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An Unusual Zinc-Promoted Decomposition of a Bis(2-{pyrid-2-yl}ethyl)amine Derivative

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The complex $[ZnBr_2L^1]$ (L^1 = ferrocenylmethyl-bis[2-{pyrid-2-yl}-ethyl]amine) contains bidentate L^1 by crystallography and NMR spectroscopy and decomposes during recrystallization from CH_2Cl_2/pentane via both C–N bond cleavage and formation steps. Other $[MBr_2L^1]$ (M = Co, Ni, Cu) compounds do not undergo this reaction and contain L^1 bound in the more usual tridentate coordination mode.

N-Alkyl or *N*-aryl derivatives of bis(2-{pyrid-2-yl}ethyl)-amine (bpea) are widely used ligands in coordination chemistry that, among other things, have been particularly important in studies of O_2 binding and activation by copper centers in chemistry and biology.[1] We have recently begun to study some aspects of their chemistry[2] and report here an unexpected, facile decomposition reaction of a zinc(II) complex of one such ligand. Ferrocenylmethyl-bis[2-{pyrid-2-yl}ethyl]amine (L^1)[3] was prepared from bis[2-{pyrid-2-yl}ethyl]amine (L^2)[2] by a modification of the literature procedure (see Supporting Information). Mixing separate MeOH solutions of equimolar amounts of L^1 and $ZnBr_2$ at room temperature led to rapid precipitation of orange microcrystals of pure $[ZnBr_2L^1]$ (**1**). However, recrystallization of **1** from CH_2Cl_2/pentane in air over a period of 1−3 days afforded mixtures of at least two different species. Single crystals of unchanged **1**, $[ZnBr_2L^2]$ (**2**), and/or bis-(ferrocenylmethyl)(2-{pyrid-2-yl}ethyl)amine (**3**) were all obtained from different crystallizations of the same initial batch of **1**.[4] The identity of **2** was confirmed by comparison of the NMR and IR spectra of its crystals, separated manually from the crystallization mixtures, with those of a bulk sample prepared from $ZnBr_2$ and L^2.[5] Unfortunately, our attempts to independently prepare **3** from 2-(2-aminoethyl)pyridine and 2 equiv of ferrocenylmethyl(trimethyl)ammonium iodide were unsuccessful, and it proved impossible to manually separate **3** in any quantity from **1**. However, formation of **3** is supported by electrospray mass spectra of the crude product mixtures, which show a molecular ion at *m*/*z* 519 (attributable to $[\mathbf{3} + H]^+$) as well as at 568 ($[^{64}Zn^{79}BrL^1]^+$, derived from **1**), 426 ($[L^1 + H]^+$), and 228 ($[L^2 + H]^+$). Inspection of the crystals obtained showed that **2** is formed from **1** in ca. 50% yield by this procedure, but that **3** is a more minor component of the product mixtures.

Single-crystal structures of **1** and **2** both show that the L^1 and L^2 ligands are bidentate, with one noncoordinate pyridyl group oriented away from the metal centers (Figure 1 and Supporting Information). This affords an irregular tetrahedral stereochemistry at the zinc ions that is distorted by the narrow ligand bite angles [N(4)−Zn(1)−N(8) = 99.97(12)° in **1** and 98.41(13)° in **2**]. The dihedral angle between the least-squares planes of Zn(1), Br(2), and Br(3) and Zn(1), N(4), and N(8) in the two structures is near-ideal for a tetrahedral geometry, at 89.18(6)° for **1** and 89.29(8)° for **2**. The tetrahedral stereochemistry of **1** and **2** is consistent with previously reported IR data from **2**,[6] but contrasts with every other crystallographically characterized zinc(II) complex of a bpea derivative, all of which have tridentate bpea ligands.[7] The N−H group in **2** hydrogen bonds to a Br^- ligand from a

