New ligand platforms for developing the chemistry of the Ti=N–NR$_2$ functional group and the insertion of alkynes into the N–N bond of a Ti=N–NPh$_2$ ligand†

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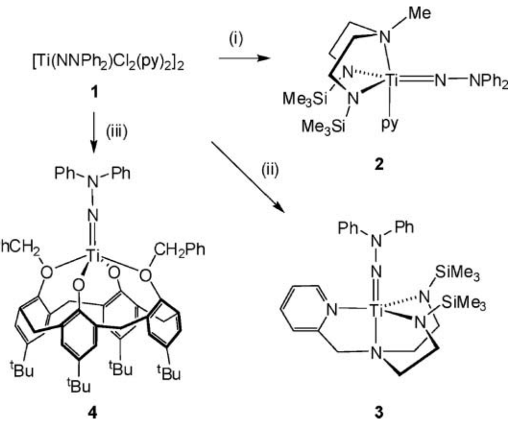
Two broadly applicable strategies for extending the available ligand platforms of the virtually unexplored terminal Ti=N–NR$_2$ functional group are described, along with the highly selective room temperature insertion of alkynes into the N–N bond of Ti{MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$}(NNPh$_2$)(py) and the catalytic *cis*-diamination of PhC≡CMe by diphenylhydrazine.

Transition metal hydrazido compounds (L)M=NNR$_2$ (L = supporting ligand set) continue to be of considerable interest, especially with regard to the biological and synthetic fixation of molecular nitrogen, which proceeds *via* such species.[1] Despite the prevalence of terminal hydrazides for the mid transition metals, there is a paucity of such compounds for Group 4. The chemistry of the M=N–NR$_2$ functional group is therefore considerably underdeveloped for these metals, not least when compared to the current situation for the related imido compounds (L)M=N–R (R = hydrocarbyl).[2–6] Titanium terminal hydrazides have, nonetheless, been implicated in the catalytic hydrohydrazination[7–13] and iminohydrazination[13,14] of alkynes, and in the synthesis of indoles[4,9,12] and tryptamines.[10] Recent DFT calculations have shown that substitution of the organic R-substituent of an imide Ti=N–R by NR$_2$ can destabilize one of the Ti=N π-bond components by *ca.* 130 kJ mol^{-1} due to an antibonding interaction between one of the Ti=N$_\alpha$ π-bond pairs and the lone pair of the β-nitrogen atom.[15] This interaction also weakens the N$_\alpha$–N$_\beta$ bond itself. One could anticipate some interesting differences between the chemistry of the Ti=NR and Ti=N–NR$_2$ functional groups. To date, there are few structurally authenticated examples of the terminal Ti=N–NR$_2$ ligand,[11,14–16] and even fewer examples of its stoichiometric chemistry.[17,18]

We have found that simple salt-elimination/metathesis reactions of the recently reported [Ti(NNPh$_2$)Cl$_2$(py)$_2$]$_2$ (**1**)[15] provide a potentially highly versatile route to new hydrazido compounds (Scheme 1). Chelating diamide-amine[5,19] and calix[4]arene (calix) ligands[20] have been highly successful for developing Group 4 imido chemistry, and so we have focused on these as proof of concept for using **1**. The reaction of **1** with the appropriate lithium or sodium salts gave the new hydrazido compounds **2–4** with a variety of N$_3$, N$_4$ and O$_4$ donor ligand sets (Scheme 1).



Scheme 1 Terminal titanium hydrazido complexes with N- and O-donor dianionic ligands. Reagents: (i) Li$_2$[MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$]; (ii) Li$_2$[(2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$NSiMe$_3$)$_2$]; (iii) Na$_2$[Bn$_2$calix].

Fig. 1 shows the X-ray structure of Ti{MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$}(NNPh$_2$)(py) (**2**), and confirms the monomeric nature of this compound.‡ The hydrazido β-nitrogen (N(2)) is planar due to conjugation with one of the phenyl substituents. The only other structurally-characterised compound with a terminal Ti=NNPh$_2$ moiety is Ti{HC(Me$_2$pz)$_3$}(NNPh$_2$)Cl$_2$,[15] which has Ti=N$_\alpha$ = 1.718(2) and N$_\alpha$–N$_\beta$ = 1.369(3) Å *vs.* values of 1.733(5) and 1.359(7) Å, respectively, in **2**.

