Single and double substrate insertion into the Ti= N_{α} bonds of terminal titanium hydrazides[†]

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Nitriles, CO₂ and isocyanates undergo net single or double insertion reactions into the Ti=N_{α} multiple bonds of terminal titanium hydrazides. These are the first such examples of this type of reactivity for any transition metal hydrazide complex.

Studies of the synthesis and reactivity of transition metal hydrazides, (L)M=NNR₂, have been of sustained interest and activity for over 25 years. Historically, this is because of their relevance to the biological conversion (fixation) of N₂ to ammonia.¹⁻⁴ For this reason, much of the early work was based around Group 6 systems⁴⁻⁶ for which M= N_{α} - $N_{\beta}R_{2}$ group reactivity is characterised by reactions of the N_{β} atom (quaternarisation or (for R = H) N–H bond chemistry) and/or N_{α} - N_{β} reductive cleavage. Although initial reactivity reports of Group 4 hydrazides appeared some time ago,^{7,8} there has recently been a surge in activity and output in this area,⁹⁻²¹ and a number of new reactions of the M=NNR₂ functional group have been discovered. These include the cycloaddition of alkynes (as in I, Fig. 1) and heteroalkynes to the $M=N_{\alpha}$ multiple bond,²¹ and N_{α} -N_{β} bond insertion reactions with several substrates, including alkynes^{18,21} and isocyanides (e.g. forming II and III, Fig. 1).^{16,22} The reactions of $Ti(N_2N^{Me})(NNPh_2)(py) (N_2N^{Me} = MeN(CH_2CH_2NSiMe_3)_2)$ which lead to "insertion" products II and III can be viewed as N_{α} atom migration processes.

Just as Group 6 hydrazides are important because of their structural and functional relevance to biological N_2 fixation,



Fig. 1 Reaction products of Ti=NNPh₂ bonds with alkynes (I, II) and XylNC (III): M=N_{α} cycloaddition and N_{α}-N_{β} bond cleavage.

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Group 4 hydrazides are closely connected with the important area of catalytic N–C bond formation.^{11,23–25} Metallacycles analogous to I are intermediates in the metal-catalysed conversion of alkynes and hydrazines to hydrazones (*i.e.*, hydrohydrazination: double N–H addition across a C≡C multiple bond^{11,23–25}). The N_α–N_β bond insertion compound II and its homologues are intermediates in the diamination of internal alkynes using Ph₂NNH₂ (N–N addition across a C≡C multiple bond).^{18,21}

The fundamental paradigm of both hydrohydrazination and diamination is net transfer of an "NNR₂" moiety from a metal hydrazide to an unsaturated substrate. In every case, the final Ti–N_{α} bond breaking step only occurs *via* protonolysis using an incoming R₂NNH₂. As part of our continuing interest in metal hydrazide and related chemistry, we have started to develop new approaches to "NNR₂" functional group transfer reactions of these emerging new classes of early transition metal compound. We report here the first M=N_{α} bond insertion reactions of any metal hydrazide compound.

Reaction of the recently reported¹⁸ terminal hydrazides Cp*Ti{MeC(NⁱPr)₂}(NNR₂) (R = Ph (1a) or Me (1b)) with an excess of CO₂ gave the dicarboxylate complexes Cp*Ti{MeC(NⁱPr)₂}{OC(O)N(NR₂)C(O)O} (R = Ph (2a) or Me (2b)) in good yields. The spectroscopic and other data for 2a and 2b are consistent with the C_s symmetric "double insertion" products depicted in Scheme 1, and the X-ray structure of 2a (Fig. 2) confirms this in the solid state.[†]

As Fig. 2 shows, two molecules of CO_2 have effectively inserted into the Ti= N_{α} (formally triple¹⁷) bond of **1a**. This type of transformation is very rare in metal-nitrogen multiple



Scheme 1 Cycloaddition and cycloaddition–insertion reactions of $Cp*Ti\{MeC(N^iPr)_2\}(NNR_2)$ with heterocumulenes. All reactions are at room temperature in toluene or C_6H_6 with 1 atm CO_2 (where relevant).

