Reversible coordination of N₂ and H₂ to a homoleptic S = 1/2 Fe(I) diphosphine complex in solution and the solid state†

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The synthesis and characterisation of the S = 1/2 Fe(I) complex [Fe(depe)₂⁺][BArF₄⁻] (I)[BArF₄⁻], and the facile reversible binding of N₂ and H₂ in both solution and the solid state to form the adducts [1·N₂]⁺ and [1·H₂]⁺, are reported. Coordination of N₂ in THF is thermodynamically favourable under ambient conditions (1 atm; ΔG°₂₉₈ = −4.9(1) kcal mol⁻¹), while heterogenous binding is more favourable for H₂ than N₂ by a factor of ~300. [1·H₂]⁺[BArF₄⁻] represents a rare example of a well-defined, open-shell, non-classical dihydrogen complex, as corroborated by ESR spectroscopy. The rapid exchange between N₂ and H₂ coordination under ambient conditions is unique for a paramagnetic Fe complex.

Methods

The ESR spectroscopic methods used for characterizing molecular structure are based on the following spin Hamiltonian, representing the electron Zeeman, nuclear Zeeman, hyperfine and nuclear quadrupole components, respectively.

$$\mathcal{H} = \sum_i s_i \mathcal{B} + \sum_i g_i s_i \mathcal{B} + \sum_i a_i I_i + \sum_k Q_k I_k$$

(1)

The bold symbols are 3 × 3 tensors (or matrices) and the vector of Cartesian spin operators are defined in appropriate Hilbert space eigenbasis. The third term of the spin Hamiltonian, hyperfine or $\mathcal{H}_{\text{HF}}$ is composed of an isotropic component, $a_{\text{iso}}$ transformed to a 3 × 3 matrix by, I defined as the identity matrix, and an anisotropic component, T.

$$\mathcal{H}_{\text{HF}} = \sum_i S_i [a_{\text{iso}} I_i + T_i]$$

(2)

It is the anisotropic tensor component that returns the structural relations of the spin system, based on the summation

Introduction

Recent years have seen great interest in the pursuit of well-defined transition metal (TM) complexes capable of catalysing the reduction of N₂ to NH₃ or N₂H₄.¹ One of the most compelling rationales for studying such systems is that their mechanistic details can be more readily discerned, in comparison with the complex proton-coupled electron transfer (PCET) steps operative within nitrogenase enzymes.² The utility of Fe in biological N₂ fixation,³ and the anthropogenic Haber–Bosch process,⁴ has prompted researchers to target Fe complexes as potential synthetic catalysts. These ‘artificial’ nitrogenases employ chemical H⁺ and e⁻ sources to reduce N₂ through PCET pathways, although this process competes with proton reduction to H₂, which can preferentially sequester active metal sites.⁵ Facile displacement of H₂ by N₂ is thus an important aspect to maintaining a productive N₂-fixing catalytic cycle, and an understanding of the binding of these small molecules to low-valent Fe centres could lead to more selective and efficient catalysts for the production of azanes. While the coordination chemistry of N₂ and H₂ to Fe(0) and Fe(II) complexes is well-documented,⁶ analogous detailed studies containing Fe(i) are scant,⁷ despite the potential relevance of this low-valent oxidation state in Fe-based synthetic nitrogenases. We recently reported that the Fe(0) bisphosphine complex, Fe(depe)₂(N₂) [1·N₂; depe = Et₂P(CH₂CH₂)PEt₂] is a highly selective catalyst for the PCET-mediated conversion of N₂ to N₂H₄ with H⁺ and e⁻ equivalents.⁸ Herein we report the related low-spin Fe(i) species [Fe(depe)₂]⁺ [([1]⁺) which is shown to reversibly coordinate N₂ or H₂ with the latter being a rare case of a thoroughly-characterised paramagnetic σ-H₂ complex. Furthermore, this behavior is found to occur both in solution and in the solid-state.

