Titanium Hydrazinediido Half-Sandwich Complexes: Highly Active Catalysts for the Hydrohydrazination of Terminal Alkynes at Ambient Temperature

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Reaction of [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] with 1 molar equiv of diphenylhydrazine yielded the hydrazinediido complex [Cp*Ti(N^{Xyl}N)(NNPh$_2$)($NH_2{}^t$Bu)] (**1a**), whereas the orange pyridine adduct [Cp*Ti(N^{Xyl}N)(NNPh$_2$)(py)] (**1b**) was obtained by reacting the imide [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] with diphenylhydrazine in the presence of pyridine. The *tert*-butylamine coordinated to the metal center in **1a** could be removed by heating the solid at 60 °C and 10^{-6} mbar for 72 h, yielding [Cp*Ti(N^{Xyl}N)(NNPh$_2$)] (**1c**). In the presence of pyridine or 4-dimethylaminopyridine (dmap) as neutral co-ligands the hydrazinediido complexes [Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (**2a**) and [Cp*Ti(N^{Xyl}N)-(NNMePh)(dmap)] (**2b**) as well as [Cp*Ti(N^{Xyl}N)(NNMe$_2$)(dmap)] (**3**) were prepared. Upon replacement of dmap by the weaker donor ligand pyridine in the synthesis of the pyridine adduct analogous to **3**, a mixture of [Cp*Ti(N^{Xyl}N)(NNMe$_2$)(py)] (**4a**) and the dinuclear complex [Cp*$_2$Ti$_2$(N^{Xyl}N)$_2$(μ-η^1,η^1-NNMe$_2$)(μ-η^1,η^2-NNMe$_2$)] (**4b**) was obtained. Reaction of the dimethylhydrazinediido complex **3** with phenylacetylene gave the Markovnikov cycloadduct, which had sufficient lifetime to allow its ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic characterization in solution. All three hydrazinediido compounds **1a**, **2a**, and **3** were found to display remarkable activities in catalytic hydrohydrazinations at ambient temperatures. For catalyst loadings of 5 mol % complete conversions of the terminal alkynes and diynes with Markovnikov regioselectivities of over 99% selectivity were observed within 1 h.

Introduction

The catalytic hydrohydrazination of alkynes provides an atom-economic access to hydrazones, which are potentially valuable reagents for further transformations.[1] Homogeneous catalysts employed for this reaction are titanium or zinc based, the latter allowing the tandem combination of hydrohydrazination and subsequent Fischer indole cyclization.[2−4] For all reported systems relatively harsh reaction conditions have been necessary for substituted acetylenes, with reaction temperatures of 75 to 120 °C. Alternative catalytic protocols for hydrazones employ more d-electron-rich transition metals, such as cobalt or manganese, for which the hydrazines are replaced by azodicarboxylates.[5]

Hydrazinediido complexes have been identified as active species in the titanium-catalyzed hydrohydrazination[6−11] and iminohydrazination[10,11] of alkynes and the subsequent transformation of the hydrazones into indoles[2,7,12−15] or tryptamine derivatives.[8] The postulated reaction mechanism of the group 4 metal-catalyzed reaction is based on the extensively studied mechanistic scheme for hydroaminations of alkynes, in which imido complexes are the key active species.

Given the considerable amount of published work on the structures and reactivity of imido group 4 metal compounds, the relative paucity of work on their corresponding hydrazides, in particular hydrazinediides, is remarkable. Despite a report of a hydrazinediidotitanium complex by Wiberg et al. as early as 1978,[16] the chemistry of this class of complexes has only begun to be developed further during the past decade, mainly through the work of Mountford[17−23] and Odom.[6,11,24] Access to the hydrazido(−1) and hydrazinediido complexes of the heavier group 4 metal homologues has been gained in the pioneering study by Bergman and co-workers[25] and in subsequent work from our group.[26−28]

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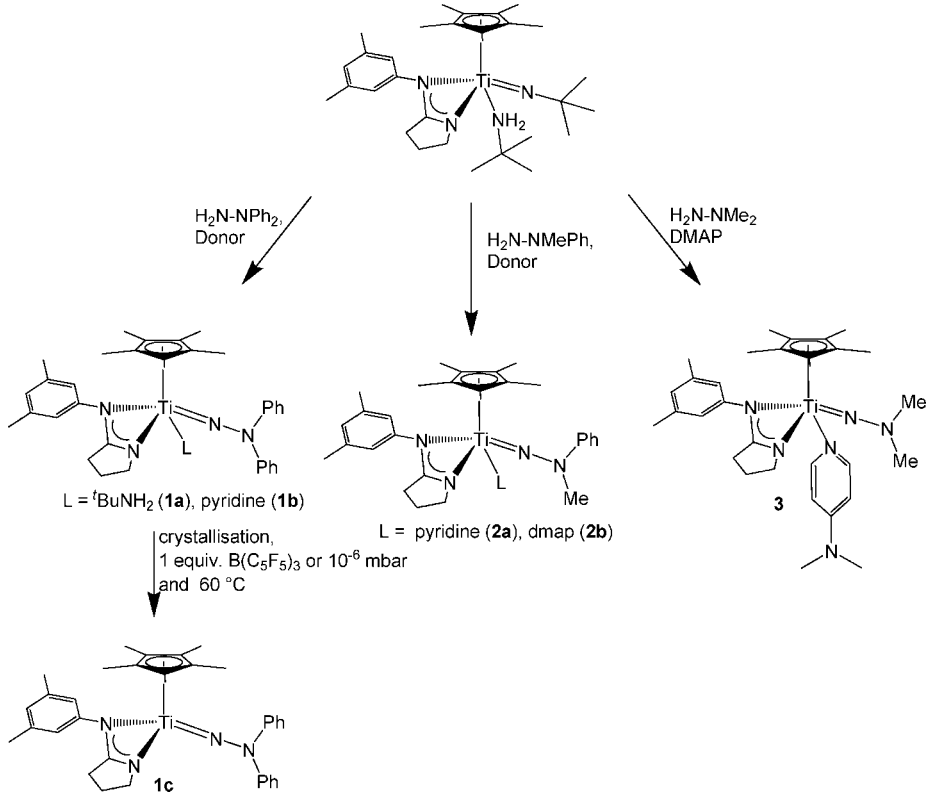
Scheme 1. Synthesis of the Hydrazinediido Complexes 1−3 by Imido/Hydrazine Exchange



The control of its reactivity by the ancillary ligand(s) is crucial for the performance of the catalyst. In recent years amidinates have been shown to be ideal ancillary ligands for a variety of early transition metals, including the group 3 elements and lanthanides,[29] as well as for metals from groups 4[30] and 5.[31] We have recently reported the synthesis of 2-aminopyrrolinato ligands in which the amidinato binding unit is exocyclic with respect to the heterocycle and which have proven to act as particularly robust spectator ligands.[32] The possibility of amidinates to convert from κ^2 to κ^1 coordination and thus temporarily to liberate a coordination site at the metal may be crucial in the development of active molecular catalysts. Their use in the preparation of a series of new titanium half-sandwich complexes, which are shown to be active catalysts for hydrohydrazination of alkynes, will be reported in this work.

Results and Discussion

Preparation and Structural Characterization of the Hydrazinediidotitanium Complexes. As starting material for the hydrazinediido complexes **1**−**3**, displayed in Scheme 1, we employed the previously published imido complex [Cp*Ti(N^{Xyl}N)(N^{t}Bu)($NH_2{}^t$Bu)],[33] which was converted to the hydrazinediide via imido/hydrazinediido exchange by reaction with the corresponding hydrazines.[34] In these transformations the half-sandwich system proved to be tolerant with respect to the nature of the N_β substituent of the hydrazido ligand. However, the less bulky and electron-withdrawing the substituents on the

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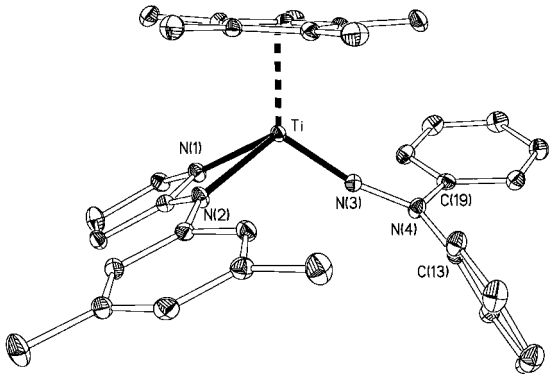

Figure 1. Molecular structure of complex **1c**. Selected bond lengths and angles are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Structurally Characterized Hydrazinediido Complexes 1c, 2a, and 3

	1c	2a	3
Ti−N(3)	1.736(2)	1.739(2)	1.735(2)
N(3)−N(4)	1.366(3)	1.351(3)	1.368(2)
Ti−N(1)	2.112(2)	2.192(2)	2.216(2)
Ti−N(2)	2.106(2)	2.203(2)	2.228(2)
Ti−N(3)−N(4)	168.2(2)	174.8(2)	172.6(1)
N(1)−Ti−N(2)	64.06(7)	60.93(8)	60.36(6)
N(4)−C(13)	1.421(3)	1.456(3)	1.458(3)
N(4)−C(14)[a], C(12), C(19)	1.407(3)	1.396(3)	1.456(3)

[a] C(14) for [Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (**2a**), C(12) for [Cp*Ti(N^{Xyl}N)($NNMe_2$)(dmap)] (**3**), and C(19) for [Cp*Ti(N^{Xyl}N)($NNPh_2$)] (**1c**).

