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Synthesis and Structure of a Titanium Hydrazido(2−) Complex

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*Summary: Reaction of 1 equiv each of $Ti(NMe_2)_2(dap)_2$ (**1**), 1-hexyne, tert-butyl isocyanide, and 1,1-dimethylhydrazine at room temperature results in the formation of $Ti(NNMe_2)(dap)[N(Bu^t)CHCHC(Bu^n)N(NMe_2)\text{-}\kappa^2N]$ (**2**), where one of the ligands is formed through iminohydrazination of the alkyne. A possible pathway for the generation of **2** and the crystal structure of this rare terminal hydrazido(2−) complex of titanium are discussed.*

Hydrazido(2−) complexes are found as important intermediates in several catalytic cycles. Of greatest importance is their role in the reductive cleavage of dinitrogen to produce ammonia, where they are known to participate in the catalytic system of Schrock[1] and may be involved in the natural nitrogenase[2] enzyme. In fact, terminal hydrazido(2−) complexes are postulated to be involved in the E_4 and E_5 states of the FeMo cofactor during nitrogen reduction.[3] These metal−ligand multiple bond complexes may also be involved in recent titanium-catalyzed hydrohydrazination processes.[4] Terminal hydrazido(2−) complexes are known for many of the transition metals.[5] A few terminal hydrazido(2−) complexes have been reported for titanium,[6] and a couple of crystal structures have recently appeared.[7] Here, we report the synthesis and structure of an unusual hydrazido(2−) complex of titanium prepared through a novel multicomponent reaction related to a new catalysis under scrutiny in our laboratory, alkyne iminohydrazination.

Hydrohydrazination of alkynes is a process for the synthesis of hydrazones by hydrazine addition to alkynes.[4] We have recently modified this process to a new multicomponent coupling reaction where an alkyne, hydrazine, and isocyanide are combined in a single titanium-catalyzed step.[8] Multicomponent coupling reactions are of interest, because they allow access to more complex products in a single step.[9] In this new titanium-catalyzed reaction, the result is formal addition of iminohydrocarbyl and hydrazinyl groups to an alkyne, iminohydrazination. Typical reaction conditions are 100 °C for 6−24 h in toluene. A possible pathway for this iminohydrazination[10] reaction is shown in Scheme 1.

In an attempt to isolate a potential intermediate in this interesting new reaction, we examined the reaction of the

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[7] (a) Li, Y.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 1794. (b) Parsons, T. B.; Hazari, N.; Cowley, A. R.; Green, J. C.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 8442.

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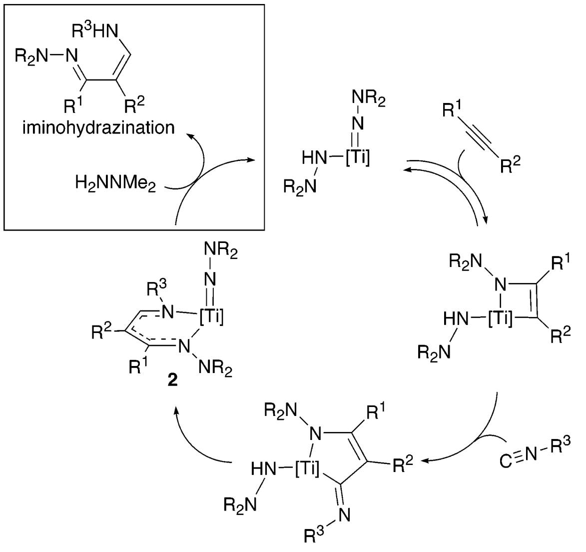
[9] For a review see: Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168.

[10] For a reference on the related reaction where a primary amine is employed instead of a hydrazine, i.e., iminoamination, see: Cao, C.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 2880.

10.1021/om060304f CCC: $33.50

Scheme 1. Possible Pathway for Iminohydrazination Catalyzed by Titanium[a]



[a] [Ti] = Ti(dap).

titanium precatalyst Ti(NMe$_2$)$_2$(dap)$_2$ (**1**) with 1 equiv each of 1-hexyne, 1,1-dimethylhydrazine, and *tert*-butyl isocyanide (Figure 1), where dap = 2-((dimethylamino)methyl)pyrrolyl. The facile reaction occurs when started in near-frozen toluene and warmed to room temperature. The isolated product contains 2 equiv of dimethylhydrazine and 1 equiv of the other reactants. In addition, one of the pyrrolyl dap ligands has been protolytically removed. The product is the terminal hydrazido(2−) complex Ti(NNMe$_2$)(dap)[N(Bu^t)CHCHC(Bu^n)N(NMe$_2$)-κ^2N] (**2**). The compound was formed in 94% yield versus limiting 1,1-dimethylhydrazine. Attempts to run the reaction with 2 equiv of hydrazine resulted in low yields of **2** and large amounts of a dinuclear species, Ti$_2$(μ_2-η^1:η^2-NNMe$_2$)$_2$(dap)$_3$(μ_1-η^1-NHNMe$_2$).[8]

