

# Unusual Electronic Features and Reactivity of the Dipyridylazaallyl Ligand: Characterizations of (smif)<sub>2</sub>M [M = Fe, Co, Co<sup>+</sup>, Ni; smif = {(2-py)CH<sub>2</sub>N}] and [(TMS)<sub>2</sub>NFe]<sub>2</sub>(smif)<sub>2</sub>

Brenda A. Frazier,<sup>†</sup> Peter T. Wolczanski,<sup>\*,†</sup> Emil B. Lobkovsky,<sup>†</sup> and Thomas R. Cundari<sup>‡</sup>

Department of Chemistry & Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853, and Department of Chemistry, University of North Texas, Box 305070, Denton, Texas 76203-5070

Received November 14, 2008; E-mail: ptw2@cornell.edu

Nitrogen donor ligands have played a historical and prominent role in coordination chemistry from its beginnings in Werner's time,<sup>1</sup> yet new variants continue to emerge. During the investigation of new chelating ligands, a degradation led to the discovery of an azaallyl ligand, (2-py)CHNCH(2-py) (smif), whose chemical properties are intriguing. A related decomposition of ((2-py)CH<sub>2</sub>)<sub>2</sub>NH led to one previous example, (smif)<sub>2</sub>Zn.<sup>2</sup> Synthesized from the condensation of 2-pyridylaldehyde and 2-pyridylmethylamine (99%), (smif)H is readily deprotonated by LiN(TMS)<sub>2</sub> to afford (smif)Li (73%). Initial synthetic studies and brief insights into the electronic features and reactivity of smif are provided herein.

Treatment of FeBr<sub>2</sub>(THF)<sub>2</sub>, CoCl<sub>2</sub>, and NiCl<sub>2</sub>(dme) in THF with 2 equiv of (smif)Li (generated in situ) afforded (smif)<sub>2</sub>M [M = Fe (**1**), 52%; Co (**2**), 87%; Ni (**3**), 67%]. Alternatively, exposure of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>THF<sup>3</sup> with 1 or 2 equiv of (smif)H provided (smif)FeN(TMS)<sub>2</sub> (**4**, 74%) or **1** (80%). Solutions of dark-green **1** and deep magenta **2** and **3** were intensely colored and afforded black-purple and gold crystalline solids, respectively, indicative of complementary reflected light. Their structures are roughly D<sub>2d</sub> according to NMR spectra, which reveal one smif environment, and X-ray crystallography, as the view of **1** in Figure 1 illustrates.

**1** is diamagnetic, and its Mössbauer spectrum (Figure 2) is consistent with a covalent, low-spin Fe(II) complex. SQUID data show that **2** exhibits a magnetic moment ( $\mu_{\text{eff}}$ ) of 1.7 at 10 K, consistent with an S = 1/2 ground state (GS), but  $\mu_{\text{eff}}$  rises to >3.0 at 300 K.<sup>4</sup> Its EPR spectrum at 30 K shows a rhombic signal with Co hyperfine couplings: g [A(Co)] = 2.01 [44 G], 2.135 [66 G] and 2.21 [64 G]. **3** is EPR-silent but manifests a  $\mu_{\text{eff}}$  of 2.8 at 300 K, with only a minor attenuation below 10 K, consistent with an S = 1 GS.

The structures of **1–3** are reminiscent of axially compressed terpy derivatives.<sup>5</sup> Iron complex **1** displays short aza (N<sub>a</sub>) and pyridine (N<sub>py</sub>) Fe–N distances of 1.9012(14) and 1.9634(12) Å, respectively (Table 1), in a symmetric (i.e., D<sub>2d</sub>) environment, corroborating its low-spin character. The distortion from idealized O<sub>h</sub> coordination is evidenced by the N<sub>py</sub>–Fe–N<sub>py</sub> angle of 164.53(11)°. In contrast to **1**, the bis(amide) complex (dpma)<sub>2</sub>Fe [dpma = ((2-py)CH<sub>2</sub>)<sub>2</sub>N] (**5**) possesses metric parameters consistent with its S = 2 ( $\mu_{\text{eff}}$  = 5.0) GS, and its UV–vis spectrum shows no band more intense than 5000 M<sup>-1</sup> cm<sup>-1</sup>.