N_β atom, the greater the donor capacity of the added donor ligand had to be, in order to obtain monomeric complexes.

Reaction of [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] with 1 molar equiv of diphenylhydrazine and subsequent workup by precipitation with hexane yielded the green diamagnetic hydrazinediido complex [Cp*Ti(N^{Xyl}N)($NNPh_2$)($NH_2{}^t$Bu)] (**1a**). Its formulation and proposed structure is supported by analytical and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic data. Apart from the hydrazinediide, one molecule of *tert*-butylamine is coordinated to the metal center as a neutral donor, which could be removed by heating solid **1a** at 60 °C for 72 h under a high vacuum (10^{-6} mbar), yielding [Cp*Ti(N^{Xyl}N)($NNPh_2$)] (**1c**). As for the starting material [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)], the proton resonances of the coordinated primary amine in compound **1a** were not observed in the ^{1}H NMR spectrum recorded at 295 K due to dissociative chemical exchange. However, upon cooling to 208 K, two doublet resonances at 7.20 and 1.67 with a geminal coupling constant $^2J_{H-H}$ of 10 Hz emerged. The large difference in chemical shifts is attributed to ring-current effects of the aromatic rings in the molecule.

Upon attempting to obtain single crystals of **1a** by slow crystallization, the donor (amine)-free derivative [Cp*Ti(N^{Xyl}N)($NNPh_2$)] (**1c**) was obtained and characterized by X-ray diffraction. Its molecular structure is depicted in Figure 1, and selected bond lengths and angles are listed in Table 1. Compound **1c** was also obtained on a preparative scale by reaction of the *tert*-butylamine adduct **1a** with $B(C_6F_5)_3$ (Scheme 1). Furthermore, the orange pyridine adduct [Cp*Ti(N^{Xyl}N)($NNPh_2$)(py)] (**1b**) was obtained directly by reacting the imide [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] with diphenylhydrazine in the presence of pyridine. The preparation of the mononuclear hydrazinediido complexes derived from 1-methyl-1-phenylhydrazine was only possible in the presence of either pyridine or 4-dimethylaminopyridine (dmap) as neutral co-ligands, yielding the two hydrazinediido complexes [Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (**2a**) and [Cp*Ti(N^{Xyl}N)(NNMePh)(dmap)] (**2b**). Finally, the isolation of a hydrazinediido compound from dimethylhydrazine [Cp*Ti(N^{Xyl}N)($NNMe_2$)(dmap)] (**3**) required the presence of the strongest donor, dmap. Single-crystal X-ray structure analyses of both **2a** and **3** were carried out, and their molecular structures are displayed in Figures 2 and 3, respectively.

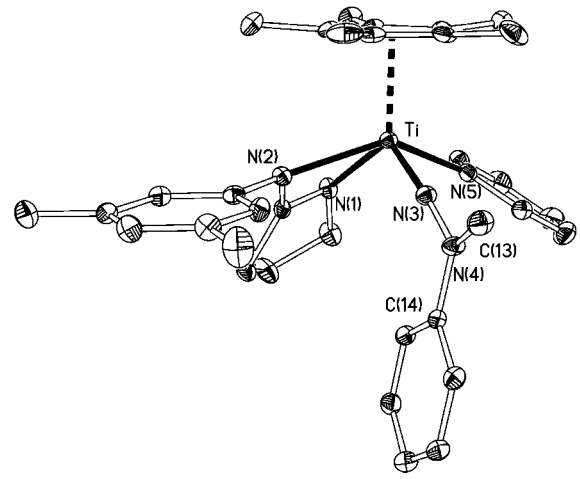

Figure 2. Molecular structure of complex **2a**. Selected bond lengths and angles are listed in Table 1.

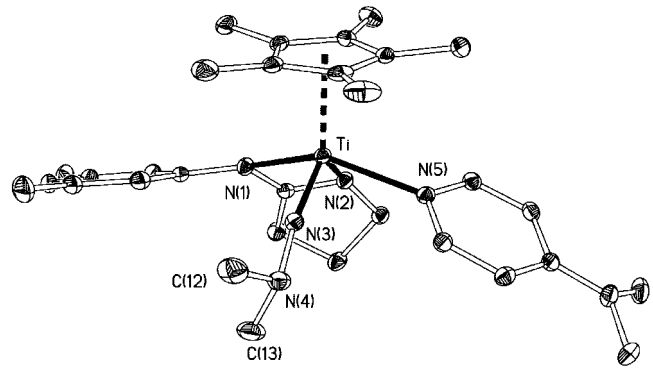

Figure 3. Molecular structure of complex **3**. Selected bond lengths and angles are listed in Table 1.

A comparative study of the metric parameters of three hydrazinediido species with different N_β substituents has been recently reported by Mountford et al. for several titanium complexes bearing calix(4)arenes as spectrator ligands.[18] The general trends established in this study are mirrored in the results of the crystal structure analyses of the three complexes reported in this work. The Ti═N bond lengths lie in a narrow range between 1.735(2) Å (for **3**) and 1.739(2) Å (for **2a**), which is very similar to previously reported Ti═N distances in terminal titanium hydrazides (14 crystallographically characterized examples: min: 1.708; max: 1.759 Å; average: 1.728 Å).[35] The hydrazinediido units in **1c**, **2a**, and **3** deviate significantly from linearity, which is attributed to the sterics of the N_β substituents. Consequently, the bending is greatest for the diphenylhydrazide in **1c**, the Ti−N(3)−N(4) angle being 168.2(2)°, whereas the 1-methyl-1-phenyl-substituted hydrazide(−2) is almost linear [174.8(2)°]. The $N_\alpha-N_\beta$ distances of between 1.351(3) (for **2a**) and 1.368(2) Å (for **3**) are also in the expected range (min: 1.344; max: 1.403 Å; average: 1.366 Å),[35] which lies charac-

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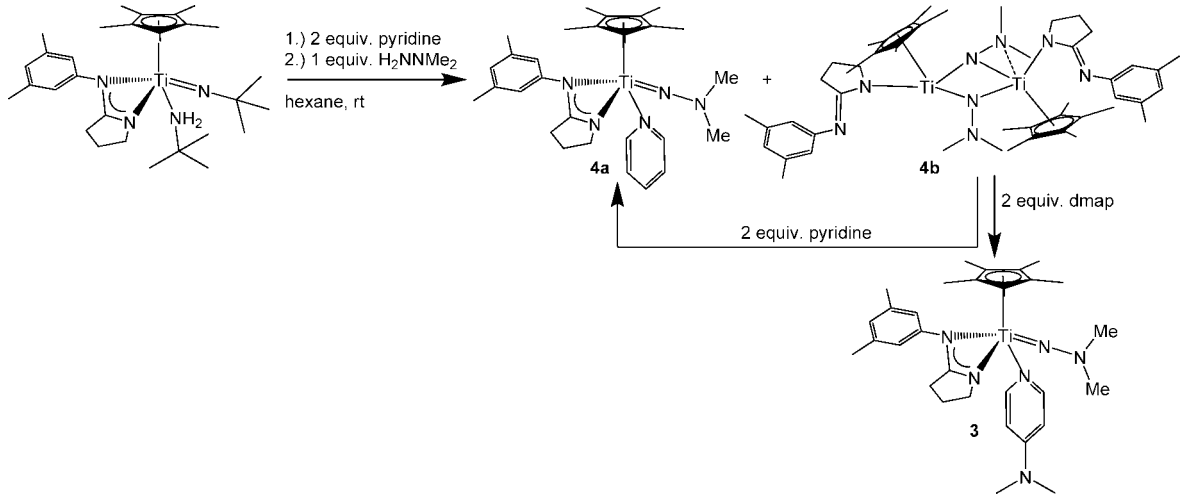
Scheme 2. Stabilization of the Dimethylhydrazinediido Complex with Pyridine as Co-ligand Resulting in the Partial Formation of the Dinuclear Compound 4b



teristically between the computed values for N−N single bonds in hydrazido(−2)-ligands and N−N double bonds in formally neutral isodiazene ligands.[36] For early transition metals in high oxidation states the hydrazido(−2) resonance formula is thought best to represent the bonding situation,[19,21,24,27] while DFT studies on late transition metal complexes imply a greater weight of the isodiazene resonance form.[37]

