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Low-Coordinate Iron Complexes Stabilized by *N*-(*tert*-Hydrocarbyl)anilide Ligation: Adduct Formation, Chemical Oxidation, and Nitric Oxide Complexation

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Monomeric iron complexes supported by the new, sterically-demanding NRAr$_F$ (R = C(CD$_3$)$_2$CH$_3$, Ar$_F$ = 2,5-C$_6$H$_3$FMe) and NR′Ar$_F$ (R′ = C(CD$_3$)$_2$Ph) ligands are described. Four-coordinate Fe(Cl)(TMEDA)(NRAr$_F$) (**1**) was isolated in 87% yield as a colorless solid. The bis(amide) complexes Fe(L)(NRAr$_F$)$_2$ (L = pyridine-*d*$_5$, **2**; L = PEt$_3$, **3**) were isolated in 91% and 80% yields as orange-red and yellow solids, respectively. The related complex Fe(py-*d*$_5$)(NR′Ar$_F$)$_2$ (**4**) was prepared in 79% yield, characterized structurally by X-ray diffraction, and found to display chelation of the Ar$_F$ residue via dative Fe···F interactions. The iodo complex Fe(I)(py-*d*$_5$)(NRAr$_F$)$_2$ (**5**) was obtained in 91% yield as a purple solid upon treatment of **2** with $^1/_2$ equiv of iodine; according to an X-ray diffraction study **5** is a pseudotetrahedral monomer. The nitric oxide complexes Fe(NO)(L)(NRAr$_F$)$_2$ (L = py-*d*$_5$, **6**; L = PEt$_3$, **7**) were obtained as wine red crystalline solids in 92% and 89% yields, respectively, upon treatment of **2** or **3** with a slight excess of gaseous nitric oxide. Nitric oxide abstraction from **6** was accomplished quantitatively upon treatment with Mo(NRAr)$_3$ (Ar = 3,5-C$_6$H$_3$Me$_2$) or with Cr(N^{i}Pr$_2$)$_3$, regenerating **2** and generating Mo(NO)(NRAr)$_3$ or Cr(NO)(N^{i}Pr$_2$)$_3$. The homoleptic iron(II) amide [Fe(NRAr)(μ-NRAr)]$_2$ (**8**) was obtained in 88% yield as a red-orange solid upon treatment of ethereal ferrous chloride with 2 equiv of Li(NRAr)(OEt$_2$). "Ate" complex (ArRN)Fe(μ-NRAr)$_2$Li(OEt$_2$) (**9**) was obtained similarly through treatment of ferrous chloride with 3 equiv of Li(NRAr)(OEt$_2$). Ferrocenium triflate oxidation of **9** gave the homoleptic iron(III) amide Fe(NRAr)$_3$ (**10**) in 85% yield. All paramagnetic complexes studied here were characterized by magnetic susceptibility studies, by ^{2}H NMR spectroscopy, and by elemental analysis.

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Introduction

Exemplary of low-coordinate iron complexes[2−4] supported by bulky amido ligands[5] are Fe[N(SiMe$_3$)$_2$]$_3$[6] and Fe[N(SiMe$_2$Ph)$_2$]$_2$[2] for iron(III) and -(II), respectively; the former was first reported in 1963,[6] and it has since been studied in greater detail.[7−9] The diphenylamido ligand also has been employed to some advantage in iron(II) chemistry, as evidenced by reports describing [Fe(NPh$_2$)(μ-NPh$_2$)]$_2$ and [Fe(NO)$_2$(μ-NPh$_2$)]$_2$.[10] The structural chemistry of these and related iron amido complexes has been described comprehensively by Power,[2] but the reaction chemistry of this unique molecular class has not been developed in great detail. A primary objective of the work reported here is to set the stage for a systematic study of reactions of low-coordinate iron amido complexes, devoting special attention to reactions involving small molecules (e.g., NO).

Iron amide complexes of the type considered here are frequently paramagnetic, prompting us to utilize a set of *N*-(*tert*-hydrocarbyl)anilide ligands which are (i) selectively deuterated to provide a convenient paramagnetic NMR spectroscopic handle[11−16] and (ii) known to suffice for the stabilization of reactive low-coordinate complexes of Ti,[17,18] V,[19] Cr,[20] and Mo.[21−25] Accordingly,

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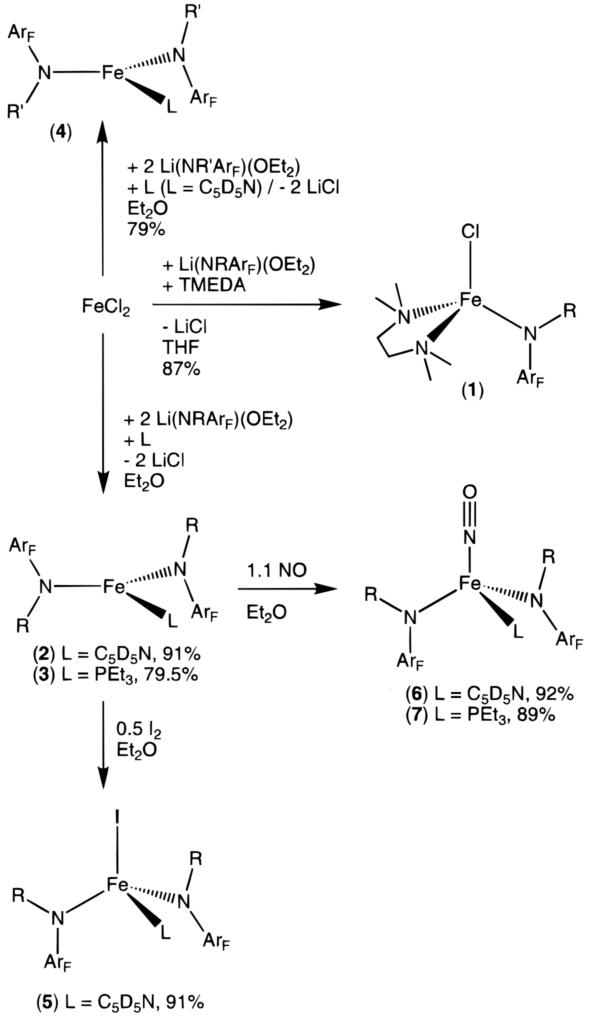
this work concerns the preparation of iron derivatives of the ligands $NRAr_F$ ($R = C(CD_3)_2CH_3$, $Ar_F = 2,5\text{-}C_6H_3\text{-}FMe$), $NR'Ar_F$ ($R' = C(CD_3)_2Ph$), and NRAr ($Ar = 3,5\text{-}C_6H_3Me_2$). Preparative procedures are given here for the first two ligands, while a synthesis of the last has been reported previously.[26] The *N*-(*tert*-hydrocarbyl)anilide ligands derived from 2-fluoro-5-methylaniline (here $NRAr_F$ and $NR'Ar_F$) are of special interest in that their *o*-fluorine substituent is potentially capable of coordination to a low-coordinate metal center[27−31] and in that they are less electron-releasing than NRAr.[32] A highlight of the present study is the synthesis and structural characterization of two formally iron(I) nitrosyl complexes and the observation that their formation by nitric oxide capture is chemically reversible.

Scheme 1



Results and Discussion

(i) Preparation and Characterization of Iron-$NRAr_F$ Complexes. Displayed in Scheme 1 are high-yield salt-elimination reactions stemming from the interaction of ferrous chloride with lithium *N*-(*tert*-hydrocarbyl)anilide etherates. Such salt-elimination reactions constitute the standard methodology for accessing iron(II) amides.[5] Peculiar to the present work is the concomitant use of salt-elimination and dative ligand complexation methodologies for the preparation of compounds **1**−**4**. Thus was $Fe(Cl)(TMEDA)(NRAr_F)$ (**1**; $TMEDA = Me_2NCH_2CH_2NMe_2$) obtained as a colorless crystalline compound in 87% yield upon treatment of $FeCl_2$ with 1 equiv of $Li(NRAr_F)(OEt_2)$ in tetrahydrofuran (THF) solvent, in the presence of TMEDA. Compound **1** exhibits a characteristic ^2H NMR signal at ca. 64 ppm, which proved to be convenient in pinpointing optimum conditions for its synthesis. Solution magnetic susceptibility measurements yielded a μ_{eff} value for **1** of 5.29 μ_B, which is typical for high-spin iron(II) and somewhat greater than the spin-only value (4.90 μ_B) for four unpaired electrons. X-ray structural data for **1** are likewise in agreement with its formulation as a four-coordinate iron(II) complex (Figure 1, Table 1). Bonding between Fe and the $NRAr_F$ ligand in **1** is restricted to a metal−nitrogen interaction, as indicated by a near-perpendicular orientation of the aryl moiety with respect to the contiguous plane defined by C(7), N(1), and Fe. The long, nonbonding Fe···F distance of 3.503(6) Å follows. The Fe−N(1) distance of 1.918(3) Å for **1** falls in the standard range for iron(II) terminal amido complexes, as evidenced by the values 1.917(2), 1.927(3) and 1.923(3), 1.895(3), 1.916(5), 1.905(2), 1.896(2) and 1.909(2), 1.914(14), 1.913(6) and 1.923(5), 1.938(2), and 1.934(3) and 1.924(3) Å for the representative compounds $Fe[N(SiMePh_2)_2]_2$,[33] $[Fe(\mu\text{-}N[SiMe_3]_2)(N[SiMe_3]_2)]_2$,[34] $[Fe(\mu\text{-}NPh_2)(NPh_2)]_2$,[34] $Fe(N[SiMe_3]_2)_2(THF)$,[34] $[Fe(\mu\text{-}OAr)(N[SiMe_3]_2)]_2$,[35] $Fe[N(SiMe_2Ph)_2]_2$,[36] $[Fe(\mu\text{-}PMes_2)(N[SiMe_3]_2)]_2$,[37] $Fe(S\text{-}2,6\text{-}C_6H_3[Mes]_2)(N[SiMe_3]_2)$,[38] $Fe[NMes(BMes_2)]_2$,[39] and $[Fe(\mu\text{-}N(R)SiMe_2OSiMe_2NR)]_2$,[40] respectively. Longer iron-nitrogen distances (2.209(4) and 2.216(4) Å) are observed to the TMEDA nitrogens, as expected on the basis of values obtained for the iron(II)−TMEDA complex $[Fe_2(H_2O)(O_2CPh)_4(TMEDA)_2]$,[41] which exhibits bonds to TMEDA of 2.265(5), 2.268(5), 2.362(4), and 2.293(4) Å. Likewise, the unremarkable iron−chlorine distance in **1** of 2.283(1) Å can be compared with 2.22(1) and 2.23(1), 2.282(1) and 2.277(1), 2.257(1) and 2.273(1), 2.227(2), and 2.287(2) and 2.295(2) Å for the four-coordinate iron(II)