Two independent molecules of **2** exhibit longer average Co–N distances [ $d(\text{CoN}_a) = 1.93(3)$  Å;  $d(\text{CoN}_{py}) = 2.08(8)$  Å] and smaller bite angles [e.g.,  $\angle\text{N}_{py}\text{CoN}_{py} = 160.9(25)^\circ$ ], and one smif is slightly canted in the plane perpendicular to the first [ $\angle\text{N}_a\text{CoN}_a' = 176.1(18)^\circ$ ]. **3** possesses two smif ligands at equivalent long

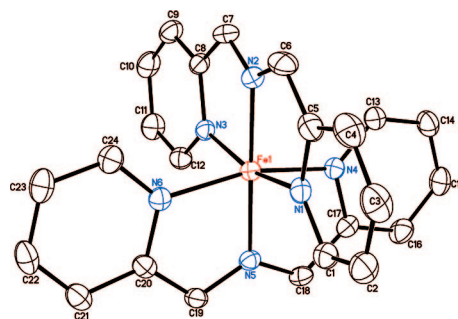


Figure 1. Molecular view of (smif)<sub>2</sub>Fe (**1**).

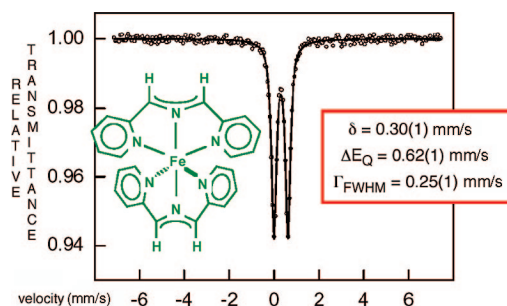


Figure 2. Zero-field Mössbauer spectrum of (smif)<sub>2</sub>Fe.

distances [ $d(\text{NiN}_a) = 2.019(5)$  Å;  $d(\text{NiN}_{py}) = 2.093(9)$ ];  $\angle\text{N}_{py}\text{NiN}_{py} = 158.1(4)^\circ$ , with a cant similar to that in **2** [ $\angle\text{N}_a\text{NiN}_a' = 176.06(8)^\circ$ ].

A better grasp of the electronic structures, geometries, and optical features of **1–3** were obtained from density functional theory (DFT) calculations. Figure 3 shows a simplified orbital diagram, which reveals occupied nonbonding azaallyl carbon-based orbitals that reside above the “t<sub>2g</sub>” set [ $d_{xy}$  (b<sub>1</sub>);  $d_{xz}$ ,  $d_{yz}$  (e) in D<sub>2d</sub>]. These orbitals maintain a roughly constant position at about -4.0 eV for **1–3** and differentiate smif from related tridentate ligands such as terpy<sup>5,6</sup> by affording high-intensity intraligand (IL) bands. Two large features in the UV–vis spectra of (smif)<sub>2</sub>M [**1**, 597 nm (16 000 M<sup>-1</sup> cm<sup>-1</sup>), 441 (42 000); **2**, 563 (29 000), 401 (20 000); **3**, 574 (50 000), 399 (18 000)] were assigned as C<sup>nb</sup> → Lπ\* IL bands on the basis of time-dependent DFT (TDDFT) calculations on **1**. Its calculated spectrum, which appeared blue-shifted by ~0.25 eV, revealed a minor MLCT component in these bands. The TDDFT study permitted a tentative identification of d–d bands at ~18 000 and 25 000 cm<sup>-1</sup>. Calculated splittings of the O<sub>h</sub> t<sub>2g</sub> orbitals into b<sub>1</sub>(d<sub>xy</sub>) and e(d<sub>xz</sub>, d<sub>yz</sub>) of D<sub>2d</sub> and of O<sub>h</sub> e<sub>g</sub> into b<sub>2</sub>(d<sub>x<sup>2</sup>-y<sup>2</sup>) and a<sub>1</sub>(d<sub>z<sup>2</sup></sub>) of D<sub>2d</sub> are <1600 cm<sup>-1</sup>. Consequently, **1** can be estimated (Tanabe–Sugano) to have Δ<sub>o</sub> ≥ 18 000 cm<sup>-1</sup> and B ≈ 470 cm<sup>-1</sup>, consistent with the covalency shown in the Mössbauer spectrum.</sub>

<sup>†</sup> Cornell University.

