scale were consistently unsuccessful. We therefore turned our attention to studies of the arylimido homolgues [Ti(NR)(Me_ntaa)]. We note, however, that the N,O-coordination found for **3** is analogous to that of the transient zirconocene complex [Zr(η^5-C_5H_5)$_2${N(Bu^t)C(NBu^t)O}] mentioned above.[48]

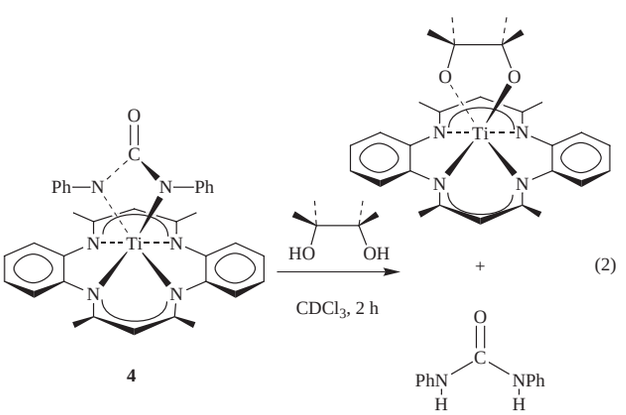
As shown (Scheme 1) addition of one equivalent of phenyl isocyante to the phenylimido complex [Ti(NPh)(Me_4taa)] gave the *N,N*-diphenylureato product [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** in 71% yield. Similarly, addition of tolyl isocyanate to the tolylimido complex [Ti(NTol)(Me_ntaa)] (n = 4 or 8) gave very good yields of [Ti{N(Tol)C(O)N(Tol)}(Me_ntaa)] (n = 4 **5** or 8 **6**). The new compounds **4**–**6** were characterised by spectroscopic and elemental analysis. The N,N-coordination of the diarylureato ligands in **4**–**6** is suggested by their NMR spectra which show effective C_{2v} symmetry for the Me_ntaa ligands and one type of chemical environment for the phenyl (for **4**) or tolyl (for **5** and **6**) substituents, and also by their IR spectra (as Nujol mulls and/or dichloromethane solutions) which revealed absorptions between 1628 and 1630 cm^{-1}, consistent with ν(C=O) of N,N-bound ureato ligands.[32,45,46,49–51] As expected, the ν(C=O) of 1628 cm^{-1} (Nujol mull) for the formally dianionic *N,N*-diphenylureato ligand in [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** is at a lower frequency compared to that for diphenylurea itself [ν(C=O) 1650 cm^{-1} as a Nujol mull].

Weakly-diffracting single crystals of [Ti{N(Tol)C(O)N(Tol)}(Me_4taa)]·1.4CH_2Cl_2 **5**·CH_2Cl_2 were obtained from a dichloromethane–hexane mixture at −25 °C. The diffraction data for the best available crystals were not of sufficient quality to merit publication [mean $I/\sigma(I)$ = 3.47, resultant R = 0.201 for a partially anisotropic model refined against all data with $I/\sigma(I) > 0$], but did define unambiguously the N,N-coordination for the ureato ligand along with other features of the coordination geometry. A structure diagram has been deposited as supplementary information (SUP 57465). Furthermore, the N,N-coordination proposed for the ureato ligands in **4**–**6** is consistent with that confirmed crystallographically for the corresponding moiety in [Zr{N($C_6H_3Pr^i_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] **7** (see below).

We have also prepared ureato complexes containing different N-substituents. Thus reaction either of [Ti(NPh)(Me_4taa)] with tolyl isocyanate or of [Ti(NTol)(Me_4taa)] with phenyl isocyanate gave the *N*-phenyl-*N*′-tolylureato complex [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] **8** in 52% and 62% yield, respectively. The NMR and IR spectra of **8** are comparable to those of the *N,N*-diphenyl- and *N,N*-ditolyl-ureato complexes **4**–**6**. The Me_4taa ligand in **8** shows effective C_{2v} symmetry in its NMR spectra, presumably because of the very similar nature of the ureato N-substituents.

NMR scale reaction of the phenylimido complex [Ti(NPh)(Me_4taa)] with *tert*-butyl isocyanate in $CDCl_3$ gave a mixture of products after 3 days. However, reaction of the 4-nitrophenylimido analogue [Ti($NC_6H_4NO_2$)(Me_4taa)] with *tert*-butyl isocyanate afforded the asymmetrically *N*-substituted ureate [Ti{N($C_6H_4NO_2$-4)C(O)N(Bu^t)}(Me_4taa)] **9** in 84% isolated yield after 3 days. Similarly, reaction of [Ti($NC_6H_4NO_2$)(Me_4taa)] with phenyl isocyanate gave [Ti{N($C_6H_4NO_2$-4)C(O)N(Ph)}(Me_4taa)] **10** in 74% isolated yield after 24 h. The NMR spectra of **9** and **10** revealed a reduction to effective C_s symmetry for the Me_4taa ligands and the IR spectrum (Nujol mull) of [Ti{N($C_6H_4NO_2$-4)C(O)N(Ph)] **10** showed ν(C=O) for the ureato ligand at 1643 cm^{-1}. This value is higher than that for [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** (1628 cm^{-1}, Nujol mull) and presumably reflects the electron-withdrawing nature of the 4-nitrophenyl substituent in **10**.