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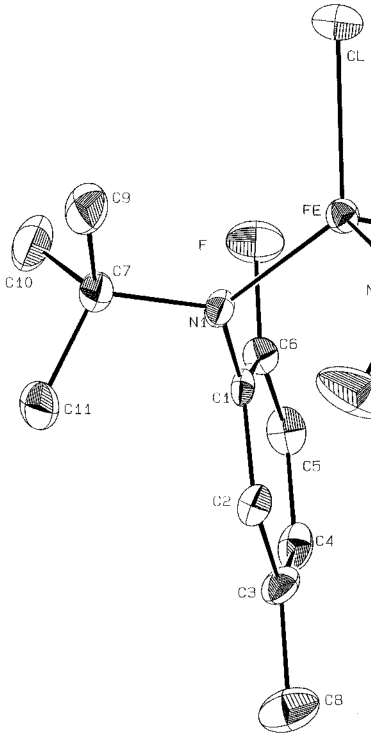

Figure 1. Structural diagram of **1** with thermal ellipsoids at the 35% probability level.

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fe(Cl)(TMEDA)(NRAr$_F$) (1)

Fe−Cl	2.283(1)	Fe−N(3)	2.216(4)
Fe−N(1)	1.918(3)	Fe−F	3.503(6)
Fe−N(2)	2.209(4)		
Cl−Fe−N(1)	125.9(1)	N(2)−Fe−N(3)	81.8(1)
Cl−Fe−N(2)	104.9(1)	Fe−N(1)−C(1)	118.8(3)
Cl−Fe−N(3)	105.6(1)	Fe−N(1)−C(7)	125.5(3)
N(1)−Fe−N(2)	117.9(1)	C(1)−N(1)−C(7)	114.9(3)
N(1)−Fe−N(3)	111.6(1)		
Cl−Fe−N(1)−C(7)	−37.7(4)		
Fe−N(1)−C(1)−C(2)	102.7(4)		

chloro complexes Fe(Cl)$_2$(dippe),[42] Fe(Cl)$_2$([*p*-tol]NCH(NH[*p*-tol]))$_2$,[43] Fe(Cl)$_2$(1-methylimidazoline-2-thione-*S*)$_2$,[44] Fe(Cl)(tris[3-*tert*-butylpyrazolyl]hydroborate),[45] and Fe(Cl)$_2$(OPMe$_3$)$_2$,[46] respectively.

Multigram quantities of the bis(amido)iron(II) complexes Fe(py-d_5)(NRAr$_F$)$_2$ (**2**; orange-red) and Fe(PEt$_3$)(NRAr$_F$)$_2$ (**3**; yellow) were prepared in 91% and 80% isolated yields, respectively, through treatment of ethereal ferrous chloride with 2 equiv of Li(NRAr$_F$)(OEt$_2$) in the presence of a slight excess of the appropriate donor ligand. Deuterium labeling in complex **2** permitted a ^{2}H NMR signal at ca. 40 ppm to be ascribed to the (CD$_3$)$_2$ portion of the NRAr$_F$ residue, on the basis of integration relative to pyridine-d_5 signals appearing at 139, 34, and 12 ppm. Triethylphosphine complex **3** exhibits a single signal at ca. 47 ppm for its deuterated NRAr$_F$ residues. A reasonable assumption would be that **2** and **3** represent mononuclear three-coordinate iron(II) complexes similar to Fe(N[SiMe$_3$]$_2$)$_2$(THF).[34] Both complexes exhibit effective magnetic moments (C$_6$D$_6$, 25 °C) consistent with high-spin iron(II): 5.29 μ_B for **2**, 5.24 μ_B for **3**. Because crystals of **2** and **3** suitable for a single-crystal X-ray structure investigation proved elusive to obtain, the related derivative Fe(py-d_5)(NR′Ar$_F$)$_2$ (**4**; orange-red) was prepared. A procedure essentially identical with that used in the preparation of **2**, utilizing Li(NR′Ar$_F$)(OEt$_2$) in place of Li(NRAr$_F$)(OEt$_2$), provided crystalline **4** in 79% yield. **4** exhibits a ^{2}H NMR signal (C$_6$H$_6$, 25 °C) at 14.5 ppm and an effective magnetic moment (C$_6$D$_6$, 25 °C) of 5.29 μ_B, these values being indicative once again of a monomeric high-spin iron(II) formulation.

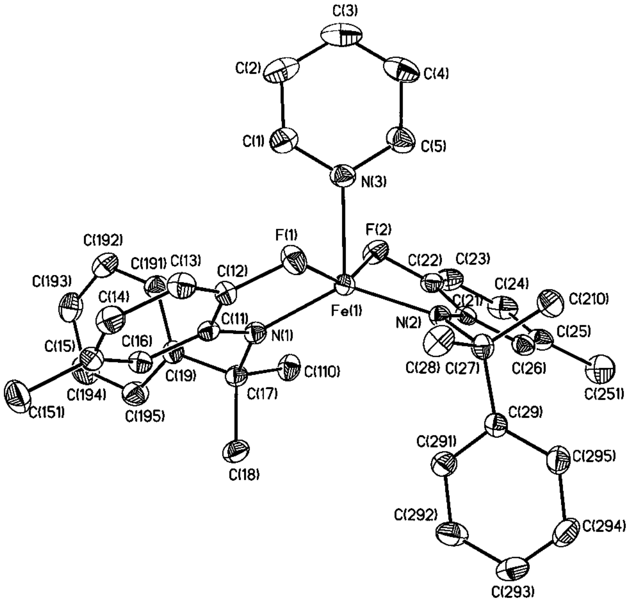

Figure 2. Structural diagram of **4** with thermal ellipsoids at the 35% probability level.

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fe(py-d_5)(NR′Ar$_F$)$_2$ (4)

Fe(1)−N(1)	1.982(2)	Fe(1)−F(2)	2.378(2)
Fe(1)−N(2)	1.992(2)	Fe(1)−F(1)	2.447(2)
Fe(1)−N(3)	2.135(2)		
N(1)−Fe(1)−N(2)	133.19(8)	N(3)−Fe(1)−F(1)	77.19(7)
N(1)−Fe(1)−N(3)	117.65(8)	F(2)−Fe(1)−F(1)	151.96(7)
N(2)−Fe(1)−N(3)	109.06(8)	C(11)−N(1)−C(17)	116.9(2)
N(1)−Fe(1)−F(2)	113.64(7)	C(11)−N(1)−Fe(1)	121.6(2)
N(2)−Fe(1)−F(2)	74.31(7)	C(17)−N(1)−Fe(1)	121.4(2)
N(3)−Fe(1)−F(2)	75.46(7)	C(21)−N(2)−C(27)	118.4(2)
C(22)−F(2)−Fe(1)	108.86(13)	C(21)−N(2)−Fe(1)	120.6(2)
N(1)−Fe(1)−F(1)	74.32(7)	C(27)−N(2)−Fe(1)	120.8(2)
N(2)−Fe(1)−F(1)	121.13(7)		
Fe(1)−N(1)−C(11)−C(12)	−1.5(2)		
Fe(1)−N(2)−C(21)−C(22)	12.1(2)		

An X-ray diffraction study (Figure 2, Table 2) revealed the expected trigonal-planar FeN$_3$ coordination polyhedron for **4**. More interesting is the finding that the NR′Ar$_F$ ligands in **4** both act as bidentate N,F-donor chelates,[27] in sharp contrast to the observation of an N-only bonding mode for the NRAr$_F$ ligand in four-coordinate **1** as described above. Metrical parameters in Table 2 reveal the two five-membered chelate rings in **4** to be nearly planar. This requires that the *o*-fluoro aryl moieties lie coplanar with their contiguous nitrogen trigonal planes, instead of perpendicular thereto as

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found for the N-only bonding mode of this ligand type. One consequence of this orientation is a reduction of the Fe−N−C(tertiary) angle due to mutual steric repulsion between the aryl *ortho* hydrogen and the tertiary hydrocarbyl substituent; these angles are 121.4(2) and 120.8(2)° in **4** as compared to 125.5(3)° in **1**. A second, more significant consequence of the aryl group orientation in **4** is to bring the fluorine substituents into close contact with the iron center: 2.447(2) and 2.378(2) Å for F(1) and F(2), respectively. By comparison with the Fe−F bond distance of 2.105(3) Å in the complex Fe(TPP)($FSbF_5$) (TTP = tetrakis(*p*-tolyl)porphyrin) with its activated Fe-F function,[47] the weak dative nature of the $Ar_F\cdots$Fe interaction in **4** becomes evident. Literature precedent exists for such chelates, with similar $Ar_F\cdots$M distances having been observed.[27] In an otherwise low-coordinate complex such as **4**, the Fe(II) cation is substantially exposed and is able to interact with polar (e.g., C−F) or polarizable (aryl) substituents that are held in close proximity through chelation.[36,38,39] It is appealing to think of such interactions as "placeholders" which may inhibit dimerization of the low-coordinate complex but which are displaced readily by aggressive incoming ligands, as in reaction chemistry to be described below for **2**. With regard to the overall coordination polyhedron in **4**, the trigonal-bipyramidal FeN_3F_2 unit is distorted such that the axial fluorine ligands are off-axis with an F⋯Fe⋯F angle of 151.96(7)°, whereas the pyridine and amide nitrogens define a plane from which the iron atom is not significantly displaced. Although it is tempting to correlate the ArF⋯Fe interactions in the observed solid-state structure of **4** with the reaction chemistry described below for **2**, caution must be exercised because this assumes (i) that such interactions obtain for **2** and (ii) that the interactions persist in solution. Specifically, the view taken here that ArF⋯Fe chelate interactions may act as placeholders, while appealing and reasonable on the basis of chemical intuition, should be viewed with some circumspection.