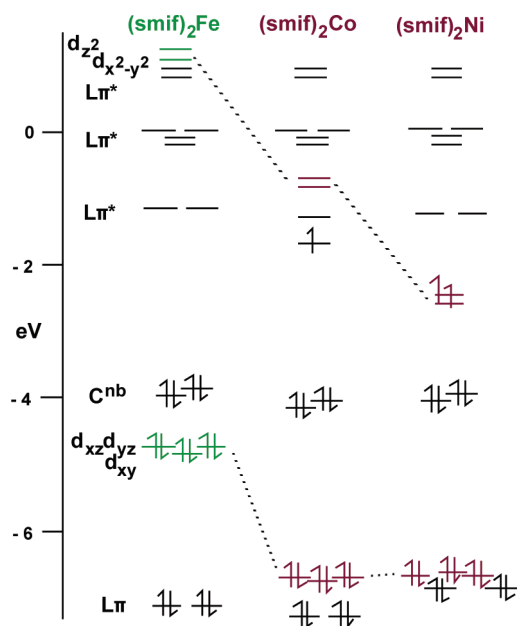
<sup>‡</sup> University of North Texas.

**Table 1.** Structural Parameters for (smif)<sub>2</sub>M (M = Fe, **1**; Co, **2**; Ni, **3**), [(smif)<sub>2</sub>Co]OTf (**2+**), (dmpa)<sub>2</sub>Fe (**5**), and [(TMS)<sub>2</sub>NFe]<sub>2</sub>(smif)<sub>2</sub> (**4**)<sup>a</sup>

compd	d(MN <sub>a</sub> )	d(MN <sub>py</sub> )	d(CN <sub>a</sub> )	∠N <sub>a</sub> MN <sub>py</sub>	∠N <sub>a</sub> MN <sub>py</sub> '	∠N <sub>a</sub> MN <sub>a</sub> '	∠N <sub>py</sub> MN <sub>py</sub>	∠N <sub>py</sub> MN <sub>py</sub> '
<b>1</b>	1.9012(14)	1.9634(12)	1.333(3)	82.3(2)	97.7(5)	179.11(6)	164.53(11)	91.0(12)
<b>2</b> <sup>b</sup>	1.93(3)	2.08(8)	1.337(7)	80.5(12)	95.1(2)–102.1(2)	177.5(3)	160.9(25)	91.6(18)
<b>2+</b>	1.8768(11)	1.9252(19)	1.331(9)	83.9(2)	96.1(7)	179.05(10)	167.68(9)	90.7(19)
<b>3</b> <sup>b</sup>	2.019(5)	2.093(9)	1.325(4)	79.1(3)	96.6(2)–104.6(2)	176.06(8)	158.1(4)	92.1(16)
<b>5</b> <sup>b</sup>	2.001(13)	2.201(13)	1.418(2)	75.5(4)	99.8(2)–109.5(2)	175.9(16)	150.9(16)	86.90(7)–101.00(7)
<b>4</b> <sup>c</sup>	1.9432(10)	2.193(3)	1.4345(16)	77.29(13)	102.7(11)	178.53(4)	154.48(4)	

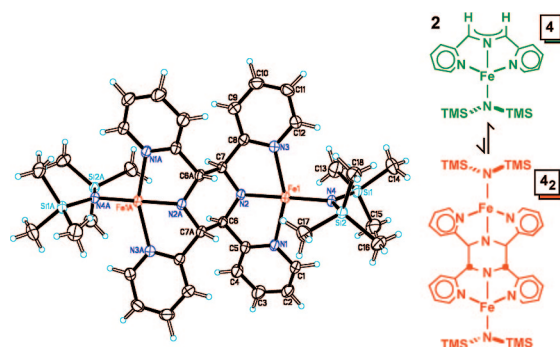
<sup>a</sup> Distances (Å) and angles (deg) are averages unless a range is given. N<sub>a</sub> is the aza nitrogen and N<sub>py</sub> a pyridine nitrogen; primes distinguish different smif ligands. <sup>b</sup> Two molecules in the asymmetric unit. <sup>c</sup> N<sub>a</sub>' is (TMS)<sub>2</sub>N at 1.9538(10) Å.

Figure 3 indicates that smif may be redox-active<sup>7–12</sup> in the case of **2**. For **1**, nonbonding, carbon-based azaallyl orbitals are the HOMO and HOMO–1. Ligand-field orbitals drop in energy in going from Fe to Co to Ni, but the additional electron in **2** (vs **1**) may reside in a ligand π\* orbital, rendering **2** formally as Co<sup>3+</sup>(smif<sup>1.5–</sup>)<sub>2</sub>. Discrete structural changes are difficult to assess because of delocalization into the py π\* framework. Oxidation of **2** with AgOTf affords magenta [(smif)<sub>2</sub>Co]OTf (**2+**, 81%), which possesses IL bands at 586 nm (23 000 M<sup>-1</sup> cm<sup>-1</sup>) and 383 nm (13 000 M<sup>-1</sup> cm<sup>-1</sup>). Symmetric (*D*<sub>2d</sub>) structural features of **2+** are consistent with its low-spin d<sup>6</sup> character. In **3**, the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (b<sub>2</sub>) and d<sub>z<sup>2</sup></sub> (a<sub>1</sub>) orbitals drop below the smif π\* orbitals, and the complex is best described as Ni(II), consistent with its long d(NiN) and EPR silence. The smif-based orbitals stay remarkably consistent for **1–3** but may be adjusted in future generations through the appropriate choice of substituents.