The sum of the angles at the N_β atom in the dimethyl-substituted complex **3** is 336.2°, indicating significant pyramidalization. On the other hand, the N_β atoms of the other two compounds are close to planar, $\Sigma(\angle_N)$ being 359.4° for [Cp*Ti(N^{Xyl}N)(NNPh$_2$)] (**1c**) and 357.0° in [Cp*Ti(N^{Xyl}N)-(NNMePh)(py)] (**2a**). This has been attributed to conjugation between the π-system of the phenyl rings and the lone pair on the N_β.[18,24] Furthermore, in [Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (**2a**), the N(4)−C(13) distance of the methyl groups is significant greater (1.456(3) Å) than that of the N_β−Ph bond [N(4)−C(14) = 1.396(3) Å], which is attributed primarily to the difference in hybridization at the C atoms.

Upon replacement of dmap by the weaker donor ligand pyridine in the synthesis of the dimethylhydrazinediido complex, a mixture of two molecular species in a relative ratio of 2.8:1 was obtained (Scheme 2). Whereas the major product could be characterized only in solution by ^{1}H and ^{13}C NMR spectroscopy, which is consistent with its formulation as the pyridine adduct [Cp*Ti(N^{Xyl}N)(NNMe$_2$)(py)] (**4a**), the analogue of the DMAP complex **3**, the minor component in this mixture, was identified as the dinuclear complex [Cp*$_2$Ti$_2$(N^{Xyl}N)$_2$(μ-η^1,η^1-NNMe$_2$)(μ-η^1,η^2-NNMe$_2$)] (**4b**).

Single crystals of **4b**, which were suitable for X-ray diffraction, were obtained by cooling a solution in diethyl ether at −18 °C. Its molecular structure is represented in Figure 4 along with the principal bond lengths and angles.

The two metal centers in the dinuclear complex **4b** are linked by two bridging dimethylhydrazido ligands. One of the μ-hydrazido(−2) units adopts a symmetrically bridging arrangement, while the second hydrazide is unsymmetrically bonded to the two Ti centers. For the latter, the N_β atom of the hydrazide is coordinated with its lone pair to the Ti(1) atom, and this additional Ti−N_β distance of 2.230(2) Å corresponds to the longest Ti−N bond in the molecule. Whereas both Ti−N_α bond lengths of the symmetrically bridging hydrazide(−2) are similar [1.931(2) Å for Ti(2)−N(3) and 1.994(2) Å for Ti(1)−N(3)], the Ti(2)−N(5) bond of the unsymmetrical bridging ligand [1.809(2) Å] is significantly shorter than the Ti−N_α bond to the second metal center [Ti(1)−N(5) 2.040(2) Å]. To date, there is only one other example of a crystallographically characterized hydrazinediidotitanium complex containing a (μ-η^1,η^1-NNMe$_2$) and a (μ-η^1,η^2-NNMe$_2$) ligand, which was reported by Leigh et al. in 1986.[38] All other structurally characterized Ti complexes with bridging hydrazides(−2) have been found to possess μ-η^1,η^2-coordination for both hydrazido ligands.[6,10,19,39] The capability of the 2-aminopyrrolinato ligands to liberate a coordination site at the metal by transferring from a κ_2 to a κ_1 coordination mode is indicated by the observation of the latter in the molecular structure of **4b** in the crystal.

By addition of dmap to **4b**, the dinuclear compound was converted into the mononuclear complex **3**. Furthermore, by

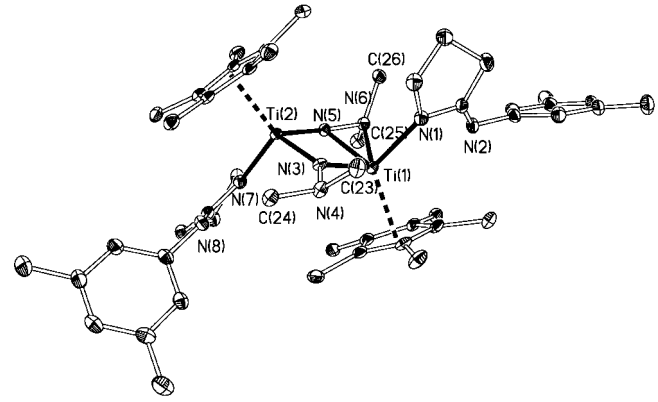


Figure 4. Molecular structure of complex **4b**. Selected bond lengths (Å) and angles (deg): Ti(1)−N(1) 2.058(2), Ti(1)−N(3) 1.994(2), Ti(1)−N(5) 2.040(2), Ti(1)−N(6) 2.230(2), Ti(1)-Cent(1) 2.110, Ti(2)−N(3) 1.931(2), Ti(2)−N(5) 1.809(2), Ti(2)−N(7) 2.087(2), Ti(2)-Cent(2) 2.105, N(3)−N(4) 1.395(2), N(5)−N(6) 1.384(2), N(4)−C(23) 1.460 (3), N(4)−N(24) 1.446(3), N(6)−C(25) 1.475(3), N(6)−C(26) 1.474(3), N(3)−Ti(1)−N(5) 80.60(7), N(3)−Ti(1)−N(6) 116.87(7), N(5)−Ti(1)−N(6) 37.51(7), N(5)−Ti(2)−N(3) 88.44(8), Ti(2)−N(3)−Ti(1) 93.96(7), Ti(2)−N(5)−Ti(1) 96.22(8).

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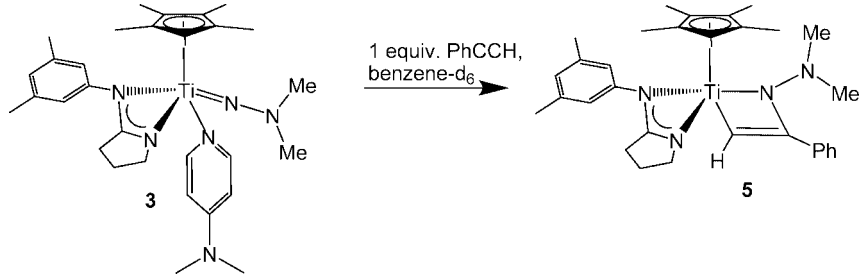
Scheme 3. *In Situ* Synthesis of a Markovnikov Cycloaddition Product via [2 + 2] Cycloaddition of Phenylacetylene to the Dimethylhydrazido Ligand



addition of an excess of pyridine to **4b** the mononuclear pyridine compound **4a** was obtained quantitatively in solution. Treating the latter under vacuum in an attempted isolation again resulted in the partial formation of the dinuclear compound **4b**. Complex **4a** could therefore not be isolated and was characterized by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy only in solution (Scheme 2).

***In Situ* Characterization of a {2 + 2} Cycloadduct of the Hydrazinediido Complex 3 with Phenylacetylene.** In contrast to the {2 + 2} cycloadducts of group 4 metal imido complexes with alkynes, which in many cases are sufficiently stable to be isolated and fully characterized, the corresponding cycloaddition products of hydrazinediides with alkynes tend to be thermally unstable. Mountford and co-workers have recently reported the spectroscopic characterization of such a species;[22] however, also in that case thermal degradation in solution prevented the growth of single crystals for an X-ray diffraction study. Of the systems reported in this work, only the stoichiometric reaction of the dimethylhydrazinediido complex **3** with phenylacetylene gave a cycloadduct of sufficient lifetime to allow its ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic characterization in solution (Scheme 3).