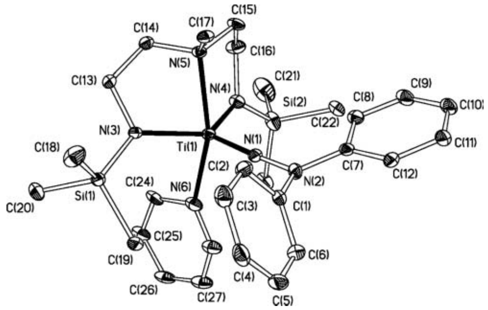


Fig. 1 Displacement ellipsoid plot (20%) of Ti{MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$}(NNPh$_2$)(py) (**2**). Selected distances (Å) and angles (°): Ti(1)–N(1) 1.733(5), N(1)–N(2) 1.359(7); Ti(1)–N(1)–N(2) 177.7(4).

Species with terminal Ti=NNR$_2$ groups have been proposed as intermediates in the catalytic hydrohydrazination of alkynes.[8,11,12]

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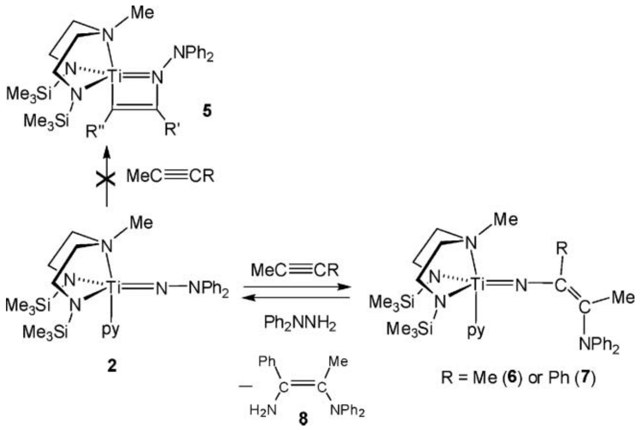


Scheme 2 Reactions of Ti{$MeN(CH_2CH_2NSiMe_3)_2$}($NNPh_2$)(py) (**2**).

We have started to examine the reactions of the new compounds herein with these and other substrates. We report here our preliminary findings for **2** (Scheme 2).

Imido complexes of a diamide-amine ligand, similar to that in **2**, form [2 + 2] cycloaddition products with certain alkynes (representing key intermediates in the alkyne hydroamination reaction) and a wide range of other unsaturated substrates.[19,21] With the expectation of a similar reactivity (products of the type **5**, Scheme 2), we carried out the reaction of **2** with four different alkynes, RC≡CR′ (R = R′ = Me or Ph; R = Ph, R′ = H; R = Ph, R′ = Me). With PhC≡CH and PhC≡CPh, mixtures were formed, but with MeC≡CMe and PhC≡CMe, single new products (**6** and **7**, respectively) were obtained. The spectroscopic data for the two compounds are analogous, and in the case of **7**, the X-ray structure was determined (Fig. 2).‡ The solid state structure of **7** is fully consistent with its spectroscopic and other analytical data, and clearly shows that in this case, cycloaddition product **5** (Scheme 2) is *not* the reaction outcome, and instead, a regiospecific net *insertion* of the alkyne into the hydrazide N_α–N_β bond has occurred, forming a vinyl imido species. Titanium vinyl imido compounds were previously available only *via* reactions of alkylidene transients and organic nitriles.[22,23]

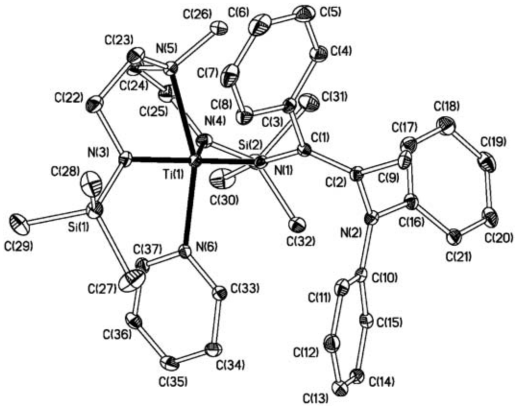
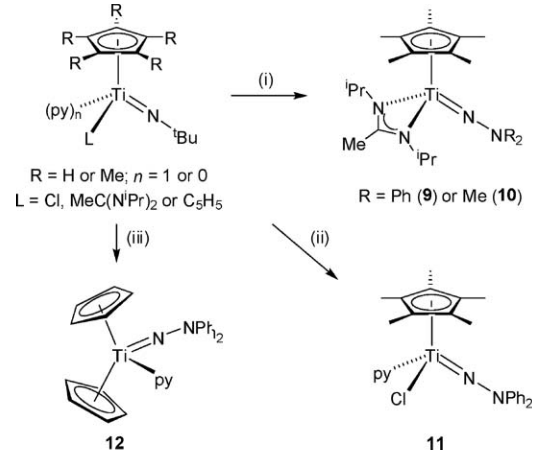


