Inorg. Chem. **2007**, *46*, 7695–7697

Inorganic Chemistry
Communication

Unusual Iron(II) and Cobalt(II) Complexes Derived from Monodentate Arylamido Ligands[#]

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Received May 3, 2007

The coordination chemistry of the N-substituted arylamido ligands [N(R)($C_6H_3R'_2$-2,6)] [R = $SiMe_3$, R′ = Me (L^1); R = CH_2Bu^t, R′ = Pr^i (L^2)] toward Fe^{II} and Co^{II} ions was studied. The monoamido complexes [M(L^1)(Cl)(tmeda)] [M = Fe (**1**), Co (**2**)] react readily with MeLi, affording the mononuclear, paramagnetic iron(II) and cobalt(II) methyl–arylamido complexes [M(L^1)(Me)(tmeda)] [M = Fe (**3**), Co (**4**)]. Treatment of 2:1 [Li(L^2)$(THF)_2$]/$FeCl_2$ affords the unusual two-coordinate iron(II) bis(arylamide) [Fe$(L^2)_2$] (**5**).

Amide ligands $[NR_2]^-$ belong to a class of versatile ligands that form stable complexes with a wide spectrum of metals.[1] Compared to the chemistry of early-transition-metal amides, which has been extensively investigated, studies of amido complexes of the later transition metals have received relatively less attention.[1−4] The bulky $[N(SiMe_3)_2]^-$ ligand has been extensively studied and proved to be successful in the isolation of divalent transition-metal amides with low coordination numbers.[5−7] Using sterically very crowded silylamides $[N(SiMe_nPh_{3-n})_2]^-$ (n = 1, 2) and diarylborylamides $[NR(BR'_2)]^-$ (R = C_6H_5, 2,4,6-$Me_3C_6H_2$; R′ = 2,4,6-$Me_3C_6H_2$, 2,6-$Me_2C_6H_3$), Power and co-workers have successfully prepared crystalline, two-coordinate Mn^{II}, Fe^{II}, and Co^{II} derivatives.[8−10] Our recent work has been centered upon the synthesis and reaction chemistry of metal amides derived from *chelating* aryl- and alkylamido ligands.[11−14] Earlier we have reported on a bidentate monoanionic 2-pyridylamido ligand system, $[N(R)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]^-$ (R = $SiBu^tMe_2$ or $SiBu^tPh_2$), that displayed interesting complexation chemistry with transition metals and the lanthanides.[11,13,14] Continuing our studies on low-valent transition-metal amides, we have extended our work to the closely related *monodentate* arylamido ligands $[N(R)(C_6H_3R'_2\text{-}2,6)]^-$, where R = $SiMe_3$ or CH_2Bu^t and R′ = Me or Pr^i. The latter ligand system has been shown to be versatile in supporting a variety of main-group, transition-metal, and lanthanide complexes.[15] Nevertheless, its chemistry with low-valent late transition metals remains relatively less explored. Cummins and co-workers have reported a few low-coordinate iron arylamido complexes derived from *N*-(*tert*-hydrocarbyl)arylamido ligands.[16] The reactivity of the latter complexes toward small molecules, such as NO, has also been investigated. In this Communication, we report the initial results of our studies on the complexation of the $[N(R)(C_6H_3R'_2\text{-}2,6)]^-$ ligand system with Fe^{II} and Co^{II} ions. Noteworthy results of the

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[#] Dedicated to Prof. Thomas C. W. Mak on the occasion of his 71st birthday.

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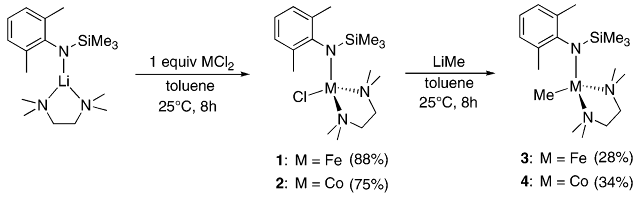
10.1021/ic700850e CCC: $37.00

Scheme 1



present work include the isolation of the mononuclear iron(II) and cobalt(II) methyl−arylamide complexes [M(L^1)(Me)(tmeda)] [M = Fe, Co; L^1 = N(SiMe$_3$)(C$_6$H$_3$Me$_2$-2,6)] and the two-coordinate iron(II) bis(arylamide) [Fe(L^2)$_2$] [L^2 = N(CH$_2$Bu^t)(C$_6$H$_3$Pr$^i{}_2$-2,6)].

