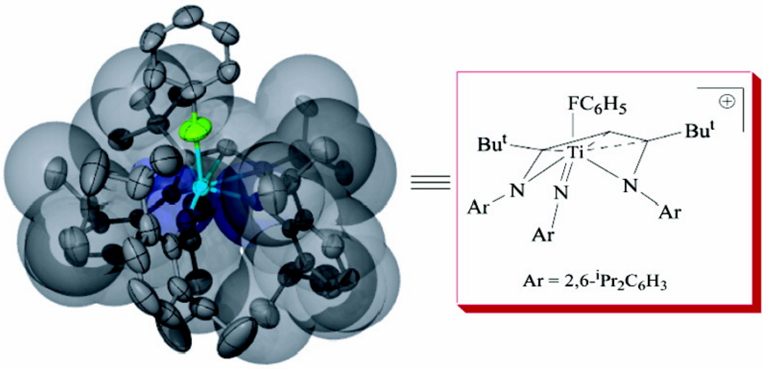
Communication

A Fluorobenzene Adduct of Ti(IV), and Catalytic Carboamination to Prepare □,β-Unsaturated Imines and Triaryl-Substituted Quinolines

Falguni Basuli, Halikhedkar Aneetha, John C. Huffman, and Daniel J. Mindiola

J. Am. Chem. Soc., **2005**, 127 (51), 17992-17993• DOI: 10.1021/ja0566026 • Publication Date (Web): 02 December 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Fluorobenzene Adduct of Ti(IV), and Catalytic Carboamination to Prepare α,β-Unsaturated Imines and Triaryl-Substituted Quinolines

Falguni Basuli, Halikhedkar Aneetha, John C. Huffman, and Daniel J. Mindiola*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received September 30, 2005; E-mail: mindiola@indiana.edu

Group 4 imido[1] complexes play a critical role in important catalytic processes, such as the intermolecular hydroamination of alkynes[1b,2−6] and alkenes,[7] hydrohydrazination of alkynes,[8] three-component coupling reactions to form α,β-unsaturated β-aminoimines,[9] and guanylation of amines,[10] among several other transformations.[1e] More recently, zirconocene imido systems have been implicated in carboamination reactions to produce α,β-unsaturated imines.[11] This carboamination process involves the insertion of aldimines into azametallacyclobutene intermediates generated by [2 + 2] cycloaddition reactions of an internal alkyne with the corresponding metal imido.[11] The latter reaction is particularly attractive since a new C=C bond is formed while C=N bonds are both cleaved and generated in such a process.

In this work, we report the synthesis and isolation of a rare example of a group 4 fluorobenzene adduct,[12] [(nacnac)Ti=NAr(FC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (nacnac- = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). This electron-deficient titanium imide can catalyze, under low catalyst loadings, carboamination reactions involving diphenylacetylene and a series of aryl aldimines to form α,β-unsaturated imines. Depending on the nature of the aldimine, the catalytic process can lead to formation of triaryl-substituted quinolines, the product resulting from a cyclization of the electron-rich α,β-unsaturated imine.

Recently, our group reported the synthesis of the *p*-dimethylaminoarene adduct, [(nacnac)Ti=NAr(η^1-C$_6$H$_5$NMe$_2$)][B(C$_6$F$_5$)$_4$].[13] FC$_6$H$_5$ solutions of the latter over an extended period of time gradually transform to a new complex, [(nacnac)Ti=NAr(FC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (**1**), which has been characterized on the basis of elemental analysis and ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy.[14] Pure samples of **1**, however, require several recrystallization steps in FC$_6$H$_5$ in order to force the equilibrium to formation of such a product. Fortunately, complex **1** can be prepared independently in one single step (74% isolated yield) utilizing [Et$_3$Si][B(C$_6$F$_5$)$_4$][15] with (nacnac)Ti=NAr(Cl) in FC$_6$H$_5$.[14]

Single-crystal X-ray diffraction studies of **1** at room temperature reveal coordination of FC$_6$H$_5$ to an electron-deficient [(nacnac)Ti=NAr]$^+$ framework (Figure 1). The Ti−F interaction is strong, thus elongating the F−C53 bond (1.417(3) Å) from that observed for free fluorobenzene (~1.36 Å). Most significantly is the coordination mode of the β-diketiminate ligand, which displays η^5 hapticity as a result of a deviated Ti atom above the NCCCN imaginary mean plane (~1.297 Å).[16] If one ignores the Ti−C$_\beta$ and −C$_\gamma$ interactions, the FC$_6$H$_5$ ligand occupies the fourth coordination site in a highly distorted tetrahedral geometry.