Fig. 2 Displacement ellipsoid plot (20%) of Ti{$MeN(CH_2CH_2NSiMe_3)_2$}{NC(Ph)C(Me)NPh_2}(py) (**7**). Selected distances (Å): Ti(1)–N(1) 1.757(3) [1.750(3)], N(1)–C(1) 1.375(4) [1.371(4)], C(1)–C(2) 1.349(5) [1.356(5)], C(2)–N(2) 1.442(4) [1.448(5)]. Values in brackets are for the other crystallographically independent molecule.

The treatment of **7** with an equivalent of Ph_2NNH_2 (NMR) at room temperature quantitatively regenerated **2**, along with the expected side-product PhC(NH_2)C(Me)NPh_2 (**8**), which was subsequently isolated and fully characterised.† Remarkably, **2** acts as a catalyst at room temperature for the overall 1,2-amination reaction. Thus, a mixture of PhC≡CMe (slight excess) and Ph_2NNH_2 in the presence of **2** (10 mol%) gave quantitative conversion to **8** as the only organic product ($t_{1/2}$ *ca.* 1 h by ^1H NMR spectroscopy).

This appears to be a new transformation of hydrazines and alkynes. Compounds of type **8** are potentially useful precursors to 1,2-diaminoalkanes by hydrogenation. The mechanism of formation of **7** is under investigation, as is the scope of this unusual reaction. It is likely that one or more of the other compounds reported herein could also catalyse this unique reaction. Furthermore, since this process proceeds at room temperature, it is likely that previously reported "classical" hydrohydrazination systems could also undergo this type of transformation in as-yet unrecognised side reactions.

Cyclopentadienyl compounds have also played a pivotal role in the development of metal–ligand multiple bonds.[5] We report here hydrazine/*tert*-butyl imide exchange reactions[17] as a second and complimentary entry route to hitherto unexplored classes of hydrazide compound (Scheme 3).



Scheme 3 Sandwich and half-sandwich terminal titanium hydrazides. Reagents: (i) R_2NNH_2 (R = Ph or Me); (ii) and (iii) Ph_2NNH_2.

The cyclopentadienyl-amidinate ligand platform has provided a rich source of Ti=NR bond reactivity in imido systems.[5] The reaction of Cp*Ti{MeC(N^iPr)$_2$}(N^tBu)[24] with either Ph_2NNH_2 or Me_2NNH_2 gave quantitative (NMR) conversion to Cp*Ti{MeC(N^iPr)$_2$}(NNR_2) (R = Ph (**9**) or Me (**10**)) in 50–60% isolated yield.† The X-ray structure‡ of **10** is shown in Fig. 3, confirming its monomeric nature. **10** is the first structurally authenticated cyclopentadienyl titanium compound featuring a terminal hydrazide ligand.

The addition of Ph_2NNH_2 to Cp*Ti(N^tBu)Cl(py) gave a clean conversion to monomeric Cp*Ti($NNPh_2$)Cl(py) (**11**) in 83% isolated yield. The remaining Ti–Cl bond of **11** could be further substituted (*vide infra*), meaning this compound will doubtless have further applications as a synthon in its own right for developing the Ti=NNR_2 ligand platform.

Reaction of $Cp_2Ti(N^tBu)(py)$[25] with Ph_2NNH_2 gave the corresponding pyridine-stabilised titanocene hydrazide,

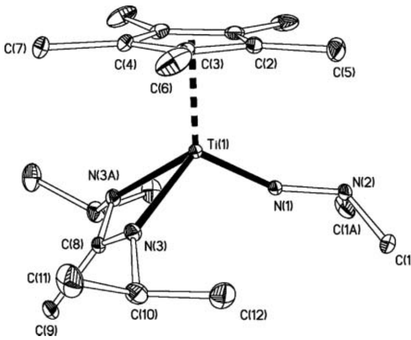


Fig. 3 Displacement ellipsoid plot (20%) of $Cp^*Ti\{MeC(N^iPr_2)_2\}(NNMe_2)$ (**10**). Selected distances (Å) and angles (°): Ti(1)–$Cp_{centroid}$ 2.063, Ti(1)–N(1) 1.723(2), N(1)–N(2) 1.386(2); Ti(1)–N(1)–N(2) 159.5(1). Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator [*x*, *y*, − *z*].

