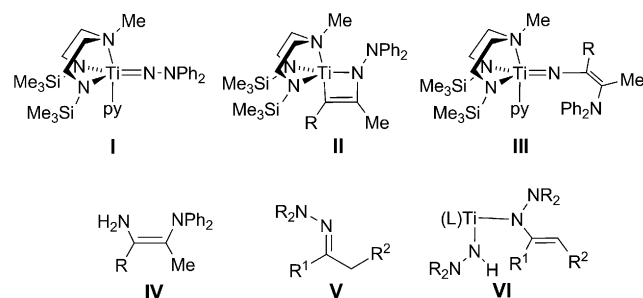


A Remarkable Switch from a Diamination to a Hydrohydrazination Catalyst and Observation of an Unprecedented Catalyst Resting State**

Andrew D. Schwarz, Chee S. Onn, and Philip Mountford*

Group 4 imido complexes, $(L)M=NR$,^[1] and, more recently, hydrazido complexes, $(L)M=NNR_2$,^[2] undergo a range of addition or insertion reactions of their $M=N$ multiple bonds with many unsaturated and saturated substrates. This reactivity has led to a number of new bond-forming methodologies. In the case of hydrazides, reductive cleavage of the $N_\alpha-N_\beta$ bond can also occur with formally oxidizable substrates, such as CO,^[2b] isocyanides,^[2g,o] and alkynes,^[2j,m] in the presence of suitably activating supporting ligand sets, such as bis(cyclopentadienyl) and diamide–amine types. We recently found^[2l,m] that the hydrazide complex **I** (Scheme 1) and

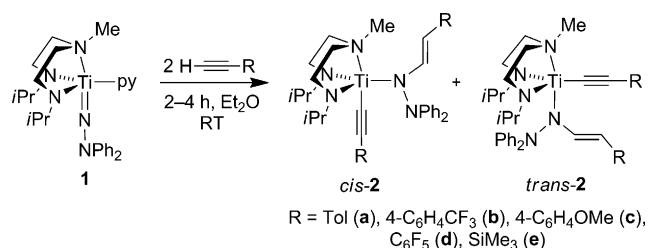


Scheme 1. Structures of the alkyne-diamination catalyst **I**, intermediates **II** and **III**, and products **IV**, as well as the proposed conventional intermediate in alkyne hydrohydrazination **VI** and the product hydrazone **V**. py = pyridine.

certain homologues react with terminal or internal alkynes to form metallacycles of the type **II**. In the case of **I**, these metallacycles cannot be isolated but proceed immediately at temperatures below 0 °C to form exclusively vinyl imides **III**. Furthermore, both **I** and **III** catalyze the 1,2-diamination of terminal alkynes to form diaminoalkenes **IV**.^[2j] This transformation is a new reaction of hydrazines with alkynes, which usually undergo hydrohydrazination, also via postulated metallacycles of the type **II**.^[1e,2c,d,3] These metallacycles undergo protonolysis of the Ti–C and Ti–N bonds to form hydrazones **V** via transient mixed bis(hydrazido(1–)) inter-

mediates **VI**. The more widely studied hydroamination reaction of alkynes, alkenes, and allenes with Group 4 metals^[1c,e,4] has been explored in a series of elegant mechanistic and computational^[3b,5] studies. Three mechanisms have been established: the “imide route” (the most common) through a [2+2] cycloaddition reaction of an $M=NR$ bond,^[3a,6] the “amide route” through substrate migratory insertion into an $M-NRR'$ amide bond,^[7] and a proton-assisted C–N bond-forming mechanism via an amide intermediate.^[8]

We have recently been developing further the chemistry of compounds of the type **I** and its homologues.^[2m,o,9] As part of this program we prepared the closely related compound $[Ti(N_2^{iPr}N)(NNPh_2)(py)]$ (**1**; $N_2^{iPr}N = MeN(CH_2CH_2NiPr)_2$) containing sterically less demanding isopropyl substituents in the ligand periphery in place of the SiMe₃ groups in **I**. Compound **1** was prepared in 72 % yield from $Li_2N_2^{iPr}N$ and $[Ti(NNPh_2)Cl_2(py)_3]$. The solid-state structure^[10] (see the Supporting Information) establishes the trigonal-bipyramidal geometry shown in Scheme 2. This geometry is also predom-



Scheme 2. Reaction of $[Ti(N_2^{iPr}N)(NNPh_2)(py)]$ (**1**) with terminal alkynes.

inantly maintained in solution according to NOE experiments. The hydrazide ligand in the solid-state structure of **1** occupies the electronically preferred^[11] axial position *trans* to the NMe donor, whereas in **I** it lies exclusively in the equatorial position, which is the sterically preferred site. Minor resonances in the ¹H NMR spectrum of **1** are attributed to the isomer with NNPh₂ in the equatorial position.

