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

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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.

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).

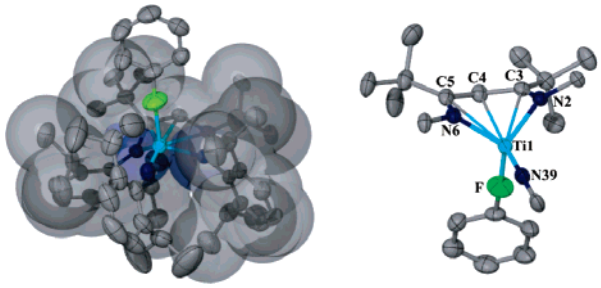

Figure 1. Molecular structure of [(nacnac)Ti═NAr(FC$_6$H$_5$)]$^+$ (left) depicting thermal ellipsoids at the 35% probability level. A simplified structure of the cationic skeleton of **1** is depicted on the right with omitted aryl groups for N6, N2, and N39. Selected metrical parameters (lengths in 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).

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.

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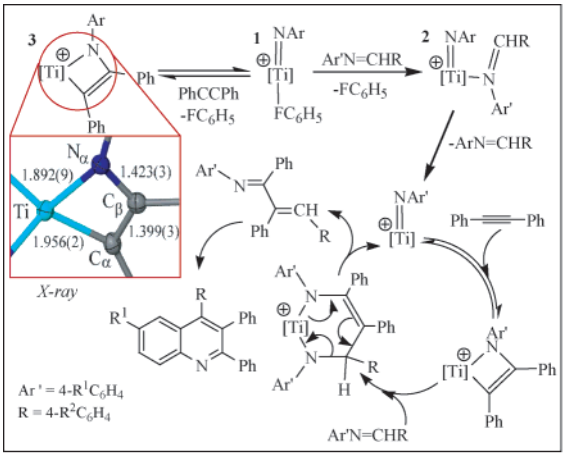
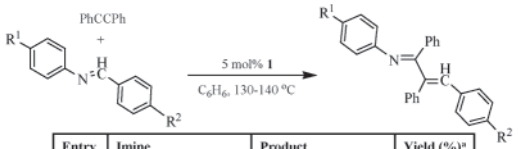
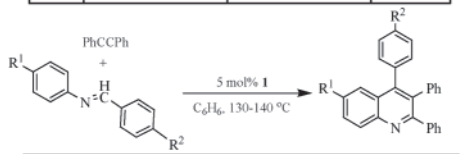




Entry	Imine	Product	Yield (%)[a]
1	$R^1 = H, R^2 = H$	$R^1 = H, R^2 = H$	74
2	$R^1 = CH_3, R^2 = CH_3$	$R^1 = CH_3, R^2 = CH_3$	72
3	$R^1 = H, R^2 = OCH_3$	$R^1 = H, R^2 = OCH_3$	71
4	$R^1 = CH_3, R^2 = OCH_3$	$R^1 = CH_3, R^2 = OCH_3$	70



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.

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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.

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