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(4) Crystal data for **1**: $C_{25}H_{27}Br_2FeN_3Zn$, M_r = 650.54, triclinic, $P\bar{1}$, a = 9.9561(1) Å, b = 10.6447(2) Å, c = 13.3663(3) Å, α = 80.5083(7)°, β = 68.8471(8)°, γ = 65.4733(12)°, V = 1201.71(4) Å^3, Z = 2, D_c = 1.798 Mg·m^{-3}, μ(Mo Kα) = 4.945 mm^{-1}, T = 150(2) K; 24378 measured reflections, 5483 unique, R1 [$I > 2\sigma(I)$] = 0.047, wR2 (all data) = 0.117. Crystal data for **2**: $C_{14}H_{17}Br_2N_3Zn$, M_r = 452.50, monoclinic, $P2_1/n$, a = 9.4430(3) Å, b = 11.7238(3) Å, c = 15.1715(5) Å, β = 105.2745(11)°, V = 1620.27(8) Å^3, Z = 4, D_c = 1.855 Mg·m^{-3}, μ(Mo Kα) = 6.441 mm^{-1}, T = 150(2) K; 18896 measured reflections, 3705 unique, R1 [$I > 2\sigma(I)$] = 0.043, wR2[all data] = 0.117. Crystal data for **3**: $C_{29}H_{30}Fe_2N_2$, M_r = 518.25, monoclinic, $P2_1/n$, a = 5.9958(1) Å, b = 19.2378(3) Å, c = 20.0839(4) Å, β = 90.7279(6)°, V = 2316.41(7) Å^3, Z = 4, D_c = 1.486 Mg·m^{-3}, μ(Mo Kα) = 1.273 mm^{-1}, T = 150(2) K; 28085 measured reflections, 5292 unique, R1 [$I > 2\sigma(I)$] = 0.042, wR2 (all data) = 0.111.

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10.1021/ic050270o CCC: $30.25

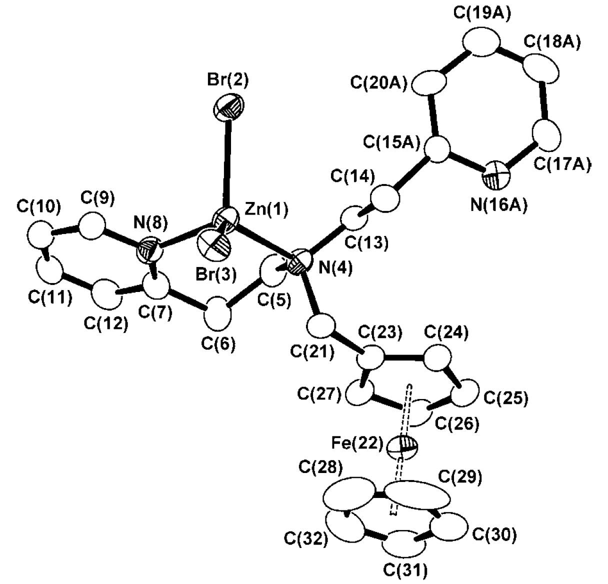

Figure 1. View of the asymmetric unit in the crystal structure of **1**. All H atoms have been omitted for clarity, and thermal ellipsoids are at the 50% probability level. Only the major orientation of the disordered pyridine ring C(15)−C(20) is shown. Selected bond lengths (Å) and angles (deg): Zn(1)−Br(2) 2.3985(6), Zn(1)−Br(3) 2.3829(5), Zn(1)−N(4) 2.079(3), Zn(1)−N(8) 2.058(3), Br(2)−Zn(1)−Br(3) 114.05(2), Br(2)−Zn(1)−N(4) 106.90(8), Br(2)−Zn(1)−N(8) 102.30(8), Br(3)−Zn(1)−N(4) 118.42(8), Br(3)−Zn(1)−N(8) 113.16(9), N(4)−Zn(1)−N(8) 99.97(12).

neighboring molecule related by $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{3}/_{2}$, yielding zigzag hydrogen-bonded chains of molecules running parallel to the crystallographic *b* direction (in the setting $P2_1/n$). There are no noteworthy intermolecular interactions in the crystal of **1**. The crystal structure of **3** (Figure 2) confirms the identity of this product, with all bond lengths and angles within this compound being in the usual ranges.