(ii) Iodine Oxidation of Fe(py-d_5)(NRAr$_F$)$_2$ (2). Chemical oxidation has been utilized previously in the preparation of manganese(III) amido complexes from manganese(II) amido precursors.[48] Such methodology can be particularly useful in instances where direct substitution on a trivalent metal ion fails to give amido complexes smoothly or in instances, as in the present case, where functionality is to be introduced. Accordingly, addition of elemental iodine in slight excess to an ether solution of **2** (Scheme 1) elicited a rapid color change to dark purple. Replacement of the ^{2}H NMR signal at ca. 40 ppm (assigned to $C(CD_3)_2CH_3$) characteristic of **2** by a single peak at ca. 47 ppm indicative of Fe(I)(py-d_5)(NRAr$_F$)$_2$ (**5**) was observed concomitantly. Purple **5** was isolated by recrystallization from ether in 97% yield. Consistent with formulation of **5** as a high-spin iron(III) complex is its observed μ_{eff} value of 5.95 μ_B (C_6D_6, 25 °C).

Characterization of **5** included a single-crystal X-ray structure determination (Figure 3, Table 3). Salient features of the structure include bond angles at iron indicative of a modest degree of distortion from the tetrahedral geometry. The Fe−N bond distances to the NRAr$_F$ nitrogens, 1.896(5) and 1.900(5) Å, fall at the low end of the range for iron amido complexes as discussed above in conjunction with the structure of **1**, nominally consistent with the smaller size of iron(III) versus iron(II). Note, however, that the Fe−N distance reported for the prototypical iron(III) amido complex Fe[N(SiMe$_3$)$_2$]$_3$ is marginally longer, 1.918(4) Å.[7] The pyridine Fe−N distance for **5** of 2.108(5) Å compares with the values 2.152(12), 2.145(9), 2.138(12) and 2.139(8) and 2.155(4) for the tetrahedral iron−pyridine and −phenanthroline complexes $Fe_4(CO)_8(py)_4$[49] and Fe(Mes)$_2$(phen),[50] respectively. With respect to the iron-iodine distance in **5** of 2.6247(9) Å, this value is longer than has been observed for simple tetrahedral iron(III) iodo complexes such as Fe(I)$_3$(SC[NMe$_2$]$_2$), Fe-I bond lengths for which are 2.533(1), 2.530(1), and 2.537(1) Å.[51] The longer Fe−I distance in **5** is perhaps a

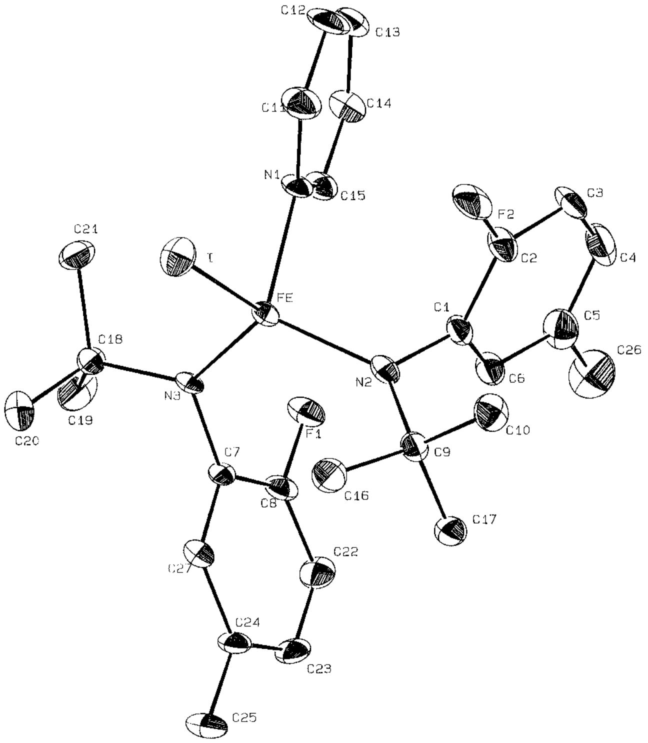

Figure 3. Structural diagram of **5** with thermal ellipsoids at the 35% probability level.

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fe(I)(py-d_5)(NRAr$_F$)$_2$ (5)

I−Fe	2.6247(9)	Fe−N(3)	1.900(5)
Fe−N(1)	2.108(5)	Fe−F(1)	3.740(5)
Fe−N(2)	1.896(5)	Fe−F(2)	3.501(5)
I−Fe−N(1)	101.6(1)	Fe−N(2)−C(1)	114.1(4)
I−Fe−N(2)	114.7(2)	Fe−N(2)−C(9)	131.1(4)
I−Fe−N(3)	114.7(2)	C(1)−N(2)−C(9)	114.8(5)
N(1)−Fe−N(2)	104.3(2)	Fe−N(3)−C(7)	116.7(4)
N(1)−Fe−N(3)	106.3(2)	Fe−N(3)−C(18)	128.2(4)
N(2)−Fe−N(3)	113.6(2)	C(7)−N(3)−C(18)	114.3(5)
Fe−N(3)−C(7)−C(27)	88.2(6)		
Fe−N(2)−C(1)−C(6)	−96.1(6)		

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reflection of the strong donor nature of the NRAr$_F$ ligand as compared with iodide. Finally, in contrast to the situation for nominally three-coordinate **4**, the *o*-fluorine substituents in **5** are distant from Fe (>3.5 Å) due to the mutually orthogonal relationship of the Ar$_F$ rings with respect to their contiguous nitrogen trigonal planes. In comparison with the structure of **4**, the structure of **5** is suggestive of iodine accommodation *via* dative Ar$_F$ displacement. A similar phenomenon is encountered below in conjunction with nitric oxide treatment of compounds **2** and **3**.

(iii) Nitric Oxide Complexes. Scheme 1 depicts direct nitrosylation of the iron(II) complexes **2** and **3** by simple addition of gaseous nitric oxide, in slight excess, to a solution of either compound at ca. 25 °C. In both cases the reaction is rapid and essentially quantitative, as assessed by ^{2}H NMR spectroscopy. The reaction is visually dramatic in that both product nitrosyl compounds are a wine red color. Removal of the ethereal solvent, followed by recrystallization of the crude material, provided nitrosyl **6** in 92% yield and nitrosyl **7** in 89% yield as faceted crystals. Nitrosyl complexes **6** and **7** are paramagnetic with μ_{eff} values of 3.92 and 4.03 μ_B, respectively, indicative of high-spin tetrahedral iron(I); this oxidation state follows if the nitrosyl ligand is counted as $(NO)^+$, giving the metal a d^7 configuration. Consistent with this picture are the nitrosyl stretching frequencies of 1708, 1675, and 1704 cm^{-1} for **6**, **6** prepared using ^{15}NO, and **7**, respectively. By comparison, the prototypical tetrahedral iron(I) nitrosyl complex $[Fe(NO)(Cl)_3]^-$, which also exhibits an effective magnetic moment indicative of three unpaired electrons, displays its NO stretch at 1802 cm^{-1}.[52] Four-coordinate iron(I) mononitrosyls exemplified by **6** and **7** constitute a rare class of compounds; among four-coordinate iron nitrosyl systems the $Fe(NO)_2(X)(L)$ (X = uninegative 2e donor, L = neutral 2e donor) class containing iron in the formal (−1) oxidation state is the most ubiquitous.[53]

From the standpoint of its overall conformation the structure (Figure 4, Table 4) of pseudotetrahedral Fe(NO)(py-d_5)(NRAr$_F$)$_2$ (**6**) is quite similar to that of iodide **5** discussed above. The observed iron−nitrogen bond distances to the pyridine and NRAr$_F$ ligands are nearly identical for the two complexes. Clearly, the most interesting metrical parameters for **6** pertain to the FeNO moiety: d(FeN) = 1.74(1) Å, d(NO) = 1.05(1) Å, and ∠(FeNO) = 174(2)°. These values should be compared with those reported[54] for $[Fe(NO)(Cl)_3]^-$ (d(FeN) = 1.70(1) Å, d(NO) = 1.12(2) Å, and ∠(FeNO) = 177(1)°) and also with those (Figure 5, Table 5) for Fe(NO)(PEt$_3$)(NRAr$_F$)$_2$ (**7**) (d(FeN) = 1.714(3) Å, d(NO) = 1.174(4) Å, and ∠(FeNO) = 167.0(3)°). In all three complexes the nitrosyl grouping is roughly linear, and the NO bond distances are close to that (1.15 Å) of free nitric oxide.[53] Multiple-bond character between iron and the nitrosyl nitrogen atom is indicated for all three complexes by short FeN bond distances, fully 0.2 Å shorter than the Fe−N distances to the NRAr$_F$ ligands. In the case of complex **6**, three different types of FeN interactions are displayed: dative to the pyridine nitrogen, 2.12(1) Å; a 1σ,1π interaction with the NRAr$_F$ nitrogen, 1.903(8) and 1.905(8) Å; and a 1σ,2π interaction with the nitrosyl nitrogen, 1.74(1) Å.

