Cycloaddition reactions of transition metal hydrazides with alkynes and heteroalkynes: coupling of Ti$=$NNPh$_2$ with PhCCMe, PhCCH, MeCN and ^{t}BuCP†

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The first structurally authenticated [2 + 2] cycloaddition products of any transition metal hydrazide complexes are reported; cycloaddition products of transition metal hydrazides with alkynes and heteroalkynes have been obtained for the first time; these are the first structurally authenticated cycloaddition products for any transition metal M$=$NNR$_2$ functional group.

Transition metal hydrazides, (L)M$=$NNR$_2$, occupy a pivotal position on the pathway for the biological and laboratory-based conversion of N$_2$ to ammonia.[1–4] From the point of view of the productive incorporation of N$_2$ into value-added products, an understanding of the chemistry of terminal metal hydrazides is clearly essential. Over the past two decades a large effort has been expended on charting the chemistry of the Group 6 metal M$=$NNR$_2$ functional groups because of their immediate relevance to biological systems.[4–6] In all of this chemistry the M$=$NNR$_2$ group reactivity is characterised exclusively by transformations involving the N$_\beta$ atom and/or N$_\alpha$–N$_\beta$ bond reductive cleavage.

Over the last 10 years, landmark achievements have also been made in the activation of N$_2$ by Group 4 compounds.[5–8] However, unlike for the Group 6 systems, the reactions of Group 4 M$=$NNR$_2$ bonds with unsaturated substrates remain very poorly understood.[9] This situation contrasts dramatically with the well-established area of imido compounds, (L)M$=$NR (R = alkyl, aryl): reactions of the M$=$NR bond are highly developed and lead to a range of valuable new NR-containing products, for example through the hydroamination of alkynes and allenes.[10–13]

Group 4 hydrazides have nonetheless been implicated in N–C bond forming processes.[13–15] Thus reactions of hydrazines and alkynes in the presence of supposed hydrazide *precursor* complexes give hydrazone products, apparently consistent with [2 + 2] cycloaddition reactions of *in situ* generated hydrazide intermediates. However, no discrete Ti$=$NNR$_2$ species have ever been observed for these systems, nor has direct evidence of the putative [2 + 2] cycloaddition of an alkyne and a hydrazide been presented. Indeed, these hydrohydrazination reactions typically require forcing temperatures around *ca.* 100 °C and long (up to 24 h) reaction times. Alternative reaction pathways such as those found in rare earth metal-catalysed hydroaminations[16] cannot *a priori* be ruled out on the available experimental evidence (*i.e.*, substrate insertion into a metal–hydrazide(1−) σ bond).

So far, all fully authenticated reactions between isolated, well-defined Group 4 hydrazides and alkynes (and also isocyanides, or chalcogenide delivery agents) have invariably led to N$_\alpha$–N$_\beta$ *bond cleavage* products (see Fig. 1 for examples).[9,17–19] Furthermore, no M$=$N$_\alpha$ cycloaddition product has been structurally authenticated for the reaction of *any* transition metal M$=$NNR$_2$ functional group.

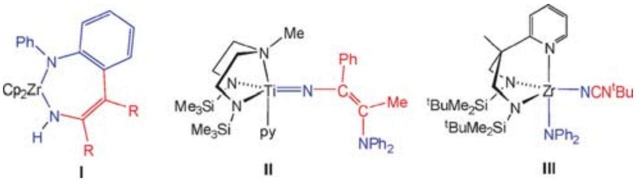

Fig. 1 Products of Group 4 M$=$NNPh$_2$ bonds with alkynes (**I**, **II**) and ^{t}BuNC (**III**): facile N$_\alpha$–N$_\beta$ cleavage rather than M$=$N$_\alpha$ bond coupling.

We recently reported general routes to a range of new titanium hydrazide complexes.[18] This has opened up the opportunity to tune and direct the reactions of the Ti$=$NNR$_2$ functional group though judicious ligand selection.

