Highly selective trimerisation of MeNC by a novel titanium imido complex containing a tridentate dianionic ligand

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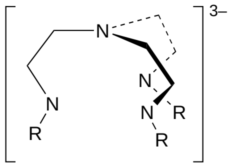
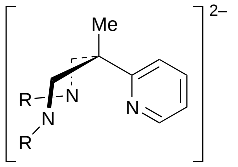
A new type of imido compound [Ti(NBu^t)L(py)] 1 containing a tripodal dianionic ligand is reported which effects the remarkably selective trimerisation of MeNC; the crystal structures of 1 and [TiL{N(Me)N(Bu^t)(C$_4$H$_3$N$_2$Me)}] 2 are described [L = MeC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$].

Transition-metal imido complexes are relevant to industrially important processes such as acrylonitrile synthesis and ring-opening metathesis polymerisation, and also to biological processes such as nitrogen fixation.[1] Highly reactive transition-metal imido transients, in particular, have demonstrated a rich chemistry including cycloaddition reactions, catalytic hydroammination and C–H bond activation.[1b] Imido complexes that have reactive {M=NR} functionalities but yet are sufficiently kinetically stable to be isolated are extremely rare. Cognisant of the very successful use of the trianionic triamidoamine ligands [(RNCH$_2$CH$_2$)$_3$N]$^{3-}$ **A** in developing groups 5–7 metal–ligand multiple bond chemistry,[2] we wished to explore the potential of the dianionic tripodal ligands [MeC(2-C$_5$H$_4$N)(CH$_2$NR)$_2$]$^{2-}$ **B**.



A



B

The ligand system **B** is related to **A**, but features several important differences. Firstly, the pyridyl nitrogen donor function in **B** is only relatively weakly coordinating (compared to amide donor groups in **A**) and this 'arm' can potentially dissociate[3] from the metal centre during reactions to open up a larger reactive site. Furthermore, **B** is only a dianionic ligand and thus allows access to neutral metal–ligand multiply bonded complexes of the group 4 metals. Here, we report the synthesis of a novel titanium imido complex containing a tridentate ligand of the type **B**, along with an example of its reactivity.

Reaction of the previously described complex [Ti(NBu^t)Cl$_2$(py)$_3$][4] with the dilithiated diamidopyridine ligand [Li$_2$L]$_2$[5] in benzene followed by standard work-up afforded [Ti(NBu^t)L(py)] **1** in good yield [L = MeC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$]. The X-ray structure of **1** is shown in Fig. 1† and is consistent with the solution ^{1}H and ^{13}C NMR data.‡ Compound **1** comprises an approximately trigonal-bipyramidal titanium centre with the *tert*-butylimide and the amide donor groups of the diamidopyridine ligand occupying the equatorial sites. The pyridyl-N atom of the diamidopyridine ligand lies in one of the apical sites and a pyridine ligand completes the coordination sphere. Compound **1** is the first fully characterised example of a terminal titanium imido complex supported by an amido ligand, although complexes of the type [Ti(NR)(NHR)$_2$] (R = SiBu$^t_3$) have been proposed as reactive transients.[6] The Ti=NBu^t bond length of 1.724(2) Å lies at the long end of the range of known titanium–*tert*-butylimido bond lengths.[1b] The pyridine molecule is substantially less tightly bound [Ti–N(51) 2.278(2) Å] than the pyridyl fragment [Ti–N(41) 2.203(2) Å] of the diamidopyridine ligand and is readily lost in reactions of **1**.