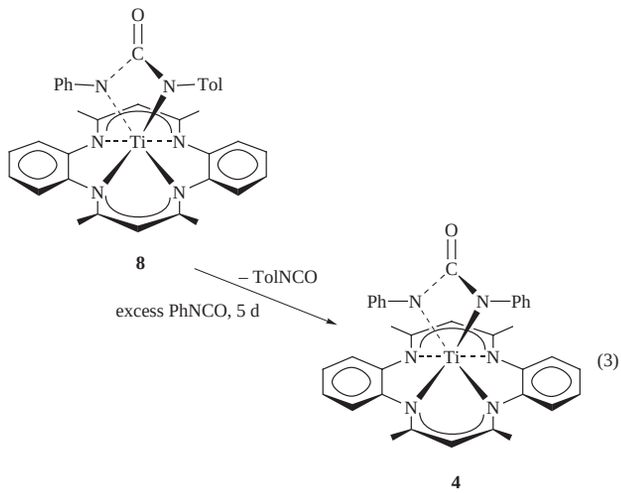
One aim of this work was to explore ways of using titanium imido complexes in the catalytic formation of new C–N bonds. Formation of the ureato complexes **4**–**6** and **8, 9** represents new C–N bond forming reactions. However, attempted removal of *N,N*-diphenylurea from the ureato complex [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** by treatment with aniline or 4-nitroaniline {thereby regenerating [Ti(NC_6H_4R-4)(Me_4taa)] (R = H or NO_2)} was unsuccessful. However, an NMR tube scale experiment demonstrated that reaction of **4** with the more Brønsted acidic pinacol readily generated *N,N*′-diphenylurea and the previously described[8] pinacolato complex [Ti{$OC(Me)_2C(Me_2)O$}(Me_4taa)] [eqn. (2)] in quantitative yield. It is thus



4 (2)

possible to remove the products of C–N bond formation (in this case *N,N*′-diphenylurea) but probably not in a way that could simultaneously regenerate titanium imido species.

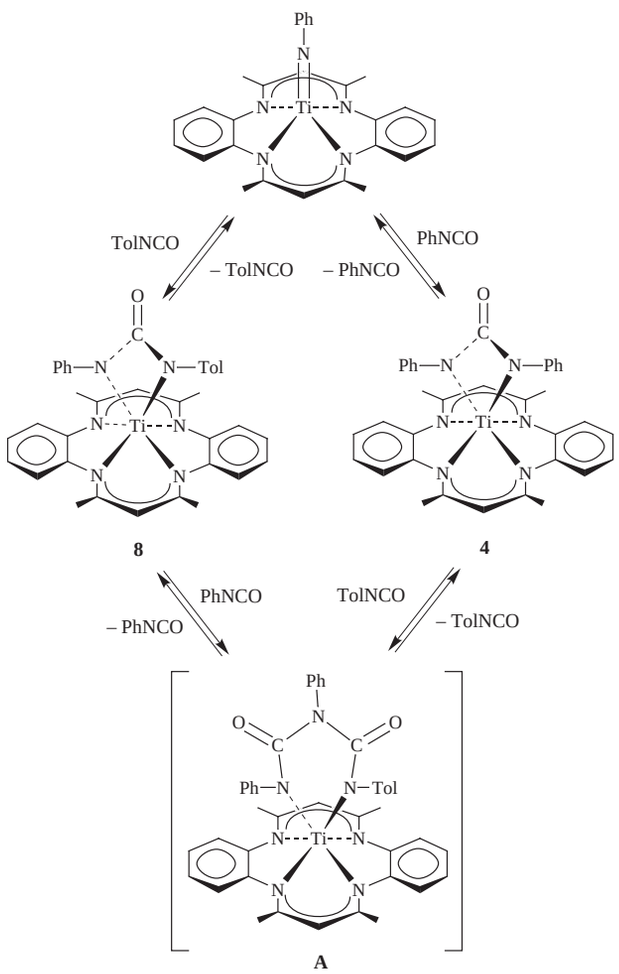
(b) Reversible carbon–nitrogen bond formation. While exploring the reaction of [Ti(NTol)(Me_4taa)] with phenyl isocyanate, we found that the *symmetric N,N*-diphenylureato complex [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** was formed along with the expected *unsymmetric N*-phenyl-*N*′-tolylureate [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] **8** when an excess of phenyl isocyanate was used. This suggested that the ureato product **8** itself could undergo a reaction with phenyl isocyanate. Subsequent NMR tube and preparative scale experiments [eqn. (3)] demonstrated that pure [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] **8** indeed reacts with an excess of phenyl isocyanate over about 5 days to give near-



8 (3) 4

quantitative conversion to the *N,N*-diphenylureato complex [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4** with displacement of tolyl isocyanate (confirmed by ^{1}H NMR).

The two mechanisms most likely to account for the transformation of **8** to **4** are an associative route *via* a biuret intermediate **A** (Scheme 2, bottom) or a dissociative route *via* the phenylimido complex [Ti(NPh)(Me_4taa)] (Scheme 2, top).



Scheme 2 Associative *versus* dissociative mechanisms for the TolNCO/PhNCO exchange reaction of [Ti{N(Tol)C(O)N(Ph)}(Me_4taa)] **8**. See the text for details.

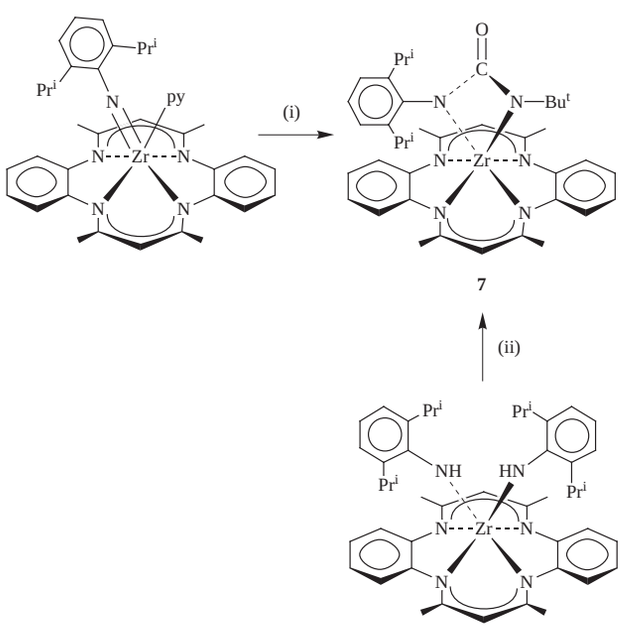
Neither **A** nor [Ti(NPh)(Me_4taa)] (or indeed any other) intermediates were detected in the NMR tube experiments and these must therefore be short-lived.

