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Reactions of Azines with Titanocene: C−H Activation, C−C Coupling, and N−N Cleavage to Heterobimetallic Complexes

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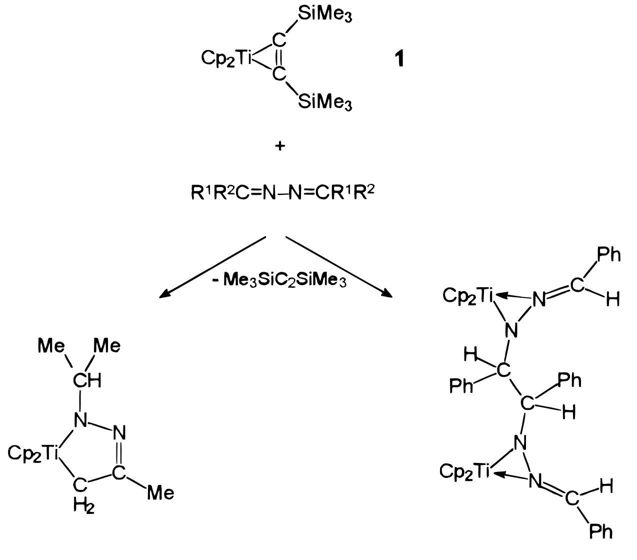
Summary: Either C−H activation or C−C coupling is observed in reactions of titanocene with azines ($R^1R^2C{=}N{-}N{=}CR^1R^2$), which lead to the formation of complexes ***2*** *and* ***3****, respectively. The reaction with two different metallocene units can yield heterobimetallic bis(alkylideneamido) complexes (****4****).*

Reactions of organic substrates containing multiple bonds with transition-metal complexes are of general interest in organometallic chemistry from the theoretical and the synthetic point of view, respectively.[1] In a series of investigations concerning the reactions of group 4 metallocenes with alkynes and substituted butadiynes[2] as well as with ketones, aldehydes, and imines we could often illustrate unexpected results which also lead to an interesting resulting chemistry.[2] Herein we report reactions of titanocene with azines and a subsequent reaction which provides an "early−late" heterobimetallic complex. Since the bis(trimethylsilyl)acetylene−titanocene complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**)[3] is an excellent starting material for the generation of the reactive Cp_2Ti fragment, reactions with azines were carried out with **1** as a metallocene precursor.

Scheme 1



2: $R^1 = R^2 = Me$ **3**: $R^1 = H$; $R^2 = Ph$

The reaction of **1** with acetone azine leads, after substitution of the alkyne with the azine, to an unexpected activation of the methyl C−H bond (Scheme 1, $R^1 = R^2 = Me$). In the resulting green complex **2**[4] a hydrogen atom is shifted from one methyl group to the carbon atom of the second C=N moiety, and a five-membered metallacycle is obtained. The NMR spectra of **2** confirm the C−H activation by signals of a CH_2 group at 1.36 ppm (very broad; becomes a sharp singlet at 330 K) and 55.9 ppm in ^1H and ^{13}C NMR, respectively. In addition, there are two different methyl signals at 1.14/2.28 ppm and 24.5/25.7 ppm in the ratio of 2:1. In the ^1H NMR spectrum the isopropyl methyl groups appear as a doublet (1.14 ppm, $^3J_{HH} = 6.3$ Hz, 6H), and consequently, the signal of the methine proton is a septet at 3.82 ppm ($^3J_{HH} = 6.3$ Hz, 1H). Very broad methylene and cyclopentadienyl resonances at ambient temperatures result from a dynamic behavior due to a folded ground-state conformation typical for azametallacycles.[5] Indeed, at higher temperatures (330 K) the NMR spectra of **2** suggest C_s molecular symmetry in solution; however, decreasing the temperature reveals a nonplanar molecular geometry and the ^1H NMR spectrum at 220 K displays two diastereotopic Cp units (5.06 (s, 5H), 5.21 (s, 5H)) as well as two nonequivalent methylene protons (0.65 (s, 1H), 2.16 (s, 1H)). The course of the reaction of acetone azine and titanocene with the activation of a strong sp^3 C−H bond in **2** is rather surprising in view of the ease of oxidative

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[4] **2**: 67% yield from **1** and acetone azine in toluene. ^1H NMR (toluene-d_8, 297 K): δ 1.14 (d, $^3J_{HH} = 6.3$ Hz, 6H, CH_3), 1.36 (br, 2H, CH_2), 2.28 (s, 3H, CH_3), 3.82 (septet, $^3J_{HH} = 6.3$ Hz, 1H, $CHMe_2$), 5.17 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (297 K): δ 24.5, 25.7 (CH_3), 55.9 (CH_2), 60.2 (CH), 105.2 (Cp), 151.7 (C=N). ^1H NMR (toluene-d_8, 220 K): δ 0.65 (s, 1H of CH_2), 1.23, 1.36 (br, 3H, CH_3), 2.16 (s, 1H of CH_2), 2.35 (s, 3H, CH_3), 3.73 (br, 1H, $CHMe_2$), 5.06, 5.21 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (220 K): δ 24.0, 25.0, 25.9 (CH_3), 55.0 (CH_2), 59.8 (CH), 102.7, 107.3 (Cp), 151.8 (C=N). IR (Nujol mull): $\nu_{C=N}$ 1603 cm^{-1}. MS: *m/e* 290 (M^+).

