Cycloaddition reactions of tetraaza macrocycle supported group 4 imido complexes and reversible addition of aryl isocyanate to a coordinated ureate ligand

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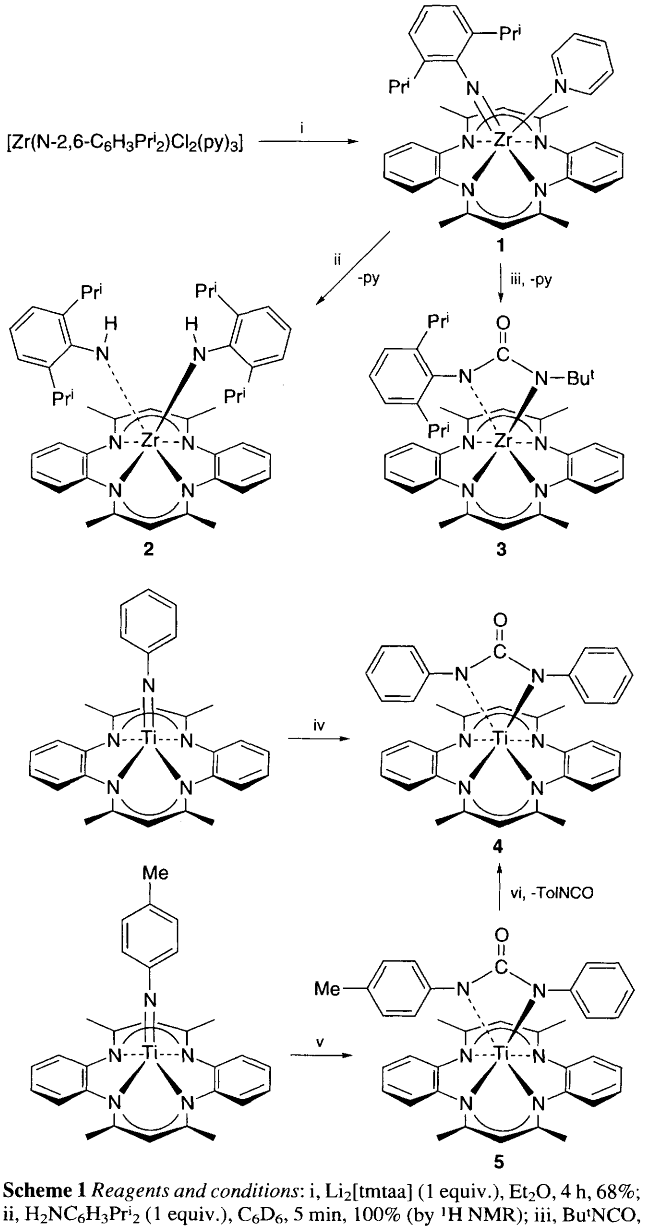
The first tetraaza macrocycle supported zirconium imido complex $[Zr(tmtaa)(NC_6H_3Pr^i_2\text{-}2,6)(py)]$ and the new titanium imido base-free analogues [Ti(tmtaa)(NAr)] (Ar = Ph or $C_6H_4Me\text{-}4$) react with isocyanates to give *N,N′*-bound ureate complexes; these can undergo exchange reactions with excess aryl isocyanate *via* reversible insertion into the Ti–N(ureate) bond; the X-ray structure of $[Zr(tmtaa)\text{-}\{(NC_2H_3Pr^i_2\text{-}2,6)(CO)(NBu^t)\}]$ is described (H_2tmtaa = tetramethyldibenzotetraaza[14]annulene).