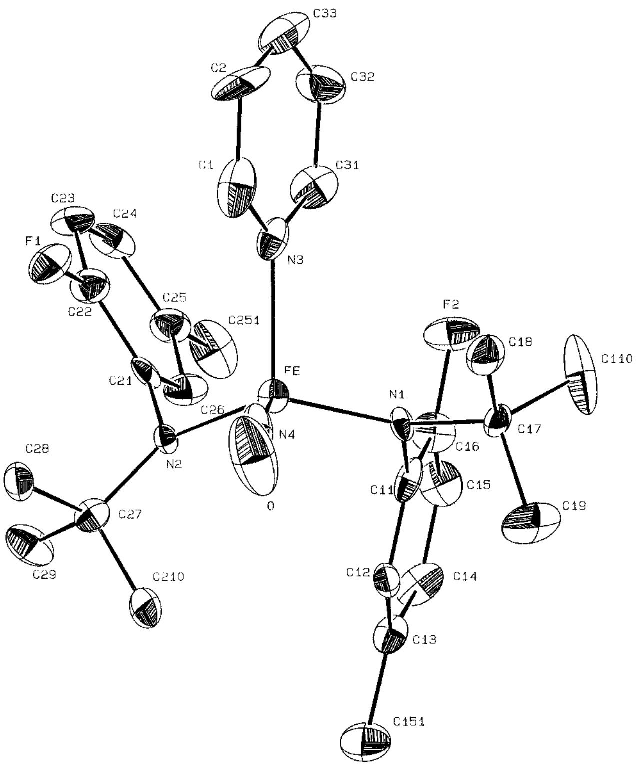

Figure 4. Structural diagram of **6** with thermal ellipsoids at the 35% probability level.

Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fe(NO)(py-d_5)(NRAr$_F$)$_2$ (6)

Fe−N(1)	1.903(8)	Fe−F(1)	3.58(1)
Fe−N(2)	1.905(8)	Fe−F(2)	4.07(1)
Fe−N(3)	2.12(1)	O−N(4)	1.05(1)
Fe−N(4)	1.74(1)		
N(1)−Fe−N(2)	114.8(4)	Fe−N(1)−C(17)	126.7(7)
N(1)−Fe−N(3)	102.3(4)	C(11)−N(1)−C(17)	113.1(8)
N(1)−Fe−N(4)	114.2(5)	Fe−N(2)−C(21)	112.8(6)
N(2)−Fe−N(3)	108.5(4)	Fe−N(2)−C(27)	128.1(7)
N(2)−Fe−N(4)	112.3(4)	C(21)−N(2)−C(27)	117.7(8)
N(3)−Fe−N(4)	103.3(5)	Fe−N(4)−O	174(2)
Fe−N(1)−C(11)	118.0(7)		
Fe−N(2)−C(21)−C(26)	96(1)		
Fe−N(1)−C(11)−C(12)	−72(1)		

Extended Hückel calculations carried out for Fe(NO)(PEt$_3$)(NRAr$_F$)$_2$ (**7**) indicate that the HOMO is singly occupied and is antibonding with respect to the Fe−P interaction; the HOMO of **6** is similarly indicated by extended Hückel analysis to be singly occupied and antibonding with respect to the iron−pyridine interaction. Since the orbital analysis suggested that some degree of lability might obtain for the dative ligands in **6** and **7**, pyridine and triethylphosphine, respectively, ligand exchange studies were carried out. Accordingly, it was found that treatment of **7** with an excess of pyridine-d_5 produced **6** in quantitative fashion but that the reverse process, displacement of pyridine from **6** in the presence of an excess of triethylphosphine, did not proceed to completion readily.

(iv) Intermetal Nitric Oxide Transfer Reactions. Metal nitrosyl complexes have been used as nitric oxide delivery agents in a number of instances. As mentioned

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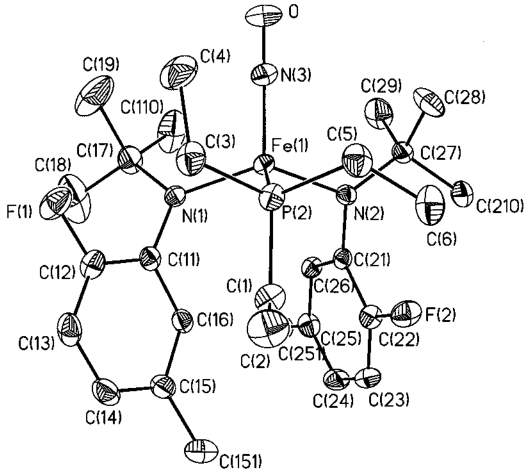
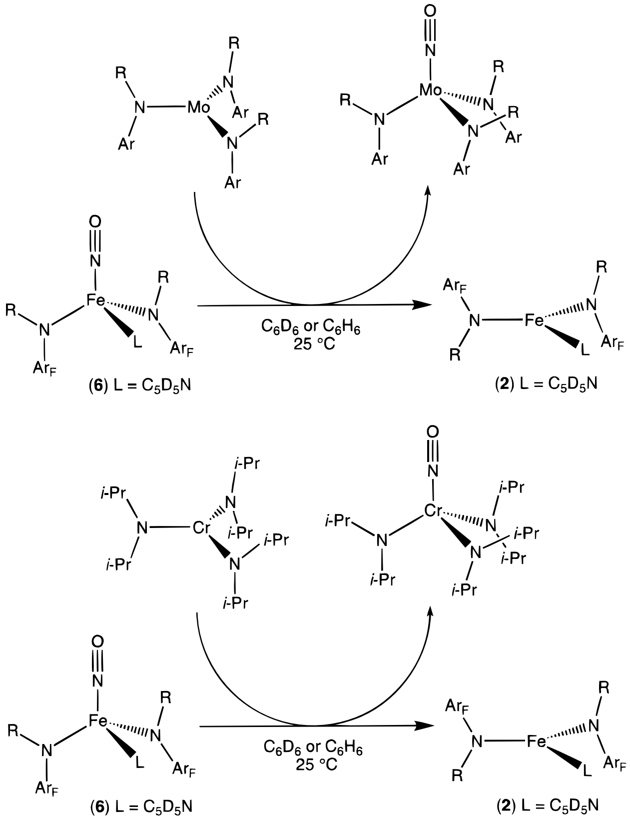


Figure 5. Structural diagram of **7** with thermal ellipsoids at the 35% probability level.

Table 5. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fe(NO)(PEt$_3$)(NRAr$_F$)$_2$ (7)

Fe(1)−N(3)	1.714(3)	N(3)−O	1.174(4)
Fe(1)−N(2)	1.925(3)	Fe(1)−F(1)	4.133(3)
Fe(1)−N(1)	1.931(3)	Fe(1)−F(2)	3.940(3)
Fe(1)−P(2)	2.4776(11)		
N(3)−Fe(1)−N(2)	107.75(14)	C(11)−N(1)−Fe(1)	115.4(2)
N(3)−Fe(1)−N(1)	108.73(14)	C(17)−N(1)−Fe(1)	126.5(2)
N(2)−Fe(1)−N(1)	121.29(12)	C(21)−N(2)−C(27)	114.0(3)
N(3)−Fe(1)−P(2)	104.51(12)	C(21)−N(2)−Fe(1)	116.4(2)
N(2)−Fe(1)−P(2)	108.20(9)	C(27)−N(2)−Fe(1)	127.2(2)
N(1)−Fe(1)−P(2)	105.15(9)	O−N(3)−Fe(1)	167.0(3)
C(11)−N(1)−C(17)	117.8(3)		
Fe(1)−N(1)−C(11)−C(16)	−69.9(3)		
Fe(1)−N(2)−C(21)−C(26)	79.7(3)		

Scheme 2. Intermetal Nitric Oxide Transfer



in the treatise by Richter-Addo and Legzdins,[53] [Co(NO)$_2$X]$_2$ (X = halide) complexes have been employed as reagents in the synthesis of other metal nitrosyls, including CpMo(NO)(CO)$_2$[55] and Mn(NO)$_3$(THF).[56] In recent work the three-coordinate molybdenum(III) complex Mo(NRAr)$_3$ was shown to react smoothly with 1 equiv of gaseous nitric oxide to provide diamagnetic, yellow Mo(NO)(NRAr)$_3$ (ν(NO) = 1604 cm^{-1}) in essentially quantitative yield.[25] This was not surprising in view of the demonstration by Bradley and co-workers that the three-coordinate chromium(III) complex Cr(N^{i}Pr$_2$)$_3$[57,58] likewise takes up 1 equiv of NO to give diamagnetic Cr(NO)(N^{i}Pr$_2$)$_3$, which is assigned a linear CrNO moiety and a low (1643 cm^{-1}) nitrosyl stretching frequency.[59,60] As shown in Scheme 2, both Mo(NRAr)$_3$ and Cr(N^{i}Pr$_2$)$_3$ effect smooth nitric oxide abstraction from Fe(NO)(py-d_5)(NRAr$_F$)$_2$ (**6**), regenerating **2** along with the corresponding nitrosyl of chromium or molybdenum. The reactions were carried out in C_6D_6 and C_6H_6 and monitored by ^{1}H and ^{2}H NMR spectroscopy, respectively. In the case of Cr(N^{i}Pr$_2$)$_3$ the abstraction reaction was accompanied by a gradual color change and shown to be complete in under 3 h, whereas in the case of Mo(NRAr)$_3$ only minutes (ca. 2 min) were required for the reaction mixture to attain its final color (orange) and NMR spectra confirmed that the transfer was complete in under 30 min. No intermediate complexes were detected in either case by NMR spectroscopy.