The treatment of **1** with HCCTol (1 equiv; Tol = 4-C₆H₄Me) in C₆D₆ led to 50 % conversion of **1** and complete conversion of the alkyne into a new compound, **2a**. A second reaction with a 2:1 ratio of the alkyne to **1** gave quantitative conversion into **2a**, which was isolated in 91 % yield when the reaction was scaled up and carried out in Et₂O. Compound **2a** is the unusual acetylide–vinylhydrazide(1–) compound $[Ti(N_2^{iPr}N)(CCTol)\{N(NPh_2)C(H)C(H)Tol\}]$ illustrated in

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Scheme 2. In solution it exists as two isomers with the vinylhydrazone moiety *cis* or *trans* to the NMe donor of $N_2^{iPr}N$, as established by NOE measurements (the ratio of *cis*-**2a** to *trans*-**2a** is ca. 10:1).

The isomer *cis*-**2a** was structurally characterized by X-ray crystallography (Figure 1).^[10] The distances and angles associated with the various ligand fragments and with the titanium

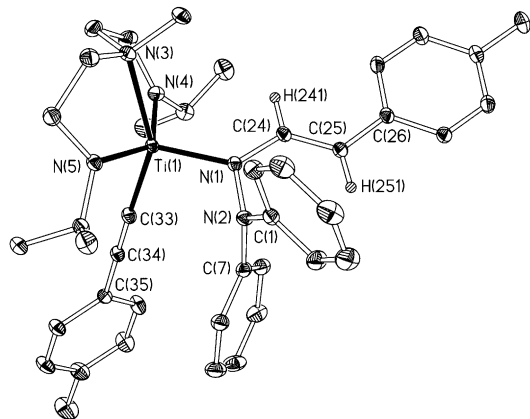


Figure 1. Displacement ellipsoid plot (20% probability level) of $[Ti(N_2^{iPr}N)(CCTol)\{N(NPh_2)C(H)C(H)Tol\}]$ (*cis*-**2a**). H atoms are omitted, except for the vinylic atoms.

center itself are within the usual ranges.^[12] Isomer *cis*-**2a** may be thermodynamically favored on steric grounds, as it positions the bulkier $N(NPh_2)C(H)C(H)Tol$ group furthest from the isopropyl substituents of $N_2^{iPr}N$. Single crystals of *cis*-**2a** immediately reform the equilibrium mixture of *cis* and *trans* isomers in solution. The vinylic hydrogen atoms of the vinylhydrazone moiety in *cis*-**2a** (H(241) and H(251) in Figure 1) appear as mutually coupled doublets at $\delta = 7.99$ and 5.79 ppm, respectively, in the 1H NMR spectrum. The absence of these 1H resonances in the isotopomer $[Ti(N_2^{iPr}N)(CCTol)\{N(NPh_2)C(D)C(D)Tol\}]$ ($[D_2]cis$ -**2a**) prepared from **1** and DCCTol (the expected resonances are present in the D NMR spectrum) shows that both of these hydrogen atoms are derived from the alkyne.

Compound **1** also reacted immediately and quantitatively in C_6D_6 with HCCR ($R = 4-C_6H_4CF_3$, $4-C_6H_4OMe$, C_6F_5 , or $SiMe_3$) to form the corresponding *cis* and *trans* analogues of **2a** (Scheme 2). These compounds were isolated in good to excellent yield when the reactions were scaled up. In contrast, HCC*t*Bu did not react with **1** at room temperature or on heating, whereas HCC*n*Bu, PhCCMe, and MeCCMe gave unidentified mixtures. Compounds **2a–e** are stable in solution in C_6D_6 over a number of days at room temperature but decompose on heating (e.g., the half-life for the decomposition of **2a** at 70 °C is ca. 3 h).

