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

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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]

$$R{-}H \xrightarrow{L_nM} L_nM\genfrac{}{}{0pt}{}{R}{H} \xrightarrow[-H_2]{+\,R{-}H} L_nM\genfrac{}{}{0pt}{}{R}{R} \longrightarrow L_nM{-}{-}\genfrac{}{}{0pt}{}{R}{R} \quad (1)$$

$$\text{a)} \qquad\qquad \text{b)} \qquad\qquad \text{c)}$$

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$_2$Ti{η^2-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]

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).

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.

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]

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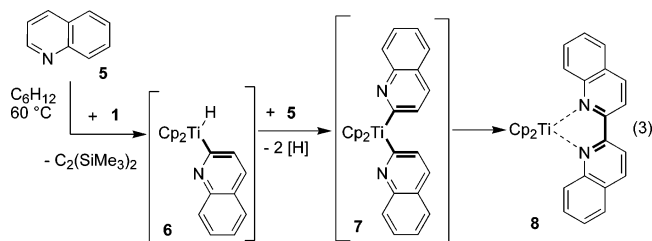
The assembly of **8** can be explained by a two-fold primary C−H bond activation, leading via **6** and **7** to **8**.

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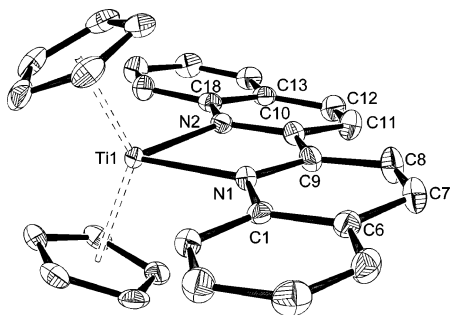
Figure 2. Molecular structure of **8** (hydrogen atoms omitted, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−N1 2.1920-(14), Ti1−N2 2.1960(12), C9−C10 1.432(2), N2−C10 1.372(2).

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**.
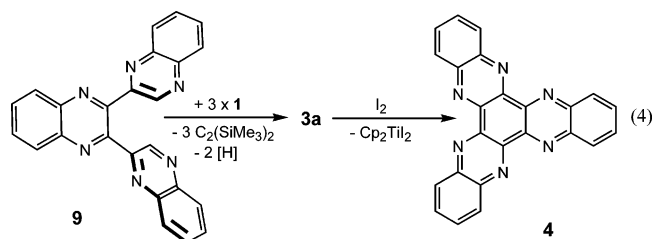
With the selective formation of carbon−carbon bonds, by dehydrogenative coupling of C−H bonds, particularly using com-

mercial starting materials, an efficient route for the coupling of *N*-heterocycles has been established.

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(w), 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$_2$Ti]$^+$, 178 (100) [Cp$_2$Ti]$^+$, 65 (27) [Cp]$^+$. C$_{54}$H$_{42}$N$_6$Ti$_3$: 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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