Transition metal imido complexes continue to attract substantial interest as potential reagents for N–C bond forming reactions.[1–3] Considerable progress has been achieved through variation of the supporting ligand set. Thus highly unsaturated imido transition metal transients, 'π-loaded' complexes with two or three imido ligands bonded to the same metal centre, and imido complexes supported by the bis(cyclopentadienyl) ligand set have proven to be especially fruitful for the development of reactive imido linkages.[3] In contrast, imido linkages supported by tetraaza macrocyclic ligands (*e.g.* porphyrins and related species) are surprisingly rare and only a small number have been characterised.[4] In Group 4, the first titanium imido macrocycle-supported complexes were only very recently described,[4,5] and their zirconium analogues have remained elusive. Recent theoretical results[6] suggested that the tetraaza macrocyclic ligand tmtaa should promote the reactivity of a terminal metal imido linkage. We now report the first tetraaza macrocycle supported imido zirconium complex, $[Zr(tmtaa)(NC_6H_3Pr^i_2\text{-}2,6)(py)]$ **1**. To demonstrate the reactivity of **1** and its titanium arylimido analogues [Ti(tmtaa)(NAr)] (Ar = $C_6H_4Me\text{-}4$ or Ph), we describe their cycloaddition reactions with isocyanates.

Treatment of the imido zirconium complex $[Zr(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_3]$[7] with one equivalent of $Li_2[tmtaa]$[8] affords the tetraaza macrocycle supported imido zirconium complex $[Zr(tmtaa)(NC_6H_3Pr^i_2\text{-}2,6)(py)]$ **1** in 68% yield.‡ The highly air and moisture sensitive complex **1** is proposed to have the structure shown in Scheme 1. In the NMR spectra of **1** the tmtaa ligand has effective C_{2v} symmetry consistent with either rapid rotation of the tmtaa ligand about Zr or facile dissociation of pyridine on the NMR timescale even at −70 °C.§ We have not yet obtained X-ray quality crystals of **1**, but the presence of a Zr=NAr linkage is supported by preliminary reactivity studies. Thus treatment of **1** with 1 equiv. of $H_2NC_6H_3Pr^i_2\text{-}2,6$ in C_6D_6 affords quantitatively the bis(amido) complex $[Zr(tmtaa)(HNC_6H_3Pr^i_2\text{-}2,6)_2]$ **2** which we have prepared and fully characterised *via* independent routes.[9] Furthermore, **1** undergoes a net cycloaddition reaction with 1 equiv. of Bu^tNCO to give the N,N′-bound ureate $[Zr(tmtaa)\{(NC_6H_3Pr^i_2\text{-}2,6)(CO)(NBu^t)\}]$ **3** whose X-ray structure is shown in Fig. 1.¶ Reactions of Group 6 to 9 imido complexes with isocyanates have been described previously.[10–12]

Tmtaa supported titanium arylimido complexes also undergo net cycloaddition reactions with a range of unsaturated substrates. For example, treatment of [Ti(tmtaa)(NPh)][13] or $[Ti(tmtaa)(NC_6H_4Me\text{-}4)]$[13] with 1 equiv. of PhNCO gives either the symmetric or asymmetric N,N′-bound ureate derivatives [Ti(tmtaa){(NPh)(CO)(NPh)}] **4** or $[Ti(tmtaa)\{(NC_6H_4Me\text{-}4)(CO)(NPh)\}]$ **5** respectively (Scheme 1). These are the first cycloaddition reactions of an isolable Group 4 metal imido complex. Until this time only Group 4 imido species



Scheme 1 *Reagents and conditions*: i, $Li_2[tmtaa]$ (1 equiv.), Et_2O, 4 h, 68%; ii, $H_2NC_6H_3Pr^i_2$ (1 equiv.), C_6D_6, 5 min, 100% (by ^1H NMR); iii, Bu^tNCO, toluene, 30 min, 50%; iv, PhNCO (1 equiv.), CH_2Cl_2, 24 h, 72%; v, TolNCO, (1 equiv.), CH_2Cl_2, 24 h, 84%; vi, PhNCO (5 equiv.), $CDCl_3$, 5 d, >95% (by ^1H NMR)

generated as reactive transients have exhibited reactivity of the M=NR linkage towards organic substrates.[3]

