

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

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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  $\text{M}=\text{NNR}_2$  functional group.**

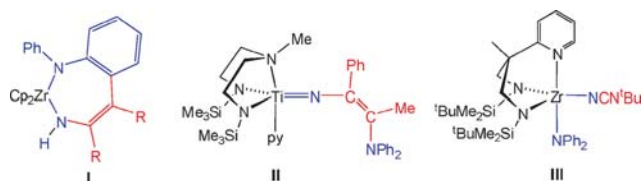
Transition metal hydrazides,  $(\text{L})\text{M}=\text{NNR}_2$ , occupy a pivotal position on the pathway for the biological and laboratory-based conversion of  $\text{N}_2$  to ammonia.<sup>1–4</sup> From the point of view of the productive incorporation of  $\text{N}_2$  into value-added products, 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  $\text{M}=\text{NNR}_2$  functional groups because of their immediate relevance to biological systems.<sup>4–6</sup> In all of this chemistry the  $\text{M}=\text{NNR}_2$  group reactivity is characterised exclusively by transformations involving the  $\text{N}_\beta$  atom and/or  $\text{N}_\alpha\text{–N}_\beta$  bond reductive cleavage.

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

Group 4 hydrazides have nonetheless been implicated in  $\text{N–C}$  bond forming processes.<sup>13–15</sup> Thus reactions of hydrazides 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  $\text{Ti}=\text{NNR}_2$  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<sup>16</sup> cannot *a priori* be ruled out on the available experimental evidence (*i.e.*, substrate insertion into a metal–hydrazide(1–)  $\sigma$  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  $\text{N}_\alpha\text{–N}_\beta$  bond cleavage products (see Fig. 1 for examples).<sup>9,17–19</sup> Furthermore, no  $\text{M}=\text{N}_\alpha$  cycloaddition product has been structurally authenticated for the reaction of *any* transition metal  $\text{M}=\text{NNR}_2$  functional group.



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

We recently reported general routes to a range of new titanium hydrazide complexes.<sup>18</sup> This has opened up the opportunity to tune and direct the reactions of the  $\text{Ti}=\text{NNR}_2$  functional group through judicious ligand selection.

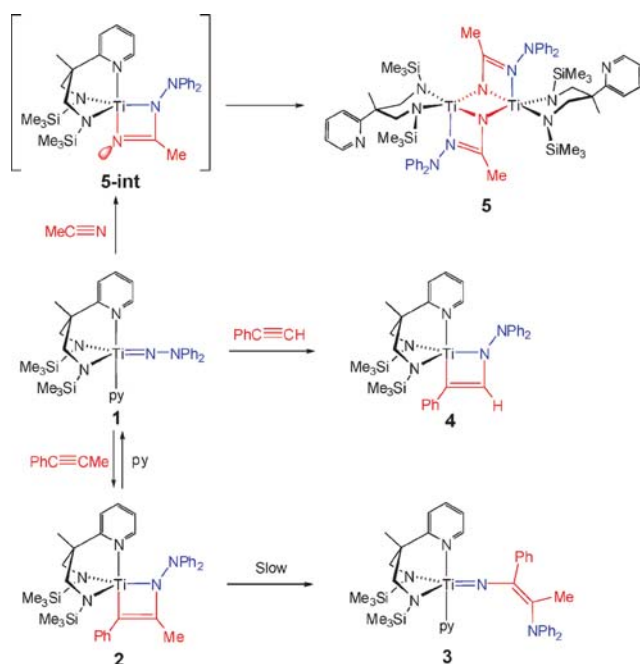
Reaction of the terminal hydrazide  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})(\text{NNPh}_2)(\text{py})$ <sup>20</sup> (**1**, Scheme 1) with  $\text{PhCCMe}$  in  $\text{C}_6\text{D}_6$  gave an equilibrium mixture containing the cycloaddition product  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}(\text{NPh}_2)\text{C}(\text{Me})\text{CPh}\}$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

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<sup>†</sup> Electronic supplementary information (ESI) available: Characterising and crystallographic data, and computational details. CCDC 698353–698355. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813911c



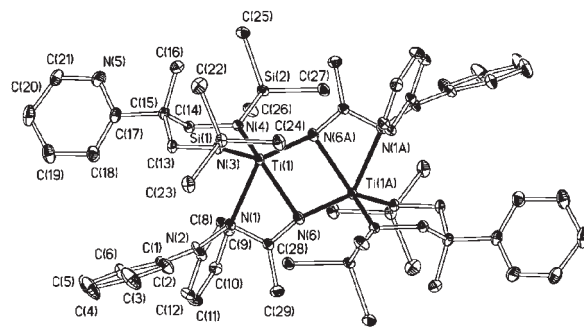
**Scheme 1** Reactions of  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})(\text{NNPh}_2)(\text{py})$  with alkynes and  $\text{MeCN}$ .

