Dinitrogen Complexes

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Terminal Fe^{I}–N_2 and $Fe^{II}\cdots H$–C Interactions Supported by Tris(phosphino)silyl Ligands**

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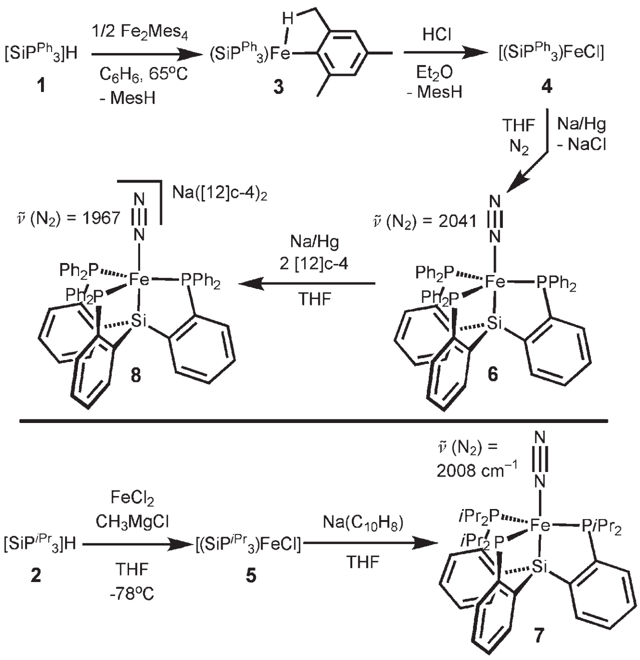
Dinitrogen complexes of iron have been the target of numerous synthetic studies in recent years.[1] An unusual and intriguing formal oxidation state to explore in such systems is iron(I), especially in the context of a Chatt-type[2] $Fe^{I/IV}$ N_2 fixation cycle (i.e. $Fe^{I}–N_2 + 3H \rightarrow Fe^{IV}{\equiv}N + NH_3$; $Fe^{IV}{\equiv}N + 3H \rightarrow Fe^{I}–N_2 + NH_3$). Yandulov and Schrock's recent work has provided impetus for such studies by establishing the synthetic viability of a conceptually related $Mo^{III/VI}$ N_2 fixation cycle.[3] Both iron and molybdenum are present in the FeMo cofactor of MoFe nitrogenases,[4] and a pseudotetrahedral $Fe^{IV}{\equiv}N$ species, a hypothetical intermediate of an $Fe^{I/IV}$ N_2 fixation mechanism, has recently been characterized.[5] Both Holland's group and our own have reported examples of three- and four-coordinate N_2 adducts of iron in the formal +1 oxidation state, but in neither case were terminally bonded N_2 species identified or isolated; dinuclear end-on Fe–NN–Fe species were inevitably obtained.[6] For the Schrock tris(amido)amine Mo–N_2 systems, it proved necessary to use a high degree of steric bulk to prevent bimetallic adduct formation before the N_2 fixation chemistry of interest could be exposed. We have attempted to retrofit the $\{(PhBP^{R}_3)Fe\}$ scaffolds ($[PhBP^{R}_3] = [PhBP(CH_2PR_2)_3]^-$) with bulky substituents at the phosphorus atoms to prevent dinuclear reaction pathways but have thus far been unable to obtain terminally bonded Fe^{I}–N_2 adducts using $[PhBP^{R}_3]$ ligands.

Recently we began to turn our attention to new derivatives of the classic Sacconi-type NP_3 ligands (e.g. $N(CH_2CH_2PR_2)_3$) to achieve access to a terminally bonded Fe^{I}–N_2 synthon.[7] While $\{Fe^{II}(N_2)(H)\}^+$ species are readily accessible using ligands of these types,[7] N_2 adducts of iron(I) have yet to be obtained. We find, however, that replacement of the apical neutral N-atom donor of a tetradentate NP_3 ligand by an anionic Si-atom donor achieves the intended goal. Herein we describe our efforts to prepare the monoanionic $[SiP^{R}_3]$ ligands ($[SiP^{R}_3] = [(2\text{-}R_2PC_6H_4)_3Si]^-$, R = Ph and *i*Pr) and to exploit them in the preparation of five-coordinate $[(SiP^{R}_3)Fe^{I}–N_2]$ complexes.