The aromatic region of the ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature is more complex than would be expected of a single C_2- or *m*-symmetric L^1 ligand environment. The peaks gradually resolve themselves upon cooling, until at 243 K resonances from the H^3, H^4, and H^5 environments of two equally populated pyridyl environments are fully resolved. The aliphatic region of the spectrum, which is very broad at room temperature, also sharpens considerably upon cooling. These data strongly imply that the molecular structure of **1** in this solvent is the same as that in the crystal, with one free and one coordinated pyridyl group. The NMR temperature dependence of the spectrum also suggests that **1** undergoes migration of the zinc center between the L^1 pyridine rings in solution, although complete coalescence was not reached at room temperature at the NMR frequency used (500 MHz).

Experiments using other metal bromide salts showed that $[CoBr_2L^1]$ (**4**), $[NiBr_2L^1]$ (**5**), and $[CuBr_2L^1]$ (**6**)[3] are recrystallized intact from CH_2Cl_2/pentane.[8] Interestingly, whereas **4** and **6** form isostructural unsolvated crystals from this solvent mixture, **5** instead crystallizes as the solvate $\mathbf{5}\cdot CH_2Cl_2$. Nonetheless, all three compounds are five-coordinate with tridentate L^1 and geometries intermediate between the square-pyramidal and trigonal-bipyramidal limits with $\tau = 0.29-0.59$[9] (Figure 3 and Supporting Information). UV/vis spectra of **4**−**6** in CH_2Cl_2 are also consistent with high-spin five-coordinate metal centers;[10] the *X*-band EPR spectrum of **6** is isotropic and uninformative, however.[3]

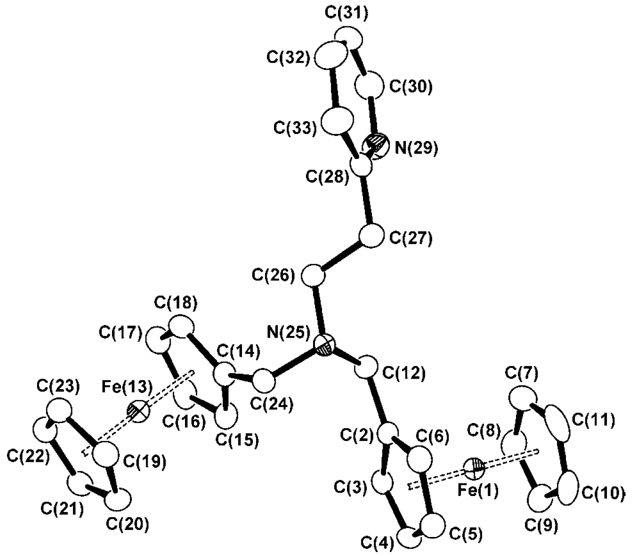

Figure 2. View of the asymmetric unit in the crystal structure of **3**. All H atoms have been omitted for clarity, and thermal ellipsoids are at the 50% probability level.

These results imply that decomposition of **1** is initiated by the bidentate coordination of L^1, which could promote the decomposition of **1** in two ways. First, the lower coordination of **1** compared to **4**−**6** should significantly increase the Lewis acidity of the zinc(II) ion.[11] That would increase the electrophilicity of the CH_2 groups α to the L^1 tertiary amine donor, facilitating C−N bond cleavage. Second, the pendant pyridyl group in **1** and **2** provides an endogenous base that could facilitate proton-transfer steps during the decomposition process. To test the importance of the latter idea, **4**−**6** were all recrystallized from CH_2Cl_2/