To distinguish between these two possibilities, NMR tube

crossover experiments were carried out. Thus a $CDCl_3$ solution containing a mixture of pure ureate [Ti{N(Ph)C(O)N(Ph)}-(Me_4taa)] **4** and tolylimido complex [Ti(NTol)(Me_4taa)] (1 : 1 ratio) was monitored for a period of 7 days. If eqn. (3) proceeds *via* a dissociative mechanism then PhNCO should be liberated from **4**. This could then either recombine with [Ti(NPh)-(Me_4taa)] to reform **4**, or be trapped by [Ti(NTol)(Me_4taa)] {present in a large excess compared to any transient [Ti(NPh)-(Me_4taa)]} to yield the known compound [Ti{N(Ph)C(O)N-(Tol)}(Me_4taa)] **8**. Hence a dissociative mechanism for eqn. (3) should lead to mixtures of **4**, **8**, [Ti(NPh)(Me_4taa)] and [Ti-(NTol)(Me_4taa)] when starting from [Ti{N(Ph)C(O)N(Ph)}-(Me_4taa)] **4** and [Ti(NTol)(Me_4taa)]. After 7 days no changes in the composition of the mixture were observed, therefore suggesting that eqn. (3) proceeds *via* an associative mechanism, probably involving the biuret complex **A**. As a check that [Ti(N-Tol)(Me_4taa)] could react with any PhNCO liberated from [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **4**, a small amount of PhNCO was added to the above NMR tube mixture after 7 days. This gave immediate formation of [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] **8** showing that [Ti(NTol)(Me_4taa)] is without doubt an effective trap for PhNCO under the conditions used for the attempted crossover experiment.

Examples of the reversible addition of isocyanates to imido complexes (to effect imido ligand exchange) have been described previously but are thought to proceed *via* ureato/imido ligand dissociative equilibria. Our results indicate that alternative, associative processes involving biuret species should not be overlooked.[1]

(c) Cycloaddition reactions of a macrocycle-supported zirconium imido complex. We have also examined the reactions of the macrocycle-supported zirconium imido complex [Zr($NC_6H_3Pr^i_2$-2,6)(py)(Me_4taa)][10] towards a range of unsaturated substrates including isocyanates. A clean product was only obtained with *tert*-butyl isocyanate, namely [Zr{$N(C_6H_3Pr^i_2$-2,6)-C(O)N(Bu^t)}(Me_4taa)] **7** (Scheme 3).



Scheme 3 Reaction of zirconium imido and bis(amido) complexes with Bu^tNCO. Reagents and conditions: (i) Bu^tNCO, toluene, r.t., 2 h, 54%; (ii) Bu^tNCO, toluene, r.t., 16 h, 38%.

The NMR spectra of **7** showed resonances for $NC_6H_3Pr^i_2$-2,6 and NBu^t groups, as well as effective C_{2v} symmetry for the Me_4taa ligand, suggestive of a dynamic process on the NMR timescale as has been found previously for certain other related Me_ntaa complexes of zirconium.[52,53] The fluxional processes

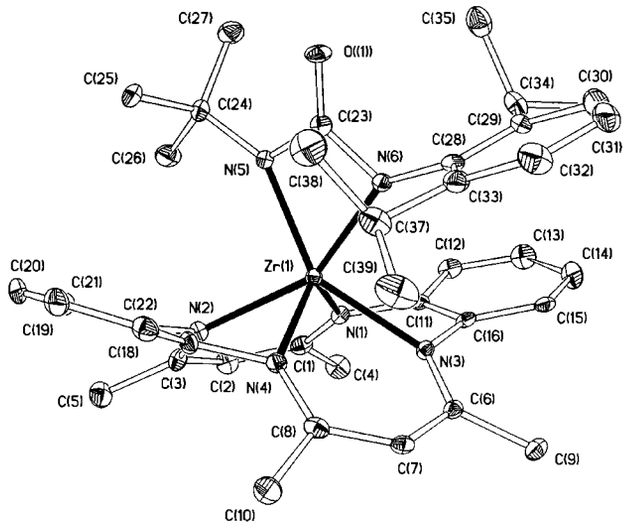


Fig. 1 Molecular structure of [Zr{$N(C_6H_3Me_2$-2,6)C(O)N(Bu^t)}-(Me_4taa)] **7** with hydrogen atoms and toluene molecule of crystallisation omitted.[10] Displacement ellipsoids are drawn at the 35% probability level.