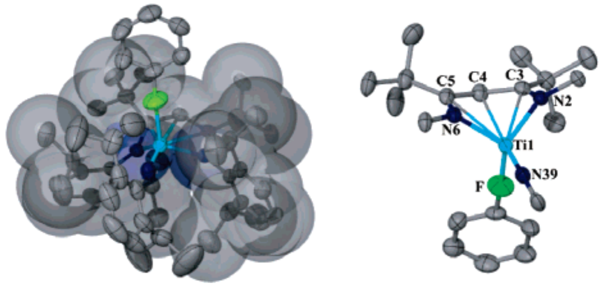


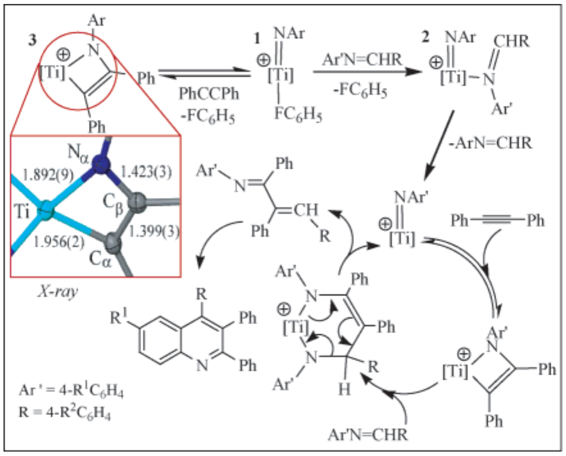
Figure 1. Molecular structure of [(nacnac)Ti=NAr(FC$_6$H$_5$)]$^+$ (left) depicting thermal ellipsoids at the 35% probability level. A simplified structure of the cationic skeleton of **1** is depicted on the right with omitted aryl groups for N6, N2, and N39. Selected metrical parameters (lengths in angstroms, angles in degrees): Ti1−N2, 1.973(7); Ti1−N6, 2.043(9); Ti1−N39, 1.707(2); Ti1−F, 2.113(7); Ti1−C3, 2.476(2); Ti1−C4, 2.518(3); Ti1−C5, 2.612(2); F−C53, 1.417(3); Ti1−N39−C40, 175.7(8); N2−Ti1−N6, 97.23(7); Ti1−F−C53, 177.5(6).

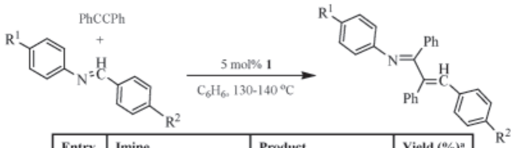
Complex **1** is exceedingly reactive and rapidly coordinates traces of THF or Et$_2$O to form the stable cations [(nacnac)Ti=NAr(THF)]$^+$ and [(nacnac)Ti=NAr(Et$_2$O)]$^+$, respectively.[13] In the absence of these poisons, complex **1** catalyzes carboamination reactions of PhCCPh and aldimines to produce highly arylated α,β-unsaturated imines with exclusive *E*,*E* configuration at the olefin and imine residues according to Figure 2. Whereas electron-poor aldimines fail to afford products, electron-rich *p*-aryl-substituted substrates react smoothly to afford eneimines in >70% isolated yield using low catalyst loads (5 mol %) and short time periods (24−36 h, entries 1−4, Figure 2). Catalyst loadings as low as 2.5 mol % also work, but reaction times extend to 84 h (Figure 2, entry 2).