$Cp_2Ti(NNPh_2)(py)$ (**12**, Scheme 3), in 62% isolated yield. A zirconium analogue of **12** has been reported by Bergman and shows interesting N–C bond coupling reactions with unsaturated substrates.[26,27] We have not yet obtained diffraction-quality crystals of **12**, but the DFT-computed structure† (Fig. 4) is in agreement both with Bergman's interesting zirconocene system and all other available data. The Ti–$Cp_{centroid}$ (2.183 and 2.168 Å) and Ti=N_α (1.743 Å) distances in **12** are comparatively long. For comparison, the DFT-computed model of **9** (namely $CpTi\{MeC(NMe)_2\}(NNPh_2)$ (**9′**)) is also shown in Fig. 4 (Ti–$Cp_{centroid}$ = 2.065, Ti–N_α = 1.714 Å). The much longer Ti–Cp_{cent} and Ti=N_α distances in **12** can be attributed to the formal 20 valence electron count of this compound, in which the π-donor Cp and $NNPh_2$ ligands compete for the same Ti $3d_\pi$ acceptor orbitals.[5] This, in turn, is expected to give rise to further interesting reactivity patterns of the Ti=NNR_2 functional group. Reactivity studies of **12** are currently under way.

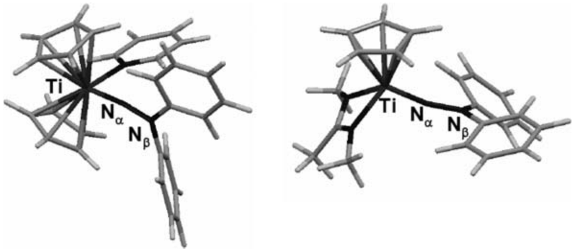


Fig. 4 DFT (B3PW91)-calculated structures. Left: $Cp_2Ti(NNPh_2)(py)$ (**12**): Ti–N_α 1.743, Ti–Cp_{cent} 2.183 and 2.168 Å. Right: $CpTi\{MeC(NMe)_2\}(NNPh_2)$ (**9′**): Ti–N_α 1.714 and Ti–$Cp_{centroid}$ 2.065 Å.

While readily isolated, **12** is sensitive to the presence of excess hydrazine, which results in its slow degradation at room temperature, tentatively attributed to loss of one of the Cp ligands. Furthermore, reaction of the mixed-ring imide $Cp^*CpTi(N^tBu)(py)$ with Ph_2NNH_2 formed a mixture of products, among which was identified $Cp^*Ti(NNPh_2)(NHNPh_2)(py)$ (**13**). Compound **13** (prepared independently from **11** in 45% yield) is the hydrazido analogue of Bergman's CpTi(NAr)(NHAr)($OPMe_3$),[7] a model for the active species formed in the Cp_2TiMe_2-catalysed hydroamination of alkynes and allenes. Several bis(cyclopentadienyl)titanium compounds act as hydrohydrazination precatalysts at elevated temperatures.[7,12] The formation of **13** at ambient temperature suggests that these catalytic systems, in fact, also proceed through half-sandwich compounds. Studies of the competence of the new cyclopentadienyl-hydrazido compounds in catalytic hydrohydrazination reactions are under way.

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Notes and references

‡ Crystal data for **2**: $C_{28}H_{44}N_6Si_2Ti$, M_w = 568.77, triclinic, *P*-1, *a* = 10.1794(5), *b* = 11.1800(7), *c* = 13.8952(8) Å, α = 89.726(3), β = 77.178(2), γ = 85.912(3)°, *U* = 1537.9(2) $Å^3$, *Z* = 2, *T* = 150 K, μ = 0.383 mm^{-1}, 3146 reflections $I > 3\sigma(I)$, R_{int} = 0.055, *R* = 0.073, w*R* = 0.080. CCDC 656394.

Crystal data for **7**: $C_{37}H_{52}N_6Si_2Ti$, M_w = 684.93, monoclinic, $P2_1/n$, *a* = 10.19100(10), *b* = 19.6879(2), *c* = 38.0089(4) Å, β = 92.0565(4)°, *U* = 7621.17(13) $Å^3$, *Z* = 8, *T* = 150 K, μ = 0.321 mm^{-1}, 6837 reflections $I > 3\sigma(I)$, R_{int} = 0.087, *R* = 0. 0397, w*R* = 0.0443. CCDC 656395.