Our initial attempts to prepare iron(II) and cobalt(II) bis(amido) complexes of the L^1 ligand via the reaction of 2 mol equiv of [Li(L^1)(tmeda)] with anhydrous MCl$_2$ (M = Fe, Co) have been unsuccessful. In our hands, only the monosubstituted iron(II) and cobalt(II) amides [M(L^1)(Cl)(tmeda)] [M = Fe (**1**), Co (**2**);[17] (Scheme 1) were isolated, despite the stoichiometry of the reagents and reaction conditions (reaction temperature and solvent polarity) we employed. Apparently, the steric stability of **1** and **2** prevents them from undergoing further ligand metathesis reactions to form the corresponding disubstituted derivatives.[18] This is consistent with our observations that both **1** and **2** were unreactive toward the bulky [N(SiMe$_3$)$_2$]$^-$ ligand, notwithstanding that they contain a terminal chloride ligand that may allow further functionalization of the compounds. Accordingly, we turned our attention to the reaction of **1** and **2** with less hindered ligands. Toward this end, we chose a prototypical alkyl ligand in organometallic chemistry, namely, the least hindered methyl ligand.

As shown in Scheme 1, treatment of **1** and **2** with equimolar amounts of LiMe in toluene afforded the 14-electron iron(II) and 15-electron cobalt(II) methyl−arylamide complexes [M(L^1)(Me)(tmeda)] [M = Fe (**3**), Co (**4**)], respectively. Both **3** and **4** are mononuclear high-spin complexes with solution magnetic moments of 5.02 μ_B (for **3**) and 4.12 μ_B (for **4**).[19] The ^{1}H NMR spectra of the methyl complexes showed well-resolved isotropically shifted resonance signals due to L^1 and tmeda (see the Supporting Information). However, like other iron(II) alkyl complexes recently reported in the literature (vide infra),[20−24] resonance signals for the metal-bound methyl ligand could not be observed, probably because of the broadness of the signals. Figure 1 depicts the single-crystal X-ray structure of **3**, which is isomorphous with the Co^{II} analogue **4** (see Figure S3 in the Supporting Information).[25] Complexes **3** and **4** exhibit a distorted tetrahedral geometry. Compared to other four-coordinate iron(II) and cobalt(II) methyl complexes, the Fe−Me distance of 2.084(6) Å for **3** is comparable to that of 2.079(3) Å for [PhTp^{tBu}]FeMe[20] but slightly longer than that of 2.013(3) Å for [PhBP$^{iPr}{}_3$]FeMe.[21] On the other hand, the Co−Me distance of 2.038(2) Å for **4** is slightly shorter than the corresponding distances of [Tp^{tBu}]CoMe [Co−C = 2.12(1) Å][22] and [PhTt^{tBu}]CoMe [Co−C = 2.052(3) Å].[23] However, they are longer than the Fe−Me and Co−Me distances of 2.009(3) and 1.963(3) Å, respectively, in the three-coordinate diketiminate complexes [LMMe] (L = β-diketiminate; M = Fe, Co).[24] The M−N(amido) distances of 1.965(4) and 1.960(2) Å in **3** and **4**, respectively, are slightly longer than the corresponding distances in the chloro derivatives **1** [1.948(2) Å] and **2** [1.922(2) Å] (see the Supporting Information). This structural difference may be

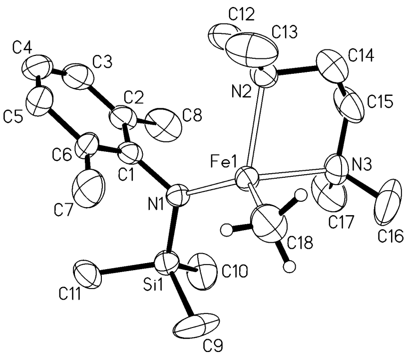


Figure 1. Molecular structure of **3** (30% thermal ellipsoid). Selected bond lengths (Å) and angles (deg) with data for **4** in square brackets are as follows: M = Fe [Co], M−N1 1.965(4) [1.960(2)], M−C18 2.084(6) [2.038(2)], N1−C1 1.423(6) [1.422(2)], N1−Si1 1.697(4) [1.715(2)]; M = Fe [Co], C18−M−N1 127.4(2) [124.90(9)], C1−N1−Si1 118.7(3) [118.5(1)], C1−N1−M 116.4(3) [116.4(1)], Si1−N1−M 122.6(2) [122.65(8)].

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(17) The molecular structures of **1** and **2** have been confirmed by X-ray crystallography. See Figures S1 and S2 in the Supporting Information. **1** and **2** are isotypic, monomeric complexes with a distorted tetrahedral geometry around the high-spin metal center (μ_{eff} = 4.79 μ_B for **1** and 3.77 μ_B for **2**[19]). Detailed structural and spectroscopic characterization of the complexes will be reported in a full article.