Although a cycloaddition species is the kinetic product for **1** and  $\text{PhCCMe}$ , over time (3 days at RT) or upon briefly heating (15 min at  $100^\circ\text{C}$ ) new products are formed from which the  $\text{N}_\alpha\text{-N}_\beta$  insertion product  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NC}(\text{Ph})\text{C}(\text{Me})\text{NPh}_2\}(\text{py})$  (**3**, Scheme 1) was obtained<sup>23</sup> (the  $\text{PhC}=\text{CMe}$  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  $\text{PhCCH}$  gave quantitative conversion to the anti-Markovnikov type cycloaddition product  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}(\text{NPh}_2)\text{C}(\text{H})\text{CPh}\}$  (**4**) in *ca.* 60% yield on the preparative scale (100% conversion by  $^1\text{H}$  NMR). Addition of pyridine to pure **4** reformed **1** along with  $\text{PhCCH}$ . The NMR data for **4** are analogous to those of **2** and also the structurally authenticated imido cycloaddition products  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}(\text{R})\text{C}(\text{H})\text{CPh}\}$  ( $\text{R} = \text{'Bu}$  or  $2,6\text{-C}_6\text{H}_3\text{Pr}_2$ ).<sup>22</sup> Like **2**, compound **4** is unstable in solution ( $t_{1/2}$  *ca.* 4 h at  $22^\circ\text{C}$ ) 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, unequivocal structural evidence for a [2+2] cycloaddition reaction of the  $\text{Ti}=\text{NNPh}_2$  group came from adding  $\text{MeCN}$  (isoelectronic with  $\text{RCCR'}$ ) to a solution of **1** in benzene. This formed the “self-trapped” dimer  $\text{Ti}_2(\text{N}_2\text{N}^{\text{py}})_2\{\mu\text{-N}(\text{NPh}_2)\text{C}(\text{Me})\text{N}\}_2$  (**5**, Scheme 1). The X-ray structure of **5** (Fig. 2)<sup>†</sup> is consistent with the likely intermediate  $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}(\text{NPh}_2)\text{C}(\text{Me})\text{N}\}$  (**5-int**) possessing the stereochemistry indicated in Scheme 1. The structural data for **5** (Fig. 2) are consistent with the drawing in Scheme 1.

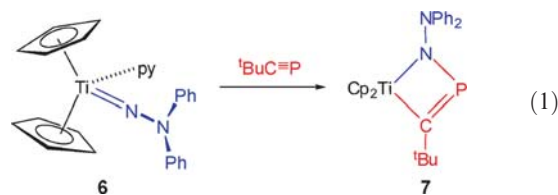
The  $\text{MeCN}$ -derived nitrogen in **5-int** (ultimately becoming C(6) and C(6A) in Fig. 2) is presumably highly nucleophilic and so leads to the “self-trapped” final product **5** which is stable in solution due to the  $\text{Ti}_2\{\mu\text{-N}(\text{NPh}_2)\text{C}(\text{Me})\text{N}\}_2$  core. The  $\text{N}_2\text{N}^{\text{py}}$  ligands in **5** respond to the steric crowding by



**Fig. 2** Displacement ellipsoid plot (20%) of  $\text{Ti}_2(\text{N}_2\text{N}^{\text{py}})_2\{\mu\text{-N}(\text{NPh}_2)\text{C}(\text{Me})\text{N}\}_2$  (**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.

adopting a  $\kappa^2(\text{N},\text{N})$  coordination mode. The addition of nitriles to transition metal–nitrogen multiple bonds is extremely rare, even in the extensively studied area of imido chemistry,<sup>10</sup> and has not been seen previously in transition metal hydrazide chemistry.

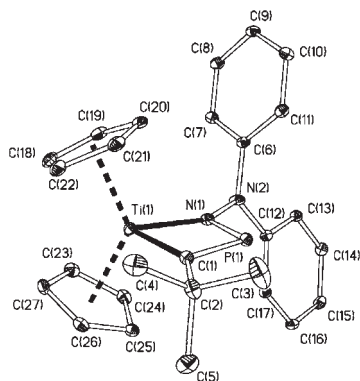
The successful use of a heteroalkyne in stabilizing **5** prompted us to explore reactions of **1** with phosphalkynes which have known similarities with alkynes.<sup>24</sup> Titanium imido compounds form a range of different products with these substrates.<sup>10,25,26</sup> Unfortunately, in the case of **1** no reaction took place with  $\text{'BuCP}$ .