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of dipolar interactions between the position vectors of the central iron atom and surrounding positions, approximated as ligand nuclei position vectors.*

\[
T = \left( \mu_0 g_e \mu_b g_N \mu_\pi / 4\pi \hbar \right) \times \sum_j f_j \left( 1 + \Delta g_j / g_\pi \right) \left( 1 r_j^2 - 3 \hat{p}_j \hat{p}_j \right) / r_j^3
\]

(Eqn (3) includes contribution of all centres, \( p_j \) of spin density \( f_j \) at distance \( r_{ij} \) to the hyperfine interaction matrix for a single nucleus position, \( p_i \). The principal axis elements in the limit of an axial tensor are \([−T, −T, 2T] \) where the perpendicular component (eqn (4)) is used to estimate a distance in a single point-dipole approximation:

\[
T = f_{e\pi} g_{e\pi} \mu_0 g_N \mu_\pi / r^3
\]

(Eqn (4) is the axial quadrupole interaction (\( = e^2 q_e Q / 4\hbar \)) and \( \eta \) is the orthorhombic asymmetry parameter. In the limit of pure quadrupole frequencies \( (\tau_i = A / 2) \) the \( m_s = +1/2 \) manifold frequencies are \( \nu_+ = K(3 + \eta) \), \( \nu_- = K(3 - \eta) \), and \( \nu_0 = 2K \eta \) for a positive hyperfine interaction.) In the opposite manifold, \( m_s = -1/2 \), there are two single quantum (sq) peaks and a double quantum (dq) transition, which corresponds to \( \nu_1 \) in the \( m_s = +1/2 \) manifold. A formula for the double quantum frequency in the limit of small hyperfine anisotropy is:

\[
\nu_{dq} = 2[\nu_{e\pi}^2 + \nu_1^2]^{1/2}
\]

where \( \nu_{e\pi} \) is the effective frequency of the Larmor and hyperfine, \( \nu_{e\pi} = \nu_1 A / 2 \), based on the DC field and unpaired electron.

### Results and discussion

Previously, we showed that \( \text{N}_2\text{H}_4/\text{NH}_3 \)-producing reactions of \( 1 \cdot \text{N}_2 \) with the acid \( \text{[Ph}_2\text{NH}_3]_2 \text{[TFO]}^+ \) (TFO = CF\(_3\)SO\(_4\)) formed an Fe(i) species, which was shown by X-ray crystallography to be \([\text{Fe(depe)}_2(\text{n}^1-\text{N}_2)]\text{[TFO]}^+ \) \([1\cdot\text{N}_2]_2 \text{[TFO]} \). Variable-temperature ESR spectra of this compound were complicated, however, and recrystallisation from Et\(_2\)O/pentane under Ar. A single crystal suitable for X-ray diffraction was subsequently isolated which solved and refined as the 15 valence electron (VE), N\(_2\)-free compound \([\text{Fe(depe)}_2]_2 \text{[BARF]}^+ \) \([1]\text{[BARF]}^+, \text{Fig. 1(a) and (b)} \). In the structure the \([1]\) and \([\text{BARF}]^+ \) ions are well separated, with no close C or F contacts between the anion and the Fe centre.

The \([1]\) cation was found to be disordered and, while the structural model is in good agreement with the X-ray crystallographic data (with the molecular connectivity and absence of an N\(_2\) ligand being conclusive), the interatomic distances are approximate and will not be discussed in detail. \( \text{FeP}_3 \) unit is pseudo square planar and exhibits a tetrahedral distortion, as seen by a dihedral angle of 12.41(11)° between the two Fe(PP) \([\text{Fe(1P)[1P]}_2(4) \) and Fe(1P)[1P] coordination planes, which is very similar to that observed in the approximately square-based pyramidal \([1\cdot\text{N}_2]_2 \text{[TFO]} \) (15.39(9)°). Evidently, coordination of N\(_2\) results in minimal reorganisation of the \([\text{Fe(depe)}_2]\) fragment. While two CH\(_4\) groups from ligand ethyl groups from each depe moiety are directed towards the vacant axial coordination sites of the Fe centre, large Fe····H separations suggest an absence of any agostic or anagostic interactions, which is supported by DFT results (vide infra).\(^{15}\)

Neither solid samples nor solutions of \([1]\text{[BARF]}^- \) under Ar showed bands attributable to an \( \nu_{\text{NH}} \) stretch in their IR or Raman spectra, further confirming the absence of N\(_2\) in the complex. \([1]\text{[BARF]}^+ \) is insoluble in alkanes, PhH and PhMe, yet highly soluble in THF and in the highly polar, non-coordinating 1,2-difluorobenzene (DFB). \(^{31}\)P NMR spectra (DFB, Ar) of \([1]\text{[BARF]}^- \) are silent, whereas very broad paramagnetically-shifted resonances for the \([1]\) moiety feature in the \( ^1\)H NMR spectrum (see ESIF). The solution-phase magnetic moment (Evans NMR, DFB, 243–298 K, Ar) was found to be 1.75 \( \mu_\text{B} \), and the X-band ESR spectrum (PhMe/DFB glass, Ar, 40 K) revealed a rhombic signal \((g_x = 2.483, g_y = 2.234, g_z = 1.985) \) with an isotropic g-value \((\text{giso} = 2.233) \) (Fig. 1(e)). These data are consistent with a low-spin (\( S = 1/2, d^7 \)) Fe(i) centre. The strong similarity between the X-band ESR spectrum
of a powdered sample of [1][BAR₄]⁻ (Ar, 1 bar, 40 K) and solution measurements implies that [1]⁺ is virtually isostuctural in solution and the solid state.