**Figure 3.** Simplified MO diagrams of **1–3**. L stands for smif and C for azaallyl carbon. The dotted lines trace the ligand-field orbitals from Fe to Co to Ni.

The C<sup>nb</sup> orbitals have ~50% ionic and ~50% covalent character and are “non-innocent” in terms of reactivity. Complex **4** is a dimer in the solid state, as Figure 4 illustrates. In solution, **4** is emerald-green, with IL bands at 633 nm (52 000 M<sup>-1</sup> cm<sup>-1</sup>) and 399 nm (37 000 M<sup>-1</sup> cm<sup>-1</sup>), but orange crystals reveal its conversion to the amide dimer [(TMS)<sub>2</sub>NFe]<sub>2</sub>(smif)<sub>2</sub> (**4**<sub>2</sub>). <sup>1</sup>H NMR spectral analysis affords a *K*<sub>eq</sub> value of ~4 × 10<sup>-4</sup> M<sup>-1</sup> (Δ*G*<sup>o</sup> ≈ 5 kcal/mol) for the reaction 2 **4** ⇌ **4**<sub>2</sub>. The dimerization can be construed as either a diradical coupling or a nucleophile/electrophile event, and polar and nonpolar reactivity is anticipated for the smif backbone.



**Figure 4.** Molecular view of [(TMS)<sub>2</sub>NFe]<sub>2</sub>(smif)<sub>2</sub> (**4**<sub>2</sub>), obtained from dimerization of **4**.

The smif ligand provides a rare opportunity to view a *new* homologous series of first-row transition-metal complexes<sup>12</sup> and manifests a unique optical density that may be exploited in various photochemical applications. Physical studies of **1–3** and variants as well as (smif)<sub>2</sub>M (M = V, Cr, Cr<sup>+</sup>, Mn) are ongoing.

**Acknowledgment.** P.T.W. thanks the NSF (CHE-0718030) and T.R.C. the DOE (DE-FG02-03ER15387), and we also thank Prof. Karsten Meyer, Dr. Suzanne Doucette, Dr. Susanne Mossin, and Dr. Joerg Sutter (Univ. Erlanger-Nuremberg) for experimental assistance.

**Supporting Information Available:** Experimental details, CIF files, NMR, UV–vis, and EPR spectra, and SQUID data for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Kauffman, G. B. *Alfred Werner: Founder of Coordination Chemistry*; Springer-Verlag: Berlin, 1966.
- (2) Westerhausen, M.; Kneifel, A. N. *Inorg. Chem. Commun.* **2004**, *7*, 763–766.
- (3) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547–2551.
- (4) Krivokapic, I.; Zerara, M.; Daku, M. L.; Vargas, A.; Enachescu, C.; Ambrus, C.; Treganna-Piggott, P.; Amstutz, N.; Krausz, E.; Hauser, A. *Coord. Chem. Rev.* **2007**, *251*, 364–378.
- (5) Constable, E. C. *Adv. Inorg. Chem.* **1986**, *30*, 69–121.
- (6) Wadman, S. H.; van der Geer, E. P. L.; Havenith, R. W. A.; Gebbink, R. J. M.; van Klink, G. P. M.; van Koten, G. J. *Organomet. Chem.* **2008**, *693*, 3188–3190.
- (7) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901–13912.
- (8) Zaresh, R. A.; Ziller, J. W.; Heyduk, A. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4715–4718.
- (9) Stanciu, C.; Jones, M. E.; Fanwick, P. E. *J. Am. Chem. Soc.* **2007**, *129*, 12400–12401.
- (10) (a) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *219*, 415–433. (b) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216*, 99–125.
- (11) (a) Spikes, G. H.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2973–2977. (b) Lu, C. C.; Bill, E.; Weyhermüller, T.; Bothe, E.; Wieghardt, K. *J. Am. Chem. Soc.* **2008**, *130*, 3181–3197.
- (12) Ray, K.; Petrenko, T.; Wieghardt, K.; Neese, F. *Dalton Trans.* **2007**, 1552–1566.

JA8089747