Generation of the α,β-unsaturated imine is proposed to occur initially by FC$_6$H$_5$ displacement with the aldimine to afford the adduct, [(nacnac)Ti=NAr(aldimine)][B(C$_6$F$_5$)$_4$] (**2**),[14] which subsequently undergoes imine metathesis with an aldimine (Figure 2, entries 1−6) to yield a much more reactive and less sterically encumbered imido cation, [(nacnac)Ti=NAr′(FC$_6$H$_5$)][B(C$_6$F$_5$)$_4$]. The latter species rapidly [2 + 2] cycloadds the internal alkyne to provide the azametallacyclobutene [(nacnac)TiNAr′CPhCPh][B(C$_6$F$_5$)$_4$]. As proposed previously by Bergman and co-workers,[11] the azametallacyclobutene intermediate undergoes insertion of the aldimine to yield a thermally unstable six-membered ring metallacycle, which carries a [4 + 2] retrocycloaddition to regenerate the Ti=NAr′ linkage and extrude the α,β-unsaturated imine (Figure 2).

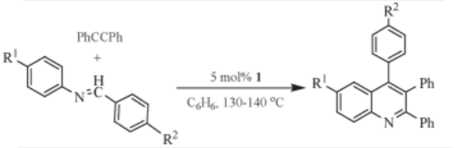
Evidence for azametallacyclobutene formation as opposed to a 1,2-insertion mechanism[8a] is supplied by structural and spectroscopic data.[2d,g,17] Accordingly, addition of 1 equiv of PhCCPh to **1** quantitatively generates [(nacnac)TiNArCPhCPh][B(C$_6$F$_5$)$_4$] (**3**) on the basis of ^{1}H and ^{13}C NMR spectra and single-crystal X-ray diffraction (Figure 2).[14] Imine metathesis taking place in the first step is strongly supported by stoichiometric reactions involving **1** and the corresponding aldimine to provide a new titanium imide cation and the hindered aldimine R^{2}CH=NAr. The latter organic product appears to be kinetically incompetent throughout the catalytic process since complex **3** does not react with such an aldimine in the catalytic reactions.[14] Unfortunately, attempts to isolate the less hindered imide have been plagued by its rapid decomposition.

10.1021/ja0566026 CCC: $30.25 © 2005 American Chemical Society





Entry	Imine	Product	Yield (%)^a
1	$R^1 = H, R^2 = H$	$R^1 = H, R^2 = H$	74
2	$R^1 = CH_3, R^2 = CH_3$	$R^1 = CH_3, R^2 = CH_3$	72
3	$R^1 = H, R^2 = OCH_3$	$R^1 = H, R^2 = OCH_3$	71
4	$R^1 = CH_3, R^2 = OCH_3$	$R^1 = CH_3, R^2 = OCH_3$	70



Entry	Imine	Product	Yield (%)^a
5	$R^1 = CH_3, R^2 = NMe_2$	$R^1 = CH_3, R^2 = NMe_2$	68
6	$R^1 = OCH_3, R^2 = NMe_2$	$R^1 = OCH_3, R^2 = NMe_2$	66

Figure 2. Mechanism for a catalytic carboamination reaction, where the [Ti] represents the (nacnac)Ti cation scaffold. Bottom tables depict carboamination reactions to prepare α,β-unsaturated imines and quinolines, respectively. In the tables, the isolated yields for the organic products are after column chromatography.

Contrary to entries 1−4, the usage of more electron-rich aldimines (entries 5 and 6) does not afford the corresponding α,β-unsaturated imines. Instead, triaryl-substituted quinolines are obtained in good yield upon workup of the reaction mixture (Figure 2). ^{1}H and ^{13}C NMR spectroscopy, single-crystal X-ray diffraction analysis (entry 6 in Figure 2), and MS data are consistent with heterocycle product formation.[14] Intuitively, quinoline production occurs from vinylic and ortho-aryl C−H bond rupture of the α,β-unsaturated imine with subsequent ring closure. Monitoring the reaction mixture by ^{1}H NMR spectroscopy (in C_6D_6) indicates that the α,β-unsaturated imine forms and decays during the catalytic process, thus suggesting that the quinoline originates from the corresponding α,β-unsaturated imine. Independently, we found that treatment of **1** with 1 equiv of an aldimine in the presence of the electron-rich α,β-unsaturated imines, where $R^1 = CH_3$ and $R^2 = NMe_2$ (prepared according to ref 11a), generates the corresponding quinoline (entry 5). As a result, we speculate that a putative $[(nacnac)Ti{=}NAr'(FC_6H_5)][B(C_6F_5)_4]$ might be responsible for the eneimine to quinoline conversion under these reaction conditions. Although we are currently uncertain about the fate of the ortho- and vinylic hydrogens for entries 5 and 6, the addition of base (2,6-di-*tert*-butyl-4-methylpyridine, 5−20 mol %) does not inhibit the carboamination and cyclization process (entry 5), thus suggesting that acid might not be playing a role in these catalytic reactions. We are currently exploring the mechanism behind formation of these quinolines since this type of reaction might involve, under a catalytic process, selective C−H activation pathways to afford multi-substituted N-heterocycles.