[5] (a) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068. (b) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661 and references therein.

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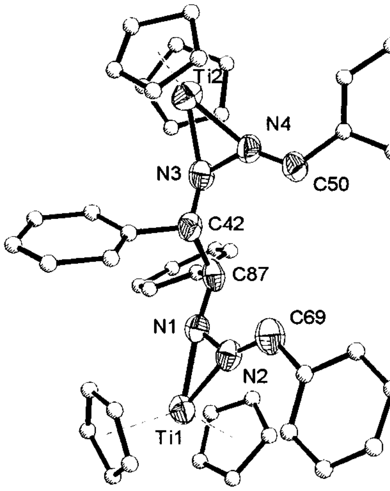


Figure 1. ORTEP view of one of the two independent molecules in the asymmetric unit of **3** (for clarity only main atoms are drawn as 50% probability ellipsoids). Selected average bond lengths (Å) and angles (deg): Ti1−N1, 2.06(2); Ti1−N2, 2.10(2); Ti2−N3, 2.06(2); Ti2−N4, 2.13(2); N1−N2, 1.33(2); N3−N4, 1.35(2); N2−C69, 1.30(2); N4−C50, 1.31(2); N1−C87, 1.46(2); N3−C42, 1.47(2); C42−C87, 1.57(2); N1−Ti1−N2, 37.4(6); N3−Ti2−N4, 37.5(6).

addition of the N−N bond of $Ph_2C{=}N{-}N{=}CPh_2$ to $Cp_2Zr(C_4H_6)$[6a] and $CpCo(C_2H_4)$.[6b]

A completely different result was obtained in the reaction of **1** with benzaldehyde azine (Scheme 1; R^1 = Ph, R^2 = H). In this case the paramagnetic complex **3**[7] is formed in a 1:1 reaction of metallocene with the azine. Due to the absence of NMR data the structure of **3** was determined by X-ray crystallography[8] (Figure 1). The structure analysis reveals a binuclear titanium(III) complex resulting from an reductive C−C coupling[9] which converts two azine molecules into a dianionic bridging ligand. Each Ti(III) center is complexed by an amido nitrogen and additionally coordinated by the electron pair of the second imine nitrogen. The structure of the ligand chain is characterized by two C−N double bonds and two C−N single bonds, respectively, intact N−N single bonds, and the newly formed central C−C single bond.

The course of the intermolecular azine coupling can only be a matter of speculation prior to further studies. However, it seems reasonable to assume that the azine unit coordinates to one titanium center via the nitrogen atoms. The metal-promoted dimerization of two monomers could proceed by a radical mechanism, which is not uncommon for early transition metals in low oxidation states.[10] A monoelectronic reduction of the azine could produce the radical Ti(III) species $Cp_2Ti[N(N{=}CHPh)C^{\bullet}HPh]$ which dimerizes to the binuclear complex **3**.

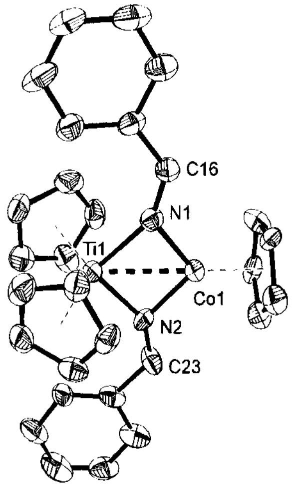
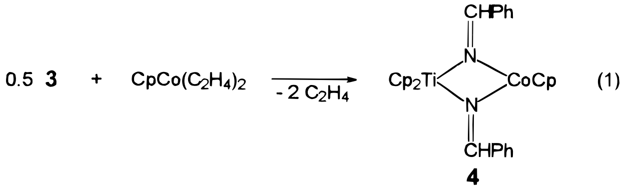


Figure 2. ORTEP view of one of the two independent molecules in the asymmetric unit of **4** (30% probability ellipsoids). Selected average bond lengths (Å) and average angles (deg): Ti−Co, 2.568(6); Ti−N1, 2.00(2); Ti−N2, 1.99(2); Co−N1, 1.86(2); Co−N2, 1.85(2); N1−C16, 1.30(4); N2−C23, 1.29(4); N1−Ti−N2, 91.4(9); N1−Co−N2, 101.2(9).

The reaction of **3** and $[CpCo(C_2H_4)_2]$[11] yields almost quantitatively the heterobimetallic product **4**[12] (eq 1).



$$0.5\ \mathbf{3} + CpCo(C_2H_4)_2 \xrightarrow[-2\,C_2H_4]{} Cp_2Ti(\mu\text{-}N{=}CHPh)_2CoCp \quad (1)$$

The interaction of the bis(titanocene) **3** with an additional Co(I) center causes the activation of the central C−C bond as well as the cleavage of the azine N−N bonds, leading to the bridged bis(alkylideneamido) complex **4**.