Reaction of the terminal hydrazide Ti(N$_2$N^{py})(NNPh$_2$)(py)[20] (**1**, Scheme 1) with PhCCMe in C$_6$D$_6$ gave an equilibrium mixture containing the *cycloaddition* product Ti(N$_2$N^{py}){N(NPh$_2$)C(Me)CPh} (**2**).† Removal of the volatiles and redissolving in C$_6$D$_6$ gave pure **2** as judged by NMR spectroscopy. The structure shown in Scheme 1 is fully compatible with the 1- and 2-D ^{1}H, ^{13}C and ROESY spectra, and other data. In particular, the Ph*C*$=$*C*Me carbons appeared at 216.1 and 146.3 ppm in typical positions for such metallacycles.[21,22] Addition of an excess of pyridine to pure **2** reformed **1** and free PhCCMe, confirming the reversibility of the cycloaddition process. Note that reaction of the closely related compound Ti(N$_2$N^{Me})(NNPh$_2$)(py) with the same alkyne gave only the N$_\alpha$–N$_\beta$ *insertion* product Ti(N$_2$N^{Me}){NC(Ph)C(Me)NPh$_2$}(py) (**II**, Fig. 1; N$_2$N^{Me}$=$MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$). No Ti$=$N$_\alpha$ cycloaddition products were seen in the reactions for **II**.

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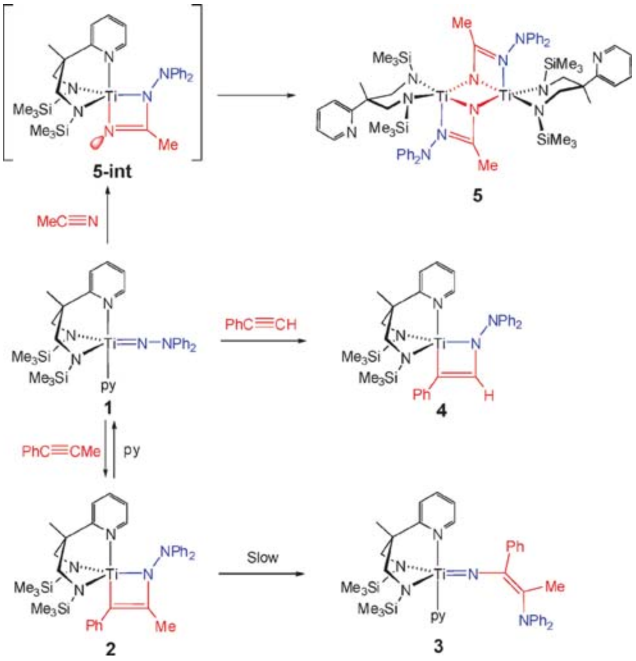


Scheme 1 Reactions of Ti(N_2N^{py})($NNPh_2$)(py) with alkynes and MeCN.

Although a cycloaddition species is the kinetic product for **1** and PhCCMe, over time (3 days at RT) or upon briefly heating (15 min at 100 °C) new products are formed from which the N_α–N_β *insertion* product Ti(N_2N^{py}){NC(Ph)C(Me)NPh_2}(py) (**3**, Scheme 1) was obtained[23] (the Ph*C*=*C*Me carbons appear at 158.2 and 112.3 ppm, these shifts being very similar to those for **II**).

Reaction of **1** with the sterically less demanding PhCCH gave quantitative conversion to the anti-Markovnikov type cycloaddition product Ti(N_2N^{py}){N(NPh_2)C(H)CPh} (**4**) in *ca.* 60% yield on the preparative scale (100% conversion by ^{1}H NMR). Addition of pyridine to pure **4** reformed **1** along with PhCCH. The NMR data for **4** are analogous to those of **2** and also the structurally authenticated imido cycloaddition products Ti(N_2N^{py}){N(R)C(H)CPh} (R = ^{t}Bu or 2,6-$C_6H_3{}^iPr_2$).[22] Like **2**, compound **4** is unstable in solution ($t_{1/2}$ *ca.* 4 h at 22 °C) but no single product could be isolated.

The high solubility of **2** and **4** and their instability prevented us from obtaining diffraction-quality crystals. However, sunequivocal structural evidence for a [2 + 2] cycloaddition reaction of the Ti=$NNPh_2$ group came from adding MeCN (isoelectronic with RCCR′) to a solution of **1** in benzene. This formed the "self-trapped" dimer $Ti_2(N_2N^{py})_2$\{μ-N(NPh_2)C(Me)N\}$_2$ (**5**, Scheme 1). The X-ray structure of **5** (Fig. 2)‡ is consistent with the likely intermediate Ti(N_2N^{py}){N(NPh_2)C(Me)N} (**5-int**) possessing the stereochemistry indicated in Scheme 1. The structural data for **5** (Fig. 2) are consistent with the drawing in Scheme 1.