The NMR spectra are consistent with the selective formation of the Markovnikov cycloaddition product **5**. A characteristic proton singlet signal at 9.68 ppm is assigned to the proton bonded in the metallacyclic ring and is shifted to higher field compared to the previously characterized metallacyclic compounds derived from half-sandwich titanium imido compounds and terminal acetylenes (TiC*H* 11.1 ppm).[33] This trend has been also observed by Mountford and co-workers for an anti-Markovnikov cycloaddition product derived from a hydrazido compound and a terminal alkyne (TiC=C*H* 9.47 ppm).[22] In the ^{15}N NMR spectra the N_α resonance of the converted hydrazinediido ligand in **5** is detected at 267.6 ppm. The assignment is based on the long-range coupling to the proton at 9.68 ppm discussed above. The regioselective formation of **5** is consistent with the results of the hydrohydrazination catalyses performed with **3**.

Application of the Hydrazinediidotitanium Complexes as Catalysts for the Hydrohydrazination of Terminal Alkynes. For all published hydrohydrazination protocols with titanium or zinc catalysts, elevated reaction temperatures between 75 and 100 °C and reaction times between 2 and 75 h at catalyst loadings of 2−10 mol % are the norm.[6–8,10,11,13,40,41] Generally, catalytic reactions of terminal alkynes with hydrazines proceeded under milder reaction conditions. In contrast to its substituted derivatives, acetylene was converted to the corresponding hydrazides at ambient temperature within 2 h.[40] In a first study into the performances of the titanium half-sandwich complexes reported in this work as hydrohydrazination catalysts for alkynes we initially focused on terminal alkynes as substrates. Depending on the hydrazine employed for the particular reactions, complexes **1a**, **2a**, and **3** were tested in this study. We note that compounds **1b** and **2b** possess very similar catalytic properties to **1a** and **2a** and give rise to the corresponding reaction products with identical selectivities. However, since **1a** and **2a** were obtained in higher preparative yields and according to somewhat simpler protocols, only these have been systematically tested.

Table 2. Hydrohydrazination of Terminal Alkynes

entry	alkyne	hydrazine	catalyst	isolated yield[a]
1	PhCCH	Ph_2N-NH_2	**1a**	99%
2	PhCCH	MePhN-NH_2	**2a**	88%
3	PhCCH	Me_2N-NH_2	**3**	99%
4	*p*-TolCCH	Ph_2N-NH_2	**1a**	96%
5	*p*-TolCCH	MePhN-NH_2	**2a**	96%
6	*p*-TolCCH	Me_2N-NH_2	**3**	99%
7	*p*-*t*BuC_6H_4CCH	Ph_2N-NH_2	**1a**	90%
8	*p*-*t*BuC_6H_4CCH	MePhN-NH_2	**2a**	95%
9	*p*-*t*BuC_6H_4CCH	Me_2N-NH_2	**3**	98%
10	*p*-MeOC_6H_4CCH	Ph_2N-NH_2	**1a**	98%
11	*p*-MeOC_6H_4CCH	MePhN-NH_2	**2a**	95%
12	*p*-MeOC_6H_4CCH	Me_2N-NH_2	**3**	94%
13	*p*-FC_6H_4CCH	Ph_2N-NH_2	**1a**	86%
14	*p*-FC_6H_4CCH	MePhN-NH_2	**2a**	98%
15	*p*-FC_6H_4CCH	Me_2N-NH_2	**3**	94%
16	1-Octyne	Ph_2N-NH_2	**1a**	95%
17	1-Octyne	MePhN-NH_2	**2a**	95%

[a] Reaction conditions: alkyne (1.2 mmol), hydrazine (1.32 mmol), 5 mol % cat. in 2 mL of toluene, 25 °C, 1 h. Yields determined after column chromatography.

All three hydrazinediido compounds **1a**, **2a**, and **3** were found to display remarkable catalytic activities even at ambient temperature. For catalyst loadings of 5 mol % complete conversions of the terminal alkynes were observed within reaction times of 1 h. All catalytic runs were performed under the same conditions to allow comparison of the different substrates. Complete conversion was confirmed by GC analysis before workup in all cases. The yields listed in Tables 2 and 3 refer to the isolated products after chromatographic purification. Remarkable regioselectivity was observed in all transformations, which were found to have >99% Markovnikov selectivity.

We studied the reactions of the three substituted hydrazine derivatives, namely, diphenyl-, 1-methyl-1-phenyl-, and dimethylhydrazine, with a series of *para*-substituted terminal arylacetylenes and, as an example of an aliphatic alkyne, 1-octyne. Whereas two of the products were obtained in only moderate yields of 86% and 88% (entries 2 and 13 in Table 2), all others were isolated in excellent yields of well over 90%.

The limitations of the catalyst system became apparent in the conversion of 1,2-diethynylbenzene. No conversion was

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(39) Pietryga, J. M.; Jones, J. N.; Macdonald, C. L. B.; Moore, J. A.; Cowley, A. H. *Polyhedron* **2006**, *25*, 259–265.
(40) Cao, C.; Shi, Y.; Odom, A. L. *Org. Lett.* **2002**, *4*, 2853–2856.
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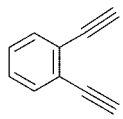
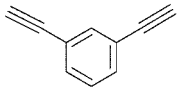
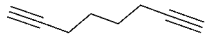
Table 3. Hydrohydrazination of Dialkynes

entry	Alkyne	Hydrazine	Conditions	Isolated yield[a]
1		Ph_2N-NH_2	**1a**	--[b]
2		McPhN-NH_2	**2a**	--[b]
3		Me_2N-NH_2	**3**	--[b]
4		Ph_2N-NH_2	**1a**	96 %
5		MePhN-NH_2	**2a**	96 %
6		Me_2N-NH_2	**3**	78 %
7		Ph_2N-NH_2	**1a**	97 %
8		MePhN-NH_2	**2a**	71 %

[a] Reaction conditions: alkyne (0.6 mmol), hydrazine (1.32 mmol), 5 mol % catalyst dissolved in 2 mL of toluene, 25 °C, 1 h. Yields determined after column chromatography. [b] Reaction conditions: alkyne (0.6 mmol), hydrazine (1.32 mmol), 5 mol % cat. in 2 mL of toluene, 105 °C, 24 h.

observed on stirring this compound for 1 h at ambient temperature with either of the three hydrazines introduced above in the presence of the respective catalyst. Likewise, heating the reactants at 105 °C for 24 h and subsequent workup only led to the almost quantitative reisolation of the hydrazines. The nonreactivity of 1,2-diethynylbenzene in the attempted hydrohydrazination is probably due to steric constraints of the two ethynyl units which are in close proximity. This interpretation is consistent with the observation that 1,3-ethynylbenzene was converted to the respective hydrazones in reactions with all three hydrazine derivatives at ambient temperature and a reaction time of 1 h. However, the yield varied somewhat more strongly than for the previously described terminal monoacetylenes (entries 4−6, Table 3). As an example of an aliphatic diyne, 1,7-octadiyne was tested and readily converted under the mild conditions employed for the other substrates (again with >99% Markovnikov selectivity). For diphenylhydrazine the isolated yield of the corresponding reaction product was 97% (entry 7, Table 3), whereas the product derived from 1-methyl-1-phenylhydrazine was only obtained in 71% yield (entry 8, Table 3).

Conclusion

In this work we have presented a simple and convenient access to a new class of hydrazinediido-titanium half-sandwich complexes, which have proven to be hydrohydrazination catalysts for terminal alkynes that are active at ambient temperature. To what extent the flexibility in the coordination of the otherwise robust 2-aminopyrrolinato ligand plays a role remains to be established. Extending the development of this class of catalysts to the heavier group 4 metals and to assess their capabilities in multicomponent reactions involving hydrazinediido intermediates will be investigated in future studies.