NMR spectra of **4** show the resonances corresponding to the phenyl groups and two different Cp units in the ratio of 2:1. In addition, the ^1H and ^{13}C signals of the azine CH function appear at 10.70 ppm (s, 2H) and 170.5 ppm, respectively. The structure of **4** was unambiguously determined by an X-ray diffraction analysis (Figure 2).[13]

The bond distances and angles support the nitrogen-bridged coordination with a central four-membered Ti−N−Co−N cycle. Additionally, there seems to be an

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[6] (a) Erker, G.; Frömberg, W.; Krüger, C.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400. (b) Carofiglio, T.; Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1957.

[7] **3**: 80% from **1** and benzaldehyde azine in toluene; paramagnetic. Anal. Calcd for $C_{48}H_{44}N_4Ti_2$ (772.6): C, 74.62; H, 5.74; N, 7.25. Found: C, 74.71; H, 5.87; N, 7.28. IR (Nujol mull): $\nu_{C=N}$ 1594, 1576 cm^{-1}. MS: *m/e* 387 ($M/2^+$).

[8] Crystal data for **3**: brown prism, 0.5 × 0.3 × 0.2 mm, monoclinic, *Pn*, a = 12.007(2) Å, b = 15.337(2) Å, c = 22.660(4) Å, β = 103.99(2)°, T = 293 K, V = 4049(1) Å^3, Z = 4, d_{calcd} = 1.267 g cm^{-3}, 10 793 reflections measured, 5982 unique data, 3181 observed data ($I > 2\sigma(I)$), R_1 = 0.048, wR_2 (all data) = 0.126, GOF (all data) = 0.922.

[9] Reviews: (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. (b) Dang, Y.; Geise, H. J. *J. Organomet. Chem.* **1991**, *405*, 1. (c) Eisch. J. J.; Shi, X.; Alila, J. R.; Thiele, S. *Chem. Ber.* **1997**, *130*, 1175.

[10] (a) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349. (b) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1996**, *35*, 5995.

[11] Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716.

[12] **4**: 84% from **3** and $CpCo(C_2H_4)_2$ in THF. ^1H NMR (C_6D_6): δ 4.51 (s, 5H, Cp), 5.44 (s, 10H, Cp), 7.28−7.35 (m, 6H, *m*-/*p*-Ph), 7.77 (m, 4H, *o*-Ph), 10.70 (s, 2H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 90.2, 108.6 (Cp), 125.3, 126.2, 129.4, 138.5 (Ph), 170.5 (C=N). Anal. Calcd for $C_{29}H_{27}N_2TiCo$ (510.4): C, 68.25; H, 5.33; N, 5.49. Found: C, 67.98; H, 5.50; N, 5.58. IR (Nujol mull): $\nu_{C=N}$ 1592 cm^{-1}. MS: *m/e* 510 (M^+).

[13] Crystal data for **4**: red-brown prism, 0.2 × 0.2 × 0.1 mm, monoclinic, *Pc*, a = 17.962(4) Å, b = 15.293(3) Å, c = 8.796(2) Å, β = 98.35(3)°, T = 293 K, V = 2390.6(9) Å^3, Z = 4, d_{calcd} = 1.418 g cm^{-3}, 7014 reflections measured, 3759 unique data, 2633 observed data ($I > 2\sigma(I)$), R_1 = 0.062, wR_2 (all data) = 0.172. GOF (all data) = 1.025.

interaction between the titanium and the cobalt center. The average Ti−Co distance of 2.568(6) Å in the bridged complex **4** is compatible with the Ti−Co distances of 2.565 Å in $(^{t}BuO)_3Ti-Co(CO)_4$[14a] and 2.614 Å in $[(CO)_9Co_3CO]Ti-Co(CO)_4$.[14b] Unequal steric demands of the different metallocene units cause a slight bending of the bridging alkylideneamido ligands toward the smaller CpCo moiety (average angles: Ti−N1−C16, 148(2)°; Ti−N2−C23, 148(2)°; Co−N1−C16, 128(2)°; Co−N2−C23, 128(2)°). Although there are bimetallic complexes known to contain bridging alkylideneamido ligands,[6,15] **4** represents the first heterobimetallic complex of its type and the facile formation could be an easy way to synthesize complexes of various metal combinations.

We have demonstrated reactions of azines with titanocene. Depending on the azine substituents, either C−H activation or C−C coupling is observed. Reactions of azines with two metal centers can lead by the cleavage of the N−N single bond to "early−late" heterobimetallic bis(alkylideneamido) complexes. Further studies aimed at the clarification of the mechanism of azine−metallocene reactions and at determination of the scope of the bimetallic reactions are currently in progress.

Acknowledgment. This work was supported by the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **3** and **4** (34 pages). Ordering information is given on any current masthead page.

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(15) For example: (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Klose, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N. *J. Am. Chem. Soc.* **1994**, *116*, 9123.