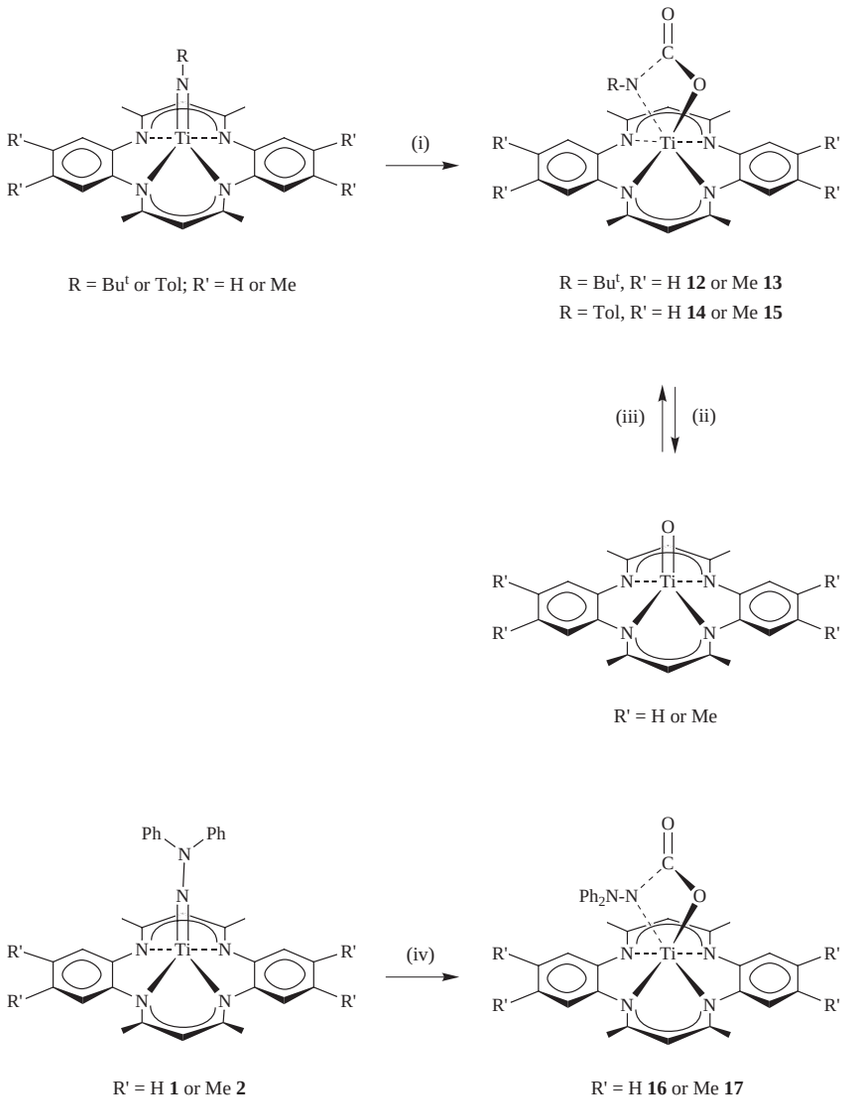
Table 2 Selected bond distances (Å) and angles (°) for [Zr{$NC_6H_3Me_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] **7**[10]

Zr(1)–N(1)	2.167(4)	C(23)–O(1)	1.243(7)
Zr(1)–N(2)	2.251(5)	N(5)–C(23)	1.388(7)
Zr(1)–N(3)	2.224(4)	N(5)–C(24)	1.480(7)
Zr(1)–N(4)	2.173(4)	N(6)–C(23)	1.372(7)
Zr(1)–N(5)	2.155(4)	N(6)–C(28)	1.430(7)
Zr(1)–N(6)	2.168(4)		
Zr(1) · · · N_4 least squares plane		1.07	

N(5)–Zr(1)–N(1)	112.1(2)	N(6)–Zr(1)–N(2)	149.7(2)
N(5)–Zr(1)–N(6)	62.0(2)	N(4)–Zr(1)–N(2)	72.3(2)
N(1)–Zr(1)–N(6)	124.2(2)	N(3)–Zr(1)–N(2)	121.5(2)
N(5)–Zr(1)–N(4)	118.3(2)	C(23)–N(5)–C(24)	119.1(4)
N(1)–Zr(1)–N(4)	122.4(2)	C(23)–N(5)–Zr(1)	94.7(3)
N(6)–Zr(1)–N(4)	103.6(2)	C(24)–N(5)–Zr(1)	145.9(4)
N(5)–Zr(1)–N(3)	145.4(2)	C(23)–N(6)–C(28)	118.9(4)
N(1)–Zr(1)–N(3)	74.2(2)	C(23)–N(6)–Zr(1)	94.6(3)
N(6)–Zr(1)–N(3)	85.9(2)	C(28)–N(6)–Zr(1)	145.0(4)
N(4)–Zr(1)–N(3)	79.7(2)	O(1)–C(23)–N(6)	125.9(5)
N(5)–Zr(1)–N(2)	92.9(2)	O(1)–C(23)–N(5)	126.6(5)
N(1)–Zr(1)–N(2)	79.3(2)	N(6)–C(23)–N(5)	107.5(5)

for **7** were not frozen out in the low temperature (toluene-d_8) spectrum. Interestingly, the ureato complex **7** is also obtained (again as the toluene solvate) in 38% yield by treatment of the bis(arylamide) [Zr($NHC_6H_3Pr^i_2$-2,6)$_2$(Me_4taa)] with *tert*-butyl isocyanate (Scheme 3). A plausible mechanism for the formation of **7** in this reaction is *via* the initial elimination of $H_2NC_6H_3Pr^i_2$-2,6 from [Zr($NHC_6H_3Pr^i_2$-2,6)$_2$(Me_4taa)] to form transient [Zr($NC_6H_3Pr^i_2$-2,6)(Me_4taa)], which then subsequently undergoes a cycloaddition reaction with Bu^tNCO.

Diffraction quality crystals of **7**·C_7H_8 were obtained from a toluene solution.[10] The molecular structure is shown in Fig. 1 and confirms that shown in Scheme 3; selected bond lengths and angles are listed in Table 2. The structure consists of a Zr(Me_4taa) moiety bound to a *N*-aryl-*N′*-*tert*-butylureate ligand. The metal atom lies *ca.* 1.07 Å from the plane of the Me_4taa nitrogen atoms with an average $Zr–N_{macrocycle}$ distance of 2.204 Å (range ± 0.042 Å); the Zr(1)–N(2) and Zr(1)–N(3) distances are significantly longer than the corresponding ones for N(1) and N(4). These features are similar to those of other Me_4taa complexes of zirconium,[9,53–58] and the Me_4taa ligand adopts the saddle-shaped geometry that is almost invariably found for this macrocycle,[13,14] with the phenylene rings oriented



Scheme 4 Reactions of titanium imido and hydrazido complexes with carbon dioxide and comparative studies for [Ti(O)(Me_ntaa)] (n = 4 or 8). Reagents and conditions: (i) CO_2 (*ca.* 1.1 atm), CH_2Cl_2, r.t., 30 min, 85–88%; (ii) $CDCl_3$ or CD_2Cl_2 solution, ambient daylight; (iii) (for **14** and **15**) TolNCO, CH_2Cl_2, r.t., 30 min, 75% or (for **13**) Bu^tNCO, $CDCl_3$, r.t., 17 days, 70% (by NMR); (iv) CO_2 (*ca.* 1.1 atm), CH_2Cl_2, r.t., 30 min, 80%.