Experimental Section

All manipulations of air- and moisture-sensitive compounds were performed under an atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were predried over molecular sieves and then dried over Na/K alloy (pentane, diethyl ether), Na (toluene), or K (THF, hexane), distilled, and stored over potassium mirrors in Teflon-valve ampoules. Deuterated solvents were dried over K (benzene-d_6, toluene-d_8), vacuum distilled, and stored under argon in Teflon-valve ampoules. The protioligand $N^{Xyl}NH$[32] and the starting materials [Cp*Ti(N^{Xyl}N)Me_2][33] and [Cp*Ti(N^{Xyl}N)-(N^tBu)($NH_2{}^t$Bu)][33] as well as the substrates 1,2-ethynylbenzene[42] and 1,3-ethynylbenzene[42] were prepared as previously described. The 1,1-disubstituted hydrazines were dried over CaH_2, vacuum distilled, and stored in Teflon valve ampoules before use. All other reagents were purchased from commercial suppliers and used as received unless otherwise stated. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. NMR spectra were recorded on Bruker Avance II 400 or Bruker Avance III 600 NMR spectrometers. NMR spectra are quoted in ppm and were referenced internally relative to the residual protio-solvent (^{1}H) or solvent (^{13}C) resonances or externally to $NH_{3(l)}$ ($^{15}NH_3$). Where necessary, NMR assignments were confirmed by the use of two-dimensional ^{1}H−^{1}H and ^{1}H−^{13}C correlation experiments. ^{15}N NMR data were obtained by two-dimensional ^{1}H-correlated experiments or by direct detection using a cryogenically cooled direct-detection NMR probe (QNP CryoProbe). Microanalyses were performed by the analytical services in the chemistry department of the Universität Heidelberg. IR spectra were recorded on a Varian 3100 Excalibur spectrometer as KBr plates. Infrared data are quoted in cm^{-1}.

(A) Preparation of the Compounds. [Cp*Ti(N^{Xyl}N)($NNPh_2$)(^{t}BuNH$_2$)] (1a). To a solution of [Cp*Ti(N^{Xyl}N)-(N^tBu)($NH_2{}^t$Bu)] (1 g, 2 mmol) in hexane (5 mL) was added diphenylhydrazine (2 mmol). The solution was stirred at room temperature for 30 min, at which stage precipitation of the product set in. The green microcrystalline solid was isolated by filtration and dried under reduced pressure. Isolated yield: 90% (1.1 g, 1.8 mmol). ^{1}H NMR (600.1 MHz, benzene-d_6, 295 K): δ 1.07 (s, 9 H, NH_2-C(CH_3)$_2$), 1.54 (br m, 2 H, NCH_2CH_2), 1.95 (s, 15 H, C_5Me_5), 2.11 (br m, 1 H, $NCCH_2$), 2.28 (s, 6 H, $C_6H_3Me_2$), 2.41 (br m, 1 H, $NCCH_2$), 3.54 (br m, 1 H, NCH_2), 3.68 (br m, 1 H, NCH_2), 6.62 (s, 1 H, *para*-$C_6H_3Me_2$), 6.68 (s, 2 H, *ortho*-$C_6H_3Me_2$), 6.85 (tr, $^3J_{H-H}$ = 7.2 Hz, 2 H, *para-Ph*), 7.19−7.15 (m, 4 H, *meta-Ph*), 7.29 (d, $^3J_{H-H}$ = 8.0 Hz, 4 H, *ortho-Ph*) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, benzene-d_6, 295 K): δ 11.4 (C_5Me_5), 21.7 ($C_6H_3Me_2$), 24.8 (NCH_2CH_2), 29.8 ($NCCH_2$), 31.8 (NH_2−C(CH_3)$_3$), 49.1 (NH_2-$C(CH_3)_3$), 55.2 (NCH_2), 119.1 (C_5Me_5), 119.7 (*ortho-Ph*), 122.6 (*ortho*-$C_6H_3Me_2$), 121.8 (*para-Ph*), 123.3 (*para*-$C_6H_3Me_2$), 128.9 (*meta-Ph*), 138.2 (*meta*-$C_6H_3Me_2$), 146.6 (*ipso-Ph*), 151.2 (*ipso*-$C_6H_3Me_2$), 164.2 (br, NCN) ppm. ^{1}H NMR (399.9 MHz, toluene-d_8, 208 K): δ 1.08 (s, 9 H, NH_2-C(CH_3)$_2$); 1.59−1.49 (m, 2 H, NCH_2CH_2), 1.67 (d, $^2J_{H-H}$ = 10 Hz, 1 H, $NH_2{}^t$Bu), 1.93 (s, 15 H, C_5Me_5), 2.18−2.13 (m, 1 H, $NCCH_2$), 2.30−2.20 (m, 1 H, $NCCH_2$), 2.36 (s, 6 H, $C_6H_3Me_2$), 3.63−3.53 (m, 1 H, NCH_2), 4.07−4.00 (m, 1 H, NCH_2), 6.60 (s, 1 H, *para*-$C_6H_3Me_2$), 6.73 (s, 2 H, *ortho*-$C_6H_3Me_2$), 6.90 (tr, $^3J_{H-H}$ = 7.0 Hz, 2 H, *para-Ph*), 7.26−7.17 (m, 9 H, *ortho-* and *meta-Ph* and $NH_2{}^t$Bu) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, toluene-d_8, 208 K): δ 11.6 (C_5Me_5), 24.0 ($C_6H_3Me_2$), 26.0 (NCH_2CH_2), 30.3 ($NCCH_2$), 30.7 (NH_2-C(CH_3)$_3$), 50.8 (NH_2-$C(CH_3)_3$), 58.0 (NCH_2), 117.2 (C_5Me_5), 120.2 (*ortho-* or *meta-Ph*), 120.8 (*ortho*-$C_6H_3Me_2$), 122.0 (*para-Ph*), 122.7 (*para*-$C_6H_3Me_2$), 128.7 (*ortho-* or *meta-Ph*), 138.0 (*meta*-$C_6H_3Me_2$), 146.5 (*ipso-Ph*), 153.4 (*ipso*-$C_6H_3Me_2$), 173.1 (NCN) ppm. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 72.5 ($NH_2{}^t$Bu), 188.5 (Ti=N-NPh_2), 201.6 (NCNXyl), 318.4 (Ti=N-NPh_2) ppm, (NCNXyl) not obsd. IR (KBr plates, cm^{-1}): 2960.8 (m), 2911.2 (m), 2861.1 (m), 1594.4 (s), 1588.0 (s), 1550.1 (s), 1489.1 (s), 1374.7 (s), 1310.5 (s), 1261.0 (s).

(42) Zeidan, T. A.; Kovalenko, S. V.; Manoharan, M.; Alabugin, I. V. *J. Org. Chem.* **2006**, *71*, 962–975.

Anal. Found (calcd for $C_{38}H_{51}N_5Ti$): C, 72.4 (72.9); H, 8.2 (8.2); N, 11.2 (11.2).

[Cp*Ti(N^{Xyl}N)($NNPh_2$)(Py)] (1b). To a solution of [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] (452 mg, 0.89 mmol) in hexane (5 mL) pyridine (72 μL, 0.89 mmol), dissolved in 1 mL of hexane, was added. Diphenylhydrazine (164 mg, 0.89 mmol) was added and the solution was stirred at room temperature for 30 min. The hydrazinediido compound started to precipitate as an orange solid at that point, and after stirring for another 1 h at room temperature, the supernatant solution was removed by filtration and the isolated solid was dried *in vacuo*. The product was obtained in 76% yield (476 mg, 0.67 mmol). ^{1}H NMR (399.9 MHz, benzene-d_6, 295 K): δ 1.60 (br m, 2 H, NCH_2CH_2), 1.90 (s, 15 H, C_5Me_5), 2.23 (s, 6 H, $C_6H_3Me_2$), 3.53 (br m, 2 H, NCH_2), 6.55−6.55 (m, 2 H, *meta*-C_5H_5N), 6.61 (s, 1 H, *para*-$C_6H_3Me_2$), 6.90−6.81 (m, 5 H, overlapping *para-Ph*, *para*-C_5H_5N, *ortho*-$C_6H_3Me_2$), 7.17−7.13 (m, 4 H, *meta-Ph,* overlapping with benzene-d_6), 7.36 (d, $^3J_{H-H}$ = 8.0 Hz, 4 H, *ortho-Ph*), 8.57 (m, 2 H, *ortho*-C_5H_5N) ppm, ($NCCH_2$) not obsd. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6, 295 K): δ 11.6 (C_5Me_5), 21.6 ($C_6H_3Me_2$), 23.9 (NCH_2CH_2), 29.4 ($NCCH_2$), 54.0 (NCH_2), 118.7 (C_5Me_5), 119.5 (*ortho-Ph*), 121.8 (*ortho*-$C_6H_3Me_2$), 122.4 (*para-Ph*), 123.4 (*meta*-C_5H_5N), 123.7 (*para*-$C_6H_3Me_2$), 129.0 (*meta-Ph*), 135.8 (*para*-C_5H_5N), 138.0 (*meta*-$C_6H_3Me_2$), 147.0 (*ipso-Ph*), 151.2 (*ipso*-$C_6H_3Me_2$), 151.2 (*ortho*-C_5H_5N), 169.3 (NCN) ppm. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 172.5 (NCNXyl or NCNXyl), 182.4 (NCNXyl or NCNXyl), 199.7 (Ti=N-NPh_2), 293.5 (C_5H_5N), 332.8 (Ti=N-NPh_2) ppm. IR (KBr plates, cm^{-1}): 2960.6 (m), 2912.1 (m), 2854.3 (m), 1593.9 (s), 1585.5 (s), 1532.4 (s), 1487.1 (s), 1441.0 (m), 1313.2 (m), 1290.2 (m), 1169.2 (m), 1024.5 (m). Anal. Found (calcd for $C_{39}H_{45}N_5Ti$): C, 74.5 (74.2); H, 7.1 (7.2); N, 10.7 (11.1).

