Reactivity of hydride bridges in a high-spin \([\text{Fe}_3(\mu-H)_3]^{3+}\) cluster: reversible \(\text{H}_2/\text{CO}\) exchange and \(\text{Fe}-\text{H}/\text{B}-\text{F}\) bond metathesis†

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The trinuclear trihydride complex \(\text{Fe}_3\text{H}_3\text{L}\) (1) [where \(\text{L}^{3-}\) is a tris(β-diketiminate)cyclophanate] reacts with \(\text{CO}\) and with BF3·OEt2 to afford \((\text{Fe}^{\text{II}}\text{CO})_2\text{Fe}^{\text{II}}(\mu_3-H)\text{L}\) (2) and \(\text{Fe}_3\text{F}_3\text{L}\) (3), respectively. Variable-temperature and applied-field Mössbauer spectroscopy support the assignment of two high-spin (HS) iron(II) centers and one HS iron(II) ion in 2. Preliminary studies support a CO-induced reductive elimination of \(\text{H}_2\) from 1, rather than CO trapping a species from an equilibrium mixture. This complex reacts with \(\text{H}_2\) to regenerate 1 under a dihydrogen atmosphere, which represents a rare example of reversible \(\text{CO}/\text{H}_2\) exchange and the first to occur at high-spin metal centers, as well as the first example of a reversible dinitrogen reductase reaction at a designed high-spin metal cluster. The formation of 3 proceeds through a previously unreported net fluoride-for-hydride substitution, and 3 is surprisingly chemically inert to \(\text{Si}-\text{H}\) bonds and points to an unexpectedly large difference between the \(\text{Fe}-\text{F}\) and \(\text{Fe}-\text{H}\) bonds in this high-spin system.

Introduction

Beginning with Hieber’s discovery of \(\text{H}_2\text{Fe(CO)}_4\) and \(\text{HCo(CO)}_4\),¹ the synthesis and reactivity studies of transition metal hydrides have remained an active area of chemical research.² Mononuclear metal hydrides have applications in industry (e.g., hydroformylation), electrocatalysis, and chemical synthesis.³ In addition, polynuclear transition metal hydrides have garnered substantial interest as these species have either been identified as or are proposed to be key intermediates in reactions in biological and chemical systems. For example, hydrides bound to iron centers are known or proposed in the Haber–Bosch⁴ and Fischer–Tropsch⁵ processes, dihydrogen oxidation/proton reduction by the nickel–iron and iron–iron hydrogenases,⁶ and the catalytic cycles for nitrogenases⁷ and nickel–iron carbon monoxide dehydrogenase.⁸ Molecular systems designed to model the multimetallic activation of \(\text{H}_2\) to generate and probe the reactivity of polynuclear metal hydrides generally use strong field donors (e.g., CO or phosphines).⁹ It remains unclear how parameters such as the metal coordination number and spin state tune reactivity of metal hydrides. This consideration is important in the context of heterogeneous and biological metal hydride clusters in which high- or intermediate-spin metal centers are typically present. The NiFe and FeFe hydrogenases are exceptions to the biological trend as the metal centers are low spin.