Mindful of previous reports of the reactions of imidozirconocenes “ $\text{Cp}_2\text{Zr}(\text{NR})$ ” ( $\text{R} = \text{'Bu}$  or aryl) with  $\text{'BuCP}$ <sup>25</sup> we carried out the reaction of the very recently reported  $\text{Cp}_2\text{Ti}(\text{NNPh}_2)(\text{py})$  (**6**, eqn (1)) with  $\text{'BuCP}$ . Brown crystals of  $\text{Cp}_2\text{Ti}\{\text{N}(\text{NPh}_2)\text{PC'Bu}\}$  (**7**) were isolated in 70% yield after 30 h at RT. The molecular structure<sup>†</sup> of **7** is shown in Fig. 3 confirming it as a monomeric [2+2] cycloaddition product. Compound **7** is the first report of a  $\text{M}=\text{NNR}_2$  species reacting with a phosphalkyne. An excess of pyridine does not displace the  $\text{'BuCP}$  from **7**. The reactions of **6** with alkynes, nitriles and other substrates are presently under investigation.

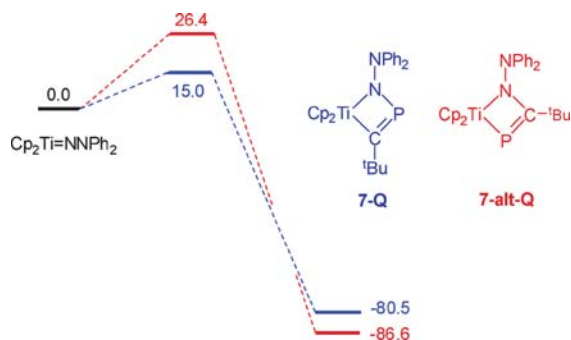
The N(1)–P(1) and C(1)–P(1) distances within the metallacyclic core of **7** are comparable to those in imido-based  $(\text{L})\text{M}\{\text{N}(\text{R})\text{PCR}\}$  units. However, the  $^{31}\text{P}$  shift of  $-28.9$  ppm for **7** is rather upfield compared to the  $\text{Cp}_2\text{Zr}(\text{NR})$ -derived examples (*ca.* 60–80 ppm)<sup>25</sup> and others formed from  $(\text{L})\text{Ti}=\text{NR}$  compounds (*ca.* 200 to 210 ppm).<sup>25,26</sup>

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,  $(\text{L})\text{M}\{\text{N}(\text{R})\text{PCR}\}$ . However, the orientation of the less sterically demanding  $\text{MeCN}$  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  $\text{Cp}_2\text{Ti}\{\text{N}(\text{NPh}_2)\text{PC}^t\text{Bu}\}$  (**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).<sup>†</sup> According to DFT, **7-alt-Q** (with a Ti–P bond) is *more* stable (but only marginally, by *ca.* 6 kJ mol<sup>−1</sup>) than the experimentally observed one in terms of electronic energies.<sup>27</sup> The calculated <sup>31</sup>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.<sup>28</sup>



**Fig. 4** Schematic representation of the two TS and product electronic energies (B3PW91, kJ mol<sup>−1</sup>) for the reaction of base-free  $\text{Cp}_2\text{Ti}(\text{NNPh}_2)$  with <sup>t</sup>BuCP. Further details of the geometries are given in the ESI.<sup>†</sup>

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 **7-Q**) is certainly kinetically favoured ( $\Delta\Delta E^\ddagger = 11.4$  kJ mol<sup>−1</sup> in favour of forming **7-Q**). Further calculations using the sterically less demanding phosphalkyne MeCP gave  $\Delta_r E$  values of −97.7 kJ mol<sup>−1</sup> for the Ti–C bound isomer  $\text{Cp}_2\text{Ti}\{\text{N}(\text{NPh}_2)\text{PCMe}\}$  (**8-Q**) but −134.1 kJ mol<sup>−1</sup> for the Ti–P bound alternative  $\text{Cp}_2\text{Ti}\{\text{N}(\text{NPh}_2)\text{C}(\text{Me})\text{P}\}$  (**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 phosphalkynes. 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<sub>α</sub>–N<sub>β</sub> 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<sub>2</sub> 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<sub>2</sub> functionalisation chemistry *via* hydrazide intermediates.

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## Notes and references

<sup>†</sup> Crystal data for **3**, **5** and **7** are provided in CIF format in the ESI.<sup>†</sup>

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- Compound **3** has been structurally characterised: see the ESI.<sup>†</sup>
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- Given their similarity, the ground state energies of **7-Q** and **7-alt-Q** could be inverted by solvent effects.
- The observed and calculated <sup>31</sup>P shifts for **7** are more upfield than expected. At first sight this could be attributed to the NNPh<sub>2</sub> in **7**. However, replacing NNPh<sub>2</sub> by NPh in **7-Q** had little effect on the <sup>31</sup>P shift (−53.1 ppm). Work is underway to rationalise these differences.