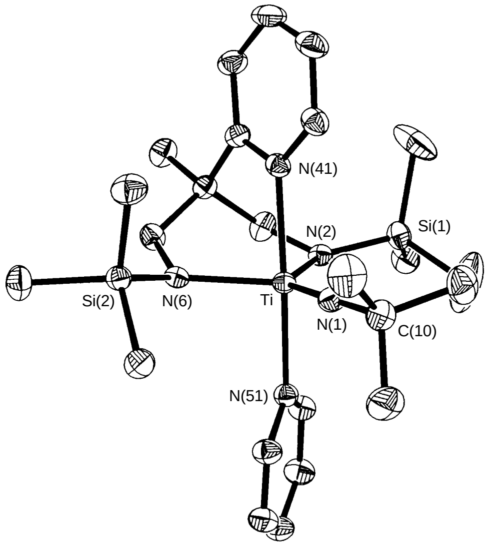
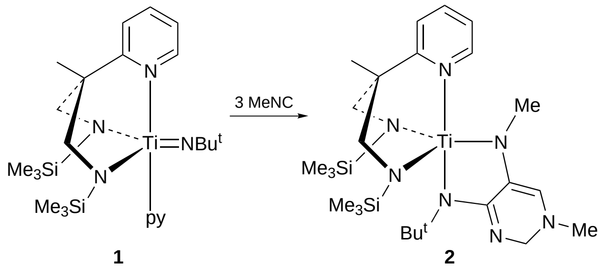


Fig. 1 Molecular structure of [Ti(NBu^t)L(py)] **1**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ti–N(1) 1.724(2), Ti–N(2) 2.025(2), Ti–N(6) 1.983(2), Ti–N(41) 2.203(2), Ti–N(51) 2.278(2); Ti–N(1)–C(10) 175.10(17), N(1)–Ti–N(2) 130.09(9), N(1)–Ti–N(6) 115.84(9), N(2)–Ti–N(6) 113.33(8), N(41)–Ti–N(51) 165.83(7).

Preliminary reactivity studies of [Ti(NBu^t)L(py)] **1** with a range of unsaturated substrates have indicated that this complex possesses a very reactive Ti=NBu^t linkage. By way of example, we describe here the novel reaction of **1** with methyl isocyanide. Thus compound **1** reacts with 3 mol equiv. of MeNC at room temp. to yield a single product [TiL{N(Me)N(Bu^t)(C$_4$H$_3$N$_2$Me)}] **2** (Scheme 1). On titration of **1** with



Scheme 1

MeNC in C_6D_6, ^1H NMR spectroscopy indicated complete cooperativity in the trimerisation (*vide infra*) of the isocyanide molecules as no intermediates were observed.

The solid-state structure of **2** was established unambiguously by X-ray crystallography (Fig. 2) which revealed a central five-coordinate Ti atom with a distorted trigonal-bipyramidal arrangement of N-donor atoms. The apical positions are occupied by the pyridyl [Ti–N(41) 2.282(2) Å] and *tert*-butyl amide fragment N-donor atoms. The Ti=NBu^t linkage of **1** has clearly undergone C–N and C–C coupling (with concomitant C–H bond migration) with three molecules of MeNC to form a coordinated 3-methyl-5,6-diamino-2,3-dihydropyrimidine derivative. The type of reaction giving rise to **2** is unprecendented in group 4 imido chemistry. Reactions of later transition-metal imido complexes with aryl isocyanides have very recently been described[7] but pyrimidine-type rings were not formed.

In conclusion, we have shown that the type of trifunctional amido-supported imido complex described can generate novel chemistry. The instantaneous formation of **2** and the absence of detectable intermediates precludes the proposal of a mechanistic pathway at this stage, but such studies will be included in further investigations into this new type of metal-mediated isocyanide cyclisation. Further preliminary results in these laboratories indicate that compounds analogous to **1** can be formed for other tridenate diamidoamines and transition metals, and work is in progress to establish the overall scope of this chemistry.