The tris(phosphino)silane precursors $[SiP^{R}_3]H$ (R = Ph (**1**) and *i*Pr (**2**)) are prepared by *ortho* lithiation of $2\text{-}R_2PC_6H_4Br$ reagents with *n*-butyllithium and subsequent addition of 1/3 equivalent of trichlorosilane. Heating a benzene solution of **1** and mesityliron(II) to 65 °C results in Si–H activation and extrusion of mesitylene, producing red $[(SiP^{Ph}_3)FeMes]$ (**3**, Mes = 2,4,6-trimethylphenyl; Scheme 1).[8] Complex **3** has an interesting solid-state structure (Figure 1) and is nominally six-coordinate; the $[SiP^{Ph}_3]$ ligand and the mesityl *ipso*-carbon atom together occupy five of the coordination sites, while the sixth site (*trans* to the silyl donor) is occupied by an agostic C–H interaction with a mesityl *ortho*-methyl group. Two molecules are found in the asymmetric unit, and both feature very short distances from the iron center to the carbon atom participating in the agostic interaction (2.564(4) and 2.569(4) Å).[9] It is plausible to attribute the structure of **3** to the presence of strongly *trans*-influencing aryl and silyl donors that do not favor a *trans* configuration.



Scheme 1.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author. CCDC-638765 through CCDC-638770 and CCDC-644269 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

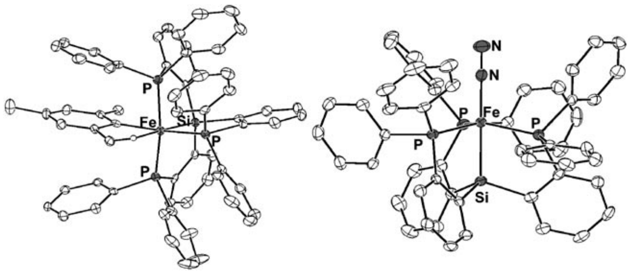

Figure 1. Left: Solid-state structure of [(SiP$^{Ph}_3$)FeMes] (**3**) (only one molecule from the asymmetric unit shown, agostic hydrogen atom shown in calculated position). Right: Solid-state structure of [(SiP$^{Ph}_3$)FeN$_2$] (**6**). Thermal ellipsoids are set at 50% probability; hydrogen atoms not involved in the agostic interaction are omitted for clarity.

Solution NMR spectra of **3** are also interesting (Figure 2). The room-temperature ^{1}H NMR spectrum (C_6D_6) of diamagnetic **3** features a sharp resonance at $\delta = 1.84$ ppm, corresponding to the mesityl *para*-methyl group, and two broad resonances at $\delta = 5.33$ ppm and 0.58 ppm, corresponding to the two *ortho*-methyl groups, which are inequivalent on the NMR time scale because of restricted Fe–C$_{ipso}$ rotation. The ^{1}H NMR spectrum at −60 °C ([D$_8$]toluene) instead features three broad resonances for the *ortho*-methyl groups ($\delta =$ 4.59 ppm, 1.10 ppm, and −0.24 ppm) in addition to the sharp *para*-methyl singlet at $\delta = 1.88$ ppm, thus indicating that at low temperature even the exchange of C–H bonds on the same methyl group is slower than the NMR time scale owing to restricted C–C rotation. Furthermore, the ^{31}P{^{1}H} NMR spectrum of **3** at −60 °C resolves the inequivalent phosphines into a doublet (2P) and a triplet (1P) with $^2J_{PP} = 11$ Hz. While iron(II) species that exhibit C–H agostic interactions are known,[9] complexes of any transition metal in which a C–H agostic interaction is stable enough to freeze rotation between the three C–H positions of a methyl group are quite rare.[10]