Crystal data for **10**: $C_{20}H_{38}N_4Ti$, M_w = 382.45, orthorhombic, *Pbnm* (non-standard setting of *Pnma*), *a* = 9.3311(2), *b* = 14.7945(4), *c* = 16.4429(4) Å, *U* = 2269.93(10) $Å^3$, *Z* = 4, *T* = 150 K, μ = 0.386 mm^{-1}, 2192 reflections $I > 3\sigma(I)$, R_{int} = 0.016, *R* = 0.038 w*R* = 0.0459. CCDC 656396.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711941k

1 R. R. Schrock, *Acc. Chem. Res.*, 2005, **38**, 955.
2 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
3 A. P. Duncan and R. G. Bergman, *Chem. Rec.*, 2002, **2**, 431.
4 A. L. Odom, *Dalton Trans.*, 2005, 225.
5 N. Hazari and P. Mountford, *Acc. Chem. Res.*, 2005, **38**, 839.
6 P. D. Bolton and P. Mountford, *Adv. Synth. Catal.*, 2005, **347**, 355.
7 J. S. Johnson and R. G. Bergman, *J. Am. Chem. Soc.*, 2001, **123**, 2923.
8 C. Cao, Y. Shi and A. L. Odom, *Org. Lett.*, 2002, **4**, 2853.
9 L. Ackermann and R. Born, *Tetrahedron Lett.*, 2004, **45**, 9541.
10 V. Khedkar, A. Tillack, M. Michalik and M. Beller, *Tetrahedron Lett.*, 2004, **45**, 3123.
11 Y. Li, Y. Shi and A. L. Odom, *J. Am. Chem. Soc.*, 2004, **126**, 1794.
12 A. Tillack, H. Jiao, I. Garcia Castro, C. G. Hartung and M. Beller, *Chem.–Eur. J.*, 2004, **10**, 2410.
13 S. Banerjee, Y. Shi, C. Cao and A. L. Odom, *J. Organomet. Chem.*, 2005, **690**, 5066.
14 S. Banerjee and A. L. Odom, *Organometallics*, 2006, **25**, 3099.
15 T. B. Parsons, N. Hazari, A. R. Cowley, J. C. Green and P. Mountford, *Inorg. Chem.*, 2005, 8442.
16 S. Patel, Y. Li and A. L. Odom, *Inorg. Chem.*, 2007, **46**, 6373.
17 A. J. Blake, J. M. McInnes, P. Mountford, G. I. Nikonov, D. Swallow and D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, 1999, 379.
18 J. L. Thorman and L. K. Woo, *Inorg. Chem.*, 2000, **39**, 1301.
19 L. H. Gade and P. Mountford, *Coord. Chem. Rev.*, 2001, **216–217**, 65.
20 S. R. Dubberley, A. Friedrich, D. A. Willman, P. Mountford and U. Radius, *Chem.–Eur. J.*, 2003, **9**, 3634.
21 B. D. Ward, A. Maisse-Francois, P. Mountford and L. H. Gade, *Chem. Commun.*, 2004, 704.
22 K. M. Doxsee, J. B. Farahi and H. Hope, *J. Am. Chem. Soc.*, 1991, **113**, 8889.
23 K. M. Doxsee, J. K. M. Mouser and J. B. Farahi, *Synlett*, 1992, 13.
24 A. E. Guiducci, C. L. Boyd and P. Mountford, *Organometallics*, 2006, **25**, 1167.
25 S. C. Dunn, P. Mountford and D. A. Robson, *J. Chem. Soc., Dalton Trans.*, 1997, 293.
26 $Cp_2Zr(NNPh_2)(DMAP)$ reacts with alkynes and CO to give products in which the N_α–N_β bond is cleaved but products analogous to **6–8** are not obtained: P. J. Walsh, M. J. Carney and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 6343.
27 Compound **12** is an analogue of $Cp_2Ti{=}NN(SiMe_3)_2$, prepared from Cp_2TiCl_2 and thermally sensitive (decomp. > −35 °C) $N_2(SiMe_3)_2$. There have been no subsequent reactivity or structural reports, and the inconvenient nature of $N_2(SiMe_3)_2$ has limited the development of this system. N. Wiberg, H.-W. Haring, G. Huttner and P. Friedrich, *Chem. Ber.*, 1978, **111**, 2708.