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Aminolysis of Bis[bis(trimethylsilyl)amido]iron and -cobalt as a Versatile Route to N-Heterocyclic Carbene Complexes

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Supporting Information

ABSTRACT: A range of new N-heterocyclic carbene complexes of iron(II) and cobalt(II) have been conveniently obtained by the aminolysis of bis[bis(trimethylsilyl)amido]iron and -cobalt precursors with imidazol(in)ium salts. Whereas sterically less hindered salts produced the tetrahedral complexes [M-(carbene)₂Cl₂] (M = Fe), bulkier salts gave the three-coordinate [M(carbene){N(SiMe₃)₂}Cl] (M = Fe, Co), which serve as versatile precursors to a range of derivatives; mechanistic aspects of the reaction are discussed.



T he chemistry of the N-heterocyclic carbene complexes of iron and cobalt is less developed than that of other transition metals. Recently, important catalytic reactions have

Scheme 1. Summary of the NHC Complexes Obtained by Aminolysis of $[M{N(SiMe_3)_2}]$ (M = Fe, Co) with Azolium Salts^{*a*}



^{*a*}Legend: (i) 2 equiv per Fe of azolium salt in THF, room temperature, 12 h; (ii) 1 equiv of 1,3-bis(*tert* butyl)imidazolinium chloride, toluene, room temperature, 12 h; (iii) 1 equiv of azolium or azolinium chloride, toluene, room temperature, 12 h.



Figure 1. Molecular structure of 1b. Selected bond lengths (Å) and angles (deg): C(1)-Fe(1), 2.132(3); C(1)-N(1), 1.348(3); C(1)-N(2), 1.349(3); N(1)-C(1)-N(2), 106.0(2); C(1)#1-Fe(1)-C(1), 103.33(13); Cl(1)#1-Fe(1)-Cl(1), 106.90(4); C(1)#1-Fe(1)-Cl(1), 104.90(7).

been reported in which the in situ formed catalyst, from an imidazolium salt and a basic organometallic reagent in the presence of iron or cobalt precursors, is presumably an N-heterocyclic carbene metal complex.^{1,2} Furthermore, a few examples where well-defined iron NHC complexes are involved in catalytic transformations³⁻⁶ or structurally mimicking [FeFe] hydrogenase enzymes have also appeared.^{7,8} However, the majority of well-characterized NHC complexes of Fe and Co bear carbonyl,⁹⁻¹¹ cyclopentadienyl,^{3,11-16} or nitrosyl¹⁷ stabi-

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Figure 2. Molecular structure of 2b (one of the two independent molecules in the asymmetric unit is shown). Selected bond lengths (Å) and angles (deg): C(1)-Fe(1), 2.138(3); C(1)-N(1), 1.340(4); C(1)-N(2), 1.345(4); Cl(1)-Fe(1), 2.2353(10); Fe(1)-N(3), 1.932(3); N(3)-Fe(1)-C(1), 127.38(12); N(3)-Fe(1)-Cl(1), 118.05(9); C(1)-Fe(1)-Cl(1), 114.57(9).



Figure 3. Molecular structure of 4. Selected bond lengths (Å) and angles (deg): Cl(1)-Fe(1), 2.3043(8); Fe(1)-N(3), 1.938(2); Fe(1)-N(4), 1.947(2); N(3)-Fe(1)-N(4), 129.38(10); N(3)-Fe(1)-Cl(1), 112.58(8); N(4)-Fe(1)-Cl(1), 117.99(8).

lizing coligands or have the NHC donor as part of a chelating framework. $^{18-23}$ In both cases, the reactivity of the complex can be modulated by these features.