Among the most important reactions of transition metal hydrides are reductive elimination (re) and oxidative addition (oa) of \(\text{H}_2\), which are ubiquitous in organometallic chemistry, including such processes as catalytic asymmetric hydrogenation.¹⁰ The study of these reactions in polynuclear high-spin iron clusters is of particular interest because of mechanistic questions related to the reduction of \(\text{N}_2\) to \(\text{NH}_3\) by the iron molybdenum cofactor in nitrogenase from Azotobacter vinelandii, which has recently been proposed to store reducing equivalents as hydrides that unmask low-valent iron centers upon elimination of \(\text{H}_2\) to facilitate binding and reduction of \(\text{N}_2\).⁷ Relatively, the chemistry of metal hydrides is also germane to chemical hydrogen storage materials for fuel cell applications, in which repetitive cycling between \(\text{H}_2\) re and oa are important reactions for discharge and recharging, respectively.¹¹ Ideally, the former would be stimuli-dependent (e.g., reduced pressure, light, exogenous agent) to allow for controlled and on-demand \(\text{H}_2\) release. A fundamental understanding of this type of reactivity is thus important to ongoing research efforts, even if transition metal hydrides lack sufficient energy density for use
in such applications. Exposure to N₂, reduced pressure, or visible light irradiation are known to instigate reductive elimination of two hydride donors from transition metal complexes.¹⁻¹³ In those cases where N₂ is involved, the interplay between N₂ binding and H₂ loss is unclear. Ideally then, compounds that can cycle between H₂ re and oa as a function of a chemical stimulus provide important insight towards tuning the energy demand for discharge and recharge of transition metal hydrides.

We previously reported the synthesis and reactivity of a series of trinuclear trithydradicate complexes, M₃(μ-H)L (M = Fe³⁺, Co³⁺, Zn³⁺), supported by the tris(β-diketiminate)cyclophanate, L⁻.⁻¹³ In those reports, we highlighted the surprisingly specific reactivity of these compounds for CO₂. These metal-hydride compounds were unreactive towards other potential substrates, including nitriles, aldehydes, and ketones. Notably, the Zn³⁺ analog demonstrated stability even towards methanol and water. In an effort to expand the substrate scope, we report here the reactivity of Fe₂H₃L (1) with carbon monoxide, which resulted in H₂ elimination to generate a formal triiron(i/ii/ii) complex, FeL₃(μ-H)₃, and with BF₃·OEt₂, which afforded Fe₃P₂L through a net fluoride-for-hydride substitution. To our knowledge, the H₂/CO reactivity demonstrated here is the first example of a reversible multielectron redox reaction occurring at a designed high-spin multimetallic compound. Similar reactivity under a minimal driving force is typically invoked as a hallmark of biological catalysis.

Results and discussion

Reaction of 1 with carbon monoxide (~1 atm) in THF results in a rapid color change from red to dark yellow-green (broad absorption with λmax = 320 nm, Fig. S14, ESI†) and formation of (FeCO)₃Fe(μ-H)L (2) in quantitative yield by ¹H NMR spectroscopy and in good crystalline yield (Scheme 1, 69%). A new resonance corresponding with H₂ is also observed in in situ NMR spectra of reaction mixtures, implying H₂ re upon reaction of 1 with CO. This formulation of 2 is supported by single-crystal X-ray diffraction (vide infra) and combustion analysis. We also observe a strong IR absorption at 1846 cm⁻¹ in spectra of 2 synthesized from ¹²CO, which shifts to 1804 cm⁻¹ for the ¹³CO labelled 2 (13CO) (theoretical/observed Δν(¹²CO-¹³CO) = 41/42 cm⁻¹).

In the solid-state structure of 2, two iron centers (Fe2 and Fe3) are in a distorted trigonal pyramidal geometry (τ₄ = 0.75) with each ligated by one semi-bridging CO, one ligand β-diketiminate (or nacnac) arm, and a μ-H hydride (Fig. 1, left). The calculated values for α (0.35 and 0.39) and the Fe2/Fe3-C≡O bond angles (163.7(2)° and 162.2(2)°) agree with Curtis’ correlation for bent-bridging CO ligands. However, bent FeL₃-C≡O bonds are known for terminal carbonyls (e.g., ~173° for a (nacnac)FeL₃(CO)₃ complex),¹³ and the geometric constraints imposed by L⁻ and μ-H likely limit the distance and angular relationships as compared with pseudo-octahedral metal centers. The Fe2/Fe3-μ₃ bond distances for 2 are significantly longer than for mononuclear nacnac Fe(i) carbonyls (~2.05 Å vs. 1.97–1.98 Å),¹⁴ suggesting differing iron spin states or steric effects. The Fe–C bond distances (1.829(2) and 1.830(2) Å) are within the range of those reported for the (β-diketimino)iron(i) di-and tri(carbonyl) complexes (1.79–1.87 Å)¹⁵ for [PhTp³⁺FeL₃(CO)] (1.789(3) Å)¹⁶ but substantially longer than those reported for Peters’ trigonal bipyramidal Fe(i)–CO series (1.679–1.769 Å).¹⁷ The energy of v(CO) for 2 is also lower than those reported for terminal FeL₃–CO species consistent with an interaction with Fe1.