(v) Preparation and Characterization of Iron−NRAr Complexes. Scheme 3 depicts synthetic procedures used for the preparation of three new NRAr-containing compounds. Salt-elimination reactions ensuing upon treatment of ferrous chloride with 2 or 3 equiv of Li(NRAr)(OEt$_2$) produced the dimer [Fe(NRAr)(μ-NRAr)]$_2$ (**8**) or the “ate” complex (ArRN)Fe(μ-NRAr)$_2$Li(OEt$_2$) (**9**) in isolated yields of 88% and 85%, respectively. That **8** is dimeric in benzene solution is indicated by ^{2}H NMR spectroscopy, in that two peaks of equal integral are observed at 11.3 and −10.8 ppm. Furthermore, two equal-integral peaks are similarly observed in crude ethereal reaction mixtures containing freshly prepared **8**, indicating that the dimer forms in preference to the putative solvate Fe(NRAr)$_2$(OEt$_2$) analogous to the known Fe[N(SiMe$_3$)$_2$]$_2$(THF).[34] Magnetic susceptibility measurements (benzene, 25 °C) are also indicative of a dimeric formulation for **8**, with $\mu_{\mathrm{eff}} = 4.21\ \mu_B$/dimer. The issue of preference for solvated monomer versus unsolvated dimer has been addressed previously for the iron(II) silylamide system,[34] where it was found that Fe[N(SiMe$_3$)$_2$]$_2$, although dimeric in the solid state, is predominantly monomeric in toluene solution at ca. 27 °C. It was asserted that [Fe(NPh$_2$)$_2$]$_2$ is a more tightly associated dimer than [Fe[N(SiMe$_3$)$_2$]$_2$]$_2$, in accord with our finding that **8** retains a dimeric structure in solution. Formation of “ate” complex **9** represents, in effect, the breakup of dimer **8** by addition of the strong nucleophile Li(NRAr)(OEt$_2$). In this respect the formation of **9** resembles the in situ production of base-stabilized complexes **2**−**4**, described above and depicted in Scheme 1. Note, however, that the putative “ate” complex (Ar$_F$-

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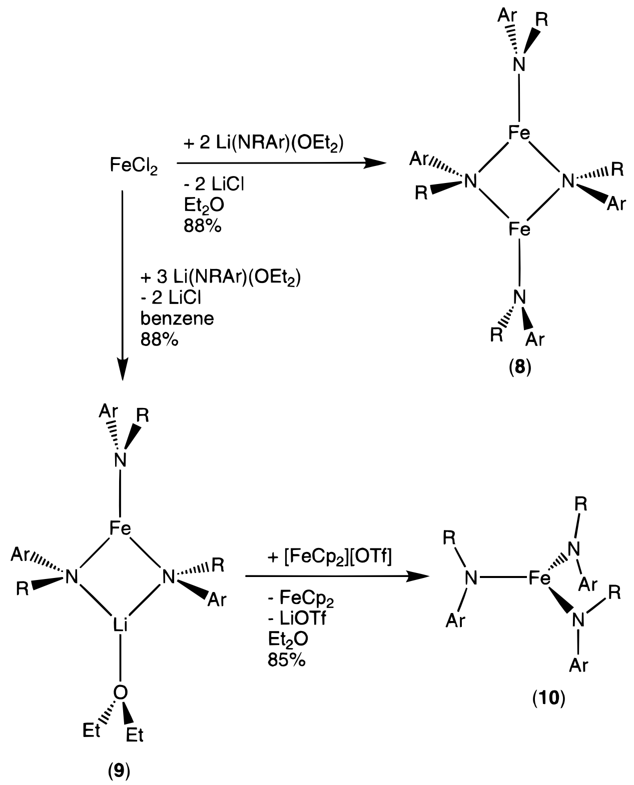
Scheme 3



RN)Fe(μ-NRAr$_F$)$_2$Li(OEt$_2$) was *not* observed upon treatment of FeCl$_2$ with 3 equiv of Li(NRAr$_F$)(OEt$_2$). ^{2}H NMR spectroscopy is indicative of the proposed structure (Scheme 3) for **9** as drawn, with two bridging and one terminal NRAr ligand: two signals appear at −2.35 and 44.2 ppm in a 2:1 ratio. The proposed structure of **9** is as found previously for the related "ate" complex [(Me$_3$Si)$_2$N]Mn[μ-N(SiMe$_3$)$_2$]$_2$Li(THF).[5,61] A tin "ate" complex of constitution similar to **9**, namely Li$^+$[Sn(NRAr)$_3$]$^-$, has been reported previously.[26]

The preparation of "ate" complex **9** provided synthetic access to a homoleptic amide of iron(III) analogous to Fe[N(SiMe$_3$)$_2$]$_3$. Treatment of ethereal **9** with ferrocenium triflate[62] (1 equiv) elicited rapid production of a homogeneous dark blue reaction mixture harboring one major NRAr-containing compound (^{2}H NMR, δ 55 ppm). Fe(NRAr)$_3$ (**10**) was obtained in 85% yield pursuant to removal of ferrocene by sublimation and lithium triflate by filtration of a hexane extract and recrystallization from pentane. Magnetic susceptibility studies (benzene, 25 °C) were consistent with the formulation of **10** as a complex of high-spin iron(III), with $\mu_{\mathrm{eff}} = 6.22\ \mu_B$. The use of ferrocenium triflate[62] to oxidize "ate" complexes has been demonstrated previously in the synthesis of neutral amides of manganese(III)[48] and iron(IV).[63] This synthetic protocol is attractive in cases where salt-elimination reactions fail with higher-oxidation-state metal halide precursors; in the present instance, for example, Fe(NRAr)$_3$ was not obtained upon treatment of ferric chloride with 3 equiv of Li(NRAr)(OEt$_2$), although dimeric **8** was produced in low yield in such attempts. Fe(NRAr)$_3$ (**10**) is the fourth known neutral compound of the type M(NRAr)$_3$, the others incorporating Ti,[17,18] Cr,[20] and Mo[21−25] as the central metal.

Concluding Remarks

This paper covers synthetic entries to iron(II) and -(III) amide complexes based on the new class of *N*-(*tert*-hydrocarbyl)anilide ligands. Salt-elimination (metathesis) reactions were used to furnish the metal amide linkage, in all cases. The quasi-three-coordinate complex Fe(py-d_5)(NRAr$_F$)$_2$ (**2**) was found to constitute a versatile platform for reaction chemistry, acting both as an iodine atom acceptor and as a chemically reversible acceptor of nitric oxide. Nitrosyl complexes **6** and **7** constitute rare examples of (formal) iron(I) nitrosyls analogous to [Fe(NO)(Cl)$_3$]$^-$. Complexes **1** and **4**−**7** were characterized structurally by X-ray diffraction, lending insight into the conformational and steric properties of the new amide ligand type. The otherwise three-coordinate complex **4** was found to incorporate supplemental dative Fe···F interactions, while the four-coordinate complexes did not exhibit short Fe···F contacts. Finally, the new homoleptic iron(III) amide Fe(NRAr)$_3$ (**10**) was prepared via chemical oxidation of the preformed iron(II) "ate" complex **9**. The synthetic and initial reactivity studies presented here are presumed to be reflective of the potential richness of iron amide chemistry.

Experimental Section

General Considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using standard Schlenk techniques under an argon atmosphere. Anhydrous ether and toluene were purchased from Mallinckrodt; *n*-pentane and *n*-hexane were purchased from EM Science. Ether was distilled under a nitrogen atmosphere from purple sodium benzophenone ketyl. Aliphatic hydrocarbon solvents were distilled under a nitrogen atmosphere from very dark blue to purple sodium benzophenone ketyl solubilized with a small quantity of tetraglyme. Toluene was refluxed over molten sodium for at least 2 days prior to its distillation under a nitrogen atmosphere. Distilled solvents were transferred under vacuum into Teflon-stopcocked glass vessels and stored, prior to use, in a Vacuum Atmospheres drybox. TMEDA was stirred over CaH$_2$ and distilled under nitrogen. Benzene-d_6 was degassed and dried over blue sodium benzophenone ketyl and transferred under vacuum into a storage vessel. Chloroform-*d* and pyridine-d_5 were degassed and dried over 4 Å sieves. Sieves (4 Å) and alumina were activated in vacuo overnight at a temperature above 180 °C. Mo(NRAr)$_3$,[21,25] Cr(N^{i}Pr$_2$)$_3$,[58] ferrocenium triflate,[62] and Li(NRAr)(OEt$_2$)[26] were prepared according to published procedures. Other chemicals were used as received. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. UV-visible spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-500, Varian XL-300, and Varian Unity-300 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported with reference to solvent resonances (residual C$_6$D$_5$*H* in C$_6$D$_6$, 7.15 ppm; *C*$_6$D$_6$, 128.0 ppm; C*H*Cl$_3$ in CDCl$_3$, 7.24 ppm; *C*DCl$_3$, 77.0 ppm). ^{2}H NMR chemical shifts are reported with respect to external C$_6$D$_6$ (7.15 ppm). ^{19}F chemical shifts are reported with reference to external CFCl$_3$ (0 ppm). Solution magnetic susceptibilities were determined by ^{1}H NMR at 300 MHz or by ^{2}H NMR at 46 MHz, using the method of Evans.[64,65] Routine coupling constants are not reported. Combustion analyses (C, H, and N) were performed by Oneida Research

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Services, Whitesboro, NY. Melting points were obtained in sealed glass capillaries and are uncorrected.