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(8) Crystal data for **4**: $C_{25}H_{27}Br_2CoFeN_3$, $M_r = 644.10$, orthorhombic, *Pbca*, $a = 14.9282(2)$ Å, $b = 11.7063(1)$ Å, $c = 27.9350(3)$ Å, $V = 4881.75(9)$ Å^3, $Z = 8$, $D_c = 1.753$ Mg·m^{-3}, μ(Mo Kα) = 4.566 mm^{-1}, $T = 150(2)$ K; 64245 measured reflections, 4801 independent, R1 $[I > 2\sigma(I)] = 0.098$, wR2 (all data) = 0.242. Crystal data for $\mathbf{5}\cdot CH_2Cl_2$: $C_{26}H_{29}Br_2Cl_2FeN_3Ni$, $M_r = 728.80$, monoclinic, $P2_1/n$, $a = 12.6712(2)$ Å, $b = 14.6662(3)$ Å, $c = 15.7818(4)$ Å, $\beta = 112.3272(9)°$, $V = 2712.99(10)$ Å^3, $Z = 4$, $D_c = 1.784$ Mg·m^{-3}, μ(Mo Kα) = 4.392 mm^{-1}, $T = 150(2)$ K; 29967 measured reflections, 6196 independent, R1 $[I > 2\sigma(I)] = 0.042$, wR2 (all data) = 0.104. Crystal data for **6**: $C_{25}H_{27}Br_2CuFeN_3$, $M_r = 648.71$, orthorhombic, *Pbca*, $a = 14.7899(2)$ Å, $b = 11.7343(2)$ Å, $c = 27.8198(4)$ Å, $V = 4828.10(13)$ Å^3, $Z = 8$, $D_c = 1.785$ Mg·m^{-3}, μ(Mo Kα) = 4.811 mm^{-1}, $T = 150(2)$ K; 44387 measured reflections, 5533 independent, R1 $[I > 2\sigma(I)] = 0.050$, wR2 (all data) = 0.125.

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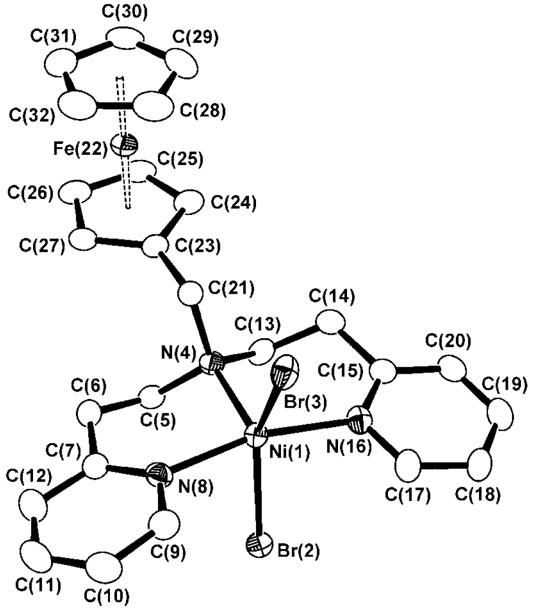
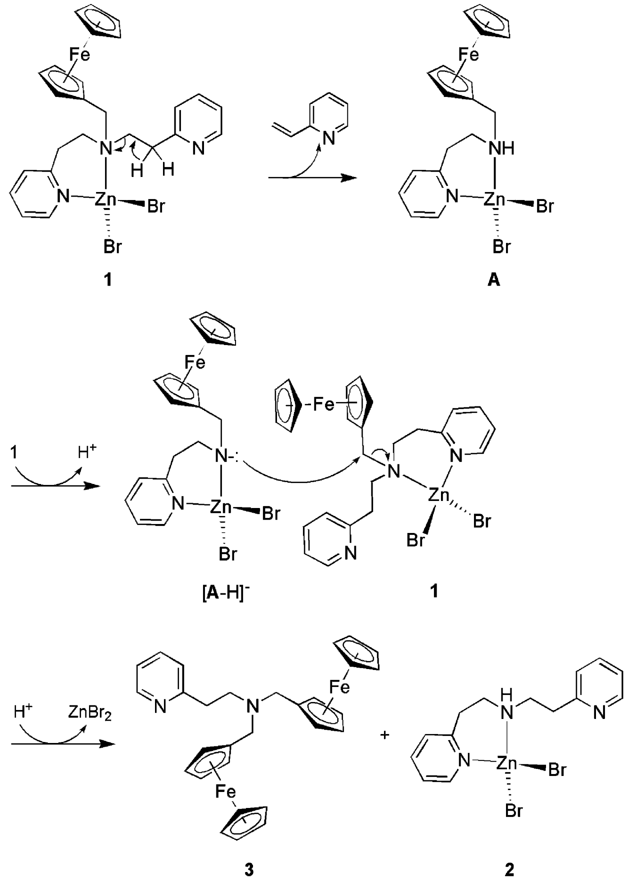


