Formation of a Guanidinate-Supported Titanium Imido Complex: A Catalyst for Alkyne Hydroamination

Tiow-Gan Ong, Glenn P. A. Yap, and Darrin S. Richeson*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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*Summary: The reaction of [{(Me$_2$N)C(N^{i}Pr)$_2$}$_2$TiMe$_2$] with 1 equiv of 2,6-dimethylphenyl isocyanide yields the terminal Ti imido complex [{(Me$_2$N)C(N^{i}Pr)$_2$}$_2$TiNAr′] (Ar′ = 2,6-Me$_2$C$_6$H$_3$) (**4**). Complex **4** is an effective catalyst for the hydroamination of alkynes and reacts with H$_2$NAr′ to yield a complex with a transformed guanidinate ligand, [{(^{i}Pr(H)N)C(N^{i}Pr)(NAr′)}$_2$TiNAr′] (**5**).*

Guanidinate anions, [R′R″NC(NR)$_2$]$^-$, are receiving increasing attention as ancillary ligands for both main-group and transition-metal complexes, due to their flexible coordination behavior and their potentially tunable steric and electronic properties invoked through variation of substituents.[1−6] We are particularly interested in species with either one or two organic substituents on the N(R′)R″ center (e.g. N(H)R′ or NR$_2$′). Guanidinate complexes are now beginning to emerge as interesting species in small-molecule activation.[3,4,7] This communication reports two pathways for the formation of a terminal imido complex of Ti(IV) possessing a guanidinate supporting framework. One route involves an unusual transformation of an aryl isocyanide on a bis(guanidinato)TiR$_2$ center. Moreover, we provide initial details on the ability of the imido complex to catalyze the hydroamination of alkynes, including an examination of the regiochemistry of this reaction and the revelation that guanidinate may not be an innocent spectator in this process.

Compound **1** was prepared by the insertion reaction of 2 equiv of diisopropylcarbodiimide into the Ti−N bonds of Ti(NMe$_2$)$_2$Cl$_2$.[3] As shown in Figure 1, **1** is readily converted to either the dimethyl or dibenzyl complex by the direct reaction with MeLi or PhCH$_2$MgCl, respectively. As is the case for complex **1**, the ^{1}H and ^{13}C NMR spectra of **2** exhibit a single isopropyl environment, indicating rapid rotation of the ligand and racemization of the C_2-symmetric complexes at room temperature.[8] In contrast, the NMR spectra of the dibenzyl species **3** are consistent with a complex that