The structure of the terminal hydrazido(2−) complex **2** was determined by single-crystal X-ray diffraction and is shown in Figure 1.[11] The structure of **2** has many features in common with the only other structurally characterized titanium dimethylhydrazido(2−) complex, Ti(NNMe$_2$)(bpy)(dpma), where dpma is *N,N*-bis(pyrrolyl-α-methyl)-*N*-methylamine.[7a] Both have approximately linear terminal hydrazido(2−) Ti−N−N angles, which measures 169.6(2)° in **2**.

The Ti═N(hydrazido) distance in **2** is 1.709(3) Å and is in the usual range for a titanium−nitrogen double to triple bond. The hydrazido(2−) N−N distance of 1.402(4) Å is slightly shorter than might be expected for an N−N single bond, which is 1.451 ± 0.005 Å in hydrazine.[12] The slightly shorter hydrazido(2−) N−N distance can be ascribed to a small amount of participation by the isodiazene resonance form (Figure 2). While the hydrazido(2−) form is favored for the quite electropositive titanium center, which would be very reducing as titanium(II), for more weakly π-donating metal centers the isodiazene form participates strongly and is known to be favored in many compounds. For example, in an isodiazene iron porphyrin complex the N−N bond distance is 1.232(5) Å,[13] indicating a bond order of ~2.0.[14]

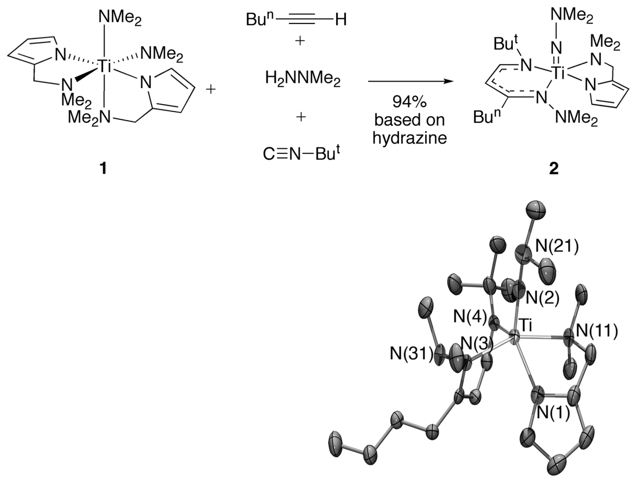


Figure 1. Synthesis and structure from X-ray diffraction of the hydrazido(2−) complex **2**. Selected bond distances (Å) and angles (deg): Ti−N(2), 1.709(3); Ti−N(3), 2.077(2); Ti−N(4), 2.055(3); Ti−N(1), 2.119(3); Ti−N(11), 2.323(3); N(2)−N(21), 1.403(4); N(3)−N(31), 1.457(3); Ti−N(2)−N(21), 169.6(2).

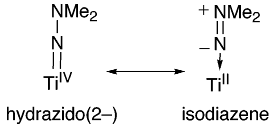


Figure 2. Possible hydrazido(2−) and isodiazene resonance forms for **2**. (The other ligands are not shown for simplicity.)

Most often, N$_\beta$ is planar in hydrazido(2−) complexes and only a few examples with pyramidalized nitrogens have been structurally characterized.[15] The angles around N$_\beta$ in **2** sum to 335.5(3)°, only slightly higher than that expected for an sp^3 NR$_3$ compound of 328°.[12] Thus far, all of the dimethylhydrazido(2−) complexes of titanium that we have structurally characterized have had a pyramidalized N$_\beta$, consistent with high participation by the hydrazido(2−) resonance form in these early-metal derivatives (Figure 2).[16]

The overall geometry of the five-coordinate complex **2** is intermediate between a square pyramid and a trigonal bipyramid. The square-pyramidal structure is only slightly favored, and the complex has a continuous symmetry parameter value of $\tau = 0.36$, where $\tau = 0$ would be a square pyramid and $\tau = 1$ would be a trigonal bipyramid.[17] The nacnac ligand[18] of **2**, although quite unsymmetrically substituted, is close to symmetrically bound with Ti−N(NMe$_2$) and Ti−N(Bu^t) distances of 2.080(3) and 2.055(3) Å, respectively. The other C−C and C−N distances within the six-membered ring are also consistent with a highly delocalized system.