"up" towards the ureato ligand. The geometry of the ureato ligand is similar to that found in other complexes of this type (eight examples in the Cambridge Structural Database[59,60]), the C=O distance [C(23)–O(1) 1.243(7) Å] being consistent with a double bond and comparable to that found in the other ureato complexes [average C=O distance 1.21(2) Å, range 1.179–1.247 Å]. Interestingly, the N,N-coordination of the ureato ligand in **7** contrasts with the N,O-bound ligand proposed for the transient species [$Zr(\eta^5\text{-}C_5H_5)_2\{N(Bu^t)C(NBu^t)O\}$].[48] To date no N,O-bound ureato complexes have been structurally authenticated.[59,60]

(d) Isocyanate cycloaddition reactions of a titanium hydrazido complex. The hydrazido complex [Ti($NNPh_2$)(Me_4taa)] **1** also undergoes cycloaddition reactions with tolyl isocyanate (Scheme 1) to form the new compound [Ti{$N(NPh_2)C(O)N(Tol)$}(Me_4taa)] **11** in 70% crystallised yield. The IR spectrum shows a ν(C=O) absorption at 1656 cm^{-1} (dichloromethane solution), and the ^1H and ^{13}C NMR spectra of **11** are also consistent with the structure shown in Scheme 1. Although the Me_4taa ligand possesses the expected C_s symmetry, the resonances for this ligand are slightly broadened at room temperature, possibly indicative of fluxionality. This was readily confirmed by spin saturation transfer experiments between the methine protons (which appear as singlets at δ 5.80 and 5.03 with $v_{1/2}$ = *ca.* 6 Hz) of the Me_4taa ligand diiminato linkage. A likely process is a net rotation of the $N(NPh_2)C(O)N(Tol)$ ligand above the Ti(Me_4taa) moiety in a similar way to that proposed for **7**, certain Me_ntaa-supported complexes of the type [M(X)(Y)(Me_ntaa)] reported previously,[52,53] and some other cycloaddition products described herein.

Reactions of titanium imido and hydrazido complexes with carbon dioxide

Cycloaddition reactions of metal imides with CO_2 are uncommon,[1] the complex [$Ir(\eta^5\text{-}C_5Me_5)\{N(Bu^t)C(O)O\}$] being the first and only structurally characterised metallacyclic product of such a process.[34] The reactions of [Ti(NR)(Me_ntaa)] (R = Bu^t or Tol; n = 4 or 8) and [Ti($NNPh_2$)(Me_ntaa)] (n = 4 **1** or 8 **2**) with carbon dioxide are summarised in Scheme 4. Exposure of dichloromethane solutions of [Ti(NR)(Me_ntaa)] (R = Bu^t or Tol; n = 4 or 8) to CO_2 (*ca.* 1.1 atm.) for 30 min gave very clean conversions to the N,O-bound carbamato complexes [Ti{N(R)C(O)O}(Me_ntaa)] (R = Bu^t, n = 4 **12** or 8 **13**; R = Tol, n = 4 **14** or 8 **15**) in 85–88% yield.

Diffraction quality crystals of [Ti{N(Tol)C(O)O}(Me_4taa)] **14** were grown at −25 °C by layering a dichloromethane solution with hexane. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are listed in Table 3. The compound **14** possesses a six-coordinate titanium atom bound

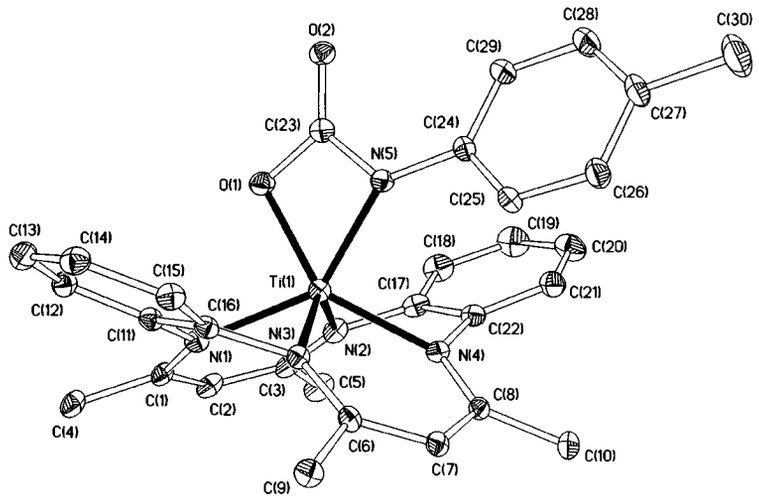


Fig. 2 Molecular structure of [Ti{N(Tol)C(O)O}(Me_4taa)] **14** with hydrogen atoms omitted. Displacement ellipsoids are drawn at the 25% probablilty level.