The titanium ureates **4** and **5** exhibit novel reactivity. Treatment of the asymmetric ureate [Ti(tmtaa){(NC_6H_4Me-4)(CO)(NPh)}] **5** with *ca.* 5 equiv. of PhNCO affords the *symmetric N,N'*-diphenylureate derivative [Ti(tmtaa)-{(NPh)(CO)(NPh)}] **4** and tolyl isocyanate (identified in an NMR tube experiment) after 5 d. The reversible C–N bond formation could proceed either *via* a dissociative {giving [Ti(tmtaa)(NPh)] and TolNCO} or *via* an associative (giving an intermediate biuret complex) route. Preliminary studies suggest that the latter possibility is the most likely. In a dissociative mechanism free aryl isocyanate would be formed in the reaction mixture, presumably in the rate-limiting step. In an NMR tube crossover experiment a 1 : 1 mixture of **4** and [Ti(tmtaa)(NC_6H_4Me-4)] did not generate any detectable **5** over a period of 7 d, as would be required if **4** is in pre-equilibrium with [Ti(tmtaa)(NPh)] and PhNCO. Addition of PhNCO to the mixture of **4** and [Ti(tmtaa)(NC_6H_4Me-4)] gave immediate formation of **5**, showing that [Ti(tmtaa)(NC_6H_4Me-4)] would effectively scavenge any free PhNCO dissociatively liberated from **4**.

The reaction of **5** with PhNCO to afford **4** is the first example of the reversible insertion of an isocyanate into the metal–N bond of a ureate ligand.[14] The reversible addition of isocyanates to imido ligands is known but such reactions are thought to proceed *via* imido/ureate dissociative equilibria.[3] Our studies show that biuret-type intermediates must also be considered.

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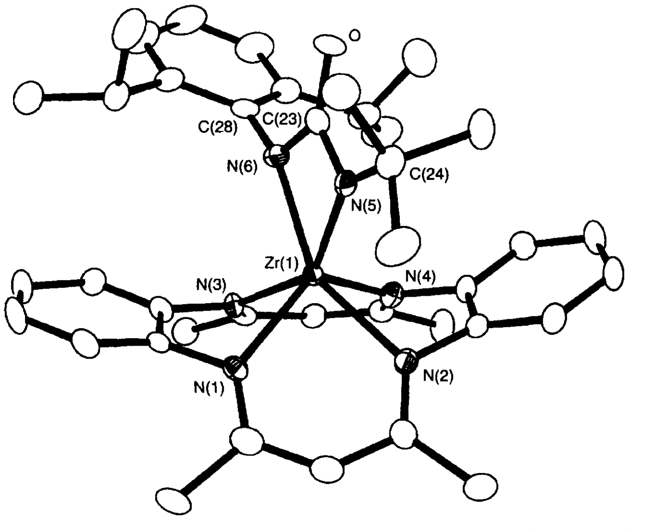

Fig. 1 Molecular structure of [Zr(tmtaa){($NC_6H_3Pr^i_2$-2,6)(CO)(NBu^t)}] **3**. Hydrogen atoms and toluene molecule of crystallisation omitted for clarity. Selected distances (Å) and angles (°): Zr(1)–N(1) 2.167(4), Zr(1)–N(2) 2.251(5), Zr(1)–N(3) 2.224(4), Zr(1)–N(4) 2.173(4), Zr(1)–N(5) 2.155(4), Zr(1)–N(6) 2.168(4), C(23)–O 1.243(7), Zr(1)···(N_4 plane of tmtaa) 1.07(1) Å; N(6)–C(23)–N(5) 107.5(5), N(6)–Zr(1)–N(5) 62.0(2), Zr(1)–N(5)–C(23) 94.7(3), Zr(1)–N(6)–C(23) 94.6(3), Zr(1)–N(5)–C(24) 145.9(4), Zr(1)–N(6)–C(28) 145.0(4)°. Displacement ellipsoids are shown at the 50% probability level.