Formation of the acetylide–vinylhydrazides **2a–e** probably proceeds by [2+2] cycloaddition reactions of **1** (or its pyridine-free analogue) via intermediate metallacycles of the type $[Ti(N_2^{iPr}N)\{N(NPh_2)C(H)C(R)\}]$ (*cis*- or *trans*-**3**; Scheme 3) as observed and/or isolated previously for **II** (Scheme 1) or its homologues.^[2m] The subsequent reaction of *cis*- or *trans*-**3** with HCCR through a σ -bond-metathesis

reaction of $Ti-C(R)$ would furnish *cis*- or *trans*-**2**, respectively. In an attempt to identify an intermediate species, we followed the reaction between **1** and $HCC-4-C_6H_4OMe$ in $[D_8]toluene$ from $-70^\circ C$ to room temperature. No intermediates were observed; however, interestingly, the first-formed product was *trans*-**2c**, which was then converted predominantly into *cis*-**2c** as room temperature was approached. This observation may suggest that the kinetically preferred reaction proceeds via *trans*-**3** at the σ -bond-metathesis step. An alternative reaction sequence based on alkyne C–H bond activation via $[Ti(N_2^{iPr}N)(CCR)\{NH(NPh_2)\}]$ (**4**) and then alkyne insertion into the $Ti-N(H)NPh_2$ bond to form $[Ti(N_2^{iPr}N)(CCR)\{C(R)C(H)N(H)NPh_2\}]$ (**5**), followed by the isomerization of **5** to form **2** is considered unlikely. Although alkyne C–H addition to titanium–ligand multiple bonds (titanocene imido, oxo, vinylidene bonds)^[13] and alkyne insertion into early-transition-metal–nitrogen single bonds^[7e,14] have precedent, these reactions are very rare.

No apparent reaction occurred when **2a** was treated with a further equivalent of HCCTol or DCCTol. The latter experiment shows that the formation of **2a** from the likely metallacycle intermediate is irreversible. However, when a solution of **2a** was treated with $HCC-4-C_6H_4CF_3$ (1 equiv), an equilibrium mixture of this alkyne, HCCTol, **2a**, and a species tentatively assigned as $[Ti(N_2^{iPr}N)(CC-4-C_6H_4CF_3)\{N(NPh_2)C(H)C(H)Tol\}]$ was formed, probably by a σ -bond-metathesis reaction as proposed for the formation of compounds **2** from intermediate metallacycles **3**.

A reaction of **1** with a mixture of HCCTol and DCCTol (**1**/HCCTol/DCCTol = 1.0:1.5:1.5) was also carried out in an NMR tube. The 1H and D NMR spectra of the organometallic product mixture showed the presence of a mixture of four isotopomers of the form $[Ti(N_2^{iPr}N)(CCTol)\{N(NPh_2)C_24-(H_aD_b)C_25(H_xD_y)Tol\}]$, in which $(a+b) = (x+y) = 1$ and C24 and C25 are labeled according to the numbering scheme in Figure 1. For C24, there was an equal amount of 1H and D attached on average ($a/b = 1$). This result implies, as expected, that there is no significant kinetic isotope effect (KIE) for the formation of the intermediate metallacycles **3a** or $[D]3a$ from **2a** and either HCCTol or DCCTol, respectively. In contrast, there was a significantly higher extent of H attachment to C25 as compared to D attachment ($x/y = 2.4(1)$ on the basis of 1H and D spectroscopic analysis); thus, a KIE value of 2.4(1) was obtained for the σ -bond-metathesis process leading from **3a** to **2a**.

Although Group 4 imide- and hydrazide-derived azametallacyclobutene species $(L)M\{N(R)C(R^1)C(R^2)\}$ are now quite well established, and unsaturated substrates can be inserted into the $M-C$ bond,^[1c,e,2e,f,o] a subsequent σ -bond-metathesis reaction has never been observed.^[15] As mentioned, catalytic hydrohydrazination and hydroamination reactions of alkynes by the “imide route” are proposed to proceed via transient species of the type **VI** (Scheme 1) containing hydrazido(1–) (or amido) and vinylhydrazido(1–) (or vinylamido) ligands formed by R_2N-H protonolysis of the $M-C(R^1)$ bond of the precursor metallacycle. Compounds **2a–e** can be viewed as the first arrested models of this type of N-bound vinylhydrazido(1–) moiety. The research groups of Odom^[14a] and Schafer^[7e] reported complementary C,N-bound

aminovinyl complexes formed by alkyne insertion into a high-energy Mo–NMe₂ or Zr–NMe₂ amide moiety, respectively. Alkyne insertion into Zr–NMe₂ is relevant to alkyne hydroamination by the “amide route”.