The synthesis of NHC complexes of Fe from preformed NHCs and FeCl₂⁶ is associated with problems of poor stoichiometry control, long reaction times, and forcing reaction conditions that are incompatible with the stability of certain preformed NHC reactants. Very recently, a synthetic method based on the substitution of tmed in [FeCl₂(tmed)] (tmed = N,N,N',N'-tetramethylethylenediamine) by the free N-heterocyclic carbene 1,3-R₂-3,4-dimethylimidazol-2-ylidene (R = Me, Et, Pr¹) was reported. The scope of this method is not yet fully known.²⁴ The aminolysis of the Fe and Co silylamides [M{N(SiMe₃)₂}₂] (M = Fe, Co³⁶)^{25,26} by suitable imidazolium halides cleanly afforded "pincer" NHC complexes; this methodology was applied very recently also to the synthesis of chelating dicarbene complexes.^{18–20} However, its scope appeared to be limited to imidazolium halides; imidazolium salts associated with noncoordinating anions (e.g., BF₄⁻, PF₆⁻) were unreactive or gave intractable mixtures under forcing





"a denotes an unsaturated and **b** a saturated NHC. Legend: (i) TlOSiPh₃/toluene; (ii) HOSiPh₃/toluene; (iii) CyNHC(Me)=NCy/toluene; (iv) LiNHDiPP/ether; (v) H_2 NDiPP/octane.

conditions. Since the silylamido species responsible for the C2 metalation of the azolium salts and the operating metalation mechanism are not established, we decided to further explore the scope and the details of the reaction, especially using simple azolium salt precursors to monodentate NHCs, with well-understood steric and electronic properties.²⁷

The reaction of $[Fe{N(SiMe_3)_2}_2]$ with 1,3-Prⁱ₂-imidazolium chloride (2 equiv per Fe) in THF at room temperature gave good yields of the colorless $[Fe(NHC)_2Cl_2]$ (1a; NHC = 1,3-diisopropylimidazol-2-ylidene) (see Scheme 1). It is analogous to a complex previously obtained^{6,24} by direct substitution or association methods.

However, the versatility and scope of the aminolysis methodology is best demonstrated by the synthesis of $[Fe(NHC)_2Cl_2]$ (**1b**; NHC = 1,3-bis(2-isopropylphenyl)-imidazolin-2-ylidene), since in this case the free NHC is not stable under the substitution reaction conditions. Complex **1b** was obtained by the reaction of 1,3-bis(2-isopropylphenyl)-imidazolinium chloride with $[Fe{N(SiMe_3)_2}_2]$ in THF and was crystallized from THF/pentane. It was characterized analytically and crystallographically (see Figure 1). Its structure is consistent with the observed magnetic behavior for a high-spin tetrahedral Fe center ($5.2 \mu_B$); the bond lengths and angles fall within the range observed for similar complexes in the literature.^{6,19,24}

In contrast, the reaction of $[Fe{N(SiMe_3)_2}_2]$ with 1,3bis(aryl)imidazol(in)ium chlorides (1 equiv per Fe) at room temperature in THF or, preferentially, toluene gave excellent yields of the colorless, air-sensitive three-coordinate species $[Fe(NHC){N(SiMe_3)_2}CI]$ (NHC = IPrⁱ (2a), SIPrⁱ (2b), IMes (3a), SIMes (3b); IPrⁱ = 1,3-(DiPP)_2-imidazol-2-ylidene, SIPrⁱ = 1,3-(DiPP)_2-imidazolin-2-ylidene; IMes =1,3-(Mes)_2imidazol-2-ylidene; SIMes =1,3-(Mes)_2-imidazolin-2-ylidene, Mes = mesityl, DiPP = 2,6-diisopropylphenyl). Interestingly, aminolysis of only one N(SiMe_3)_2 group took place, irrespective of the stoichiometry of the added reagents. Magnetic measurements show the presence of one high-spin iron center (5.5 μ_B). The structure of 2b is shown in Figure 2. The iron center adopts a distorted-trigonal-planar geometry with the NHC plane at an angle of ca. 45° from the trigonal coordination plane. Complexes **2** and **3** can be considered as Lewis base adducts of "FeCl{N(SiMe₃)₂}" and constitute rare examples of neutral mononuclear three-coordinate Fe complexes.^{28–31} It is plausible that the combination of the steric requirements of the SIPrⁱ and the silylamide and their strong σ donating properties are responsible for the coordinative and electronic unsaturation of the complexes.