(18) In order to verify that **1** and **2** are not kinetic products of the reactions, we have also examined the reaction of MCl$_2$ (M = Fe or Co) with 2 mol equiv of [Li(L^1)(tmeda)] at a higher temperature (80 °C). Only the monoamido complexes **1** and **2** were isolated under the latter reaction conditions.

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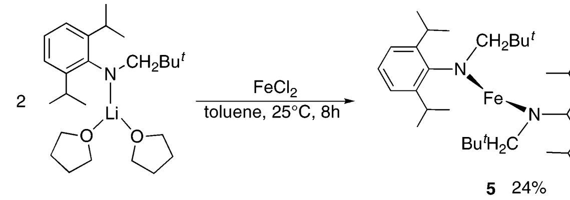
(25) Data collection for **3**: C$_{18}$H$_{37}$FeN$_3$Si, M_r = 379.45, crystal dimensions 0.4 × 0.3 × 0.2 mm^3, triclinic ($P\bar{1}$), a = 8.036(14) Å, b = 10.296(16) Å, c = 14.97(2) Å, α = 75.74(3)°, β = 76.18(3)°, γ = 70.79(3)°, V = 1114(3) Å^3, Z = 2, ρ_{calcd} = 1.131 g/cm^3, μ = 0.734 mm^{-1}, Mo Kα radiation λ = 0.710 73 Å, T = 273(2) K, reflections measured = 6817, independent reflections = 4788 (R_{int} = 0.0506), observed reflections = 2522 [$I > 2\sigma(I)$], final R indices R1 = 0.0615 and wR2 = 0.1514. Data collection for **4**: C$_{18}$H$_{37}$CoN$_3$Si, M_r = 382.53, crystal dimensions 0.3 × 0.2 × 0.18 mm^3, triclinic ($P\bar{1}$), a = 8.0103(5) Å, b = 10.2402(6) Å, c = 15.1224(9) Å, α = 76.1290(10)°, β = 76.1650(10)°, γ = 70.2830(10)°, V = 1116.54(12) Å^3, Z = 2, ρ_{calcd} = 1.138 g/cm^3, μ = 0.826 mm^{-1}, Mo Kα radiation λ = 0.710 73 Å, T = 273(2) K, reflections measured = 6019, independent reflections = 4266 (R_{int} = 0.0132), observed reflections = 3786 [$I > 2\sigma(I)$], final R indices R1 = 0.0331 and wR2 = 0.0945. Data collection for **5**: C$_{34}$H$_{56}$FeN$_2$, M_r = 548.66, crystal dimensions 0.4 × 0.3 × 0.2 mm^3, monoclinic ($C2/c$), a = 20.236(3) Å, b = 17.716(2) Å, c = 9.7692(12) Å, α = 90°, β = 100.340(3)°, γ = 90°, V = 3445.4(8) Å^3, Z = 4, ρ_{calcd} = 1.058 g/cm^3, μ = 0.459 mm^{-1}, Mo Kα radiation λ = 0.710 73 Å, T = 293(2) K, reflections measured = 11 620, independent reflections = 4163 (R_{int} = 0.0663), observed reflections = 1663 [$I > 2\sigma(I)$], final R indices R1 = 0.0528 and wR2 = 0.1115.

Scheme 2



attributed to a stronger methyl ligand as compared to a chloride ligand.

The majority of alkyl complexes of Fe^{II} and Co^{II}, which have been well-characterized, contain cyclopentadienyl ligands or π-acid supporting ligands (such as CO, PR_3, or bipyridine).[26] To our knowledge, the simple *monodentate* arylamido ligand system has not been reported to be effective in the stabilization of iron(II) and cobalt(II) methyl complexes. Mixed methyl−arylamide complexes of Fe^{II} and Co^{II} are particularly rare. Recently, a number of coordinatively and electronically unsaturated iron(II) and cobalt(II) methyl complexes supported by "tetrahedral-enforcing" borato ligands have been reported by several research groups led by Parkin,[20] Peters,[21] Theopold,[22] and Riordan,[23] respectively. Holland and co-workers have also reported three-coordinate methyl complexes of Fe^{II} and Co^{II}, which were supported by a sterically demanding bidentate diketiminate ligand.[24] It is noteworthy that the bulky "tetrahedral-enforcing" borato and chelating diketiminate supporting ligands can provide a rigid structural framework, which may enhance the stability of the corresponding methyl complexes.

