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Communication

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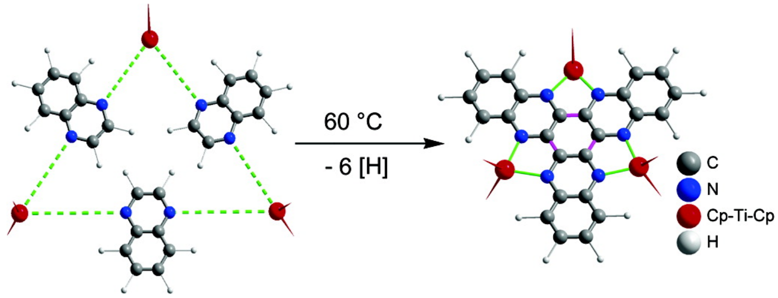

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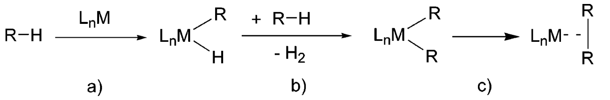
Dehydroaromatization of Quinoxalines: One-Step Syntheses of Trinuclear 1,6,7,12,13,18-Hexaazatrinaphthylene Titanium Complexes

Ingmar M. Piglosiewicz, Ruediger Beckhaus,* Wolfgang Saak, and Detlev Haase

Institute of Pure and Applied Chemistry, University of Oldenburg, D-26111 Oldenburg, Germany

Received July 15, 2005; E-mail: ruediger.beckhaus@uni-oldenburg.de

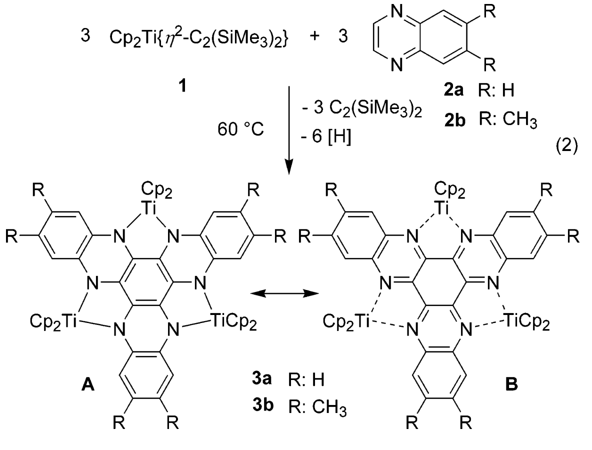
C−C formation reactions are of fundamental interest in various applications of organometallic substrates. A great deal of work has been devoted to the combination of transition metal initiated C−H bond activations (a, b) and subsequent C−C bond formation (c, eq 1).[1]


$$R{-}H \xrightarrow{L_nM} L_nM\begin{smallmatrix}R\\H\end{smallmatrix} \xrightarrow[-\ H_2]{+\ R{-}H} L_nM\begin{smallmatrix}R\\R\end{smallmatrix} \longrightarrow L_nM{-}{-}\begin{smallmatrix}R\\|\\R\end{smallmatrix} \qquad (1)$$

The C−H bond activation steps are well established.[2] From the practical point of view, a dehydrogenative coupling reaction from two C−H bonds makes synthetic procedures shorter and more efficient.[3] While reductive coupling of aryl ligands is well documented for group 10 biaryls,[4] the analogous process on biaryl zirconocene derivatives can only be induced under photochemical conditions,[5] and a radical decomposition seems to be preferred when titanocenes are irradiated.[6] The most commonly observed carbon−carbon reductive elimination process involving complexes of group 4 metals is the coupling of 1-alkenyl groups[7−9] and the coupling of alkyl and acyl ligands.[10,11]

We have found that by reacting pyrazine, triazine, or pyrimidine with the titanocene acetylene complex $Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}$ (**1**) or its permethylated analogue, as excellent titanocene sources,[12] multinuclear titanium complexes are formed,[13] often accompanied by simultaneously occurring C−C couplings of the primary formed radical anions.[14] Using pyrazine a three-fold C−C coupling reaction occurs, leading to a HAT[15] type complex characterized by a central cyclohexane ring.

Here we report the spontaneous coupling of *N*-heterocycles, initiated by C−H bond activation reactions. The reaction of quinoxalines **2a** and **2b** with **1** results in the formation of **3a** and **3b**, respectively (eq 2).