Table 3 Selected distances (Å) and bond angles (°) for [Ti{N(Tol)-C(O)O}(Me_4taa)] **14**

Ti(1)–N(1)	2.078(5)	Ti(1)–O(1)	1.981(4)
Ti(1)–N(2)	2.031(4)	N(5)–C(23)	1.381(6)
Ti(1)–N(3)	2.033(4)	N(5)–C(24)	1.424(6)
Ti(1)–N(4)	2.066(4)	C(23)–O(1)	1.321(6)
Ti(1)–N(5)	2.018(4)	C(23)–O(2)	1.221(6)
Ti(1) · · · N_4 least squares plane		0.85	
N(1)–Ti(1)–N(2)	83.5(2)	N(2)–Ti(1)–O(1)	96.3(2)
N(1)–Ti(1)–N(3)	76.9(2)	N(3)–Ti(1)–O(1)	123.5(2)
N(2)–Ti(1)–N(3)	132.1(2)	N(4)–Ti(1)–O(1)	144.1(2)
N(1)–Ti(1)–N(4)	129.8(2)	N(5)–Ti(1)–O(1)	65.0(2)
N(2)–Ti(1)–N(4)	76.8(2)	Ti(1)–N(5)–C(23)	92.9(3)
N(3)–Ti(1)–N(4)	83.1(2)	Ti(1)–N(5)–C(24)	141.8(3)
N(1)–Ti(1)–N(5)	141.6(2)	C(23)–N(5)–C(24)	124.7(4)
N(2)–Ti(1)–N(5)	119.3(2)	N(5)–C(23)–O(1)	105.3(4)
N(3)–Ti(1)–N(5)	102.4(2)	N(5)–C(23)–O(2)	129.3(5)
N(4)–Ti(1)–N(5)	87.4(2)	O(1)–C(23)–O(2)	125.4(5)
N(1)–Ti(1)–O(1)	83.1(2)	Ti(1)–O(1)–C(23)	96.4(3)

to the four nitrogen atoms of a saddle-shaped Me_4taa moiety and to a N,O-coordinated *N*-tolylcarbamate ligand, thereby unambiguously confirming the addition of CO_2 to the imido linkage of [Ti(NTol)(Me_4taa)]. The average Ti–$N_{macrocycle}$ distance of 2.052 Å (range ± 0.025 Å) is somewhat longer than the Ti–$N_{carbamate}$ distance of 2.018(4) Å, but comparable to those of other titanium(IV) complexes of this ligand.[59] The internal C=O, C–O and C–N distances of the tolylcarbamate moiety [1.221(6), 1.321(6) and 1.381(6) Å, repectively] are comparable to the corresponding average values of 1.196 (range ± 0.024), 1.344 (range ± 0.024) and 1.388 (range ± 0.014) Å found for three other crystallographically characterised complexes, namely: [Re(η^5-C_5Me_5)(O){N(Ph)C(O)O}],[61] [Mo(η^5-C_5H_5)$_2${N(Ph)-C(O)O}],[62] and [Ir(η^5-C_5Me_5){N(Bu^t)C(O)O}].[34] Although the Re and Mo complexes contain carbamato ligands, they were prepared from oxo precursors and PhNCO, rather than from imido complexes and CO_2.

The solution ^{1}H and ^{13}C NMR data for the *N*-*tert*-butylcarbamato complexes [Ti{N(Bu^t)C(O)O}(Me_ntaa)] (*n* = 4 **12** or 8 **13**) are consistent with the N,O-bound structures shown in Scheme 4 since the Me_ntaa ligand resonances indicate only effective C_s symmetry (*e.g.*, two types of diiminato linkage methine and methyl groups). The NMR spectra for the *N*-tolyl homologues **14** and **15**, however, show C_{2v} symmetry for the macrocycles, which may *a priori* be either indicative of O,O-bound *N*-tolylcarbamate ligands or of N,O-bound ligands which are fluxional on the NMR timescale at room temperature. Cooling a CD_2Cl_2 solution of [Ti{N(Tol)C(O)O}-(Me_4taa)] **14** to −90 °C led to a substantial broadening of the macrocycle methyl, diiminato methine, and phenylene ^{1}H resonances, while those of the *N*-tolyl moiety were unaffected (*i.e.* the broadening of the Me_4taa ligand resonances is probably due to slowing down of a dynamic process rather than being caused by general viscoity broadening at low temperature). Although there was no change in the appearance of the resonances in the ^{13}C-{^{1}H} NMR spectra, the temperature dependence of the ^{1}H NMR spectra is nevertheless consistent with **14** (and therefore **15**) possessing the N,O-bound *N*-tolylcarbamate geometry as found in the solid state, and being highly fluxional *via* some type of rapid rotation of the {N(Tol)C(O)O} ligand about the Ti · · · C=O vector. This is analogous to the dynamic NMR behaviour of the zirconium ureato complex [Zr-{N($C_6H_3Pr^i_2$-2,6)C(O)N(Bu^t)}(Me_4taa)] **7** and the hydrazido cycloaddition product [Ti{N(NPh_2)C(O)N(Tol)}(Me_4taa)] **11** described above. As mentioned, there is no noticeable broadening of the macrocycle resonances for **12** or **13** at room temperature, nor were we able to detect any chemical exchange by spin saturation transfer experiments for **13**. The different solution dynamic NMR behaviour of the *N*-*tert*-butyl (**12** and **13**) and N-tolyl (**14** and **15**) presumably reflects the different steric requirements of the respective N-substituents.