Synthesis of $(CD_3)_2C{=}NAr_F$. A solution of 2-fluoro-5-methylaniline (12.3 g, 98.23 mmol) in acetone-d_6 (41 mL, 560 mmol) was stirred over activated 4 Å molecular sieves for 6 h. The mixture was filtered onto fresh sieves and stirred for an additional 3 h. The latter step was repeated once more, leading to complete consumption of the aniline according to ^{19}F NMR analysis. The mixture was then filtered through a bed of Celite-545 on a sintered-glass frit, and the sieves were washed with small portions of cold acetone-d_6. The excess acetone-d_6 present in the combined filtrate was then vacuum-transferred to another vessel (for reuse). The nonvolatile, pale yellow liquid that remained was the desired product (12.19 g, 71.2 mmol, 72.5%). The yield can be increased slightly by storing the molecular sieves with pentane overnight, filtering, and removing the volatiles in vacuo. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 6.89 (t, 1H, *para* C_6H_3FMe), 6.75 (d, 1H, *meta* C_6H_3FMe), 6.57 (d, 1H, *ortho* C_6H_3FMe), 2.17 (s, 3H, C_6H_3FMe). ^{13}C NMR (75 MHz, benzene-d_6, 22 °C): δ 21.6 (q, $ArCH_3$), 28.3 (sept, CD_3), 114.6 (d, C_6H_3FMe), 116.7 (d, C_6H_3FMe), 123.9 (t, $NC(CD_3)_2$), 133.9 (s, C_6H_3FMe), 138.2 (s, C_6H_3FMe), 150.1 (d, CF), 172.5 (s, C_6H_3FMe). ^{19}F NMR (282 MHz, C_6D_6, 22 °C): δ −132.8.

Synthesis of $H(NRAr_F)$. A chilled solution (−35 °C) of the imine (12.17 g, 71.06 mmol) in ether (40 mL) was added dropwise to a cold 1.4 M solution of MeLi (−116 °C) in ether (152 mL, 213.18 mmol). After it was stirred overnight, the yellow reaction mixture was removed from the drybox and poured over 300 mL of ice. Petroleum ether (300 mL) was added, and the aqueous layer was separated and extracted with additional petroleum ether (2 × 150 mL). The organic layers were combined and flushed through an alumina column (20 × 1 cm). Additional petroleum ether can be used to elute the product from the column. The solvent was removed from the filtrate in vacuo, leaving a yellow oil (11.77 g, 61.87 mmol, 87.07%). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 6.89 (t, 1H, *meta* C_6H_3FMe), 6.85 (d, 1H, *para* C_6H_3FMe), 6.50 (s, 1H, *ortho* C_6H_3FMe), 3.74 (s, 1H, NH), 2.31 (s, 3H, C_6H_3FMe), 1.38 (s, 3H, $C(CD_3)_2(CH_3)$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ 21.5 (C_6H_3FMe), 29.9 ($C(CD_3)_2(CH_3)$), 51.4 ($C(CD_3)_2(CH_3)$), 114.2 (C_6H_3FMe), 118.4 (C_6H_3FMe), 133.5 (C_6H_3FMe), 134.9 (C_6H_3FMe), 150.3 (CF), 153.4 (C_6H_3FMe). ^{19}F NMR (282 MHz, C_6D_6, 22 °C): δ −138.9.

Synthesis of $Li(NRAr_F)(OEt_2)$. A solution of $H(NRAr_F)$ (8.00 g, 42.71 mmol) in pentane (25 mL) and ether (13 mL) was chilled to −35 °C. Addition of *n*-BuLi (30 mL of a 1.6 M solution in hexane, 47 mmol) *via* pipet resulted in the initial formation of a homogeneous mixture from which the lithium amide slowly started to precipitate. The reaction mixture was stirred for 3 h, and then the white solid product was collected by filtration. The white solid, on a sintered-glass frit, was washed with cold pentane and dried *in vacuo*. The yellow filtrate was concentrated and stored at −35 °C overnight. A second crop of white solid was isolated, washed, and dried *in vacuo*. The total yield was 8.35 g (31.17 mmol, 72.9%). ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 6.92 (d, 1H, *meta* C_6H_3FMe), 6.79 (t, 1H, *para* C_6H_3FMe), 6.00 (t, 1H, *ortho* C_6H_3FMe), 3.23 (q, 4H, OCH_2), 2.27 (s, 3H, C_6H_3FMe), 1.56 (s, 3H, $C(CD_3)_2CH_3$), 1.01 (t, 6H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 22 °C): δ 15.6 (OCH_2CH_3), 22.6 (C_6H_3FMe), 31.6 ($C(CD_3)_2CH_3$), 51.9 ($C(CD_3)_2CH_3$), 66.0 (ether CH_2), 107.1 (C_6H_3FMe), 113.3 (C_6H_3FMe), 119.0 (C_6H_3FMe), 134.7 (C_6H_3FMe), 149.1 (C_6H_3FMe), 156.8 (CF). ^{19}F NMR (300 MHz, C_6D_6, 22 °C): δ −152.1.

Synthesis of $H(NR'Ar_F)$. A chilled solution (−35 °C) of the imine $(CD_3)_2C{=}NAr_F$ (10.0 g, 58.39 mmol) in ether (40 mL) was added dropwise to a cold ether solution (−116 °C) of PhLi (126 mL of a 1.4 M cyclohexane/ether solution, 178 mmol). After it was stirred overnight, the dark orange-brown reaction mixture was removed from the drybox and poured onto 300 mL of ice contained in a 1 L Erlenmeyer flask. Petroleum ether (400 mL) was added, and the aqueous layer was separated and extracted with additional petroleum ether (2 × 200 mL). The organic layers were combined and flushed through an alumina column (20 × 2 cm). Additional petroleum ether can be used to fully elute the product. Volatile material was then removed *in vacuo*, leaving the crude product as a yellow-orange oil (9.89 g, 39.50 mmol, 67.1%). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 7.30 (d, 2H, *ortho* C_6H_5), 7.12 (t, 2H, *meta* C_6H_5), 7.01 (t, 1H, *para* C_6H_5), 6.62 (dd, 1H, C_6H_3FMe), 6.10 (m, 1H, C_6H_3FMe), 5.74 (dd, 1H, C_6H_3FMe), 4.07 (s, 1H, NH), 1.77 (s, 3H, C_6H_3FMe). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ 21.4 (C_6H_3FMe), 29.8 ($C(CD_3)_2$), 55.5 ($C(CD_3)_2$), 114.1, 116.5, 117.0, 125.7, 126.7, 128.8, 133.3, 134.4, 147.4, 150.7.

Synthesis of $Li(NR'Ar_F)(OEt_2)$. A solution of $H(NR'Ar_F)$ (9.89 g, 39.50 mmol) in pentane (40 mL) and ether (20 mL) was chilled to −35 °C. Addition of *n*-BuLi (27 mL of a 1.6 M hexane solution, 43.5 mmol) *via* pipet resulted in the initial formation of a homogeneous mixture from which the lithium amide slowly started to precipitate. The reaction mixture was stirred for 3 h, and then the precipitated product was collected by filtration on a frit. The beige product was washed with cold pentane and dried in vacuo (11.15 g, 33.7 mmol, 85.4%). This compound has low solubility in C_6D_6, precluding characterization by ^1H NMR in that solvent. A ^1H NMR spectrum obtained in tetrahydrofuran-d_8 was complex, possibly indicative of complex equilibria or multiple species of low symmetry.

$Fe(Cl)(TMEDA)(NRAr_F)$ (1). $FeCl_2$ (470 mg, 3.71 mmol, 0.50 equiv) and TMEDA (700 mg, 6.02 mmol) were added sequentially to a stirred colorless solution of $Li(NRAr_F)(OEt_2)$ (1.00 g, 3.74 mmol) in THF (30 mL) at 28 °C. After the solution was stirred overnight, all volatile material was removed in vacuo from the amber reaction mixture. The residue was extracted with ether (50 mL) while the mixture was stirred, and LiCl was removed by filtration. The filtrate was concentrated to a volume of ca. 30 mL and stored at −35 °C overnight. $Fe(Cl)(TMEDA)(NRAr_F)$ (**1**) was thereby obtained as transparent, colorless crystals (1.27 g, 3.23 mmol, 86.9% yield). ^2H NMR (46 MHz, C_6H_6, 22 °C): δ 63.8 (s, $\Delta\nu_{1/2}$ = 26 Hz). μ_{eff} (46 MHz, C_6H_6, 22 °C): 5.29 μ_B. Anal. Calcd for $C_{17}H_{25}D_6N_3FFe$: C, 51.85; H, 7.93; N, 10.67. Found: C, 51.77; H, 7.85; N, 10.67.

X-ray Structure of $Fe(Cl)(TMEDA)(NRAr_F)$ (1). A crystal of approximate dimensions 0.25 × 0.32 × 0.32 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at −72 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 2963 reflections were collected to a 2θ value of 44.9°, 2746 of which were unique (R_{int} = 0.037); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined either anisotropically or isotropically. Refinement was hampered by the disorder that was discovered in the TMEDA ligand CH_2CH_2 fragment. The disorder is one that has been observed in a wide variety of structures and is best described as a conformational disorder. The disorder was successfully modeled. Due to the disorder it was not possible to refine all of the carbons in the TMEDA ligand as anisotropic scatterers. One carbon, C(12), was refined isotropically. The final cycle of least-squares refinement was based on 2060 observed reflections ($I > 3.00\sigma(I)$) and 231 variable parameters and converged (largest parameter shift was 0.15 times its esd) with $R = 0.042$ and $R_w = 0.051$. A final difference Fourier map showed no chemically significant features. Crystal data are $a = 8.416(2)$ Å, $b = 16.019(2)$ Å, $c = 15.043(2)$ Å, $V = 2023(1)$ Å^3, $\beta = 93.93(2)$°, space group $P2_1/n$, $Z = 4$, $M_r = 393.71$ for $C_{17}H_{25}D_6N_3FClFe$, and ρ(calcd) = 1.273 g/cm^3.