The compounds can be isolated in yields of 17% (**3a**) and 62% (**3b**) as crystalline products in one-pot syntheses at 60 °C (24 h).[16] These hexaazatrinaphthylene (HATN) titanium complexes are thermally stable (mp > 350 °C **3a**, 353 °C **3b**), but very sensitive to air and moisture. The molecular peaks can be observed (**3a** *m*/*z* 919 (3%) [M$^+$], **3b** *m*/*z* 1002 (4%) [M$^+$]). **3a** is nearly insoluble in common solvents, whereas **3b** is soluble in aromatic solvents.[17,18] Products formed by reactions of the free HATN ligands[19] with **1**, are in every respect identical to **3a** and **3b**, respectively.[18] However, due to the general poor solubility of HATN ligands, their complexation often ends up in poor yields and reveals significant disadvantages compared to the presented route.

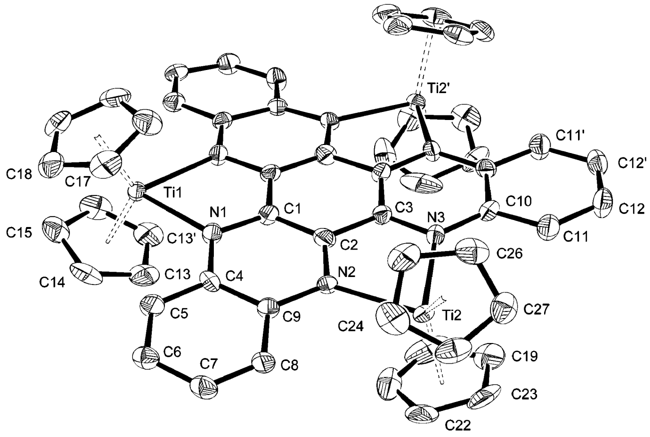


Figure 1. Molecular structure of **3a** (hydrogen atoms omitted, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−N1 2.187(4), Ti2−N2 2.170(4), Ti2−N3 2.195(3), C1−C2 1.420(7), C2−C3 1.426(7), C1−N1 1.353(6), C2−N2 1.370(6), C3−N3 1.352(6), C4−N1 1.396(6), C9−N2 1.389(6), C10−N3, 1.384(6), C1−C1′ 1.411(9), C3−C3′ 1.438(9).

Suitable crystals for X-ray diffraction are obtained directly from the reaction solutions (**3a**, Figure 1).[18] Disorder problems in **3b** prohibit further discussion of structural parameters. **3a** is *Cm*-symmetrical with the Ti1 center on the mirror plane.

The HATN ligand of **3a** is nearly planar with a slight deviation of the outer fused benzene rings. Bond distances and angles in **3a** suggest a reduced *N*-heterocyclic system with characteristic patterns of low-valent *N,N′*-chelated titanium complexes[14,20] Whereas uncomplexed HATN (**4**) shows for the central six-membered ring three long (average 1.479 Å) and three short C−C bonds (average 1.425 Å),[19] for **3a** shorter and more balanced distances (1.411(9)−1.438(9) Å) are found. The central C−C bonds of the chelate positions in **3a** (1.411(9)−1.426(7) Å) appear shorter compared to the free ligand **4** (1.472(6)−1.491(6) Å).[19] The C−N distances in **3a** are elongated (1.396(6)−1.352(6) Å) compared to **4** (1.318(5)−1.382(5) Å,[19] 1.323(3)−1.363(3) Å[21]), indicating contributions from the mesomeric amid form **A**. The Ti−N distances (2.170(4)−2.195(3) Å) lie in the upper limit for Ti−N σ bonds without $p_\pi{-}d_\pi$ interactions and correspond to the values expected for titanium-coordinated *N*-heterocycles in agreement with the mesomeric form **B**.[14]

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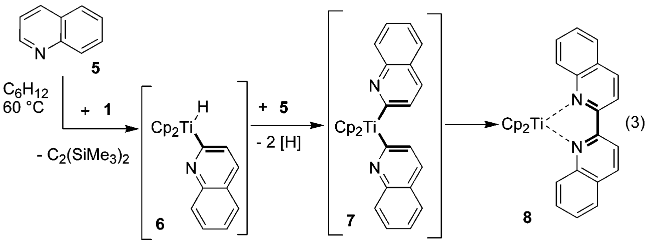
Reactions of pyridine and **1** lead to stable binuclear pyridyl titanium hydrides through C−H bond activation and ortho titanation.[22] Subsequent C−C bond formations are not observed.[23] Dehydrogenative coupling proceeds if benzannelated *N*-heterocycles with at least one ortho C−H bond are reacted with **1**. The simplest representative of this type of heterocycle is quinoline (**5**). With the formation of biquinoline **8**, another example for the dehydrogenative coupling is given what allows to present the potential mechanism of the reactions to **3a** and **3b** in a concise manner (eq 3).



