[7] For an example and for leading references, see: F. Agnelli, G. A. Sulikowski, *Tetrahedron Lett.* **1998**, *39*, 8807–8810.

[8] The coordination in Pd-enolate complex is likely to be by the carbon atom (rather than by the oxygen atom). For stoichiometric studies involving analogous intermediates and leading references see: D. A. Culkin, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 5816–5817.

[9] Note that the base employed must not bear a β-hydrogen (because of the potential for undesired Pd^{II} reduction by β-H transfer). *tert*-Butoxide bases proved sluggish whereas hexamethyldisilazide compounds proved useful.

[10] It is not evident why this works, although there is some discussion of M–O (M = Na, Li) covalency. Perhaps surprisingly, given the reduction of diarylation on switching from NaHMDS to LiHMDS, ethyl phenylacetate can be α-arylated in good yield (based on arylating agent) at 80 °C under essentially the same conditions.

[11] With very hindered aryl substrates, Hartwig et al., found that $t\mathrm{Bu}_3\mathrm{P}$ proved to be better than the carbene ligand.

[12] With hindered propionates (those with branching at the α- or β-positions) or glycinates, the ethyl, or methyl ester was preferred over the *tert*-butyl ester.

[13] The higher C–H acidity of ketimine and aldimine derivatives of glycinates allows the weaker base K_3PO_4 to be employed.

[14] Homologues (which require generation of a quaternary center) have not yet been successfully prepared by this method.

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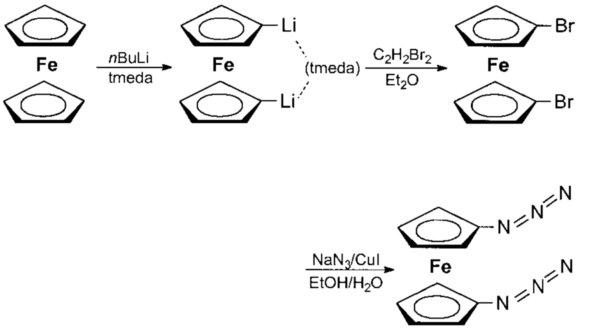
1,1′-Ferrocenedi(amido) Chelate Ligands in Titanium and Zirconium Complexes

Max Herberhold*

Although known for more than four decades,[1, 2] the sandwich compound $[\mathrm{Fe}(\mathrm{C_5H_4\text{-}NH_2})_2]$ (**1**) ($[\mathrm{fc(NH_2)_2}]$; fc = ferrocene-1,1′-diyl),[2, 3] has not really been used either as a building block in polymers or as a chelate ligand in transition metal complexes. Recently, however, an improved synthesis—via 1,1′-di(azido)ferrocene ($[\mathrm{fc(N_3)_2}]$;[2] Scheme 1)—has been worked out and the molecular structure of **1** has been determined.[3]



Scheme 1. Synthesis of 1,1′-di(azido)ferrocene; tmeda = tetramethylethylenediamine.

According to the crystal structure analysis of **1**, the lattice contains two (ecliptic) rotamers, that is the 1,1′ and the 1,2′ isomer.[3] The diamine **1** can be protonated, or oxidized (at the iron atom; Scheme 2) to give a green, paramagnetic cation **1a** ($\mu_{\mathrm{eff}} = 2.1\ \mu_B$), of which salts of the type $[\mathrm{fc(NH_2)_2}]^+\mathrm{A}^-$ (anion $\mathrm{A}^- = \mathrm{PF_6}^-$, OTf^- or TCNE^- (TCNE = tetracyanoethylene) were obtained.[3]

Starting from the primary diamine **1**, the silylated derivative $[\mathrm{fc(NH\text{-}SiMe_3)_2}]$ (**2**) can be prepared,[5] while condensation with benzaldehyde and subsequent hydrogenation generates 1,1′-di(benzylamino)ferrocene, $[\mathrm{fc(NH\text{-}CH_2Ph)_2}]$ (**3**).[6]

Titanium and Zirconium Complexes

With regard to the development of new catalysts for the olefin polymerization, during the last few years an increasing number of complexes of the electron-poor transition metals titanium and zirconium with di(amido) chelate ligands has been investigated[5–8] instead of the highly reactive di(cyclopentadienyl)titanium and -zirconium complexes ("metallocene catalysts"). The doubly deprotonated derivatives of the secondary diamines **2**–**4** serve as examples for 1,1′-ferrocenedi(amido) ligands (Scheme 2 and 5).