Comparison of the Fe–C and C–O bond distances in 2 with those reported for other complexes featuring the monocarbonyl iron motif demonstrates that 2 is atypical with unusually long C–O bonds given the Fe–C bond lengths (Fig. S16–S17†). We cannot discount libration effects as one reason for the unexpected differences in the bond lengths, although these values are reasonable given the IR data. The (nacnac)Fe(L)CO units in 2 represent the second example of a four coordinate Fe¹ bearing only one CO donor, the first being [PhTp³⁺FeL₃(CO)].¹⁶ The Fe(L)CO fragment is known for P– and N-donor compounds,¹⁸ hydrogenase model compounds,¹⁹ and in metal carbonyl cluster chemistry,²⁰ but is unknown for lower than 5-coordinate iron centers. Fe1 is held within a distorted trigonal bipyramidal coordination environment comprising the μ-H hydride and two N-atoms from the nacnac arm, and two long axial interactions of 2.481(2) Å and 2.545(2) Å to the semi-bridging CO donors.²¹ The bond metrics suggest minimal direct overlap between the iron centers in 2, which is evident from the formal shortness ratios for the Fe1 contacts (FSR = 1.24 and 1.31).²² Specifically, the Fe2–Fe3 (3.8612(4) Å) and Fe2/Fe3–Fe1 (2.9038(5), 3.0428(5) Å) distances are longer than typically associated with iron–iron bonds. The cyclophanate is distorted
based on the bond metrics and angles relative to those of the M₄X₃L series (M = Mn, Fe, Co, Zn, Cu; X = Br⁻, Cl⁻, and H⁺),
which highlighted the surprising flexibility of Lᵢᵢ. The (μ₂-H)
Fe₂ fragment (n > 2) was previously unknown in the high-spin
state (vide infra), and 2 is the first example of an internal μ₁-
hydride in polyiron chemistry; face-capping μ₁-hydrides are
well-known in iron carbonyl clusters.¹³

Reductive elimination of H₂ from 1 should afford a triiron
complex with 20 d electrons with formal oxidation states of
Fe₃FeIV. This assignment is supported by the zero-field
Mössbauer spectrum (Fig. 2), which comprises two different
quadrupole doublets with a 2 : 1 area ratio. From the Mössbauer
parameters, we assign the doublet with double integration as FeI
(δ = 0.66 mm s⁻¹; ΔE_Q = 2.60 mm s⁻¹) and corresponding to Fe2
and Fe3, whereas the parameters of the other doublet are char-
acteristic of high-spin FeII (δ = 0.98 mm s⁻¹; ΔE_Q = 2.15 mm s⁻¹)
and attributed to Fe1. The δ values assigned to Fe2 and Fe3 are
comparable to those for the high-spin (β-diketiminate)-supported
iron(I) complexes with two tert-butylisocyanides⁴⁴ or one di-
trig bound (c.f. 0.64 or 0.62, respectively), and distinct from
the analogous low-spin iron(I) di- and tris(carbonyl)⁴⁵ and tris(tert-
butylisocyanide) compounds (c.f. 0.12–0.25).⁴⁴ This comparison
suggests that 2 likely contains high-spin Fe²I centers, which is rare
for a CO ligated iron center with tris[pyrazoly]borate Fe(CO)
compounds as the only characterized examples.⁴⁶-⁴⁷ Applying
a magnetic field of 2 T at 4.8 K resulted in a slight line broadening
for the doublet assigned to Fe(n), revealing an internal field
of less than 4 T (Fig. S19†). This is indicative of an integer-spin
system with a relatively well-isolated M₉ = 0 ground state within
the spin manifold. On the contrary, the doublet assigned to Fe(i)
may be strongly coupled Fe centers. Consistently, we observe
a broad signal near g = 16 in X-band EPR spectra collected
in parallel mode on 2 (Fig. S13†). Similar spectra are
reported for biological and other synthetic polyiron systems and
are attributed to weak coupling between integer-spin multi-
plets.⁴⁸ As a first approximation, we have simulated the high-field
Mössbauer spectra assuming three uncoupled iron centers, two
of which account for the two Fe(i) centers, with identical
parameters. The overall splittings were well reproduced
assuming an S = 3/2 ground state for the Fe(i). Additionally,
the solution magnetic susceptibility of 2 (μ̃eff = 5.6 μB) is lower than
that of all triiron(n) complexes supported by Lᵢᵢ (6.2–7.5 μB) and
is therefore consistent with the Fe²IFeIV oxidation state assign-
ment.¹³,²⁵