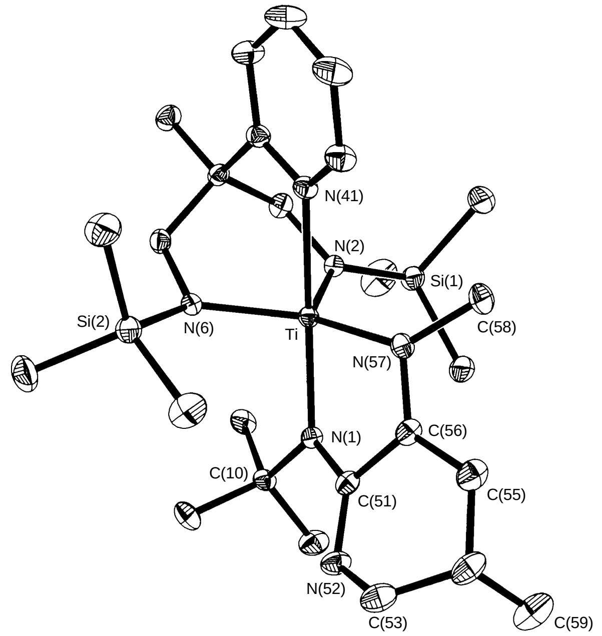


Fig. 2 Molecular structure of [TiL{N(Me)N(Bu^t)($C_4H_3N_2Me$)}] **2**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (°): Ti–N(1) 2.034(2), Ti–N(2) 1.890(2), Ti–N(6) 1.936(2), Ti–N(41) 2.282(2), Ti–N(57) 1.965(2), N(1)–C(51) 1.379(3), C(51)–N(52) 1.299(4), N(52)–C(53) 1.457(4), C(53)–N(54) 1.448(4), N(54)–C(55) 1.414(4), C(55)–C(56) 1.349(4), C(51)–C(56) 1.484(4); N(1)–Ti–N(1)–N(2) 109.87(9), N(1)–Ti–N(6) 98.66(9), N(2)–Ti–N(6) 108.53(10), N(1)–Ti–N(41) 163.94(9).

This work was supported by grants from the EPSRC (to P. M. and M. McP.), the Deutsche Forschungsgemeinschaft (SFB 347 to L. H. G.) and the Leverhulme Trust (to P. M.). L. H. G., P. M. and M. McP. thank the British Council and DADD for support under the ARC programme.

Footnotes and References

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† *Crystal data* for [Ti(NBu^t)L(py)] **1**: $C_{24}H_{43}N_5Si_2Ti$, M = 505.71, triclinic, space group $P1$, a = 9.535(3), b = 10.125(3), c = 15.948(3) Å, α = 90.63(3), β = 99.22(3), γ = 105.40(2)°, U = 1416.1(7) Å^3, Z = 2, D_c = 1.186 g cm^{-3}, $F(000)$ = 544, T = 150 K, Mo-Kα, $5.2 \leqslant 2\theta \leqslant 50°$. The structure was solved by direct methods (SHELXS = 96) and 289 parameters were refined (SHELXL-96) on F^2 for 4983 data to give final conventional R_1 = 0.0416 [for 4308 data with $F_o > 4\sigma(F_o)$] and wR_2 = 0.1084 (all data). For [TiL{N(Me)N(Bu^t)($C_4H_3N_2Me$)}] **2**: $C_{25}H_{47}N_7Si_2Ti$, M = 549.78, triclinic, space group $P1$, a = 10.031(2), b = 11.4608(14), c = 15.465(2) Å, α = 94.333(8), β = 108.378(13), γ = 111.976(11), U = 1526.4(4) Å^3, Z = 2, D_c = 1.196 g cm^{-3}, $F(000)$ = 592, T = 298 K, Mo-Kα, $2.85 \leqslant 2\theta \leqslant 50°$. The structure was solved by direct methods and 316 parameters were refined on F^2 for 5346 data. All computations were performed with SHELXTL PC 5.03. Refinement converged at R_1 = 0.0437 [for 3900 data with $F_o > 4\sigma(F_o)$] and wR_2 = 0.1102 (all data). CCDC 182/525.

‡ NMR spectroscopic and elemental analytical data for the new compounds have been deposited for scrutiny by the referees.

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Received in Basel, Switzerland, 12th May 1997; 7/03275G