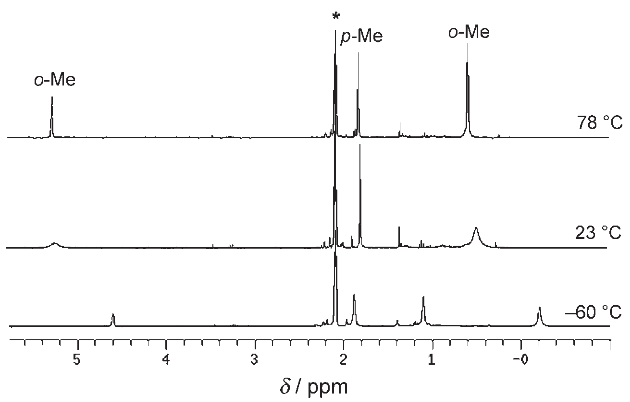

Figure 2. ^{1}H NMR spectra of [(SiP$^{Ph}_3$)FeMes] (**3**) at different temperatures (* = residual solvent peak).

Protonolysis of ethereal solutions of **3** with HCl cleanly produces mesitylene and paramagnetic, light orange [(SiP$^{Ph}_3$)FeCl] (**4**; Scheme 1). Though reaction between **2** and mesityliron(II) does not produce a tractable reaction mixture, light orange [(SiP$^{iPr}_3$)FeCl] (**5**) can be accessed by addition of CH$_3$MgCl to a mixture of **2** and FeCl$_2$ (Scheme 1).[11] The crystal structures of **4** and **5** feature iron centers with trigonal-bipyramidal coordination geometries (Figure 3), and solution magnetic data indicate triplet ground states for both ($\mu_{eff} = 2.9\,\mu_B$ (**4**) and $3.3\,\mu_B$ (**5**)). The cyclic voltammogram (CV) of **4** in THF features two reversible redox events, an Fe$^{III/II}$ couple at $E^{0\prime} = -0.40$ V and an Fe$^{II/I}$ couple at $E^{0\prime} = -2.10$ V (vs. Fc$^+$/Fc). The corresponding redox events for **5** are shifted to more negative potentials by approximately 300 mV each owing to the more strongly electron-donating phosphine substituents. The Fe$^{II/I}$ couple in **5** is irreversible at 500-mV s^{-1} scan rates, presumably because of the enhanced lability of the chloride ligand in the more electron-rich system.

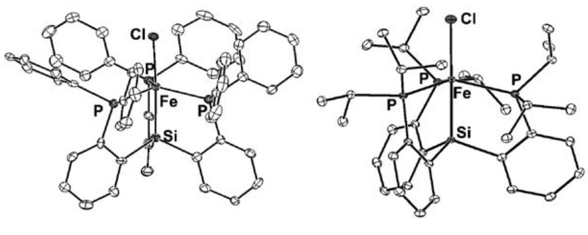

Figure 3. Solid-state structures of [(SiP$^{Ph}_3$)FeCl] (**4**; left) and [(SiP$^{iPr}_3$)FeCl] (**5**; right). Thermal ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