The use of amino-functionalized 1,1′-ferrocenedi(amido) sandwich compounds as chelate ligands provides two particular advantages:

1) Owing to the rotational mobility of the two cyclopentadienyl rings around the axis which is defined by the ring centers and the iron atom, the bidentate 1,1′-ferrocenedi(amido) ligand can easily adapt to the steric situation in the coordination sphere of the central metal,—as known for $[\mathrm{fc(PPh_2)_2}]$.[4b]
2) Owing to the relatively high charge density in the electron-rich ferrocene sandwich, the iron center can be readily oxidized which may also be controlled by cyclovoltammetry.[3, 7]

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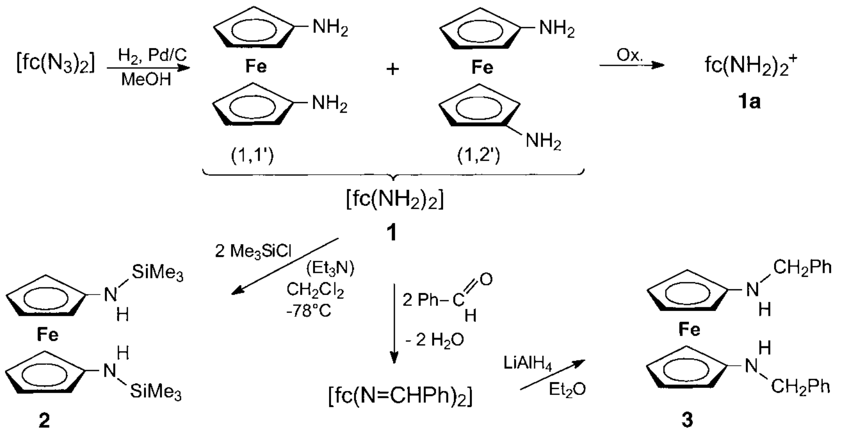
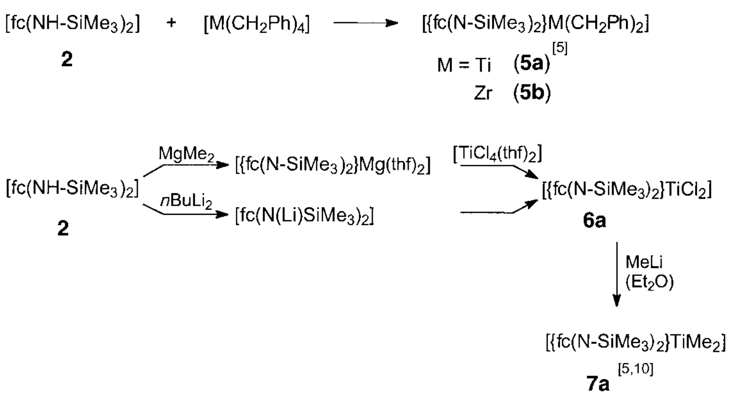
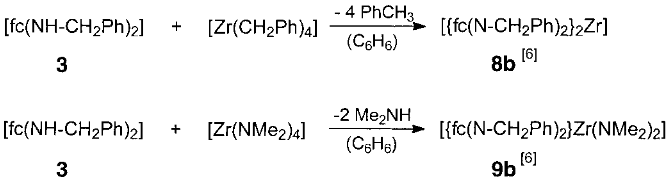


Scheme 2. Formation and reactivity of **1**.

The 1,1′-ferrocenedi(amido) complexes are formed either by aminolysis of tetrabenzyltitanium or -zirconium, respectively, or via metalated intermediates of the N-substituted 1,1′-di(amino)ferrocene (Scheme 3). Instead of the tetrabenzyl complexes $[M(CH_2Ph)_4]$ (M = Ti, Zr), tetrakis(dimethylamino) complexes $[M(NMe_2)_4]$ (M = Ti, Zr) can be subjected to aminolysis with **3** or **4** to give the corresponding di(amido) complexes (Scheme 4 and 5). In the case of the zirconium complexes containing 1,1′-ferrocenedi(phenylamido) ligands (Scheme 5), the Zr center behaves as a Lewis acid which eagerly adds dimethylamine.[7]

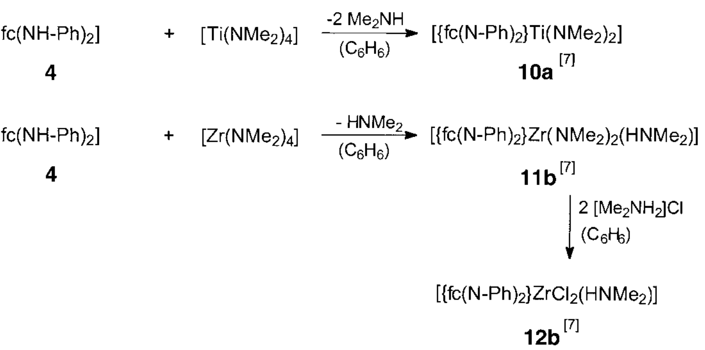


Scheme 3. Preparation of 1,1′-ferrocenedi(trimethylsilylamido) complexes of titanium and zirconium.



Scheme 4. Preparation of 1,1′-ferrocenedi(benzylamido) complexes of zirconium starting from the benzyl-substituted di(amido) ligand **3**.