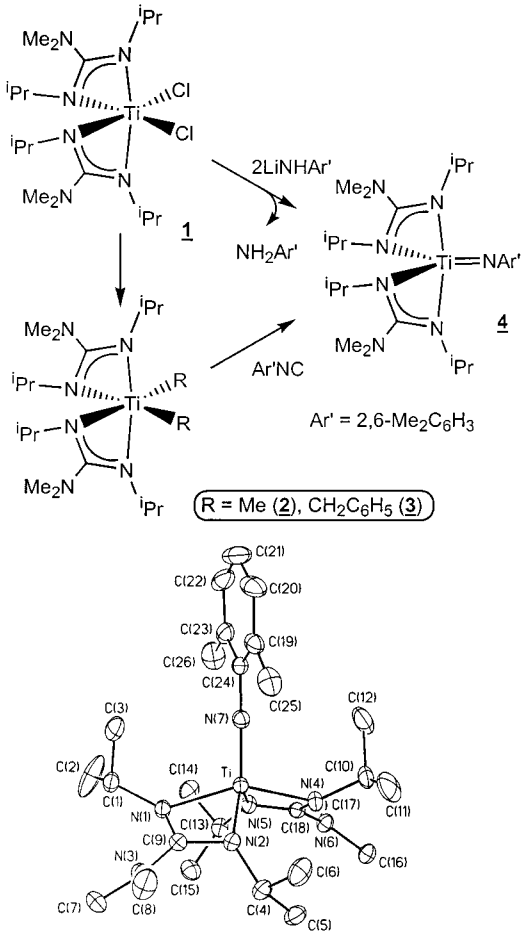

Figure 1. Reaction scheme for the formation of complexes **2**−**4** and a thermal ellipsoid plot of **4** with hydrogen atoms deleted. Selected bond distances (Å) and angles (deg) for **4**: Ti−N(7) = 1.723(2), N(1)−C(9) = 1.344(2), N(2)−C(9) = 1.333(2), N(3)−C(9) = 1.382(2), N(7)−C(24) = 1.380(2); N(7)−Ti−N(2) = 118.86(7), N(7)−Ti−N(1) = 103.39(7), N(2)−Ti−N(1) = 63.68(6), N(7)−Ti−N(4) = 104.63(7), N(2)−Ti−N(4) = 101.08(6), N(1)−Ti−N(4) = 151.96(6), N(7)−Ti−N(5) = 116.04(7), N(2)−Ti−N(5) = 125.10(6), N(1)−Ti−N(5) = 104.23(6), N(4)−Ti−N(5) = 63.88(6).

is stereochemically rigid at room temperature. Specifically, the spectra for this compound display four distinct doublets for the methyl groups of the isopropyl substituents and an AB splitting pattern for the methylene groups of the benzyl substituents.

Our recent observation that related hydrocarbyl zirconium complexes react with 2,6-dimethylphenyl isocyanide to generate a terminal imido complex provided the impetus for examining the product of the analogous reactions with **2**.[7] The reaction of **2** with (2,6-Me$_2$C$_6$H$_3$)NC proceeds rapidly to form a red solution

(1) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91 and references therein.

(2) (a) Lu, Z.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (b) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **2000**, 1515. (c) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2000**, *19*, 2573. (d) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **1999**, 2483.

(3) (a) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952. (b) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808.

(4) Giesbrecht, G. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923.

(5) Bailey, P. J.; Grant, K. J.; Mitchell, L. A.; Pace, S.; Prakin, A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **2000**, 1887.

(6) Coles, M. P.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1169.

(7) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1.

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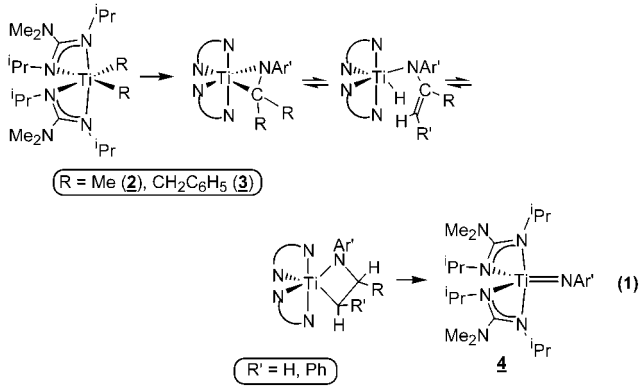
from which red crystals of **4** could be isolated. The identity of **4** as the imido complex was first supported by the NMR spectra. This species is fluxional at room temperature, as indicated by the single set of isopropyl resonances. Furthermore, the intensity of the signals for the eight ^{i}Pr groups are of appropriate integration ratio for a single 2,6-dimethylphenyl moiety. While the observation of a single set of ^{i}Pr signals is in contrast with the case for the zirconium analogue, which exhibited two signals of equal intensity for these groups, the appearance of these spectra is akin to the only other reported imido Ti complex with guanidinate ligands.[3]

Attempts to isolate an intermediate in the formation of **4** have so far failed. However, a reasonable mechanism for this transformation would follow a similar pathway we observed for the generation of $\{(Me_2N)C(N^i\text{-}Pr)_2\}_2Zr{=}N(2,6\text{-}Me_2C_6H_3)$ from $\{(Me_2N)C(N^iPr)_2\}_2ZrR_2$ (R = Me, CH_2Ph):[7] double insertion of one isocyanide into the two Ti hydrocarbyl moieties to form a transient metallaaziridine complex that could transform, via a sequential β-H elimination/insertion, to generate an azatitanacyclobutane (eq 1). A retro 2 + 2 cycloaddition