Na/Hg reduction of **3** in THF produces the target terminal iron(I) dinitrogen adduct [(SiP$^{Ph}_3$)FeN$_2$] (**6**; Scheme 1). The closely related dinitrogen complex [(SiP$^{iPr}_3$)FeN$_2$] (**7**) is synthesized by Na(C$_{10}$H$_8$) reduction of **5** (Scheme 1). Solution magnetic data indicate $S = 1/2$ spin states for these iron(I) complexes **6** ($\mu_{eff} = 1.8\,\mu_B$) and **7** ($\mu_{eff} = 2.2\,\mu_B$). Accordingly, the X-band EPR spectrum of **6** at 4 K (2-MeTHF glass) features an intense rhombic signal with $g_1 = 2.013$, $g_2 = 2.051$, $g_3 = 2.187$ that is coupled to three P atoms ($A_1 = 58.0$, $A_2 =$ 55.0, $A_3 = 5.8$ G). The solid-state structures of these red-orange complexes (Figure 1) confirm their identities as terminally bonded N$_2$ adducts of iron(I). Complex **6** has an Fe–N bond length of 1.819(2) Å and a short N–N bond of 1.106(3) Å, consistent with the weak N$_2$ activation implied by the relatively high-energy N–N stretching vibrations observed by IR spectroscopy (2041 cm^{-1} for **6** and 2008 cm^{-1} for **7**).[12] For comparison, tetrakis(phosphine)iron(0) dinitrogen complexes have N–N vibrations ranging from 1955 cm^{-1} in [Fe(N$_2$)(depe)$_2$][13] to 2068 cm^{-1} in [Fe(N$_2$)(dppe)$_2$].[14] As expected, the N$_2$ ligands in **6** and **7** are in positions *trans* to the silyl donors. This structural feature is unusual; transition-metal N$_2$ complexes that also feature silyl donors are rare,[15] especially where the ligands are *trans*-disposed. Such an arrangement of ligands might be expected to labilize the N$_2$ ligand. Indeed, prolonged exposure of **6** to vacuum results in loss of some of the N$_2$-adduct species (determined by ^{1}H NMR spectroscopy, Toepler pump analysis, and combustion analysis). The N$_2$ ligand of **7** is similarly labile. Hence, while each complex can be generated cleanly in solution and crystallographically characterized, neither provides satisfactory combustion analysis data upon rigorous solvent removal.

Comparative examination of the solid-state structures of **6** and **7** provides insight as to why dinuclear complex formation is observed for $[\{(PhBP^{iPr}_3)Fe\}_2(\mu\text{-}N_2)]$ but not in the case of **6** and **7**. Figure 4 shows space-filling models of the hypothetical $\{(PhBP^{iPr}_3)Fe{-}N_2\}$ fragment, derived from the X-ray structure of $[\{(PhBP^{iPr}_3)Fe\}_2(\mu\text{-}N_2)]$ after stripping away one of the $\{(PhBP^{iPr}_3)Fe\}$ units, alongside its five-coordinate relative **7**. The N_2 ligand of $\{(PhBP^{iPr}_3)Fe{-}N_2\}$ extends well beyond the protective pocket provided by the isopropyl substituents of the phosphine donors, whereas even the β-N atom of the N_2 ligand of **7** is nicely shrouded by the isopropyl substituents. Energetically unfavorable interactions can be anticipated for **7** under the approach of another $\{(SiP^{iPr}_3)Fe\}$ unit, thus precluding formation of the dinuclear species. A similar analysis holds for $[(SiP^{Ph}_3)FeN_2]$ (**6**), where the terminal N_2 ligand is buried even more deeply in the protective pocket than in the case of **7** (Figure 4).

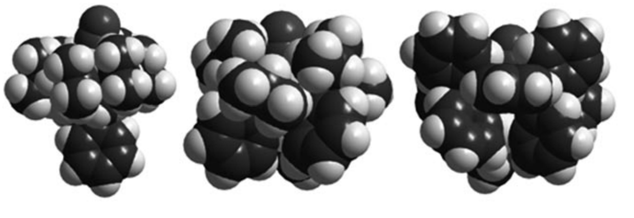

Figure 4. Space-filling models of $[\{(PhBP^{iPr}_3)Fe\}_2(\mu\text{-}N_2)]$ (left, one $\{(PhBP^{iPr}_3)Fe\}$ fragment omitted), $[(SiP^{iPr}_3)FeN_2]$ (**7**; center), and $[(SiP^{Ph}_3)FeN_2]$ (**6**; right).