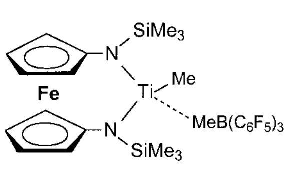
The titanium and zirconium complexes **5**–**12** can be considered as 1,3-diaza-2-metalla[3]ferrocenophanes.[4c] The crystal structure analyses (of **5b**, **6a**, **7a**[5] and of **11b** and **12b**[7]) indicate that the two cyclopentadienyl rings always adopt a nearly ecliptic conformation, although the cyclopentadienyl ring planes slightly diverge at the di(amido)–metal bridge. The dihedral angle α between the ring planes lies in the range of 4–12°. In all complexes **5**–**12** the amido-nitrogen atoms are coordinated in a trigonal-planar arrangement (sp^2 hybridization). Considering the distances between iron and zirconium center (333.9 pm in **11b**, 331.0 pm in **12b**), a direct interaction between the two metals can be excluded.



Scheme 5. Preparation of 1,1′-ferrocenedi(phenylamido) complexes of titanium and zirconium starting from the phenyl-substituted di(amido) ligand **4**.

Complexes Containing Heterodimetal Interactions

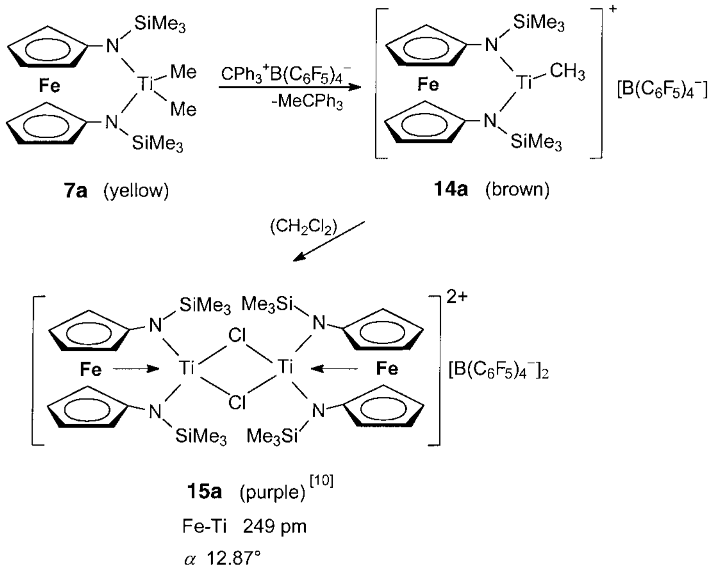
In Ziegler–Natta olefin polymerization processes, the catalyst must be activated by generation of a vacant coordination position at titanium or zirconium, respectively.[9] As recently shown by Shafir and Arnold,[10] this activation may be simulated by the reaction of **7a** with the strong Lewis acid $B(C_6F_5)_3$. In the resulting adduct **13a** one of the two methyl groups has been shifted towards boron with concomitant formation of a pseudo-tetrahedral anion $[MeB(C_6F_5)_3]^-$; the distance from the titanium center to this methyl group (Ti–C 229.7(4) pm) is significantly longer than that to the remaining terminal methyl ligand (208.1(5) pm). Simultaneously, the Fe···Ti distance in **13a** shortens to 307 pm.



13a (dark red)[10]

Fe····Ti 307 pm
∢ N-Ti-N 145.2(2)°
α 7.64°

Like $B(C_6F_5)_3$, the salt $[CPh_3][B(C_6F_5)_4]$ can be used to split off a methyl ligand from **7a**;[10] the titanium cation thus formed is stabilized by the 1,1′-ferrocenedi(amido) chelate ligand (Scheme 6). The cation in **14a**, which is coordinatively unsaturated at titanium, activates dichloromethane to generate the chloro-bridged dimer **15a**. The short Fe–Ti distance (249 pm) in **15a** can be ascribed to the formation of a dative Fe →Ti bond. The sandwich structure is more distorted in **15a** than in **7a** and **13a**; the amido-nitrogen atoms in **15a** now possess trigonal-pyramidal coordination (sp^3), and the titanium center is no longer in the FeN$_2$ plane.



Scheme 6. Formation of a dative Fe →Ti bond in **15a**.

Experience has shown that it is difficult to extract the iron atom from the sandwich cave of the ferrocene and to force it into a dative bond to a metal (M) available in the vicinity, although its Lewis basicity is beyond doubt.[4c, 10, 11] It is assumed that, as a prerequisite for a Fe →M heterodimetallic interaction, M has to be a Lewis-acidic, electron-poor center with a vacant coordination site. Some [3]ferrocenophanes such as [{fcS$_2$}M(PPh$_3$)] (M = Pd (**16**),[12] Pt (**17**)[13]) and corresponding cations[11] like **18** and **19** fulfill these requirements, and the relatively short distance (Fe →M < 300 pm)—in addition to the distortion of the sandwich structure—is considered as an indication for a direct Fe–M interaction. Compound **15a** contains the shortest Fe–M bond (249 pm) observed so far in a ferrocene-containing heterodimetallic coordination compound. Evidently, the stabilization of cationic titanium centers by a 1,1′-ferrocenedi(amido) chelate ligand leads to the formation of a dative Fe →Ti bond.

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