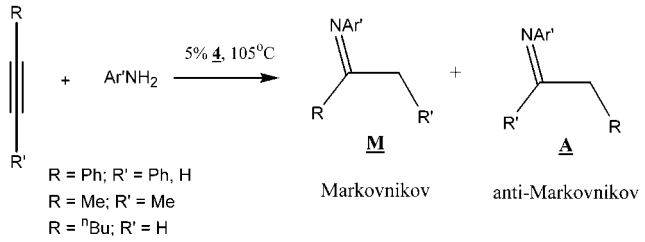


with elimination of olefin would generate the imido ligand of **4**. This is only the second reported observation of this transformation. The closely related conversion of an η^2-imine complex, [Zr(tropocoronand){η^2-Ar′NC-$(CH_2Ph)_2$}] (Ar′ = 2,6-$Me_2C_6H_3$), to yield a μ-imido species proceeds via an alternative mechanism.[9]

Complex **4** can be prepared directly from **1**, as depicted in Figure 1. The reaction of **1** with 2 equiv of $LiN(H)(2,6\text{-}Me_2C_6H_3)$ proceeds smoothly and quantitatively to **4** when monitored by NMR spectroscopy. Isolation of **4** was hampered by the presence of free amine, resulting in a 62% crystallized yield.

The degree of aggregation for complex **4** was determined by X-ray crystallographic analysis, and the results are presented in Figure 1.[10] Complex **4** is a terminal imido complex with the metal coordination environment completed by two chelating, bidentate guanidinate monoanions.[3,11] The coordination geometry of **4** is derived from a distorted trigonal bipyramid, with the imido ligand occupying an equatorial site. The limitations of the guanidinate bite angles (average 63.8°) require substantial distortions from an ideal tbp geometry. The Ti−N bond length of 1.723(2) Å and the near-linearity of the aryl imido group suggest the Ti−N(7) interaction may be viewed as a triple bond, giving a 14-electron metal center.

Table 1. Results for the Reaction of 2,6-Dimethylaniline with Alkynes Catalyzed by $\{(Me_2N)C(N^iPr)_2\}_2Ti{=}N(2,6\text{-}Me_2C_6H_3)$ (4)



entry	substrate	time (h)	yield (%)	**A**:**M**[a]
1	PhC≡CPh	120	55	
2	MeC≡CMe	18	18	
3	PhC≡CH	18	94	73:27
4	$C_4H_9C{\equiv}CH$	48	88	14:86

[a] Ratio of anti-Markovnikov to Markovnikov products determined by GC-MS comparison with authentic samples.

Our proposed mechanism for formation of imido complex **4** involves a retro 2 + 2 cycloaddition in the final step. A convincing case has been made that the reverse of this reaction, cycloaddition of an unsaturated substrate to M=N, is the key step in the mechanism of catalytic hydroamination of alkynes using cyclopentadienyl-supported group 4, U, and Th imido complexes.[12−14] Recent reports that homoleptic Ti amides and Ti complexes with mixed pyrrolyl amido ligand arrays are competent precatalysts for this reaction demonstrate that Cp ligands are not essential for hydroamination activity.[15] Given that hydroamination of unsaturated substrates is a promising route to the formation of new N−C bonds and that **4** possessed the appropriate imido function for catalysis, we examined the ability of **4** to facilitate this transformation.

The results for the hydroamination of four representative alkynes with 2,6-dimethylaniline as catalyzed by complex **4** are summarized in Table 1. These data indicate that **4** is a capable catalyst for these reactions and represents the first reported Cp-free imido complex for this transformation. Initial data suggest that terminal alkynes react more rapidly, with higher yields of imine, than internal alkynes. Complex **4** appears to exhibit reactivity comparable with that of Cp_2TiMe_2 or $Cp_2Zr(NHAr)_2$ catalyst precursors.[13b,16] However, the recently reported imido complex Cp(Ar′NH)(py)Ti=NAr′

(8) Complexes **2** and **3** have been structurally characterized, and details will be provided in the full paper.