Preliminary experiments have shown that **1** is a catalyst for the hydrohydrazination of certain terminal alkynes with Ph₂NNH₂ [Eq. (1) and Table 1]. This reactivity contrasts

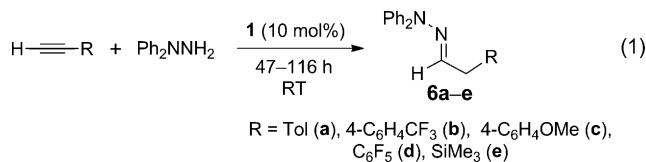


Table 1: Hydrohydrazination of alkynes HCCR with Ph₂NNH₂ and [Ti(N₂^{ipr}N)(NNPh₂)(py)] (**1**).^[a]

Entry	Alkyne R group	Reaction time [h]	<i>k</i> _{obs} [h ^{−1}] ^[b]	Conversion [%] ^[c]	Yield [%] ^[d]
1	4-C ₆ H ₄ Me	48	6.8(3) × 10 ^{−2}	96	90
2	4-C ₆ H ₄ CF ₃	68	4.7(2) × 10 ^{−2}	94	75
3	4-C ₆ H ₄ OMe	47	4.2(1) × 10 ^{−2}	74	58
4	4-C ₆ H ₄ CF ₃	47	—	91	—
5	C ₆ F ₅	116	0.66(5) × 10 ^{−2}	55	40
6	C ₆ F ₅	45	—	20	—
7	SiMe ₃	65	4.4(1) × 10 ^{−2}	95	73
8	<i>t</i> Bu	116	0	0	0

[a] Reactions were carried out in C₆D₆ with a 10 mol% loading of **1**.

[b] The rate constant *k*_{obs} was determined on the basis of first-order rate plots (*R*² = 0.995–0.996) for ≥ 90% substrate consumption, except for the reaction in entry 3, which showed significant decay of the catalyst after 27 h (67% conversion, *R*² = 0.997; no further reaction beyond 47 h), and the reaction in entry 6 (116 h, 55% conversion, *R*² = 0.974).

[c] Conversion was determined by NMR spectroscopy by integration of the hydrazine and/or alkyne, and hydrazone resonances. [d] Yield of the isolated product after purification by column chromatography.

remarkably with that of the SiMe₃-substituted homologue **I** (Scheme 1), which is a 1,2-diamination catalyst under these conditions.^[21,16] The catalysis is totally specific for the formation of the anti-Markovnikov hydrazones **6a–e**, as confirmed for (*E*)-HC(NNPh₂)CH₂–4-C₆H₄CF₃ (**6b**) by X-ray crystallography (see the Supporting Information).^[10]

The catalysis is relatively slow at room temperature. The best conversions were observed for **6a**, **6b**, and **6c**: 91–95% conversion after 47–68 h at room temperature with a catalyst loading of 10 mol%. However, with the exception of a system reported recently by Gade,^[3d] these performances are not untypical of titanium hydrohydrazination catalysts at room temperature.^[2c,d,3c] All systems showed first-order consumption of the hydrazine (see Figure 2 for the reaction with HCC–4-C₆H₄CF₃ and Figure S3 in the Supporting Information for HCCTol). For **6c**, the catalyst system seemed to degrade after approximately 1 day, whereas with HCCC₆F₅, the catalysis was about an order of magnitude slower.

We monitored the reactions in Equation (1) by NMR spectroscopy and found that the acetylide–vinyl hydrazido compounds **2a–e** were the only titanium species observed and were present throughout the catalytic process. Furthermore,

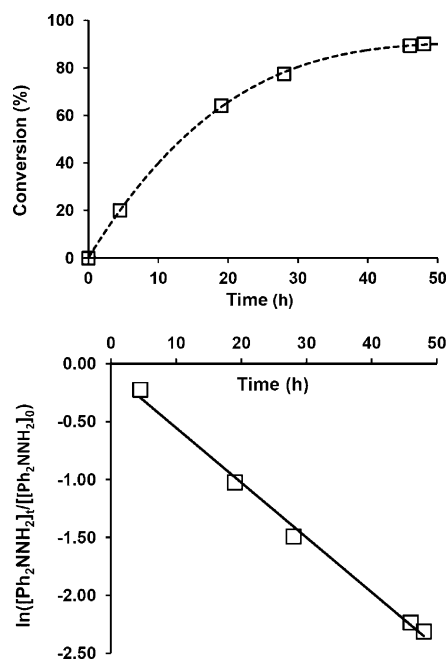
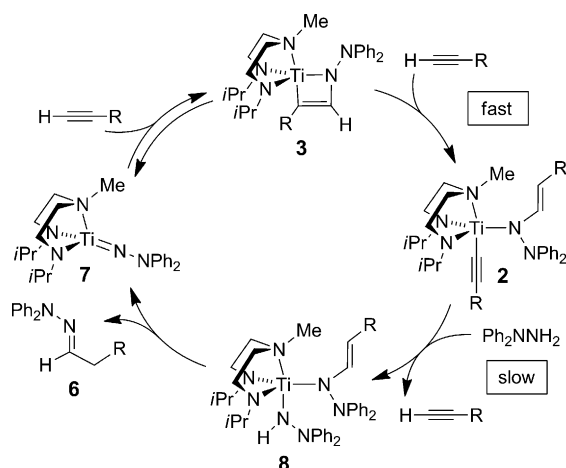