$Fe(py\text{-}d_5)(NRAr_F)_2$ (2). $FeCl_2$ (1.93 g, 15.2 mmol) and pyridine-d_5 (1.40 g, 16.64 mmol, 1.09 equiv) were added to a stirred colorless solution of $Li(NRAr_F)(OEt_2)$ (8.11 g, 30.7 mmol) in ether (50 mL) at 28 °C. The reaction mixture was stirred overnight. The orange-red reaction mixture was then filtered, and the filtrate was concentrated to ca. 25 mL and cooled to −35 °C for several hours to provide the product as

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orange-red crystals, which were collected and dried *in vacuo* (7.00 g, 13.7 mmol, 90.9%). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 139.1 (s, $\Delta\nu_{1/2} = 105$ Hz, 2D, *ortho* C_5D_5N), 40.1 (s, $\Delta\nu_{1/2} = 34$ Hz, 12D, $C(CD_3)_2$), 34.3 (s, $\Delta\nu_{1/2} = 16$ Hz, 2D, *meta* C_5D_5N), 11.6 (s, $\Delta\nu_{1/2} = 19$ Hz, 1D, *para* C_5D_5N). μ_{eff} (46 MHz, C_6H_6, 22 °C): 5.29 μ_B. Anal. Calcd for $C_{27}H_{18}D_{17}N_3F_2Fe$: C, 63.91; H, 6.95; N, 8.28. Found: C, 63.98; H, 7.03; N, 8.19.

$Fe(PEt_3)(NRAr_F)_2$ (3). $FeCl_2$ (254 mg, 2.00 mmol, 0.501 equiv) and triethylphosphine (300 mg, 2.54 mmol, 0.647 equiv) were added to a stirred colorless solution of $Li(NRAr_F)(OEt_2)$ (1.07 g, 3.99 mmol) in diethyl ether (20 mL) at 28 °C. Within 4 h, the reaction mixture was yellow-orange. At this point, the solution was filtered and volatile material was removed under reduced pressure, leaving a crystalline yellow solid. The solid was dissolved in a minimum of diethyl ether, and stored at −35 °C for several hours. The product was isolated in three crops as faceted yellow crystals (870 mg, 1.59 mmol, 79.5%). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 47.4 (s, $\Delta\nu_{1/2} = 49$ Hz). μ_{eff} (300 MHz, C_6D_6, 23 °C): 5.28 μ_B. Anal. Calcd for $C_{28}H_{33}D_{12}N_2F_2PFe$: C, 61.53; H, 8.29; N, 5.13. Found: C, 61.78; H, 8.34; N, 5.23.

$Fe(py\text{-}d_5)(NR'Ar_F)_2$ (4). $FeCl_2$ (0.253 g, 1.99 mmol) and pyridine-d_5 (0.175 g, 2.08 mmol, 1.04 equiv) were added to a stirred pale yellow solution of $Li(NR'Ar_F)(OEt_2)$ (1.32 g, 3.99 mmol) in ether (50 mL) at 25 °C. The reaction mixture was stirred for 3 h. Then the orange-red reaction mixture was filtered through a bed of Celite-545 on a sintered-glass frit, and the filtrate was concentrated to ca. 15 mL. The product was isolated as orange crystals after storage at −35 °C for several hours. The crystals were collected and dried in vacuo (1.01 g, 1.58 mmol, 79%). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 146.1 (s, $\Delta\nu_{1/2} = 125$ Hz, 2D, *ortho* C_5D_5N), 14.7 (s, $\Delta\nu_{1/2} = 41$ Hz, 12D, $C(CD_3)_2$), 27.9 (s, $\Delta\nu_{1/2} = 60$ Hz, 2D, *meta* C_5D_5N), 9.14 (s, $\Delta\nu_{1/2} = 36$ Hz, 1D, *para* C_5D_5N). μ_{eff} (46 MHz, C_6H_6, 23 °C): 5.29 μ_B. Anal. Calcd for $C_{37}H_{27}D_{17}N_3F_2Fe$: C, 69.80; H, 6.60; N, 6.17. Found: C, 69.73; H, 6.32; N, 6.47.

X-ray Structure of $Fe(py\text{-}d_5)(NR'Ar_F)_2$ (4). A crystal of approximate dimensions 0.70 × 0.40 × 0.30 mm (triclinic) was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at 293(2) K on a Siemens Platform goniometer with a CCD detector at 188(2) K using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 6568 reflections ($-10 \le h \le 10$, $-13 \le k \le 15$, $-15 \le l \le 16$) were collected, of which 4482 were unique ($R_{int} = 0.0321$). Semiempirical absorption corrections (from ψ-scans) were applied. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. The final cycle of least-squares refinement was based on 4475 observed reflections ($I > 3.00\sigma(I)$) and 389 variable parameters. The least-squares refinement converged with residuals of R1 = 0.0361 and wR2 = 0.0940, and GOF = 1.067. Crystal data: $a = 9.1217(7)$ Å, $b = 13.8387(10)$ Å, $c = 14.4944(10)$ Å, $V = 1599.9(2)$ Å^3, $\alpha = 113.6480(10)$°, $\beta = 91.8950(10)$°, $\gamma = 104.9520(10)$°, space group $P\bar{1}$, $Z = 2$, $M_r = 636.67$ for $C_{37}H_{27}D_{17}N_3F_2Fe$, and ρ(calcd) = 1.286 g/cm^3.

$Fe(I)(py\text{-}d_5)(NRAr_F)_2$ (5). Iodine (1.171 g, 4.61 mmol) was added to a stirred orange solution of $Fe(py\text{-}d_5)(NRAr_F)_2$ (**2**; 4.73 g, 9.23 mmol) in ether (30 mL) at 28 °C. The reaction mixture rapidly turned dark purple. After l h, the ^{2}H NMR spectrum of an aliquot showed that $Fe(py\text{-}d_5)(NRAr_F)_2$ had been consumed. The reaction mixture was filtered and the solvent was removed *in vacuo*, leaving crude $Fe(I)(py\text{-}d_5)(NRAr_F)_2$ (**5**) as a dark purple solid. Recrystallization from ether at −35 °C resulted in the formation of dark purple faceted crystals of **5** (5.72 g, 8.95 mmol, 96.9% yield). Mp: 139−141 °C dec. ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 155.0 (s, $\Delta\nu_{1/2} = 126$ Hz, 2D, *ortho* C_5D_5N), 99.9 (s, $\Delta\nu_{1/2} = 25$ Hz, 2D, *meta* C_5D_5N), 46.8 (s, $\Delta\nu_{1/2} = 61$ Hz, 12D, $C(CD_3)_2$), −6.9 (s, $\Delta\nu_{1/2} = 15$ Hz, 1D, *para* C_5D_5N). μ_{eff} (46 MHz, C_6H_6, 22 °C): 5.95 μ_B. Anal. Calcd for $C_{27}H_{18}D_{17}N_3F_2FeI$: C, 50.71; H, 5.52; N, 6.57. Found: C, 51.04; H, 5.54; N, 6.44.

X-ray Structure of $Fe(I)(py\text{-}d_5)(NRAr_F)_2$ (5). A crystal of approximate dimensions 0.22 × 0.28 × 0.30 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at −86 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 3931 reflections were collected to a 2θ value of 44.9°, 3879 of which were unique ($R_{int} = 0.038$); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of least-squares refinement was based on 3718 observed reflections ($I > 3.00\sigma(I)$) and 307 variable parameters and converged (largest parameter shift was 0.02 times its esd) with $R = 0.033$ and $R_w = 0.043$. A final difference Fourier map showed no chemically significant features. Crystal data are $a = 10.043(4)$ Å, $b = 14.993(5)$ Å, $c = 10.572(4)$ Å, $V = 1411(2)$ Å^3, $\beta = 117.58(2)$°, space group $P2_1$, $Z = 2$, $M_r = 639.45$ for $C_{27}H_{23}D_{12}N_3F_2FeI$, and ρ(calcd) = 1.465 g/cm^3.

$Fe(NO)(py\text{-}d_5)(NRAr_F)_2$ (6). Nitric oxide (55 mL at STP, 2.28 mmol, 1.12 equiv) was added to a stirred orange solution of **2** (1.04 g, 2.03 mmol) in ether (15 mL) at 22 °C. The reaction mixture rapidly assumed a wine red color. After l0 min the solvent was removed *in vacuo*. Recrystallization of the crude product from ether (15 mL, −35 °C) resulted in the formation of wine red faceted crystals of $Fe(NO)(py\text{-}d_5)(NRAr_F)_2$ (**6**, 1.01 g, 1.86 mmol, 91.8% yield). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 98.9 (s, $\Delta\nu_{1/2} = 143$ Hz, 2D, *ortho* C_5D_5N), 60.1 (s, $\Delta\nu_{1/2} = 48$ Hz, 2D, *meta* C_5D_5N), 10.4 (s, $\Delta\nu_{1/2} = 37$ Hz, 12D, $C(CD_3)_2$), −4.3 (s, $\Delta\nu_{1/2} = 26$ Hz, 1D, *para* C_5D_5N). μ_{eff} (300 MHz, C_6D_6, 22 °C): 3.92 μ_B. EIMS (70 eV; m/z (%)): 542(0.52) [M$^+$]. IR (Et_2O, KBr, 25 °C): ν(NO) 1708 cm^{-1}. Anal. Calcd for $C_{27}H_{18}D_{17}N_4F_2OFe$: C, 59.77; H, 6.50; N, 10.32. Found: C, 60.61; H, 6.67; N, 10.40. The ^{15}N-labeled analog $Fe(^{15}NO)(py\text{-}d_5)(NRAr_F)_2$ was prepared similarly using 99%-^{15}N nitric oxide purchased from Cambridge Isotopes. IR (Et_2O, KBr, 25 °C): $\nu(^{15}NO)$ 1675 cm^{-1}.