(9) Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857.

(10) Crystal data: empirical formula $C_{26}H_{49}N_7Ti$, T = 203(2) K, λ = 0.710 73 Å, space group $P2_1/c$, a = 11.248(2) Å, b = 13.151(3) Å, c = 20.677(3) Å, β = 92.551(14)°, V = 3055.6(10) Å^3, Z = 4, R indices ($I > 2\sigma(I)$) R1 = 0.0441 and wR2 = 0.1361.

(11) For recently published complexes with Ti−imido groups see: (a) Trosch, D. J. M.; Collier, P. E.; Bashall, A.; Gade, L. H.; McPartlin, M.; Mountford, P.; Radojevic, S. *Organometallics* **2001**, *20*, 3308−3313 and refernces therein. (b) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216*, 65−97 and references therein. (c) Guiducci, A. E.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2001**, 1392−1394 and references therein.

(12) (a) Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 2923. (b) Straub, B. F.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4632.

(13) (a) Haak, E.; Siebeneicher, H.; Doye, S. *Org. Lett.* **2000**, *13*, 1935. (b) Haak, E.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3389.

(14) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773.

(15) (a) Cao, C.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2001**, *20*, 5011. (b) Shi, Y.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2001**, *20*, 3967.

(py = pyridine) is considerably more active and carries out the reaction exemplified by entry 1 with a half-life of less than 15 min at 75 °C.[12a] Our preliminary investigations indicate that less bulky arylamines (e.g. aniline) and aliphatic amines (e.g. cyclohexylamine) are effective for the hydroamination of alkynes with catalyst **4** and that they give reaction rates and yields similar to those presented in Table 1. Further details will be presented in our full report.

The two terminal alkynes employed in this reaction reveal an interesting regiochemical selectivity for catalyst **4**. A comparison of entries 3 and 4 indicates that phenylacetylene preferentially undergoes anti-Markovnikov addition, while hydroamination of 1-hexyne generated predominantly Markovnikov products. The regioselectivity in early-metal-catalyzed alkyne hydroamination reactions is a complex matter. For example, reported cyclopentadienyl-supported group 4 catalysts proceed with anti-Markovnikov addition to aryl alkynes,[12,13] while catalysts derived from $Ti(NMe_2)_4$ strongly favored Markovnikov products for phenylacetylene (>50:1 M:anti-M) with substantially reduced selectivity with 1-hexyne (3:1 M:anti-M).[15] Interestingly, the regioselectivity of intermolecular hydroamination of alkynes using $Cp^*_2AcMe_2$ (Ac = Th, U) is dependent on the identity of the metal.[14] The U complex gave products of Markovnikov addition, while the reverse selectivity was observed for the Th analogue. A focus of our ongoing investigations is to clarify this issue with regard to compound **4**.

When a mixture of **4**, alkyne, and amine was heated to 110 °C and monitored by NMR, we observed hydroamination products along with formation of a new metal complex and concomitant disappearance of **4**. This same species was formed when **4** and $Ar'NH_2$ were allowed to react at 110 °C and was accompanied by a color change of the reaction mixture from red to purple. This reaction was carried out on a preparative scale, and a new complex, **5**, was isolated as purple crystals in 70% yield (Figure 2). The most obvious changes in the NMR spectra from **4** to **5** were the loss of the resonances for the ligand NMe_2 groups and the appearance of three new singlets assigned to $Ar-CH_3$ groups and four doublets for the ^{i}Pr methyl groups. A structure consistent with the spectroscopic features and later confirmed by an X-ray crystallographic study is shown in Figure 2.[17] Complex **5** is more stereochemically rigid than **4**, as indicated by the appearance of the inequivalent methyl groups within this species. Like **4**, the Ti coordination environment of **5** consists of two chelating, bidentate guanidinate monoanions and a terminal imido ligand. The Ti=NAr′ bond is aligned with an approximate C_2 axis, making the two guanidinate ligands magnetically equivalent in solution. In contrast to **4**, the coordination geometry of **5** is derived from a distorted square pyramid with the apex formed by the imido moiety. Support for this assessment is provided by the uniform values obtained for the four N(7)−Ti−N(guanidinate) angles (range from 108.79(7) to 114.76(7)°) and the N−Ti−N angles of the pseudo-basal plane.