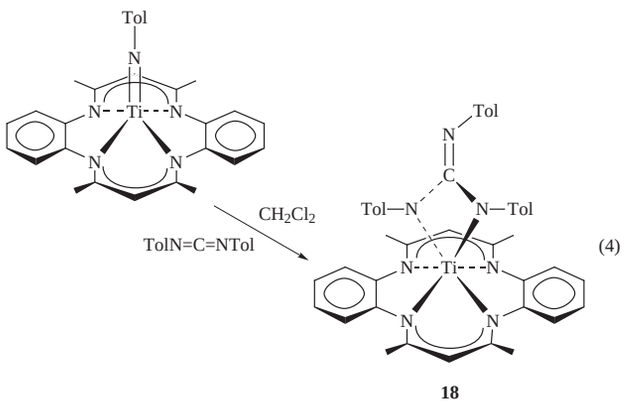
The IR *ν*(C=O) absorptions for dichloromethane solutions of the carbamato complexes **12**–**15** (1636, 1642, 1663, 1657 cm^{-1}, respectively) are also consistent with all of them possessing N,O-bound isomers in the solution state. The increased *ν*(C=O) found for the *N*-tolyl substituted isomers probably reflects the better electron-withdrawing ability of tolyl *versus tert*-butyl groups.

The hydrazido complexes [Ti($NNPh_2$)(Me_ntaa)] (*n* = 4 **1** or 8 **2**) readily give the corresponding cycloaddition products [Ti{N(NPh_2)C(O)O}(Me_ntaa)] (*n* = 4 **16** or 8 **17**) on reaction with *ca.* 1.1 atm CO_2 (Scheme 4). The IR spectra show *ν*(C=O) absorptions at 1685 and 1681 cm^{-1}, respectively, consistent with N,O-bound ligands. As for the *N*-tolyl carbamato complexes [Ti{N(Tol)C(O)O}(Me_ntaa)] (*n* = 4 **14** or 8 **15**), however, the NMR spectra are suggestive of fast dynamic behaviour since the Me_ntaa ligand resonances indicate effective C_{2v} symmetry on the NMR timescale.

All of the imido/CO_2 cycloaddition products **12**–**15** are apparently light-sensitive both in solution and the solid state, giving rise to the corresponding oxo titanium complexes [Ti(O)(Me_ntaa)] and either Bu^tNCO (for **12** and **13**) or TolNCO (Scheme 4). For example, a $CDCl_3$ solution of [Ti{N(Bu^t)-C(O)O}(Me_8taa)] **13** quantitatively formed [Ti(O)(Me_8taa)] and

Bu^{t}NCO on standing in ambient lighting conditions for 5 days. A control sample of **13** kept in the dark did not undergo any significant decomposition over the same time period. The corresponding hydrazido/CO_2 cycloaddition products **16** and **17** do not appear to be as light-sensitive as **12**–**15**.

For completeness and for comparison we also carried out the reaction of [Ti(NTol)(Me$_4$taa)] with ditolylcarbodiimide: this gives the triazatrimethylene (or *N,N′,N″*-tri-*p*-tolylguanidine) complex [Ti{N(Tol)C(NTol)N(Tol)}(Me$_4$taa)] **18** in 64% recrystallised yield [eqn. (4)]. Unfortunately, we were not able to obtain analytically pure samples of **18** and so this compound was characterised only by ^{1}H NMR spectroscopy and by comparison with the other well-characterised cycloaddition products described herein. The NMR spectrum of **18** shows two types of tolyl group (integral ratio 2:1) together with resonances for an Me$_4$taa ligand possessing effective C_{2v} symmetry. These data are fully consistent with the structure shown for **18** in eqn. (4).



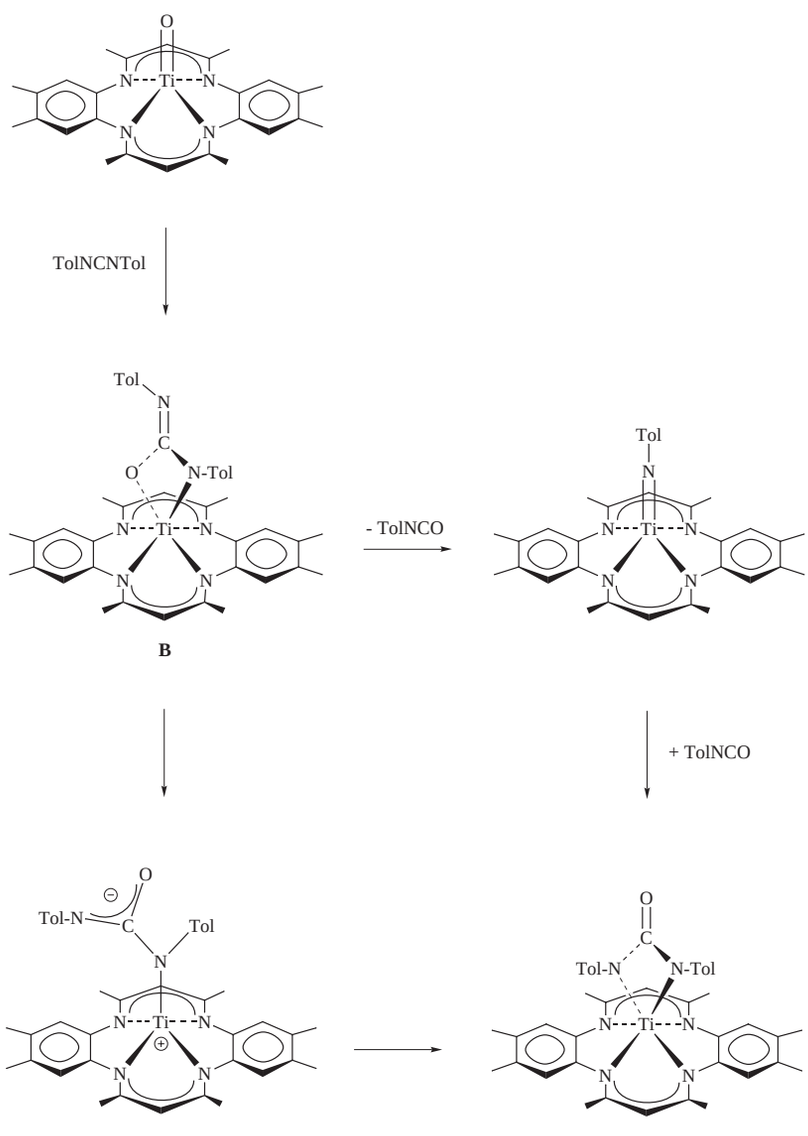
(4)