Apart from the trimethylsilyl-substituted L^1 ligand, we have also investigated the coordination chemistry of the closely related N-alkylated $[N(CH_2Bu^t)(C_6H_3Pr^i{}_2\text{-}2,6)]^-$ (L^2) ligand toward Fe^{II} and Co^{II} ions.[27] Because tmeda forms part of the steric protection around the metal center in the monoamido complexes **1** and **2**, it was expected that the absence of tmeda in the reaction mixture may facilitate a complete anion metathesis reaction of 1:2 MCl_2/lithium amide. Therefore, in an effort to synthesize bis(amido) derivatives, we treated anhydrous $FeCl_2$ with 2 equiv of the tmeda-free lithium salt $[Li(L^2)(THF)_2]$ in toluene (Scheme 2).

Interestingly, a red crystalline complex was isolated, and both X-ray data and elemental analysis indicated that the product is the two-coordinate iron(II) bis(arylamide) **5** (Figure 2).[25] Complex **5** conforms closely to an idealized C_2 molecular symmetry, with the Fe^{II} ion being coordinated to a pair of monodentate L^2 ligands. It is noteworthy that the Fe^{II} center in **5** is protected from the surroundings by the neopentyl and isopropyl groups of the two L^2 ligands. The Fe−N distance of 1.842(2) Å in **5** is slightly shorter than those reported for other iron(II) bis(amide) complexes, namely, 1.896(2) and 1.916(2) Å for $[Fe\{N(SiMe_nPh_{3-n})_2\}_2]$[9] and 1.938(2) Å for $[Fe\{N(Mes)(BMes_2)\}_2]$ (Mes = 2,4,6-$Me_3C_6H_2$).[10] The next-closest atoms to the Fe^{II} center in **5** are C1 and C1A, which are located at ca. 2.728 Å from the metal center. The N−Fe−N angle [168.8(2)°] in **5** has a minor deviation from linearity, which is similar to those observed for $[Fe\{N(SiMe_nPh_{3-n})_2\}_2]$[9] and $[Fe\{N(Mes)(BMes_2)\}_2]$.[10]

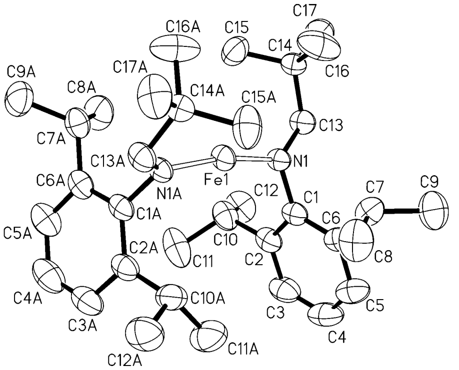


Figure 2. Molecular structure of **5** (30% thermal ellipsoid). Only one of the two orientations of the disordered neopentyl group is shown for clarity, Selected bond lengths (Å) and angles (deg): Fe1−N1 1.842(2), N1−C1 1.437(4), N1−C13 1.46(1), N1−Fe1−N1A 168.8(2), C1−N1−C13 111.1(5), C1−N1−Fe1 112.0(2), C13−N1−Fe1 136.1(4).

In summary, the *monodentate* arylamido ligands $[N(R)(C_6H_3R'_2\text{-}2,6)]^-$ [R = $SiMe_3$, R′ = Me (L^1); R = CH_2Bu^t, R′ = Pr^i (L^2)] have been shown to be promising candidates for the stabilization of electronically and coordinatively unsaturated Fe^{II} and Co^{II} complexes, namely, the methyl−arylamide complexes $[M(L^1)(Me)(tmeda)]$ [M = Fe (**3**), Co (**4**)] and the two-coordinate iron(II) bis(arylamide) $[Fe(L^2)_2]$ (**5**). Further studies on the coordination chemistry of the present arylamido ligand system with other late-transition-metal ions and a detailed investigation on the reaction chemistry of the corresponding metal complexes are currently in progress in our laboratory.

Acknowledgment. We thank The Chinese University of Hong Kong for financial support of this work in the form of a Direct Grant (A/C 2060253) and a postgraduate studentship to H.Y.A.-Y. We thank George Fai Wong and Lai Fong Yeung for their kind assistance.

Supporting Information Available: Detailed synthetic procedures for **1**−**5**, ORTEP drawings of **1**, **2**, and **4**, and tables (in CIF and PDF formats) listing selected X-ray crystallographic data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) We anticipated that different electronic properties of the $SiMe_3$ and CH_2Bu^t substituents on L^1 and L^2, respectively, may lead to a variation in their coordination properties.