The MeCN-derived nitrogen in **5-int** (ultimately becoming C(6) and C(6A) in Fig. 2) is presumably highly nucleophilic and so leads to the "self-trapped" final product **5** which is stable in solution due to the Ti_2\{μ-N(NPh_2)C(Me)N\}$_2$ core. The N_2N^{py} ligands in **5** respond to the steric crowding by adopting a κ^2(*N*,*N*) coordination mode. The addition of nitriles to transition metal–nitrogen multiple bonds is extremely rare, even in the extensively studied area of imido chemistry,[10] and has not been seen previously in transition metal hydrazide chemistry.

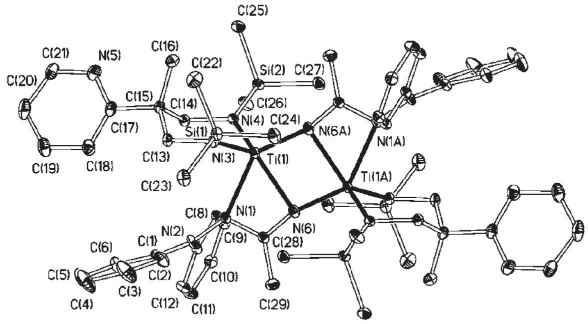
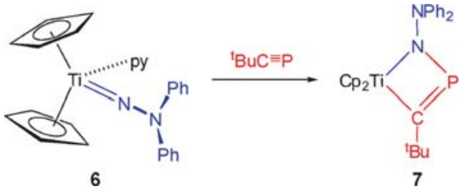


Fig. 2 Displacement ellipsoid plot (20%) of $Ti_2(N_2N^{py})_2$\{μ-N(NPh_2)C(Me)N\}$_2$ (**5**). Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $-x + 2/3$, $-y + 1/3$, $-z + 1/3$: Ti(1)–N(1) 2.3084(13), Ti(1)–N(6) 2.1687(16), Ti(1)–N(6A) 1.8684(14), N(1)–C(28) 1.318(2), N(6)–C(28) 1.334(2), N(1)–N(2) 1.4137(18) Å; H atoms, solvent and minor disorder omitted.

The successful use of a heteroalkyne in stabilizing **5** prompted us to explore reactions of **1** with phosphaalkynes which have known similarities with alkynes.[24] Titanium imido compounds form a range of different products with these substrates.[10,25,26] Unfortunately, in the case of **1** no reaction took place with ^{t}BuCP.



(1)

Mindful of previous reports of the reactions of imidozirconocenes "Cp_2Zr(NR)" (R = ^{t}Bu or aryl) with ^{t}BuCP[25] we carried out the reaction of the very recently reported Cp_2Ti($NNPh_2$)(py) (**6**, eqn (1)) with ^{t}BuCP. Brown crystals of Cp_2Ti\{N(NPh_2)PC^{t}Bu\} (**7**) were isolated in 70% yield after 30 h at RT. The molecular structure‡ of **7** is shown in Fig. 3 confirming it as a monomeric [2 + 2] cycloaddition product. Compound **7** is the first report of a M=NNR_2 species reacting with a phosphaalkyne. An excess of pyridine does not displace the ^{t}BuCP from **7**. The reactions of **6** with alkynes, nitriles and other substrates are presently under investigation.

The N(1)–P(1) and C(1)–P(1) distances within the metallacyclic core of **7** are comparable to those in imido-based (L)M{N(R)PCR} units. However, the ^{31}P shift of −28.9 ppm for **7** is rather upfield compared to the Cp_2Zr(NR)-derived examples (*ca.* 60–80 ppm)[25] and others formed from (L)Ti=NR compounds (*ca.* 200 to 210 ppm).[25,26]

The orientation of the [2 + 2] cycloaddition process in **7** appears to be favoured on steric grounds and is analogous to that found previously for imido-derived examples, (L)M{N(R)PCR}. However, the orientation of the less sterically demanding MeCN in **5-int** (and **5**) is the opposite of that in **7** (Ti–heteroatom formation in **5-int** *vs.* Ti–C formation