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[11] Crystal data: monoclinic, $P2_1/c$, formula $C_{22}H_{43}N_7Ti$, $a = 9.180(1)$ Å, $b = 19.161(3)$ Å, $c = 15.043(2)$ Å, $\beta = 102.598(3)°$, $Z = 4$, $D_{calcd} = 1.167$ g/mL, $\mu = 0.353$ mm^{-1}, $F(000) = 984$, θ range 1.75−23.33°, 22 066 total reflections, 3737 unique reflections, 272 parameters, GOF = 1.012, $\epsilon = 0.020(2)$, largest peak and hole +0.414 and −0.398 e Å^{-3}, R1($I > 2\sigma(I)$) = 0.0436, wR2($I > 2\sigma(I)$) = 0.1040.

[12] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972. Here the parentheses denote estimated standard deviations from model used in the X-ray diffraction experiment, and the ± denotes standard deviations from the average found from multiple experiments.

[13] Mahy, J.-P.; Battioni, P.; Mansuy, D.; Fisher, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699.

[14] Allman, R. Structural Chemistry. In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: London, 1975; Part 1, p 23.

[15] Kahlal, S.; Saillard, J.-Y.; Hamon, J.-R.; Manzur, C.; Carrilo, D. *J. Chem. Soc., Dalton Trans.* **1998**, 1229.

[16] There are two reported examples of diphenylhydrazido(2−) complexes of group 4. The nitrogens in these complexes are planar, due to interactions with the phenyl groups.[5e,7b]

[17] (a) Alvarez, S.; Llunell, M. *Dalton Trans.* **2000**, 3288. (b) Zabrodsky, H.; Peleg, S.; Avnir, D. *J. Am. Chem. Soc.* **1992**, *114*, 7843.

[18] For some recent examples of titanium nacnac chemistry see: (a) Basuli, F.; Aneetha, H.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 17992. (b) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 3321.

Examination of the ^{1}H NMR spectrum of this hydrazido(2−) complex revealed a slight broadening of the methyl groups associated with the multiply bonded ligand due to relatively slow exchange. The barrier associated with the exchange of the two methyl groups was found with the aid of variable-temperature NMR spectroscopy to be 12 kcal/mol. The nature of the barrier was explored using density functional theory; see the Supporting Information for details. Apparently, the barrier is associated with steric interactions between the hydrazido(2−) methyl groups and the groups on the nacnac ligand.

New C−C and C−N bonds are formed in **2** at or below room temperature. A possible mechanism for the formation of **2** is shown in Scheme 1, without the protonolysis of the nacnac ligand and product release (boxed portion of Scheme 1). The complex forms despite the fact that the optimized conditions for the iminohydrazination catalysis involve heating to 100 °C for 16 h.[8] Considering the ease with which **2** is formed, it seemed reasonable that the catalysis involved protonation of the product from **2** to reenter the catalytic cycle, the slow step possibly being this final protonolysis. Consistent with this, reaction of **2** with 10 equiv of H_2NNMe_2 to release the iminohydrazination product does not occur until the temperature is raised to ~90 °C, with no reaction occuring overnight at room temperature.

The synthesis of this unusual terminal hydrazido(2−) titanium complex suggests that hydrazido(2−) formation, [2 + 2] cycloaddition, 1,1-insertion of isonitrile, and protonolysis of the Ti−C bond in the five-membered metallacycle are quite favorable in our catalytic system. Studies are ongoing to further elucidate the mechanism of this iminohydrazination reaction and to discern the role of this complex in the catalytic cycle. The composition and ease with which the complex is formed are certainly suggestive of it having a role in the catalysis. The kinetic competence of **2**, its reactions with hydrazine, and its reaction with Hdap are currently under investigation.

Aside from its potential role in these new C−N bond forming reactions, the complex is a readily formed, rare terminal hydrazido(2−) complex of titanium. The complex exhibits a dimethylhydrazido(2−) ligand with a pyramidalized N_β. The metric parameters are consistent with only small participation by the isodiazene resonance form.

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Supporting Information Available: Text, tables, and figures giving synthetic details and characterization data for **2**, details of the X-ray diffraction experiment, and DFT calculations on the nature of the hydrazido(2−) barrier to rotation and a CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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