Acknowledgment. D.J.M. thanks Indiana University−Bloomington, the Dreyfus Foundation, the Sloan Foundation, and the NSF (CHE-0348941, PECASE) for financial support of this research. The authors also thank Dr. Donald L. Morrison and Boulder Scientific for a generous gift of $[CPh_3][B(C_6F_5)_4]$.

Supporting Information Available: Complete experimental preparation (compounds **1**−**3** and organic products), and crystallographic data (compounds **1**−**3**, and the quinoline from entry 6, Figure 2). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For some comprehensive reviews on imides and their reactivity, see: (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−482. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988. (c) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216−217*, 65−97. (d) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123−175. (e) Duncan, A. P.; Bergman, R. G. *Chem. Rec.* **2002**, *2*, 431−445.

(2) For some representative examples, see: (a) Anderson, L. L.; Arnold, J.; Bergman, R. G. *Org. Lett.* **2004**, *6*, 2519−2522. (b) Lee, S. Y.; Bergman, R. G. *Tetrahedron* **1995**, *51*, 4255−4276. (c) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753−2763. (d) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719. (e) Ackermann, L. *Organometallics* **2003**, *22*, 4367−4368. (f) Lorber, C.; Choukroun, R.; Vendier, L. *Organometallics* **2004**, *23*, 1845−1850. (g) Ward, B. D.; Maisse-Francois, A.; Mountford, P.; Gade, L. H. *Chem. Commun.* **2004**, 704−705. (h) Tillack, A.; Jiao, H.; Castro, I. G.; Hartung, C. G.; Beller, M. *Chem.−Eur. J.* **2004**, *10*, 2409−2420 and references therein. (i) Straub, B. F.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4632−4635. (j) Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305−2308.

(3) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664−665.

(4) (a) Haak, E.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3389−3391. (b) Pohlki, F.; Bytschkov, I.; Siebeneicher, H.; Heutling, A.; König, W. A.; Doye, S. *Eur. J. Org. Chem.* **2004**, 1967−1972. (c) For a review on hydroamination reactions involving alkynes, see: Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104−114.

(5) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839−2841.

(6) Zhang, Z.; Schafer, L. L. *Org. Lett.* **2003**, *5*, 4733−4736 and references therein.

(7) Ackermann, L.; Kaspar, L. T.; Gschrei, C. J. *Org. Lett.* **2004**, *6*, 2515−2518.

(8) (a) Odom, A. *Dalton Trans.* **2005**, 225−233 and references therein. (b) Li, Y.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 1794−1803.

(9) Cao, C.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 2880−2881.

(10) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 8100−8101.

(11) (a) Ruck, R. T.; Zuckermann, R. L.; Krska, S. W.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 5372−5374. (b) Ruck, R. T.; Bergman, R. G. *Organometallics* **2004**, *23*, 2231−2233.

(12) A Ti(III) fluorobenzene adduct has been structurally characterized. (a) Bouwkamp, M. W.; de Wolf, J.; del Hierro Morales, I.; Gercama, J.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 10956−10957. (b) Bouwkamp, M. W.; Budzelaar, P. M. H.; Gercama, J.; del Hierro Morales, I.; de Wolf, J.; Meetsma, A.; Troyanov, S. I.; Teuben, J. H.; Hessen, B. *J. Am. Chem. Soc.* **2005**, *127*, 14310−14319.

(13) Basuli, F.; Clark, R. L.; Bailey, B. C.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2005**, 2250−2252.

(14) See Supporting Information for complete experimental details.

(15) (a) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430−2443. (b) Scott, V. J.; Celenligil-Cetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852−2853.

(16) Thalladi, V. R.; Weiss, H.-C.; Blaser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702−8710.

(17) (a) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405−13414. (b) Wang, H.; Chan, H.-S.; Xie, Z. *Oganometallics* **2005**, *24*, 3772−3779. (c) Vaughan G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994−8001.

JA0566026