[Cp*Ti(N^{Xyl}N)($NNPh_2$)] (1c). To a stirred solution of [Cp*Ti(N^{Xyl}N)($NNPh_2$)(^{t}BuNH$_2$)] (**1a**) (135 mg, 0.26 mmol) in hexane (5 mL) $B(C_6F_5)_3$ (133 mg, 0.26 mmol) was added at room temperature. Immediately, an oily black precipitate formed, and the mixture was stirred an hour at room temperature. The supernatant solution was subsequently removed by filtration, and all volatiles, were removed *in vacuo*. The residue was triturated in pentane, and the supernatant solution was removed by filtration from the undissolved oily precipitate. The extract was evaporated to dryness, yielding analytically pure [Cp*Ti(N^{Xyl}N)($NNPh_2$)] (**1c**) in 49% yield. (72 mg, 0.13 mmol). Suitable crystals for X-ray diffraction were obtained from a concentrated hexane solution at −18 °C. ^{1}H NMR (399.9 MHz, benzene-d_6, 295 K): δ 1.55−1.47 (m, 2 H, NCH_2CH_2), 1.94 (s, 15 H, C_5Me_5), 1.99−1.90 (m, 2 H, $NCCH_2$, overlapping with C_5Me_5), 2.25 (s, 6 H, $C_6H_3Me_2$), 3.58−3.54 (m, 2 H, NCH_2), 6.60 (s, 2 H, *ortho*-$C_6H_3Me_2$), 6.62 (br s, 1 H, *para*-$C_6H_3Me_2$), 6.82 (tr, $^3J_{H-H}$ = 7.2 Hz, 2 H, *para-Ph*), 7.17−7.15 (m, 4 H, *meta-Ph*, overlapping with benzene-d_6), 7.34 (d, $^3J_{H-H}$ = 7.8 Hz, 4 H, *ortho-Ph*) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6, 295 K): δ 11.3 (C_5Me_5), 21.6 ($C_6H_3Me_2$), 24.1 (NCH_2CH_2), 28.1 ($NCCH_2$), 53.8 (NCH_2), 118.1 (*ortho-Ph*), 119.2 (br, *para*-$C_6H_3Me_2$ and C_5Me_5), 120.2 (*para-Ph*), 123.7 (*ortho*-$C_6H_3Me_2$), 128.1 (*meta-Ph*, overlapping with benzene-d_6), 138.4 (*meta*-$C_6H_3Me_2$), 147.3 (br, *ipso*-$C_6H_3Me_2$ or *ipso-Ph*), 148.9 (br, *ipso*-$C_6H_3Me_2$ or *ispo-Ph*) ppm, (NCN) not obsd. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 174.5 (NCNXyl), 330.6 (Ti=N-NPh_2) ppm, (NCNXyl), (Ti=N-NPh_2) not obsd. IR (KBr plates, cm^{-1}): 2960.3 (w), 2909.7 (m), 2856.9 (w), 1592.9 (s), 1489.1 (s), 1375.0 (m), 1290.5 (s), 1275.1 (s), 1263.1 (s), 1185.2 (m), 1166.8 (m), 1101.2 (m), 1073.0 (m), 1025.6 (m), 838.9 (m), 788.3 (s), 745.0 (s), 691.7 (s). Anal. Found (calcd for $C_{34}H_{40}N_4Ti$): C, 73.2 (73.9); H, 7.6 (7.30); N, 9.8 (10.1).

General Procedure for the Synthesis of the Hydrazinediido Complexes 2a, 2b, and 3. To a solution of [Cp*Ti(N^{Xyl}N)(N^tBu)($NH_2{}^t$Bu)] (1 equiv) in hexane (5 mL) the donor (pyridine or dmap 1 equiv) dissolved in 1 mL of toluene was added. The respective hydrazine (1 equiv) was added, and the solution was stirred at room temperature for 30 min. The hydrazinediido compounds started to precipitate as orange or red solids at that point, and after stirring for another 1 h at room temperature, the supernatant solution was removed by filtration and the isolated solid was dried *in vacuo*. Isolated yields of the reaction products: [Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (**2a**) 605 mg (1.06 mmol, 74%), [Cp*Ti(N^{Xyl}N)(NNMePh)(dmap)] (**2b**) 414 mg (0.67 mmol, 68%), [Cp*Ti(N^{Xyl}N)($NNMe_2$)(dmap)] (**3**) 176 mg (0.32 mmol, 62%).

[Cp*Ti(N^{Xyl}N)(NNMePh)(py)] (2a). Suitable crystals for X-ray diffraction were grown from a concentrated hexane solution at −18 °C. ^{1}H NMR (399.9 MHz, benzene-d_6, 295 K): δ 1.68−1.61 (m, 2 H, NCH_2CH_2), 1.99 (s, 15 H, C_5Me_5), 2.21 (s, 6 H, $C_6H_3Me_2$), 2.50−2.21 (br, 2 H, $NCCH_2$), 3.47 (s, 3 H, NMePh), 3.71−3.25 (br 2 H, NCH_2), 6.48−6.45 (m, 2 H, *meta*-C_5H_5N), 6.58 (s, 1 H, *para*-$C_6H_3Me_2$), 6.63 (tr, $^3J_{H-H}$ = 7.2 Hz, 1 H, *para*-C_5H_5N), 6.78 (s, 2 H, *ortho*-$C_6H_3Me_2$, overlapping with *para-Ph*), 6.81−6.78 (m, 1 H, *para-Ph*, overlapping with *ortho*-$C_6H_3Me_2$), 6.93 (d, $^3J_{H-H}$ = 8.1 Hz, 2 H, *ortho-Ph*), 7.14−7.10 (m, 2 H, overlapping with benzene-d_6, *meta-Ph*), 8.53 (d, $^3J_{H-H}$ = 4.7 Hz, 2 H, *ortho*-C_5H_5N) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6, 295 K): δ 12.1 (C_5Me_5), 21.6 ($C_6H_3Me_2$), 23.9 (NCH_2CH_2), 29.4 ($NCCH_2$), 41.5 (NMePh), 54.0 (NCH_2), 110.7 (*ortho-Ph*), 117.0 (*para*-C_5H_5N), 117.5 (C_5Me_5), 122.4 (*ortho*-$C_6H_3Me_2$), 123.3 (*meta*-C_5H_5N), 123.4 (*para*-$C_6H_3Me_2$), 128.8 (*meta-Ph*), 136.2 (*para-Ph*), 137.6 (*meta*-$C_6H_3Me_2$), 148.1 (*ipso-Ph*), 151.3 (*ipso*-$C_6H_3Me_2$), 152.2 (*ortho*-C_5H_5N), 169.7 (NCN) ppm. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 172.0 (NCN-Xyl), 180.2 (Ti=N-NMePh), 290.2 (NC_5H_5), 340.0 (Ti=N-NMePh) ppm, (NCN-Xyl) not obsd. IR (KBr plates, cm^{-1}): 2960.3 (m), 2906.2 (m), 2854.4 (m), 1598.8 (s), 1544.8 (s), 1489.8 (s), 1441.0 (s), 1324.7 (m), 1287.8 (s), 1174.1 (m), 1088.0 (w). Anal. Found (calcd for $C_{34}H_{43}N_5Ti$): C, 71.3 (71.7); H, 7.6 (7.6); N, 12.2 (12.3).