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Fig. 2 Displacement ellipsoid plot (20%) of $Cp^*Ti\{MeC(N^iPr)_2\}-\{OC(O)N(NPh_2)C(O)O\}$ (2a). Ti(1)–O(1) 1.937(2), Ti(1)–O(3) 1.951(2), Ti(1)–Cp_{cent} 2.051, Ti(1)–N(3) 2.059(2), Ti(1)–N(4) 2.090(2), N(1)–N(2) 1.394(3), C(13)–O(2) 1.206(3), C(14)–O(4) 1.218(3) Å.

bond chemistry in general,^{26,27} and without precedent in metal hydrazide chemistry at all. While the OC(O)N(NR₂)C(O)O moiety in **2a** and **2b** is a new structural unit in transition metal chemistry, we note Chirik's recent reports of metal-bound 1,1- or 1,2-NN(CO₂)₂ ligands prepared from metallocene–N₂ complexes and CO₂.^{28,29}

When the reaction between 2a and CO₂ was followed by ¹H NMR an intermediate cycloaddition product 3a (Scheme 1) was observed. Subsequent scale up led to isolated 3a in 54% yield. Reaction of 3a with CO₂ quantitatively forms 2a. No intermediate analogous to 3a was observed for 1b at room temperature. The stepwise formation of 2a from 1a *via* 3a suggested that mixed Ti=N_{α} insertion products should be accessible. Reaction of 1a with TolNCO gave 4a (Scheme 1), and subsequent addition of CO₂ to 4a gave the mixed double insertion product 5a in 37% isolated yield (quantitative when followed by ¹H NMR). The IR spectrum of 5a shows ν (C=O) and ν (C=N_{Tol}) bands at 1699 and 1628 cm⁻¹, respectively.



Compounds **2a**, **2b** and **5a** form *via* a cycloaddition–insertion mechanism leading to new homo-coupled and cross-coupled products. As shown in eqn (1) we have also discovered another type of Ti= N_{α} insertion reaction starting from the previously reported Ti(N_2N^{Me})(NNPh₂)(py) (6) mentioned in the introductory paragraphs. In this case a single molecule of Ar^FCN ($Ar^F = C_6F_5$) has inserted into the Ti= N_{α} bond of **6** forming the hydrazonamide derivative **7**. The solid state structure of **7** (Fig. 3) confirmed the formation of the new hydrazonamide fragment NC(Ar^F)NNPh₂. The Ti(1)–N(1) distance of 1.781(1) Å is consistent with substantial multiple bond character, and is only slightly longer than Ti= N_{α} (1.733(5) Å) in **6** itself.

Compound 7 is the first example of a terminal hydrazonamide complex. Mono- and di-metallated hydrazonamides have been reported by sequential reaction of $AlMe_3$ or dialkyl zincs with Me_2NNH_2 and MeCN,^{30,31} but formed polynuclear



Fig. 3 Displacement ellipsoid plot (20%) of $Ti(N_2N^{Me})$ -{ $NC(Ar^F)NNPh_2$ }(py) (7). Ti(1)-N(1) 1.781(1), Ti(1)-N(4) 1.964(1), Ti(1)-N(5) 1.964(1), C(1)-N(1) 1.338(2), C(1)-N(2) 1.308(2), C(1)-C(2) 1.514(2), N(2)-N(3) 1.441(2) Å.

clusters. Since the metal-bound hydrazonamide moiety in 7 still possesses a Ti=N multiple bond, further reaction chemistry of this moiety should be possible, allowing development of this hitherto unexplored functional group.

The reactions of metal hydrazido (or indeed imido) complexes with nitriles are almost without precedent, and only one previous system has been described (eqn (2)).^{21,32} This leads to the dimeric products **9** on reaction of $Ti(N_2N^{py})(NR)(py)$ (**8**, **R** = 'Bu or NPh₂) with MeCN. Terminal hydrazonamides analogous to **7** were not observed. Interestingly, when **6** was reacted with MeCN or PhCN equilibrium mixtures of unreacted starting materials and unidentified product(s) were observed.

To probe the factors and mechanism leading to the formation of the insertion product 7, we carried out DFT(B3PW91) calculations[†] on the model system $Ti(N_2^{SiH_3}N^{Me})(NNMe_2)(py)$ (6Q, $N_2^{SiH_3}N^{Me} = MeN(CH_2CH_2NSiH_3)_2)$ and Ar^FCN (Fig. 4). All energies given in the text are Gibbs free energies (T = 298 K, P = 1 atm) estimated from separated 6Q and nitrile.