Figure 2. Plot of hydrazine conversion into the hydrazone (top, dotted line drawn as an aid to the eye) and the corresponding first-order ln plot of hydrazine consumption (bottom, linear regression fit, *k*_{obs} = 4.7(2) × 10^{−2} h^{−1}). Data are for the hydrohydrazination of HCC–4-C₆H₄CF₃ with Ph₂NNH₂ and [Ti(N₂^{ipr}N)(NNPh₂)(py)] (**1**; C₆D₆, room temperature, 10 mol% catalyst loading).

when the same catalytic reaction of HCCTol and Ph₂NNH₂ was carried out with **2a** (10 mol%) as the added catalyst rather than **1**, the reaction proceeded at approximately the same rate to form **6a**, and once again **2a** was the only titanium species observed. Further experiments in NMR tubes showed that the reaction of **2a** with 1 equivalent of Ph₂NNH₂ liberated 1 equivalent of **6a** and consumed 0.5 equivalents of **2a** in accordance with Scheme 3.^[17] The corresponding reaction with XylOH (Xyl = 2,6-C₆H₃Me₂) immediately formed HCCTol (no **6a** was formed), which is consistent with preferential protonolysis of the Ti–CCTol moiety of **2a** over [Ti–N(NNPh₂)C(H)C(H)Tol]. The metal product of this reaction was not identified, but the kinetically favored protonation of **2** at the Ti–C(sp) bond is reminiscent of the well-established protonation reactions of [2+2] Group 4 metallacycles at the M–C(sp²) bond during hydroamination/hydrohydrazination catalysis.

Overall, these results are consistent with the catalytic cycle shown in Scheme 3. Alkyne [2+2] cycloaddition to base-free **7** (previously established as an intermediate in 1,2-diamination reactions catalyzed by **I**) forms transient **3**, which, in turn, rapidly forms **2**. Alternatively, the cycle can be entered directly from **2**. Protonolysis of Ti–CCR forms **8**, analogous to the intermediates (e.g. **VI**, Scheme 1) proposed in direct reactions of metallacycles with hydrazines or amines. Finally, elimination from **8** generates the hydrazone **6**. Since the rates of the reactions in Scheme 2 of **1** with HCCR to form **2a–e** are effectively independent of R, whereas hydrohydrazination with R = C₆F₅ is approximately 10 times slower (owing to the lower basicity of the acetylenic carbon atom in



Scheme 3. Proposed mechanism for the catalytic hydrohydrazination of alkynes via $[\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{CCR})\{\text{N}(\text{NPh}_2)\text{C}(\text{H})\text{C}(\text{H})\text{R}\}]$ (**2**). Only the *cis* isomers of **2**, **3**, and **6** are illustrated for clarity. Compound **5** may also be formed by pyridine loss from **1** (this step is omitted for clarity).

2d), the turnover-limiting step (TLS) appears to be from **2** to **8**. This conclusion is also consistent with the observation that **2** is the resting state.

These results alone do not rule out the direct conversion of **3** into **8** as proposed in the conventional “imide” mechanism for alkyne hydroamination, although such a transformation seems unlikely from our observations that 1) **2** is an active (pre)catalyst; 2) **2** is also the resting state of the titanium in the system; 3) the formation of **3** from **2** does not occur (according to labeling studies). To probe this possibility further, we carried out a stoichiometric competition reaction of **1** with HCCTol and Ph_2NNH_2 (1:1:1 molar ratio) in an NMR tube. All of the HCCTol and half of **1** were immediately converted into **2a**. No hydrazone **6a** was formed and no hydrazine was consumed until 30 min after consumption of the alkyne to form **2**. Therefore, in the presence of equimolar amounts of the alkyne and the hydrazine (the ratio used in the catalytic reactions, Table 1), the formation of **2a** from **3a** is much faster than a possible reaction of **3a** with Ph_2NNH_2 to form **8a**. This result is consistent with the observations we made when we monitored the catalytic reactions by NMR spectroscopy: complete conversion of all of the starting **1** into **2** occurred well in advance of the appearance of any hydrazone.