[Cp*Ti(N^{Xyl}N)(NNMePh)(dmap)] (2b). ^{1}H NMR (600.1 MHz, benzene-d_6, 295 K): δ 1.79−1.74 (NCH_2CH_2), 2.04 (s, 6 H, $NC_5H_4NMe_2$), 2.13 (s, 15 H, C_5Me_5), 2.23 (s, 6 H, $C_6H_3Me_2$), 2.28−2.12 (br m, 1 H, $NCCH_2$), 2.64 (br m, 1 H, $NCCH_2$), 3.67−3.52 (m, 2 H, NCH_2), 3.66 (s, 3 H, s, NMePh), 5.80 (br s, 2 H, *meta*-$NC_5H_4NMe_2$), 6.58 (s, 1 H, *para*-$C_6H_3Me_2$), 6.59 (m, 1 H, *para-Ph*), 6.89 (br s, 2 H, *ortho*-$C_6H_3Me_2$), 7.12−7.05 (m, 4 H, *ortho-Ph* and *meta-Ph*), 8.33 (d, $^3J_{H-H}$ = 4.2 Hz, 2 H, *ortho*-$NC_5H_4NMe_2$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, benzene-d_6, 295 K): δ 12.6 (C_5Me_5), 21.7 ($C_6H_3Me_2$), 23.8 (NCH_2CH_2), 29.4 ($NCCH_2$), 38.0 ($NC_5H_4NMe_2$), 41.8 (NMePh), 54.3 (NCH_2), 105.8 (*meta*-$NC_5H_4NMe_2$), 110.5 (*ortho-* or *meta-Ph*), 116.3 (C_5Me_5), 116.6 (*para-Ph*), 119.2 (*ortho*-$C_6H_3Me_2$), 123.6 (*para*-$C_6H_3Me_2$), 128.8 (*ortho-* or *meta-Ph*), 137.3 (*meta*-$C_6H_3Me_2$), 148.4 (*ipso-Ph*), 152.2 (*ortho*-$NC_5H_4NMe_2$), 152.4 (*ipso*-$C_6H_3Me_2$), 153.9 (*para*-$NC_5H_4NMe_2$), 171.6 (NCN) ppm. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 57.9 ($NC_5H_4NMe_2$), 183.3 (NCNXyl), 180.4 (Ti=N-NMePh), 245.8 ($NC_5H_4NMe_2$), 345.4 (Ti=N-NMePh) ppm, (NCNXyl) not obsd. IR (KBr plates, cm^{-1}): 2944.4 (m), 2906.2 (m), 2853.2 (m), 1607.8 (s), 1543.1 (s), 1489.3 (s), 1291.8 (m), 1225.3 (m), 1006.7 (m). Anal. Found (calcd for $C_{36}H_{48}N_6Ti$): C, 70.8 (70.6); H, 8.0 (7.9); N, 13.4 (13.7).

[Cp*Ti(N^{Xyl}N)($NNMe_2$)(dmap)] (3). Suitable crystals for X-ray diffraction were grown from a concentrated hexane solution at −18 °C. ^{1}H NMR (600.1 MHz, benzene-d_6, 295 K): δ 1.74−1.66 (br m, 2 H, NCH_2CH_2), 2.13 (s, 21 H, C_5Me_5 and $NC_5H_4NMe_2$), 2.34 (s, 6 H, $C_6H_3Me_2$), 2.52−2.39 (br m, 2 H, $NCCH_2$), 2.79 (s, 6 H, NMe_2), 3.74−3.58 (br m, 2 H, NCH_2), 5.97 (d, $^3J_{H-H}$ = 5.9 Hz, 2 H, *meta*-$NC_5H_4NMe_2$), 6.56 (s, 1 H, *para*-$C_6H_3Me_2$), 7.02 (br s, 2 H, *ortho*-$C_6H_3Me_2$), 8.59 (d, $^3J_{H-H}$ = 4.9 Hz, 2 H, *ortho*-$NC_5H_4NMe_2$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, benzene-d_6, 295 K): δ 12.2 (C_5Me_5), 21.7 ($C_6H_3Me_2$), 24.3 (NCH_2CH_2), 29.7 ($NCCH_2$), 38.2 ($NC_5H_4NMe_2$), 49.1 (NMe_2), 105.9 (*meta*-$NC_5H_4NMe_2$), 115.9 (C_5Me_5), 122.3 (*para*-$C_6H_3Me_2$), 122.6 (*ortho-*

Table 4. Details of the Crystal Structure Determinations of the Complexes 1c, 2a, 3, and 4

	1c	2a	3	4
formula	$C_{34}H_{40}N_4Ti$	$C_{34}H_{43}N_5Ti$	$C_{31}H_{46}N_6Ti$	$C_{53}H_{84}N_8Ti_2$
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	14.6088(15)	11.483(2)	11.1384(13)	10.5635(13)
b/Å	11.0619(11)	17.855(3)	11.9027(14)	16.591(2)
c/Å	19.2644(19)	15.233(3)	12.5326(15)	29.458(4)
α/deg			89.894(2)	
β/deg	108.926(2)	92.644(4)	88.023(2)	96.168(2)
γ/deg			66.001(2)	
V/Å^3	2944.8(5)	3120.0(10)	1516.9(3)	5132.9(11)
Z	4	4	2	4
M_r	552.60	569.63	550.64	929.08
d_c/Mg·m^{-3}	1.246	1.213	1.206	1.202
F_{000}	1176	1216	592	2008
μ(Mo Kα)/mm^{-1}	1.246	0.305	0.312	0.354
max., min transmn factors	0.7464, 0.6908	0.7464, 0.6598	0.7464, 0.6908	0.7456, 0.6923
X-radiation, λ/Å	Mo Kα, graphite monochromated, 0.71073			
θ range/deg	2.1 to 29.6	2.1 to 27.5	1.6 to 30.0	1.4 to 27.6
index ranges (indep set) h,k,l	−20... 19, 0... 15, 0... 26	−14... 14, 0... 23, 0... 19	−15... 15, −16... 16, 0... 17	−13... 13, 0... 21, 0... 38
reflns measd	68 100	62 584	35 412	103 733
unique [R_{int}]	8261 [0.0868]	7153 [0.0940]	8860 [0.0546]	11 856 [0.0768]
observed [$I \geq 2\sigma(I)$]	5223	4572	6105	8206
params refined	359	369	354	541
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0472, 0.1011	0.0484, 0.1078	0.0456, 0.1017	0.0478, 0.1222
R indices (all data) $R(F)$, $wR(F^2)$	0.1082, 0.1403	0.1073, 0.1444	0.0855, 0.1254	0.0828, 0.1383
GooF on F^2	1.114	1.069	1.031	1.065
largest residual peaks/e·Å^{-3}	0.491, −0.467	0.450, −0.623	0.429, −0.382	1.242, −0.426

$C_6H_3Me_2$), 137.3 (*meta*-$C_6H_3Me_2$), 151.9 (br, *ortho*-$NC_5H_4NMe_2$ and *ipso*-$C_6H_3Me_2$), 154.0 (*para*-$NC_5H_4NMe_2$), 171.9 (N*C*N) ppm, (N*C*H$_2$) not obsd. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 56.5 (NC_5H_4*N*Me$_2$), 251.3 (*N*$C_5H_4NMe_2$), 379.9 (Ti=*N*-NMe$_2$) ppm, (Ti=N-*N*Me$_2$), (NC*N*Xyl) and (*N*CNXyl) not obsd. IR (KBr plates, cm^{-1}): 2962.9 (w), 2910.9 (w), 2856.4 (w), 1602.9 (2), 1536.8 (m), 1444.8 (m), 1226.3 (m), 789.1 (s). Anal. Found (calcd for $C_{31}H_{46}N_6Ti$): C, 67.5 (67.6); H, 8.5 (8.4); N, 14.6 (15.3).

[Cp*Ti(N^{Xyl}N)(NNMe$_2$)(py)] (4a) and [Cp*Ti(N^{Xyl}N)(NNMe$_2$)]$_2$ (4b). Using pyridine for the stabilization of the mononuclear dimethylhydrazinediido complex in the synthesis of **[Cp*Ti(N^{Xyl}N)(NNMe$_2$)(py)]** (**4a**) gave a mixture of two compounds in a 2.8:1 ratio. Single crystals of the minor compound, which proved to be a dinuclear complex, were obtained from a concentrated pentane solution at −18 °C and were used for the X-ray diffraction study (*vide infra*). The major component was characterized in solution by NMR spectroscopy.