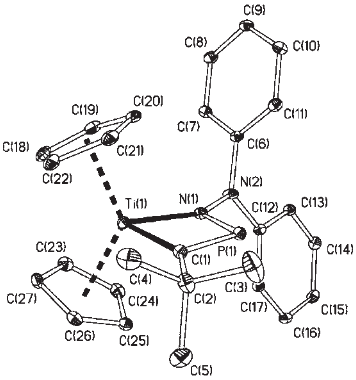


Fig. 3 Displacement ellipsoid plot (20%) of $Cp_2Ti\{N(NPh_2)PC^tBu\}$ (**7**): Ti(1)–N(1) 1.9770(17), Ti(1)–C(1) 2.115(2), N(1)–P(1) 1.7329(18), C(1)–P(1) 1.677(2), N(1)–N(2) 1.400(2) Å; N(1)–P(1)–C(1) 98.93(9), N(1)–Ti(1)–C(1) 78.51(7)°; H atoms omitted.

in **7**). We have calculated the two alternative regioisomers of **7** using DFT (B3PW91), namely **7-Q** and **7-alt-Q** (see Fig. 4).† According to DFT, **7-alt-Q** (with a Ti–P bond) is *more* stable (but only marginally, by *ca.* 6 kJ mol^{-1}) than the experimentally observed one in terms of electronic energies.[27] The calculated ^{31}P shifts of **7-Q** and **7-alt-Q** are −47.8 and +319 ppm. This supports the suggestion that **7-Q** represents the experimental solution and solid-state species.[28]

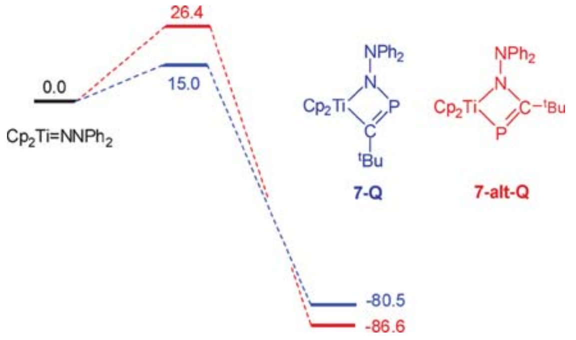


Fig. 4 Schematic representation of the two TS and product electronic energies (B3PW91, kJ mol^{-1}) for the reaction of base-free $Cp_2Ti(NNPh_2)$ with ^tBuCP. Further details of the geometries are give in the ESI.†

Although Fig. 4 shows that formation of **7-alt-Q** is thermodynamically competitive with **7-Q**, the transition state (TS) energies predict that the experimentally observed species (modeled by **7Q**) is certainly kinetically favoured ($\Delta\Delta E^{\ddagger}$ = 11.4 kJ mol^{-1} in favour of forming **7-Q**). Further calculations using the sterically less demanding phosphaalkyne MeCP gave Δ_rE values of −97.7 kJ mol^{-1} for the Ti–C bound isomer $Cp_2Ti\{N(NPh_2)PCMe\}$ (**8-Q**) but −134.1 kJ mol^{-1} for the Ti–P bound alternative $Cp_2Ti\{N(NPh_2)C(Me)P\}$ (**8-alt-Q**). This confirms that the Ti–P/N–C orientated [2+2] cycloaddition process is the electronically preferred one.

In conclusion, we have reported the first [2+2] cycloaddition reactions of transition metal hydrazides with internal and terminal alkynes, and also aza- and phosphaalkynes. These reactions demonstrate the potential breadth of substrate functionalisation chemistry available using Group 4 hydrazides. Compounds **5** and **7** are the first structurally authenticated cycloaddition products for *any* metal hydrazide. The reactions of **1** with PhCCMe show that the [2+2] cycloaddition reactions to hydrazides can be reversible and that systems capable of forming azametallacycles like **2** (the proposed intermediates in hydroamination catalysis) are also capable of N_α–N_β insertion chemistry (formation of **3**). This has significant implications for the design and rationalisation of hydroamination and related catalyst systems using hydrazines. The DFT calculations for **7** and its analogues show that alternative coupling modes of $M{=}NNR_2$ with unsaturated substrates should be accessible through tuning of substrate and supporting ligand set. Finally, these results will be of benefit in developing Group 4 based N_2 functionalisation chemistry *via* hydrazide intermediates.

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Notes and references

‡ Crystal data for **3**, **5** and **7** are provided in CIF format in the ESI.†

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27 Given their similarity, the ground state energies of **7-Q** and **7-alt-Q** could be inverted by solvent effects.
28 The observed and calculated ^{31}P shifts for **7** are more upfield than expected. At first sight this could be attributed to the $NNPh_2$ in **7**. However, replacing $NNPh_2$ by NPh in **7-Q** had little effect on the ^{31}P shift (−53.1 ppm). Work is underway to rationalise these differences.