In previous mechanistic and computational studies of hydroamination catalysis by an imide mechanism, both the [2+2] cycloaddition and subsequent protonation of the metallacycle have been proposed to be the TLS (as well as the generation of the free imido species $(\text{L})\text{M}=\text{NR}$ from a bis(amide) or dimeric resting state), depending on the system under study.^[3a,b,5,6] In our system, it is apparent that the reaction of **3** with the alkyne to form **2** is significantly faster than that of **7** with the alkyne, and the protonolysis of **2** is considerably slower than the conversion of **1** into **2**.

We carried out additional experiments to investigate further the contribution of steps $7 \rightarrow 3$, $3 \rightarrow 2$, and $2 \rightarrow 8$ to the overall rate of hydrohydrazination. When the experiment with $[\text{HCCTol}]_0/[\text{Ph}_2\text{NNH}_2]_0/[\mathbf{1}]_0 = 10:10:1$ (Table 1, entry 1;

$k_{\text{obs}} = 6.8(3) \times 10^{-2} \text{ h}^{-1}$) was repeated with $[\text{HCCTol}]_0/[\text{Ph}_2\text{NNH}_2]_0/[\mathbf{1}]_0 = 5:10:1$ (i.e., a 50 % decrease in the alkyne loading) the experimental k_{obs} value was identical ($6.7(1) \times 10^{-2} \text{ h}^{-1}$; see Figure S3 in the Supporting Information), which indicates that the k_{obs} value and the TLS are independent of $[\text{alkyne}]_t$. The use of monodeuterated tolyl acetylene with $[\text{DCCTol}]_0/[\text{Ph}_2\text{NNH}_2]_0/[\mathbf{1}]_0 = 10:10:1$ gave $k_{\text{obs}(\text{D})\text{alkyne}} = 6.2(3) \times 10^{-2} \text{ h}^{-1}$ (the KIE value based on HCCTol and DCCTol is 1.1(1); Figure 3, top); again no experimentally significant effect of the deuterated alkyne on the overall reaction rate was found (recall that we showed independently above that the (fast) σ -bond-metathesis step $3\text{a} \rightarrow 2\text{a}$ has a KIE value of 2.4(1)).

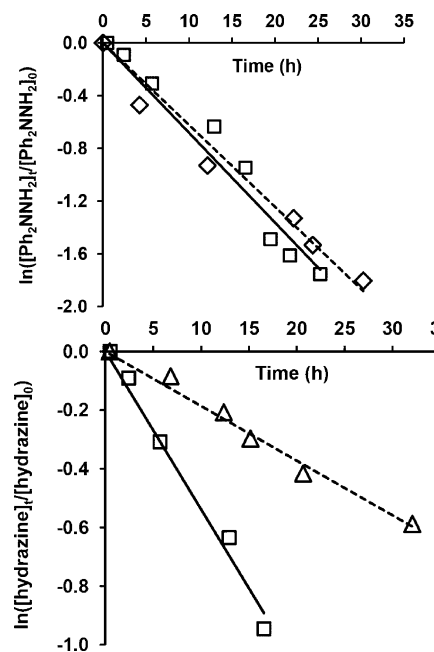


Figure 3. Top: First-order \ln plot of hydrazine conversion and linear regression fits for the hydrohydrazination of HCCTol (squares and solid line, $k_{\text{obs}} = 6.8(3) \times 10^{-2} \text{ h}^{-1}$) and DCCTol (diamonds and dotted line, $k_{\text{obs}} = 6.2(3) \times 10^{-2} \text{ h}^{-1}$) with Ph_2NNH_2 . Bottom: Corresponding first-order plots of hydrazine conversion and linear regression fits for the hydrohydrazination of HCCTol with Ph_2NNH_2 (squares and solid line, $k_{\text{obs}} = 6.8(3) \times 10^{-2} \text{ h}^{-1}$) and Ph_2NND_2 (triangles and dotted line, $k_{\text{obs}} = 1.9(1) \times 10^{-2} \text{ h}^{-1}$). All experiments were carried out with $[\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NNPh}_2)(\text{py})]$ (**1**; C_6D_6 , room temperature, 10 mol % catalyst loading).