The assembly of **8** can be explained by a two-fold primary C−H bond activation, leading via **6** and **7** to **8**.

This reductive coupling to the diazadiene like complex **8** shows similarities to well-established vinyl−diene rearrangement.[7] Corresponding intermediates in the reactions of **1** and **2** enable further C−H activation and subsequent C−C bond formation steps to give **3**. However, attempts to isolate intermediates such as **6** or **7** have not been successful yet, even at lower temperatures. The 2,2′-biquinoline complex **8** can be isolated as crystalline product (61%), exhibiting comparable structural characteristics as 2,2′-bipyridine titanium complexes,[20a] proven by X-ray diffraction (Figure 2). The shortening of the C9−C10 bond (1.432(2) Å), e.g. compared to free 2,2′-bipyridine (1.50 Å,[24a] 1.490(3) Å[24b]), indicates the reduced nature of the chelating ligand.

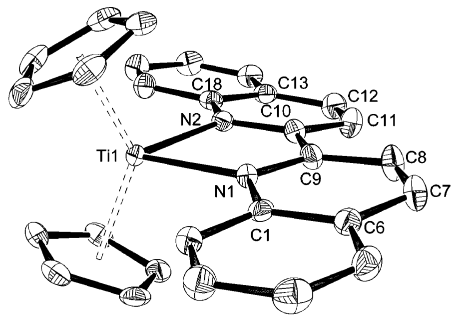
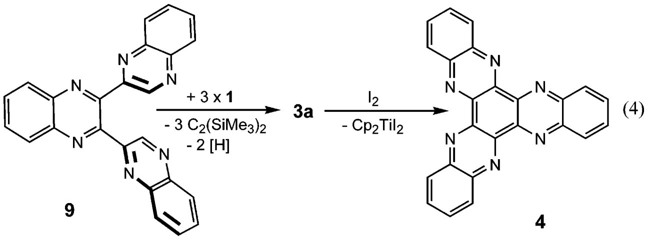


Figure 2. Molecular structure of **8** (hydrogen atoms omitted, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−N1 2.1920(14), Ti1−N2 2.1960(12), C9−C10 1.432(2), N2−C10 1.372(2).

The HATN complex **3a** is also formed by dehydrogenative coupling of 2,3-(2′,2″)-diquinoxalylquinoxaline (**9**) with **1**, which is in agreement with the proposed mechanism (eq 4).[18] Reacting **3a** with I_2 (3 equiv) in *n*-hexane as solvent gives **4**.



With the selective formation of carbon−carbon bonds, by dehydrogenative coupling of C−H bonds, particularly using commercial starting materials, an efficient route for the coupling of *N*-heterocycles has been established.

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Supporting Information Available: Experimental details and X-ray crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) HAT: 1,4,5,8,9,12-hexaazatriphenylene.

(16) **1** (0.600 g, 1.72 mmol) and **2a** (0.224 g, 1.72 mmol) were dissolved in THF (110 mL) at 25 °C. The solution turned dark violet and became dark green after a few minutes. The reaction mixture was heated to 60 °C, for 24 h leading to dark crystals of **3a**, separated by filtration from the hot mixture, washed with *n*-hexane (20 mL), and dried in vacuo. (yield 0.092 g, 17%) IR (KBr): $\tilde{\nu}$ = 2949(w), 2922(w), 2361(w), 2342(w), 1559(m), 1465(s), 1409(m), 1361(m), 1301(s), 1275(m), 1250(s), 1222(m), 1128(m), 1015(m), 805(s), 743(s), 626(m) cm^{-1}. MS (70 eV): *m/z* (rel intensity) = 918 (3) $[M^+]$, 740 (2) $[M - Cp_2Ti]^+$, 178 (100) $[Cp_2Ti]^+$, 65 (27) $[Cp]^+$. $C_{54}H_{42}N_6Ti_3$: calcd. C 70.61, H 4.61, N 9.15; found C 70.36, H 4.75, N. 9.26. Further details are given in ref 18.

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