Footnotes

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‡ Satisfactory elemental analyses have been obtained. Selected ^{1}H NMR data for **1** (250 MHz, C_6D_6) δ 8.42 (d, 2 H, 2-NC_5H_5, *J* 4.5 Hz), 7.09 (d, 2 H, 3-$C_6H_3Pr^i_2$, *J* 7.5 Hz), 6.99 (m, 8 H, C_6H_4 of tmtaa), 6.80 (t, 1 H, 4-NC_5H_5, *J* 5 Hz), 6.77 (t, 1 H, 4-$C_6H_3Pr^i_2$, *J* 7.5 Hz), 6.53 (dd, 2 H, 3-NC_5H_5, *J* 5 and 4.5 Hz), 4.90 [s, 2 H, C(=N)C*H*C(=N) of tmtaa], 2.84 (sept, 2 H, C*H*Me_2, *J* 6.8 Hz), 1.96 [s, 12 H, *Me*C (=N) of tmtaa] and 1.03 (d, 12 H, CHMe_2, *J* 6.8 Hz). For **3** (250 MHz, C_6D_6) δ 7.23–6.98 (overlapping m, 11 H, 3- and 4-$C_6H_3Pr^i_2$ and C_6H_4 of tmtaa), 4.99 [br s, 2 H, C(=N)C*H*C(=N) of tmtaa], 2.50 (sept, 2 H, C*H*Me_2, *J* 6.7 Hz), 1.84 [s, 12 H, *Me*C(=N) of tmtaa], 1.36 (s, 9 H, Bu^t), 1.31 (d, 6 H, CHMe_2, *J* 6.7 Hz) and 1.22 (6 H, CHMe_2, *J* 6.7 Hz). For **4** (300 MHz, $CDCl_3$) δ 7.08 to 6.80 (overlapping multiplets, 14 H, 3- and 4-C_6H_5 and C_6H_4 of tmtaa), 6.36 (d, 4 H, 2-Ph, *J* 7.3 Hz), 5.78 [s, 2 H, C(=N)C*H*C)=N) of tmtaa], 2.49 [s, 12 H, *Me*C(=N) of tmtaa]. For **5** (250 MHz, $CDCl_3$) δ 7.15 –6.80 (overlapping multiplets, 13 H, 3- and 4-Ph, 3-C_6H_4Me and C_6H_4 of tmtaa), 6.33 (d, 2 H, 2-Ph or 2-C_6H_4Me, *J* 7.5 Hz), 6.22 (d, 2 H, 2-C_6H_4Me or 2-Ph, *J* 7.5 Hz), 5.75 [s, 2 H, C(=N)C*H*C(=N) of tmtaa], 2.47 [s, 12 H, *Me*C(=N) of tmtaa] and 2.28 (s, 3 H, C_6H_4*Me*).

§ We cannot exclude *a priori* an alternative structure with the pyridine *trans* to the Zr=N vector although we consider this less likely.

¶ *Crystal data* for **3**.C_7H_8: $C_{39}H_{48}N_6OZr.C_7H_8$, M = 800.19, monoclinic, $P2_1/n$, a = 13.744(3), b = 24.729(5), c = 13.796(3) Å, β = 109.00(3)°, U = 4434(2) Å^3, Z = 4, D_c = 1.199 g cm^{-3}, $F(000)$ = 1688, T = 150 K, Mo-Kα radiation, $5 \leqslant 2\theta \leqslant 50°$. The structure was solved by direct methods (SHELXS-86[15]) and 542 parameters were refined (SHELXL-93[16]) on F^2 for 7789 data to give final conventional $R1$ = 0.0606 [5201 data with $F_o > 4\sigma(F_o)$] and $wR2$ = 0.1681 (all data). Non-hydrogen atoms of one half-occupied, disordered toluene solvate could be refined anisotropically while the other could only be refined isotropically. Hydrogen atoms on the disordered toluene solvates were omitted. Other non-hydrogen atoms were refined anisotropically with hydrogen atoms riding. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/154.

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