In contrast, use of the *N*-dideuterated hydrazine with $[\text{HCCTol}]_0/[\text{Ph}_2\text{NND}_2]_0/[\mathbf{1}]_0 = 10:10:1$ gave $k_{\text{obs}(\text{D})\text{hydrazine}} = 1.9(1) \times 10^{-2} \text{ h}^{-1}$, which corresponds to a significant KIE value of 3.7(2) based on Ph_2NNH_2 and Ph_2NND_2 (Figure 3, bottom). Taken together, these results imply a tentative rate expression of $d[\text{hydrazone}]/dt = k_{\text{obs}}[\text{Ph}_2\text{NNH}_2]$. Further studies are in progress to fully characterize the k_{obs} term, but our results unambiguously establish $2 \rightarrow 8$ as the TLS for the hydrazines and alkynes studied to date with **1**.

The high selectivity of the catalytic process is controlled by the sense of addition of the alkyne to the $\text{Ti}=\text{NNPh}_2$ bond of **3** as found in related systems.^[1c,3b,4d,18] We have explained

the origin of this preference previously in the 1,2-diamination reactions of **1** with alkynes.^[2m] The lack of reaction of **1** with HCCtBu is attributed to the unfavorable energy of formation of the metallacycle **3** with the bulky, electron-releasing *tert*-butyl substituent, which destabilizes the electron-rich metallacycle.^[2m]