18

The first structurally characterised mononuclear triazatrimethylene (*N,N′,N″*-triarylguanidine) complex was only recently reported by Dinger and Henderson.[63] We note also that triazatrimethylene (*N,N′,N″*-triarylguanidine) intermediates are implicated (but have never been observed) in the carbodiimide metathesis reactions of [W(NR)Cl$_3$(μ-Cl)]$_2$ and [V(NTol)X$_3$] (X = Cl or OBu^t).[47,64]

Comparative reactions of the titanium oxo complexes [Ti(O)(Me$_n$taa)] (*n* = 4 or 8)

Goedken[15] and Geoffroy and co-workers[16] have previously reported cycloaddition reactions of [Ti(O)(Me$_n$taa)] (*n* = 4 or 8) with a range of unsaturated substrates including organic and organometallic carbonyl complexes, SO_2, COS and CO_2. Reactions with isocyanates or carbodiimides, however, were not described and so we include here for comparison some new cycloaddition reactions of [Ti(O)(Me$_n$taa)].[65]



B **C** **6**

Scheme 5 Two possible mechanisms for the formation of [Ti{N(Tol)C(O)N(Tol)}(Me$_8$taa)] **6** from [Ti(O)(Me$_8$taa)] and TolNCNTol. See the text for further details.

Reaction of [Ti(O)(Me_ntaa)] (n = 4 or 8) with tolyl isocyanate gave the corresponding carbamato complexes [Ti{N(Tol)-C(O)O}(Me_ntaa)] (n = 4 **14** or 8 **15**) in 75% isolated yield after 30 min (Scheme 4). In contrast, the reaction of [Ti(O)(Me_8taa)] with 1.5 equivalents of *tert*-butyl isocyanate in $CDCl_3$ showed only 70% conversion to the expected cycloaddition product [Ti{N(Bu^t)C(O)O}(Me_8taa)] **13** after 17 days, once again demonstrating the considerably different reactivity of the *N*-aryl- and *N*-*tert*-butyl-substituted heterocumulenes. These results contrast with the reactions of oxovanadium complexes [V(O)($OR)_3$] (R = Bu^t or Pr^i) with certain isocyanates R′NCO which form the corresponding carbodiimides R′NCNR′ catalytically,[47] rather than isolable ureato derivatives. However, several other metal oxo complexes do react with isocyanates to form isolable carbamato complexes.[34,61,62]

As mentioned, the compounds [Ti{N(R)C(O)O}(Me_ntaa)] are light-sensitive and give rise to [Ti(O)(Me_ntaa)] and RNCO under ambient lighting conditions. We note that the addition of CO_2 to [Ti(O)(Me_ntaa)] (n = 4 or 8) to form [Ti{OC(O)O}-(Me_ntaa)] is also reversible, although it is not reported whether the retrocyclisation process is light-induced in this case.[15,16] Our observation that [Ti{N(Tol)C(O)O}(Me_ntaa)] (n = 4 **14** or 8 **15**) can be obtained either by reaction of [Ti(O)(Me_ntaa)] with tolyl isocyanate or from [Ti(NTol)(Me_ntaa)] and CO_2 is analogous to the synthesis of [Ir(η^5-C_5Me_5){N(Bu^t)C(O)O}], which can be obtained from [Ir(η^5-C_5Me_5)(O)]$_2$ or [Ir(η^5-C_5Me_5)(NBu^t)] by reaction with Bu^tNCO or CO_2, respectively.[34]

Reaction of [Ti(O)(Me_8taa)] with ditolylcarbodiimide in dichloromethane for 24 h yields the *N,N′*-bound ureato isomer [Ti{N(Tol)C(O)N(Tol)}(Me_8taa)] **6** in 60% isolated yield (Scheme 1). The ^{1}H and ^{13}C NMR and IR spectra of samples of **6** obtained in this way were completely identical to those obtained from reaction of [Ti(NTol)(Me_8taa)] with tolyl isocyanate. The formation of **6** in this reaction is surprising since a simple cycloaddition reaction might be expected to yield the N,O-bound ditolylureato product [Ti{N(Tol)C(NTol)O}(Me_8-taa)] (**B**, Scheme 5) in which the original Ti–O connectivity is retained.

Scheme 5 shows two possible mechanisms for the formation of **6**. The reaction probably proceeds *via* an intermediate **B**. Subsequent retrocyclisation to give transient [Ti(NTol)-(Me_8taa)], followed by cycloaddition of liberated TolNCO then gives rise to **6**. Alternatively, partial ring-opening of **B** to form the resonance-stabilised zwitterion **C**, followed by ring-closure, also gives a satisfactory explanation for the formation of **6**.[66] By either mechanism, the overall synthesis of **6** from [Ti(O)(Me_8taa)] amounts to the insertion of carbodiimide into the Ti=O multiple bond. This process, which gives complete rupture of a Ti=O linkage with concomitant transfer of the oxygen atom to an organic substrate, is reminiscent of the reaction of [Ti(O)(Me_4taa)] with COS to form [Ti(S)(Me_4taa)] and CO_2, although in this latter case the product (CO_2) is released from the metal centre.[16]

Conclusions

We have described the cycloaddition chemistry of macrocycle-supported imido, hydrazido and oxo complexes with hetero-cumulenes, together with the first structurally characterised Group 4 carbamato and ureato complexes. Certain ureato species undergo reversible C–N bond cleavage reactions, and ditolylcarbodiimide has been shown to insert into a Ti=O multiple bond. It does not appear likely, however, that Me_ntaa-supported imido complexes are suitable candidates for catalytically active imido-transfer reagents.

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