[Cp*Ti(N^{Xyl}N)(NNMe$_2$)(py)] (4a). ^{1}H NMR (600.1 MHz, benzene-d_6, 295 K): δ 1.68−1.64 (m, 2 H, NCH$_2$C*H*$_2$), 2.00 (s, 15 H, C_5*Me*$_5$), 2.30 (s, 6 H, C_6H_3*Me*$_2$), 2.32−2.24 (br m, 2 H, NCC*H*$_2$, overlapping with $C_6H_3Me_2$), 2.72 (s, 6 H, N*Me*$_2$), 2.83−2.69 (br m, 2 H, NC*H*$_2$, overlapping with NMe$_2$), 6.65−6.63 (m, 3 H, *para*-$C_6H_3Me_2$ and *meta*-C_5H_5N), 6.94−6.91 (m, 3 H, *ortho*-$C_6H_3Me_2$ and *para*-C_5H_5N), 8.65 (d, $^3J_{H-H}$ = 4.4 Hz, 2 H, *ortho*-C_5H_5N) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, benzene-d_6, 295 K): δ 12.0 (C_5*Me*$_5$), 21.4 (C_6H_3*Me*$_2$), 23.7 (NCH$_2$*C*H$_2$), 29.4 (NC*C*H$_2$), 49.0 (N*Me*$_2$), 55.2 (N*C*H$_2$), 115.9 (*C*$_5$Me$_5$), 122.4 (*para*-$C_6H_3Me_2$), 122.5 (*ortho*-$C_6H_3Me_2$), 122.7 (*meta*-C_5H_5N), 135.5 (*para*-C_5H_5N), 137.1 (*meta*-$C_6H_3Me_2$), 151.2 (*ortho*-C_5H_5N), 152.0 (*ipso*-$C_6H_3Me_2$), 171.3 (N*C*N) ppm. ^{15}N NMR (60.8 MHz, benzene-d_6, 295 K): δ 155.0 (Ti=N-*N*Me$_2$), 303.6 (C_5H_5*N*), 380.1 (Ti=*N*-NMe$_2$) ppm, (*N*CN-Xyl), (NC*N*-Xyl) not obs.

[Cp*Ti(N^{Xyl}N)(NNMe$_2$)]$_2$ (4b). ^{1}H NMR (600.1 MHz, benzene-d_6, 295 K): δ 1.65−1.53 (br m, 4 H, NCH$_2$C*H*$_2$), 2.11 (br s, 30 H, C_5*Me*$_5$), 2.32−2.23 (br m, 4 H, NCC*H*$_2$), 2.38 (s, 12 H, C_6H_3*Me*$_2$), 2.51−2.46 (br m, 4 H, NCC*H*$_2$), 2.83 (s, 6 H, N*Me*$_2$), 3.12−3.02 (br m, 2 H, NC*H*$_2$), 3.35−3.26 (br m, 1 H, NC*H*$_2$), 3.38 (s, 6 H, N*Me*$_2$), 3.55−3.50 (br m, 1 H, NC*H*$_2$), 6.69 (br s, 2 H, *para*-$C_6H_3Me_2$), 6.79 (br s, 4 H, *ortho*-$C_6H_3Me_2$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, benzene-d_6, 295 K): δ 13.3 (C_5*Me*$_5$), 21.9 (C_6H_3*Me*$_2$), 25.4 (NCH$_2$*C*H$_2$), 29.8 (NC*C*H$_2$), 54.2 (N*Me*$_2$), 54.6 (N*Me*$_2$), 59.4 (N*C*H$_2$), 120.8 (*ortho*-$C_6H_3Me_2$), 122.5 (*para*-$C_6H_3Me_2$), 122.6 (*C*$_5$Me$_5$), 137.9 (*meta*-$C_6H_3Me_2$), 155.3 (*ipso*-$C_6H_3Me_2$), 171.5 (N*C*N) ppm. IR (KBr plates, cm^{-1}): 2955.9 (m), 2910.5 (m), 2859.2 (m), 1608.0 (sh), 1577.6 (s), 1450.7 (w), 1353.2 (w), 1261.3 (m), 1247.8 (m), 1159.1 (w). Anal. Found (calcd for $C_{48}H_{72}N_8Ti_2$ + 1 equiv pentane): C, 68.3 (68.5); H, 9.1 (9.1); N, 11.9 (12.0).

[Cp*Ti(N^{Xyl}N){κ^2N(NMe$_2$)CPh=CH}] (5). [Cp*Ti(N^{Xyl}N)(NNMe$_2$)(dmap)] (**3**) (40 mg, 0.07 mmol) was dissolved in toluene-d_8 (0.5 mL) and cooled to −78 °C. Phenylacetylene (8 μL, 0.07 mmol) was then added, leading to an immediate change of color from red to deep brown. The NMR spectra were recorded within 2 h after the *in situ* preparation. ^{1}H NMR (600.1 MHz, toluene-d_8, 295 K): δ 1.45−1.41 (m, 1 H, NCH$_2$C*H*$_2$), 1.52−1.46 (m, 1 H, NCH$_2$C*H*$_2$), 1.96 (s, 15 H, C_5*Me*$_5$), 2.14 (s, 6 H, C_6H_3*Me*$_2$, overlapping with NCC*H*$_2$), 2.17−2.12 (m, 2 H, NCC*H*$_2$, overlapping with C_6H_3*Me*$_2$), 2.83 (br s, 3 H, N*Me*$_2$), 3.30−3.20 (m, 2 H, NC*H*$_2$), 6.23 (s, 1H, *para*-$C_6H_3Me_2$), 6.39 (s, 2 H, *ortho*-$C_6H_3Me_2$), 7.08−7.02 (m, 3 H, *meta*- and *para*-*Ph*), 7.81 (d, $^3J_{H-H}$ = 7.2 Hz, 2 H, *ortho*-*Ph*), 9.68 (s, 1 H, C=C*H*) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, toluene-d_8, 295 K): δ 12.4 (C_5*Me*$_5$), 21.5 (C_6H_3*Me*$_2$), 24.2 (NCH$_2$*C*H$_2$), 31.2 (NC*C*H$_2$), 52.8 (N*C*H$_2$), 53.2 (N*Me*$_2$, br), 53.4 (N*Me*$_2$, br), 118.3 (*C*$_5$Me$_5$), 120.2 (*ortho*-$C_6H_3Me_2$), 121.8 (*para*-$C_6H_3Me_2$), 124.6 (overlapping with toluene-d_8, *meta*- or *para*-*Ph*), 127.2 (*ortho*-*Ph*), 127.5 (*meta*- or *para*-*Ph*), 131.1 (*ipso*-C_6H_5), 136.7 (*meta*-$C_6H_3Me_2$), 138.2 (*C*=CH), 149.3 (*ipso*-$C_6H_3Me_2$), 167.3 (br, *C*=*C*H), 174.0 (N*C*N) ppm. ^{15}N NMR (60.8 MHz, toluene-d_8, 295 K): δ 172.3 (NC*N*Xyl), 267.6 (Ti=*N*-NPh$_2$) ppm, (Ti=N-*N*Ph$_2$), (*N*CN-Xyl) not obsd.

(B) General Procedure for the Intermolecular Hydrohydrazination of Terminal Alkynes. A Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was charged with the terminal alkyne (1.2 mmol for monoalkyne and 0.6 mmol for dialkyne), the hydrazine (1.32 mmol), and the catalyst (0.06 mmol, 5 mol %) dissolved in 2 mL of toluene. The resulting mixture was stirred for 1 h at room temperature. At that stage the complete conversion of the starting materials was confirmed by GC analysis. The reaction mixture was subsequently filtered through a pad of silica and washed with diethyl ether. After removing all volatiles the crude product was subjected to column chromatography.

X-ray Crystal Structure Structure Determinations. Crystal data and details of the structure determinations are listed in Table

4. Intensity data were collected at 100(2) K with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). Data were corrected for air and detector absorption and Lorentz and polarization effects;[43] absorption by the crystal was treated with a semiempirical multiscan method.[44,45]

The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[46] (complexes **1c**, **2a**, and **3**) or by the charge flip procedure[47,48] (complex **4**) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[49] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model. Due to severe disorder, electron density attributed to solvent of crystallization (pentane) was removed from the structures (and the corresponding F_{obs}) of **4** with the SQUEEZE procedure,[50] as implemented in PLATON.[51]

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Supporting Information Available: Characterization data of the hydrazones obtained in the catalysis and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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