The steric parameter $\% V_{bur}$ for the 1,3-bis(2isopropylphenyl)imidazolin-2-ylidene and 1,3-diisopropylimidazol-2-ylidene (25.4% and 29.2%, respectively)³² compared with those for SIPrⁱ/IPrⁱ and Imes/SImes (35% and 33.3%, respectively) is a useful tool to quantify the observed reactivity. In order to test further the hypothesis that steric effects are dictating the degree of substitution, we carried out the reaction with 1,3-bis(*tert*-butyl)imidazolinium chloride ($\% V_{bur} = 39.5\%$) with [Fe{N(SiMe₃)₂}₂]. Surprisingly, we isolated the ionic complex [SIBu^tH][Fe{N(SiMe₃)₂}₂Cl] (4), in almost quantitative yield (see Figure 3),³³ which proved to be stable toward aminolysis at least up to 70 °C in toluene.

It became therefore reasonable to assume that the anionic $[Fe{N(SiMe_3)_2}_2Cl]^-$ may be the initial intermediate that is activated toward aminolysis by the azolium salts; this is also consistent with the expected increased basicity of the coordinated silvlamide in the more electron-rich anionic species. In order to verify this assumption, we attempted the aminolysis of $[Fe{N(SiMe_3)_2}_2]$ with $(SIPr^iH)^+(BF_4)^-$. Under conditions comparable to those of the formation of 2b, we could not observe any reaction. However, after prolonged heating of a mixture of $[Fe{N(SiMe_3)_2}_2]$ and $(SIPr^iH)^+(BF_4)^-$ (1/1) in octane/THF (95/5) (120 °C for 48 h), we isolated colorless crystals of the adduct SIPrⁱ·BF₃, which was characterized spectroscopically and crystallographically (see the Supporting Information), presumably resulting from dehydrofluorination of the imidazolinium salt facilitated by the presence of the iron amide. The mechanism of this transformation is not clear. Dehydrofluorination of imidazolium tetrafluoroborates has recently been reported under more forcing conditions (T > 230 °C, at 10^{-4} mbar).³⁴

Interestingly, H bonding between azolium cations and various anions is well established crystallographically,^{35a} spectroscopically, and computationally and has been implied as a factor responsible for the selectivity in the formation of the normal or abnormal NHC complexes by direct metalation.^{35b} The occurrence of this interaction would lead to weakening of the azolium C–H bond and facilitate a C2 metalation assisted by a coordinated base. However, in the aminolysis reactions described here an increase of the basicity of the silylamide and the steric accessibility of the C2–H acidic site by the coordinated base (i.e., silylamide) may be the crucial factors determining reactivity and chemoselectivity.

Extension of the aminolysis methodology to cobalt seems also to support these ideas. For example, the reaction with $(IMesH)^+Cl^-$ or $(SIMesH)^+Cl^-$ produces the three-coordinate $[Co(IMes)\{N(SiMe_3)_2\}Cl]$ (5a) and $[Co(SIMes)\{N-(SiMe_3)_2\}Cl]$ (5b), respectively, in excellent yields, while the reaction of $[Co\{N(SiMe_3)_2\}_2]$ with $(SIPr^iH)^+Cl^-$ at room temperature leads to the ion pair $[SIPr^iH][Co\{N(SiMe_3)_2\}_2Cl]$ (6), which crystallized together with minor amounts of $[SIPr^iH][Co(SIPr^i)Cl_3]$ (both characterized crystallographically).

The new three-coordinate complexes 2, 3, and 5 provide versatile entries for the synthesis of numerous new NHC complexes by either metathetical and/or further aminolytic reactions. Selected preliminary examples for iron are shown in Scheme 2. All complexes in the scheme have been characterized by analytical, spectroscopic, and diffraction methods and will be reported in detail in forthcoming papers. The chemistry and catalytic properties of all new complexes are currently being investigated in our group.

In conclusion, the methodology described above provides a new route to the synthesis of versatile Fe and Co monodentate NHC complexes, some with low coordination numbers and possessing functional groups, opening the way for the mild and selective synthesis of numerous derivatives suitable for further chemical studies. The method is particularly advantageous in cases where the generation and/or stability of the NHCs are problematic.³⁷

ASSOCIATED CONTENT

Supporting Information

Text and figures giving experimental details and characterization data of the complexes reported and CIF files giving crystallographic data for **1b**, **2b**, **4**, and the complex $SIPr^{i}BF_{3}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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