Figure 3. View of the complex molecule in the crystal structure of $5 \cdot CH_2Cl_2$. All H atoms have been omitted for clarity, and thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni(1)−Br(2) 2.5472(6), Ni(1)−Br(3) 2.4793(6), Ni(1)−N(4) 2.049(3), Ni(1)−N(8) 2.060(3), Ni(1)−N(16) 2.047(3), Br(2)−Ni(1)−Br(3) 148.48(2), Br(2)−Ni(1)−N(4) 103.63(9), Br(2)−Ni(1)−N(8) 85.51(9), Br(2)−Ni(1)−N(16) 86.82(9), Br(3)−Ni(1)−N(4) 107.88(9), Br(3)−Ni(1)−N(8) 91.78(9), Br(3)−Ni(1)−N(16) 88.45(8), N(4)−Ni(1)−N(8) 95.62(11), N(4)−Ni(1)−N(16) 97.94(11), N(8)−Ni(1)−N(16) 165.67(11).

pentane in the presence of 2 equiv of 2,6-lutidine. In each case, **4**−**6** were recovered essentially unchanged according to IR and ESMS analysis, although microanalysis implied that the purity of **4** and **6** obtained this way was lower than in the absence of 2,6-lutidine (2−3% errors in C, 0.5% errors in H and N). Importantly, the mass spectra of these impure samples showed the same molecular ions as those of the pure compounds and provided no mass peaks that could be assigned to degradation of L^1. Thus, although we have not identified any impurities from the 2,6-lutidine-modified products, any such compounds are unlikely to involve modification of the L^1 ligand.

A possible mechanism for the formation of **2** and **3** from **1**, that takes account of these observations, is shown in Scheme 1. The first step of this sequence is a retro-Michael elimination of 2-vinylpyridine from **1** to yield intermediate **A**. Some bpea-type ligands are known to decompose in this way upon heating,[12] and this step might also be promoted by bidentate coordination of L^1 to a Lewis acidic metal ion. Importantly, however, this sequence implies that equal yields of **2** and **3** should result from the decomposition of **1**. Because the yield of **2** is apparently greater, an alternative mechanism must also exist for the conversion of **1** into **2**. Although functionalization of the pendant arms of copper/bpea complexes by oxygenation is well-known,[1] it is unlikely to be occurring in this system. A more plausible mechanism for the dealkylation of **1** is nucleophilic attack at the benzylic $FcCH_2$ moiety by adventitious water, yielding **2** and ferrocenylmethanol. Given that we have not detected ferrocenylmethanol in our product mixtures, however, this latter suggestion remains speculative.

Scheme 1. Possible Mechanism for the Conversion of **1** into **2** and **3**



It is noteworthy that **2** as well as both of other known transition metal complexes containing bidentate bpea derivatives as ligands[13,14] are all thermally stable in chlorinated solvents at room temperature and, in one case, in hot EtOH. These results imply that bidentate coordination of a bpea ligand is not in itself enough to induce its decomposition and that **1** must therefore be particularly susceptible to this reaction.

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Supporting Information Available: Synthetic procedures and characterization data for L^1 and the new complexes in this study; figures of the complex molecules in the crystal structures of **2**, **5**, and **6**; ^{1}H NMR spectra of **1** and a representative mass spectrum of a decomposed sample of **1**; and crystallographic data in CIF format for **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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