Reversible one-electron reduction events at $E^{0\prime} = -1.93$ V for **6** and $E^{0\prime} = -2.72$ V for **7** (vs. Fc^+/Fc) are observed by CV, along with irreversible oxidations at higher potentials. Chemical reduction of **6** with an additional equivalent of Na/Hg in the presence of [12]crown-4 affords the dark purple formally iron(0) species assigned as $[(SiP^{Ph}_3)FeN_2][Na([12]c\text{-}4)_2]$ (**8**) on the basis of a strong N_2 vibration at 1967 cm^{-1} in its IR spectrum, its diamagnetic ^1H and $^{31}P\{^1H\}$ ($\delta = 84.3$ ppm) NMR spectra, and combustion analysis (Scheme 1). On the other hand, one-electron oxidation of **6** with $[FeCp_2][BAr^F_4]$ releases N_2 and produces the high-spin solvento species $[(SiP^{Ph}_3)Fe(thf)][BAr^F_4]$ (**9**; $Ar^F = 3,5\text{-}(F_3C)_2C_6H_4$).[16] Note that anion **8** features a less labile N_2 ligand than its neutral precursor **6** (see above) owing to stronger backbonding from the more electron-rich Fe center, and it therefore gives satisfactory combustion analysis data.

The N_2 ligand in **6** can be displaced by CO (1 atm) to provide $[(SiP^{Ph}_3)Fe(CO)]$ (**10**; $\tilde{\nu}(CO) = 1881\ cm^{-1}$). The CO stretching frequency for **10** is virtually identical to that for the structurally related but cationic Fe^I carbonyl complex $[\{N(2\text{-diisopropylphosphino-4-methylphenyl})_3\}Fe(CO)][BPh_4]$, where isopropyl rather than phenyl substituents decorate the phosphine donors.[7a] No reaction, however, is observed between **6** and excess PMe_3 or NH_3. The Fe^I site *trans* to the silyl ligand therefore appears preferentially disposed to coordination of π-acidic ligands, whereas Fe^{II} accommodates pure σ donors, as in the thf-adduct complex **9**.

Previously characterized iron dinitrogen complexes have been reported to release low yields (less than 15% per Fe equivalent) of hydrazine and/or ammonia under strongly protolytic conditions.[17] However, the addition of protic reagents to either the previously reported diiron(I) systems $[\{(PhBP^{iPr}_3)Fe\}_2(\mu\text{-}N_2)]$ or the diiron(I) β-diketiminato complex $[L^RFeNNFeL^R]$[6a] did not lead to any detectable production of either NH_3 or N_2H_4. Therefore, our observation of low yields of hydrazine upon addition of acids HX to **6** (17% per Fe equivalent for $X = BF_4$; 7% per Fe equivalent for $X = Cl$) represents a promising initial lead for the $\{(SiP^R_3)Fe\}$ systems. More interesting is the observation that performing such protonations in the presence of CrX'_2 as a one-electron reductant increases yields of hydrazine significantly (47% per Fe equivalent for $X' = Cl$; 42% per Fe equivalent for $X' = Cp^*$; $Cp^* = C_5Me_5$). The addition of similar protic reagents to **8** rapidly and cleanly regenerates **6** with no evidence for protonation at the N_2 ligand. Analogous conditions result in substantially lower yields of hydrazine for **7** (9% per Fe equivalent) even in the presence of $[CrCp^*_2]$, presumably because the more reducing nature of **7** causes direct H^+ reduction to H_2 to vastly outcompete N_2 reduction. Complex **7** is more basic than **6**, and therefore weaker acids that fail to react with **6** instead provide low yields of hydrazine with **7** (e.g. 13% per Fe equivalent for $HX = [HNiPr_2Et][BPh_4]$). One key to further advancing this N_2-reduction chemistry will be to control the delivery of protons and electrons more carefully so that N_2 reduction is favored over H_2 evolution.

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[11] Precomplexation of **2** with $FeCl_2$ is observed upon mixing, and the $[L_2FeCl_2]$ ($L_2 = \kappa^2$-$[SiP^{iPr}{}_3]H$) intermediate has been characterized by X-ray crystallography (See Supporting Information). Though no reaction is observed between **1** and $FeCl_2$, adding CH_3MgCl to the mixture does produce **4** in modest yields.

[12] In the X-ray structure of **7**, a Cl ligand is present in place of the N_2 ligand with approximately 3% occupancy. As a result, Fe−N and N−N bond lengths are not discussed here.

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