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- [1] a) D. E. Wigley, *Prog. Inorg. Chem.* **1994**, *42*, 239; b) P. Mountford, *Chem. Commun.* **1997**, 2127; c) A. P. Duncan, R. G. Bergman, *Chem. Rec.* **2002**, *2*, 431; d) N. Hazari, P. Mountford, *Acc. Chem. Res.* **2005**, *38*, 839; e) A. L. Odom, *Dalton Trans.* **2005**, 225; f) P. D. Bolton, P. Mountford, *Adv. Synth. Catal.* **2005**, *347*, 355; g) A. R. Fout, U. J. Kilgore, D. J. Mindiola, *Chem. Eur. J.* **2007**, *13*, 9428.
- [2] A range of new hydrazide reactions have been reported in the last 7–8 years in particular. For early landmark studies and more recent examples, see: a) D. J. Mindiola, *Angew. Chem.* **2008**, *120*, 1580; *Angew. Chem. Int. Ed.* **2008**, *47*, 1557; b) P. J. Walsh, M. J. Carney, R. G. Bergman, *J. Am. Chem. Soc.* **1991**, *113*, 6343; c) C. Cao, Y. Shi, A. L. Odom, *Org. Lett.* **2002**, *4*, 2853; d) Y. Li, Y. Shi, A. L. Odom, *J. Am. Chem. Soc.* **2004**, *126*, 1794; e) S. Banerjee, A. L. Odom, *Organometallics* **2006**, *25*, 3099; f) A. A. Dissanayake, A. L. Odom, *Chem. Commun.* **2012**, *48*, 440; g) H. Herrmann, J. L. Fillol, H. Wadepohl, L. H. Gade, *Angew. Chem.* **2007**, *119*, 8578; *Angew. Chem. Int. Ed.* **2007**, *46*, 8426; h) T. Gehrman, J. L. Fillol, H. Wadepohl, L. H. Gade, *Angew. Chem.* **2009**, *121*, 2186; *Angew. Chem. Int. Ed.* **2009**, *48*, 2152; i) T. Gehrman, M. Kruck, H. Wadepohl, L. H. Gade, *Chem. Commun.* **2012**, *48*, 2397; j) T. Gehrman, S. A. Scholl, J. L. Fillol, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2012**, *18*, 3925; k) A. J. Blake, J. M. McInnes, P. Mountford, G. I. Nikonov, D. Swallow, D. J. Watkin, *J. Chem. Soc. Dalton Trans.* **1999**, 379; l) J. D. Selby, C. D. Manley, M. Feliz, A. D. Schwarz, E. Clot, P. Mountford, *Chem. Commun.* **2007**, 4937; m) A. D. Schofield, A. Nova, J. D. Selby, C. D. Manley, A. D. Schwarz, E. Clot, P. Mountford, *J. Am. Chem. Soc.* **2010**, *132*, 10484; n) P. J. Tjong, A. D. Schofield, J. D. Selby, A. Nova, E. Clot, P. Mountford, *Chem. Commun.* **2010**, *46*, 85; o) A. D. Schofield, A. Nova, J. D. Selby, A. D. Schwarz, E. Clot, P. Mountford, *Chem. Eur. J.* **2011**, *17*, 265; p) P. J. Tjong, A. Nova, A. D. Schwarz, J. D. Selby, E. Clot, P. Mountford, *Dalton Trans.* **2012**, *41*, 2277.
- [3] a) J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923; b) A. Tillack, H. Jiao, I. Garcia Castro, C. G. Hartung, M. Beller, *Chem. Eur. J.* **2004**, *10*, 2409; c) S. Banerjee, E. Barnea, A. L. Odom, *Organometallics* **2008**, *27*, 1005; d) K. Weitershaus, H. Wadepohl, L. H. Gade, *Organometallics* **2009**, *28*, 3381.
- [4] a) S. Doye, *Synlett* **2004**, 1653; b) K. C. Hultsch, *Adv. Synth. Catal.* **2005**, *347*, 367; c) L. L. Schafer, A. V. Lee, *Eur. J. Inorg. Chem.* **2007**, 2243; d) T. E. Müller, K. C. Hultsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795.
- [5] a) B. F. Straub, R. G. Bergman, *Angew. Chem.* **2001**, *113*, 4768; *Angew. Chem. Int. Ed.* **2001**, *40*, 4632; b) S. Tobisch, *Dalton Trans.* **2006**, 4277; c) S. Tobisch, *Chem. Eur. J.* **2007**, *13*, 4884; d) C. Müller, R. Koch, S. Doye, *Chem. Eur. J.* **2008**, *14*, 10430; e) S. Tobisch, *Chem. Eur. J.* **2008**, *14*, 8590.
- [6] a) P. J. Walsh, A. M. Baranger, R. G. Bergman, *J. Am. Chem. Soc.* **1992**, *114*, 1708; b) A. M. Baranger, P. J. Walsh, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 2753; c) F. Pohlki, S. Doye, *Angew. Chem.* **2001**, *113*, 2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2305; d) L. E. N. Allan, G. J. Clarkson, D. J. Fox, A. L. Gott, P. Scott, *J. Am. Chem. Soc.* **2010**, *132*, 15308.
- [7] a) D. V. Gribkov, K. C. Hultsch, *Angew. Chem.* **2004**, *116*, 5659; *Angew. Chem. Int. Ed.* **2004**, *43*, 5542; b) P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2004**, 894; c) B. D. Stubbert, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 6149; d) S. Majumder, A. L. Odom, *Organometallics* **2008**, *27*, 1174; e) D. C. Leitch, C. S. Turner, L. L. Schafer, *Angew. Chem.* **2010**, *122*, 6526; *Angew. Chem. Int. Ed.* **2010**, *49*, 6382.
- [8] a) D. C. Leitch, R. H. Platel, L. L. Schafer, *J. Am. Chem. Soc.* **2011**, *133*, 15453; b) K. Manna, S. Xu, A. D. Sadow, *Angew. Chem.* **2011**, *123*, 1905; *Angew. Chem. Int. Ed.* **2011**, *50*, 1865.
- [9] a) J. D. Selby, C. D. Manley, A. D. Schwarz, E. Clot, P. Mountford, *Organometallics* **2008**, *27*, 6479; b) A. D. Schwarz, A. Nova, E. Clot, P. Mountford, *Chem. Commun.* **2011**, *47*, 4926; c) A. D. Schwarz, A. Nova, E. Clot, P. Mountford, *Inorg. Chem.* **2011**, *50*, 12155–12171.
- [10] CCDC 894174 (**1**), 894175 (**6b**), and 894176 (*cis-2a*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [11] B. D. Ward, G. Orde, E. Clot, A. R. Cowley, L. H. Gade, P. Mountford, *Organometallics* **2004**, *23*, 4444.
- [12] D. A. Fletcher, R. F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746 (The UK Chemical Database Service: CSD version 5.33 updated May 2012).
- [13] a) J. L. Polse, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 13405; b) J. L. Polse, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 5393; c) R. Beckhaus, J. Sang, T. Wagner, B. Ganter, *Organometallics* **1996**, *15*, 1176.
- [14] a) E. Katayev, Y. Li, A. L. Odom, *Chem. Commun.* **2002**, 838; b) P. J. Walsh, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1990**, *112*, 894.
- [15] We make a formal distinction between the metathesis reaction observed with C–H bonds and protonolysis-type chemistry well-known with N–H bonds.
- [16] J. D. Selby, DPhil thesis, University of Oxford **2009**.
- [17] Scheme 3 predicts that a stoichiometric reaction of Ph₂NNH₂ with **2a** should initially form base-free **7** (1 equiv), **6a** (1 equiv), and HCCtTol (1 equiv). However, the rapid reaction of **7** with the liberated HCCtTol (1:2 ratio) leads to the regeneration of **2a** (0.5 equiv) through the [2+2]/σ-bond-metathesis reaction.
- [18] I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2003**, 935.