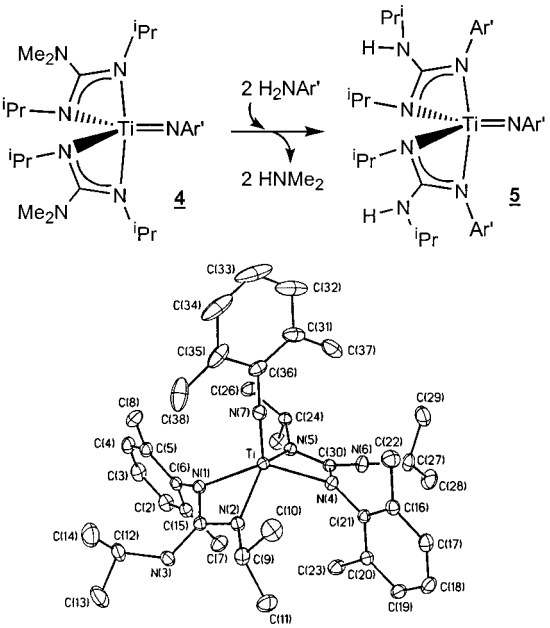


Figure 2. Reaction of complex **4** with 2,6-dimethylaniline and a thermal ellipsoid plot of **5** with hydrogen atoms deleted. Selected bond distances (Å) and angles (deg) for **5**: Ti−N(7) = 1.7223(16), N(1)−C(15) = 1.341(2), N(2)−C(15) = 1.342(2), N(3)−C(15) = 1.368(2), N(7)−C(36) = 1.375(2); N(7)−Ti−N(5) = 108.79(7), N(7)−Ti−N(2) = 114.76(7), N(5)−Ti−N(2) = 136.46(6), N(7)−Ti−N(1) = 111.88(7), N(5)−Ti−N(1) = 99.99(6), N(2)−Ti−N(1) = 63.83(6), N(7)−Ti−N(4) = 110.86(7), N(5)−Ti−N(4) = 63.96(6), N(2)−Ti−N(4) = 99.53(6), N(1)−Ti−N(4) = 137.22(6), C(36)−N(7)−Ti = 175.77(15).

Compounds **4** and **5** are related by the exchange of a dimethylamine group within the guanidinate ligand of **4** for a dimethylaniline group. Several possible mechanisms for this transformation can be envisioned; however, we have not yet determined details for this reaction. This transformation is formally a transamination reaction with exchange of a more basic dimethyl amido group for a more acidic aromatic amido group. Noteworthy is our observation that, while **5** is also a catalyst for the hydroamination of phenylacetylene, it exhibits a much lower turnover frequency. It appears that formation of **5** actually hinders the hydroamination activity of **4**.

We have shown that the bis(guanidinate) framework offers a scaffold for interesting metal-centered reactivity. We are currently exploring the generality of these reactions with isocyanides and related small molecules as well as attempting to further develop and clarify the mechanism of the hydroamination reactions presented herein.

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Supporting Information Available: Text giving experimental details for compounds **1**−**5** and tables of crystal data and structural solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708.

(17) Crystal data: empirical formula $C_{44}H_{63}N_7Ti$, T = 203(2) K, λ = 0.710 73 Å, space group $P\bar{1}$, a = 12.589(4) Å, b = 13.324(3) Å, c = 14.743(4) Å, α = 85.06(3)°, β = 69.844(19)°, γ = 70.835(18)°, V = 2191.8(10) Å^3, Z = 2, R indices ($I > 2\sigma(I)$) R1 = 0.0488 and wR2 = 0.1385.