The reaction of **6Q** with $Ar^{F}CN$ starts with dissociation of py leading to **Int1**. This process, unfavorable by $\Delta G =$ 9.4 kcal mol⁻¹, generates a vacant site for coordination of $Ar^{F}CN$. Two different orientations are possible for the η^{2} - $Ar^{F}CN$ adduct, namely **Int2** (with Ar^{F} towards NNMe₂, see Fig. 4) and **Int2b** (with N toward NNMe₂, not shown in Fig. 4). **Int2** is more stable than **Int2b** by 6.0 kcal mol⁻¹, and only **Int2** was considered in the mechanism. From this intermediate, [2+2] cycloaddition to form the diaza-metallacycle **Int3** is thermodynamically favored ($\Delta G = -7.3$ kcal mol⁻¹) with a low activation barrier ($\Delta G^{\#} = 6.5$ kcal mol⁻¹). The Ti–N_{nitrile} distance in **Int3** is 0.22 Å shorter than Ti–N_{α} (Fig. 4), while C–N_{α} and C–N_{nitrile} distances have similar values (1.35 and



Fig. 4 Energy profile for reaction of $\text{Ti}(N_2^{\text{SiH}_3}\text{N}^{\text{Me}})(\text{NNMe}_2)(\text{py})$ (6Q) with $\text{Ar}^{\text{F}}\text{CN}$. All energies are ΔG in kcal mol^{-1} . [Ti] = $\text{Ti}(N_2^{\text{SiH}_3}\text{N}^{\text{Me}})$.

1.32 Å, respectively). Ring-opening of Int3 (*via* Int4) and coordination of pyridine is exoergic by $\Delta G = -3$ kcal mol⁻¹ and yields 7Q (a model for the product 7 observed experimentally).

The reactions of 6Q with MeCN and PhCN were also examined computationally. In contrast to the situation with the fluorinated substrate, the products of MeCN (70 Me) and PhCN (7Q_Ph) insertion into the Ti= N_{α} bond were computed to be endoergic ($\Delta G = 3.1 \text{ kcal mol}^{-1}$ for MeCN; 5.1 kcal mol⁻¹ for PhCN). The η^2 -RCN adducts (Int2_Me and Int2_Ph) and the cycloaddition products (Int3_Me and Int3_Ph) have also energies above those of the reactants ($\Delta G = 6.3$ kcal mol⁻¹ for Int2 Me; $\Delta G = 8.5$ kcal mol⁻¹ for Int2 Ph; $\Delta G =$ 0.2 kcal mol⁻¹ for Int3_Me; $\Delta G = 3.2$ kcal mol⁻¹ for Int3_Ph). There is thus no thermodynamic driving force towards formation of the insertion products 7Q Me or 7Q Ph. This could explain the experimental observation of equilibrium mixtures of products and starting materials in the reactions of the real system 6 with MeCN and PhCN. Note that self-trapping (dimerisation) of species of the type Int3 would lead to dimeric compounds such as 9 (eqn (2)) observed experimentally. An NBO analysis of the electronic structure of 7Q indicated that the electron-withdrawing character of the Ar^F group plays a crucial role in formation of the insertion product through stabilisation of the N_{α} lone pair. Accordingly, the insertion product with CF₃CN (7Q CF₃) was computed to lie below separated **6Q** and CF₃CN by $\Delta G = -11.6$ kcal mol⁻¹.

The proposed mechanism is reminiscent of a classical Chauvin-type metathesis reaction,³³ in that it proceeds through [2+2] cycloaddition (**Int3**) and reverse cycloaddition steps, leading to **7Q**. However, whereas in alkyne or alkene metathesis (mediated through metal alkylidyne or alkylidene species), separation of the bond-exchanged partners can occur, this does not happen in the reactions of hydrazides and nitriles since the required species, $Ti(N_2N^{Me})(py)(=N^{\bullet})$ and $Me_2NN=C^{\bullet}Ar^{F}$, are evidently radical-like in nature. Thus eqn (1) and Fig. 4 can be thought of as an "arrested" or "frustrated" $Ti=N/C\equiv N$ metathesis reaction.

In conclusion, we have reported the first $M = N_{\alpha}$ insertion reactions of any transition metal hydrazide. Two different mechanisms have been observed: (i) cycloaddition-insertion leading to homo- or cross-coupled bis(heterocumulene) derivatives; (ii) "arrested" metathesis giving single-substrate insertion, again with $Ti = N_{\alpha}$ bond cleavage. In this latter case (7, eqn (1)), a new Ti = N multiple bond is formed which could in principle be a site of additional functionalisation. These results will be of benefit in developing Group 4 based substrate functionalisation chemistry *via* hydrazide intermediates.

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