The formal metal oxidation state assignments and the overall
cofactor charge in the resting state (E₀) of FeMoco remain
unclear. Early formulations considered Mo(IV) and various ratios
of Fe(n) and Fe(II); some of the Fe(n) and Fe(II) centers could be
treated as mixed-valent pairs (i.e., 2Fe²⁺).²⁸-²⁹ Currently, the Mo
is proposed to be a non-Hund’s S = 1/2 Mo center based on high-
energy resolution fluorescence detected Mo K-edge XAS.²⁹ Spatially resolved anomalous scattering (SpReAD) experiments
support the Mo(m) assignment and suggest an [Mo⁰Fe²⁺Fe²⁺Fe²⁺-]
cluster.²⁹ Recent DFT studies by Björnsson, et al. benchmarked
to the Mössbauer parameters reported by Yoo, et al. are
consistent with the SpReAD result or the related isoelectronic
mixed-valent formalism (i.e., [Mo⁰Fe²⁺Fe²⁺Fe²⁺]-).²⁹ Similar
ambiguities arise for the one-electron reduced (M⁻) and
the CO-bound forms of FeMoco, although differences in the
experimental conditions (i.e., extracted FeMoco vs. holo-MoFe
protein) may account for these discrepancies.²⁹-³⁰ Relatively,
the extent of charge delocalization may be critical to dinitrogen
activation. Local iron(n) character would be required should N₂
binding and activation by FeMoco parallel synthetic systems.⁴³
Our results and the possible coordination number changes for
iron center(s) in FeMoco during catalytic turnover¹²,¹³ hint that
these uncertainties should be expected in the reduced states
of FeMoco. For example, the isomer shift and quadrupole splittings
for Fe2 and Fe3 could lead to the mistaken assignment of these
centers as di-rather than mono-valent, since isomer shifts of 0.66
mm s⁻¹ are well within the range of many iron(n) species.