X-ray Structure of $Fe(NO)(py\text{-}d_5)(NRAr_F)_2$ (6). A crystal of approximate dimensions 0.45 × 0.38 × 0.13 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at −100 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 6851 reflections were collected, of which 6459 were unique ($R_{int} = 0.056$); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1982 observed reflections ($I > 3.00\sigma(I)$) and 317 variable parameters and converged with $R = 0.078$ and $R_w = 0.084$. A final difference Fourier map showed no chemically significant features. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. Crystal data are $a = 9.155(4)$ Å, $b = 18.372(3)$ Å, $c = 16.507(9)$ Å, $V = 2724(2)$ Å^3, $\beta = 101.18(4)$°, space group $P2_1/c$, $Z = 4$, $M_r = 542.40$ for $C_{27}H_{18}D_{17}N_4F_2FeO$, and ρ(calcd) = 1.281 g/cm^3.

$Fe(NO)(PEt_3)(NRAr_F)_2$ (7). $Fe(PEt_3)(NRAr_F)_2$ (**3**; 600 mg, 1.10 mmol) was dissolved in 10 mL of diethyl ether. The solution was transferred to a Schlenk flask fitted with a septum. Nitric oxide (29 mL, 1.20 mmol, 1.09 equiv) was added via syringe to the stirred yellow-orange solution. The solution quickly darkened to a deep wine red color. After 15 min, volatile material was removed under reduced pressure, leaving the product as a dark powder. The product was recrystallized in a minimum of pentane at −35 °C (565 mg, 0.979 mmol, 89.3%). ^{2}H NMR (46 MHz, pentane, 22 °C): δ 3.09 (s, $\Delta\nu_{1/2} = 14$ Hz). μ_{eff} (300 MHz, C_6D_6, 25 °C): 5.28 μ_B. Anal. Calcd for $C_{28}H_{33}D_{12}N_3F_2POFe$: C, 58.33; H, 7.87; N, 7.29. Found: C, 58.26; H, 8.27; N, 7.32.

X-ray Structure of $Fe(NO)(PEt_3)(NRAr_F)_2$ (7). A crystal of approximate dimensions 0.75 × 0.50 × 0.25 mm was obtained from a chilled pentane solution. The crystal was mounted on a glass fiber. Data collection was carried out at

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188(2) K on a Siemens Platform goniometer with a CCD detector using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 11 822 reflections ($-39 \leq h \leq 34$, $-10 \leq k \leq 12$, $-10 \leq l \leq 18$) were collected, of which 4353 were unique ($R_{\mathrm{int}} = 0.0299$). Corrections applied: semiempirical from ψ-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. The final cycle of least-squares refinement was based on 4350 observed reflections ($I > 3.00\sigma(I)$) and 326 variable parameters. Least-squares refinement converged with residuals of $R1 = 0.0541$ and wR2 = 0.1208, and GOF = 1.132. Crystal data: $a = 35.215(2)$ Å, $b = 10.9050(6)$ Å, $c = 16.5830(10)$ Å, $V = 6075.9(6)$ Å^3, $\beta = 107.4280(10)°$, space group $C2/c$, $Z = 8$, $M_r = 576.56$ for $C_{28}H_{33}D_{12}N_3F_2FePO$, and ρ(calcd) = 1.234 g/cm^3.

Reaction of Fe(NO)(py-*d*$_5$)(NRAr$_F$)$_2$ (6) with Cr(N^{i}Pr$_2$)$_3$. NMR experiments were performed in C_6D_6 and C_6H_6. As an example, conditions for the C_6H_6 experiment are described. Benzene solutions of Cr(N^{i}Pr$_2$)$_3$ (0.0223 g, 0.0632 mmol) and **6** (0.0343 g, 0.0632 mmol) were transferred to an NMR tube. The initial wine red reaction mixture adopted an orange-brown color within 3 h. Analysis using ^{2}H and ^{1}H NMR showed that the NO group had been transferred to form known Cr(NO)(N^{i}Pr$_2$)$_3$ and **2**. According to the spectroscopy the reaction was clean and quantitative. ^{1}H NMR (300 MHz, C_6D_6, 22 °C): δ 3.59 (sep, 2H, C*H*Me$_2$), 1.29 (d, 12H, CH*Me*$_2$). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 142.3 (s, $\Delta\nu_{1/2} = 79$ Hz, 6D, *ortho* C_5D_5N), 40.6 (s, $\Delta\nu_{1/2} = 32$ Hz, 12D, C(C*D*$_3$)$_2$), 35.0 (s, $\Delta\nu_{1/2} = 17$ Hz, 2D, *meta* C_5D_5N), 11.9 (s, $\Delta\nu_{1/2} = 22$ Hz, 1D, *para* C_5D_5N).

Reaction of Fe(NO)(py-*d*$_5$)(NRAr$_F$)$_2$ (6) with Mo(NRAr)$_3$. NMR tube experiments were performed in C_6D_6 as well as C_6H_6. As an example, reaction conditions for the C_6H_6 experiment are described. Benzene solutions of Mo(NRAr)$_3$ (0.0363 g, 0.0564 mmol) and **6** (0.0304 g, 0.0560 mmol) were transferred to an NMR tube. The wine red reaction mixture turned orange within 2 min. After 30 min, analysis by ^{2}H and ^{1}H NMR spectroscopy showed that the nitrosyl group had been transferred, forming Mo(NO)(NRAr)$_3$ and **2**. ^{1}H NMR (299 MHz, C_6D_6, 22 °C): δ 6.65 (s, 3H, *para* $C_6H_3Me_2$), 6.01 (s, 6H, *ortho* $C_6H_3Me_2$), 2.03 (s, 18H, $C_6H_3Me_2$), 1.49 (s, 9H, C(CD$_3$)$_2$C*H*$_3$). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 142.3 (s, $\Delta\nu_{1/2} = 79$ Hz, 2D, *ortho* C_5D_5N), 40.6 (s, $\Delta\nu_{1/2} = 32$ Hz, 12D, C(C*D*$_3$)$_2$CH$_3$), 35.0 (s, $\Delta\nu_{1/2} = 17$ Hz, 2D, *meta* C_5D_5N), 11.9 (s, $\Delta\nu_{1/2} = 22$ Hz, 1D, *para* C_5D_5N), 4.28 (s, $\Delta\nu_{1/2} = 8.02$ Hz, 18D, C(C*D*$_3$)$_2$CH$_3$).

[Fe(NRAr)(μ-NRAr)]$_2$ (8). To a stirred ether solution of Li(NRAr)(OEt$_2$) (2.14 g, 7.99 mmol) was added 0.5 equiv of FeCl$_2$ (0.515 g, 4.06 mmol). After it was stirred overnight at 30 °C, the orange reaction mixture was filtered through a bed of Celite-545 on a sintered-glass frit. The orange filtrate was concentrated to ca. 20 mL and chilled to −35 °C overnight. The product was isolated as dark orange microcrystalline material after recrystallization from ether (two crops, 1.45 g, 1.72 mmol, 87.9%). ^{2}H NMR (46 MHz, C_6H_6, 23 °C): δ 11.3 ($\Delta\nu_{1/2} = 13$ Hz) and −10.8 ($\Delta\nu_{1/2} = 14$ Hz). μ_{eff} (300 MHz, C_6D_6, 25 °C): 4.21 μ_B. Anal. Calcd for $C_{36}H_{36}D_{18}N_3Fe$: C, 68.55; H, 8.63; N, 6.66. Found: C, 68.56; H, 8.52; N, 6.60.

(ArRN)Fe(μ-NRAr)$_2$Li(OEt$_2$) (9). To a stirred benzene solution (50 mL) of Li(NRAr)(OEt$_2$) (4.00 g, 14.93 mmol) was added FeCl$_2$ (1.00 g, 7.89 mmol). After the mixture was stirred for 6 h, LiCl was removed by filtration. The crude green product was lyophilized in benzene. Recrystallization from a minimum of pentane at −35 °C gave **9** as a yellow-green solid (2.63 g, 3.84 mmol, 86%). ^{2}H NMR (C_6H_6): −2.35 ($\Delta\nu_{1/2} = 78$ Hz, μ-NRAr), 44.2 ($\Delta\nu_{1/2} = 121$ Hz, NRAr). μ_{eff} (300 MHz, C_6D_6, 25 °C): 5.56 μ_B. Combustion analysis was not attempted for this compound, which was expected to contain varying amounts of ether on a batch-to-batch basis.

Fe(NRAr)$_3$ (10). "Ate" complex **9** (1.31 g, 1.92 mmol) was dissolved in 25 mL of diethyl ether. Upon addition of ferrocenium triflate (0.643 g, 1.92 mmol), the reaction mixture turned dark blue. Ether was removed *in vacuo* after the reaction mixture was stirred for several hours. White lithium triflate was removed by hexane extraction followed by filtration. A mixture of dark blue and orange solid remained after hexane was removed from the filtrate. Ferrocene was removed by sublimation, leaving 1.05 g of blue solid, which was >95% pure according to ^{1}H and ^{2}H NMR spectroscopy. Recrystallization (pentane, −35 °C) provided dark blue crystals of **10** ((2) crops, 0.98 g, 1.63 mmol, 85%). ^{2}H NMR (46 MHz, C_6H_6, 22 °C): δ 54.6 ($\Delta\nu_{1/2} = 93$ Hz). Anal. Calcd for $C_{36}H_{36}D_{18}N_3Fe$: C, 71.73; H, 9.03; N, 6.97. Found: C, 71.90; H, 8.96; N, 6.87. Evans' method μ_{eff} (300 MHz, C_6D_6, 25 °C): 6.22 μ_B.

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Supporting Information Available: Tables of positional and thermal equivalent parameters, anisotropic thermal parameters, intramolecular distances, bond angles, and torsion angles for compounds **1** and **4**−**7** (30 pages). Ordering information is given on any current masthead page.

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