We previously suggested that loss of H₂ from 1 may be
sterically controlled based on the large H⋯H distances (2.93–
3.05 Å).¹⁴ H₂ re from 1 is not observed either thermally or under
broad wavelength irradiation. For an H₂ re step to precede CO
binding, an H₂ re/oa equilibrium would likely have to exist in
which any liberated H₂ reacts rapidly to regenerate 1, but
affords 2 in the presence of high concentrations of CO relative
to H₂ (Scheme 2). H₂/D₂ exchange should occur in this mech-
anism, thereby scrambling the respective isotopic labels. No
changes were observed in ¹H NMR spectra recorded on reaction
mixtures of Fe₂D₃L (1-D₃) with H₂ (~1 atm) at temperatures up
to 80 °C for 20 h (Fig. S5†). The lack of observable H/D exchange
suggests CO binding preceding H₂ loss and contrasts the
exchange reported for dimeric β-diketiminate complexes.³¹ As
noted in Scheme 2, we cannot exclude a tightly associated
Kubas-type complex between the eliminated H₂ and the triiron
species, which does not exchange with dissolved H₂ or D₂. CO
can then coordinate to the Kubas-type species, liberating H₂
and generating 2. However, such tightly bound M–H₂ complexes
on a high-spin metal center are rare,¹⁴ and this pathway
assumed unlikely. A similar substrate-binding prior to H₂
elimination was recently reported for reaction of a di(μ-hydrido)
diiron(n) complex with diazo compounds.³⁴ In the simplest
mechanism, retention of one hydride in 2 would arise from an

![Fig. 2 Mössbauer spectrum of 2 recorded at 80 K and zero-applied field. Black bars and colored lines represent the experimental data points and simulated quadrupole doublets, respectively (Table S11). Solid black line is a composite spectrum obtained by combining individual doublets.](image-url)
intramolecular step for H2 loss upon reaction of 1 with CO (Scheme 2). Previously, we provided crystallographic evidence demonstrating that the β-diketiminate and benzene substituents on the ligand for two triiron complexes could interdigitate in the presence of K+ cations.35 A similar bis(triiron) intermediate could form during H2 re; however, the predicted long H···H distance and the absence of K+ cations suggests that such an intermediate is also unlikely. Consistent with an intraligand H2 re mechanism, we observe only H2 and not HD in the 1H-NMR spectra of reactions containing 1 and 1-D3 under a CO atmosphere (Fig. S7†).

Given that we have hitherto been unable to isolate Fe3-containing complexes for 1–3,35 we were intrigued if reactivity characteristic of Fe3 centers could be accessed starting from 2. To that end, we examined the conversion of 2 to 1 upon addition of H2. Notably, we observed complete reaction of a toluene solution of 2 with H2 at 20 bar and 80 °C to yield 1 in 75% spectroscopic yield as a 6.3 : 1 mixture of 1 and 1-D3 under a CO atmosphere (Fig. S7†).

Because the reactions of mononuclear or self-assembled dinuclear β-diketiminate iron hydrides with CO lead to low-spin polycarbonyl products whose formation is presumably irreversible,36 we hypothesize that our use of a relatively rigid polynucleating ligand is the key factor that enables the unusual ability to convert between the two species that we observe. Additionally, the interchange between 1 and 2 represents a reversible two-electron redox reaction occurring at a high-spin polyiron cluster, and the starting species 1 demonstrates unusually high substrate specificity.36 As such, the reactivity demonstrated here bears resemblance to the biological reactivity of multimetallic cofactors; the proposed dihydride species in the E4 state of FeMoco is stable to protonation but readily undergoes reversible re/oa of H2. These observations suggest that the bio-inspired design of polynucleating ligands to stabilize high-spin clusters of base metals is a promising strategy for developing base-metal promoted multi-electron chemistry similar to that performed by multimetallic enzymes in biology.

If the dihydrogen reductive elimination is intramolecular, the distance between two hydride donors must necessarily decrease from the solid-state structure of 1 to form H2. We posit that CO binds to 1 and stabilizes a structure in which two H2 donors are sufficiently close to liberate H2. Fluxional coordination of hydrides37 was proposed in 1 based on our previous reaction study, and a shift of a μ-hydride in 1 towards the internal cavity or to a μ3 position would generate an open coordination site for CO to bind. With this in mind, we hypothesized that small Lewis acids could coordinate to one or more hydrides in 1 and stabilize such a distorted conformation of [Fe2H4]3+. We probed the reaction of 1 with BF3·OEt2 as others have isolated species with R3B···H–M interactions.38 To our knowledge, the M–H···BF3 adduct is rare with the only reported example for a bis(cyclopentadienyl)niobium dihydride.39 We considered, however, the size of the R group and the need for an electron deficient borane in our choice of BF3·OEt2.

Reaction of 1 with BF3·OEt2 resulted in formation of a bright yellow solution of Fe3[(μ-F)3L]3, 3 (λmax = 321 nm, 392 nm, 431 nm, Fig. S15†) in near quantitative spectroscopic yield and moderate crystalline yield (Scheme 3, 57%). Our assignment of 3 is supported by combustion analysis, HR-ESI/MS†, and 1H-NMR; the latter is consistent with a D3h symmetric species in solution and on the method timescale. The solution magnetic susceptibility of 3 is 7.4 μB, consistent with that of similar tririron[n] complexes.36,37 The solid-state structure of 3 evidences three bridging fluoride ligands and a planar [Fe3F3]3+ core in 3 (Fig. 3) with comparable bond metrics to related mono- and di-metallic complexes (Table S2†) as well as those in tririron[μn] and -iron[μn] complexes of L3–1,3b,3e,3g Given the quantitative conversion of 1 to 3, the reaction is a net metathesis of Fe–H for B–F bonds. Consistently, treatment of the reaction mixture with NEt3 allowed observation of BH3 as the amine-borane adduct, Et3NBH3, in 1B-NMR spectra. To our knowledge,
this reaction represents the first example of a controlled B–F/Fe–H for B–H/Fe–F bond metathesis. This transformation is enthalpically disfavored (~21 kcal mol\(^{-1}\) per B–F/Fe–H bond metathesis) based on the average empirical values for the respective bonds.\(^{40}\) The fact that this reaction proceeds at ambient temperature, however, implies that the bond dissociation energies for the Fe–H and Fe–F bonds in 1 and 3 differ significantly from the reported average empirical values. This deviation from the expected bond enthalpies is likely due to the ligand’s unique geometric constraints and the differences in bridging ligand properties of fluoride versus hydride. The B–Fe–F/H bond metathesis further illustrates the unexpected reactivity profile of 1 and related trihydride compounds.\(^{13}\) Previously, monometallic (nacac)iron fluoride complexes were reported to react rapidly with trialkylsilanes to generate the corresponding iron hydride complexes.\(^{44}\) However, 3 is unreactive towards the silanes tested based on IR and \(^{1}H\)-NMR spectroscopy. This reaction should be only slightly enthalpically disfavored relative to the reaction of 1 with BF\(_3\), but our result is consistent with an unusually large difference between the Fe–F and Fe–H bond strengths in 3 vs. 1. Other factors such as approach of the silyl reagent, access to the transition state geometry, or poor access to the fluoride ligands may also modulate the reaction rate.

Conclusions

We have expanded on the prior reactivity studies reported for 1, demonstrating that CO triggers reductive elimination of H\(_3\) from 1 to generate an unusual high-spin mixed-valent triiron(III/II) complex, 2, and that reaction with BF\(_3\)–OEt\(_2\) affords the tri(μ-fluoride) species 3. These results add to the growing evidence that hydrides act as effective masks or protecting groups for low-valent high-spin metal centers. In addition, 2 reacts with H\(_2\) to regenerate 1, which is a rare example of reversible H\(_2\) re/oa involving CO and the first to occur at high-spin metal centers. Ongoing work focuses on continuing to develop the multi-electron reactivity profiles of 1 as well as that of 2.

Acknowledgements

LJM: University of Florida (UF), ACS Petroleum Research Fund (ACS-PRF 52704-DN13), National Science Foundation (CHE-1464876, CHE-1048604), J. Goodsell and Prof. A. Angerhofer for help collecting EPR data. RGS: Labex ARCANE (ANR-11-LABX-0003-01). KAA: National Science Foundation (CHE-0821346) and UF for funding of the purchase of the X-ray equipment. KJA: UF University Scholars Program.

Notes and references