Dissolution of [1][BAR₄]⁻ in N₂-saturated solvents (1 atm; DFB or THF) afforded forest-green solutions at room temperature, which became pale yellow upon cooling to −30 °C; either heating these solutions above room temperature, or degassing with Ar, resulted in the rapid reappearence of the characteristic blue colour of [1][BAR₄]²⁻. An IR active ρN atoms stretch at 2067 cm⁻¹ confirmed coordination of N₂ to [1]⁺ to form [1-N₂]⁺, which is intermediate in value between those seen for 2102 cm⁻¹ saturated DFB or THF solutions (40 K) of [1][BAR₄]⁻ and the related Fe(u) [trans-Fe(d)(N₂)(depe)]²⁺ (1975 cm⁻¹ and 2102 cm⁻¹ respectively);¹⁶ this trend may be readily accounted for by decreased Fe → N₂ π-backbonding as the oxidation state increases.

The thermodynamics of N₂ coordination were obtained from variable temperature UV-vis spectroscopy by monitoring the concentrations of [1]⁺ and [1-N₂]⁺ via their absorption features (λ_max (nm) = 618 and 1018, respectively; Fig. 2). N₂ association with [1]⁺ is accordingly found to be exoergic (ΔG¹⁻ = −4.9(1) kcal mol⁻¹) with, as expected, a favourable enthalpy (ΔH¹⁻ = −13.1(1) kcal mol⁻¹) and an unfavourable entropy (ΔS¹⁻ = −27.6(1) cal K⁻¹ mol⁻¹) contribution; these values compare well with those for N₂ binding by (P₃B)Co [P = o-(PPr₂)₂C₆H₄; ΔH¹⁻ = −13.9(7) kcal mol⁻¹, and ΔS¹⁻ = −32(5) cal K⁻¹ mol⁻¹], which also produces an S = 1/2 dinitrogen complex.¹⁸¹⁹

The X-band ESR spectra of rapidly freeze-quenched N₂-saturated DFB or THF solutions (40 K) of [1][BAR₄]⁻ revealed a pseudo-axial signal which differs markedly from the rhombic signal characteristic of the N₂-free complex (g_iso = 2.07; simulated g tensors = 2.0014, 2.0922, 2.125). Additionally, hyperfine coupling to the four ¹⁴P nuclei was resolved for the THF glass giving A(¹⁴P) = 62.7(1) MHz (Fig. S5†), which is very similar to A(¹⁴P) previously obtained for [1·N₂][TFO]⁻ [66.2(2) MHz].⁸

Similar spectroscopic observations have been described for the Fe(s) complex [Fe(DMeOPrPE)₂(N₂)]⁺ (DMeOPrPE = R₂-PCH₂CH₂PR₂; R = CH₂CH₂CH₂OMe), which were attributed to an equilibrium between yellow [Fe(DMeOPrPE)₂(N₂)]⁺ and a purple N₂-bridged bimetallic S = 1 species [Fe(DMeOPrPE)₂]⁺[N₂]⁻; the latter is favoured at higher temperatures and/or low p(N₂).²⁰ We noted that comparable optical absorptions were observed for [1]⁺ and [1-N₂]⁺ (see Table S1, ESI†), and accordingly 2D-ESR (HYSCORE; HYperfine Sublevel CORrelation) experiments were performed on equivalent ¹⁴N₁⁻ and ¹⁵N₂-saturated PhMe/DFB (7 : 1) solutions of [1][BAR₄]²⁻, to fully ascertain the solution-phase coordination mode of N₂ to [1]⁺. As shown in Fig. 3, two ¹¹N signals were clearly detected at the perpendicular field position, in panels a, b, e, f.

The proximal nitrogen, ¹⁴N₁⁺, gives intense double quantum d₀ dq correlation peaks in the (−, +) quadrant corresponding to the ¹⁴N directly bound to Fe(i) centre, leading to peaks at (± 16.2, ±12.2) MHz and, from eqn (6), A(¹⁴N₁⁺) may correspondingly be calculated as 14.3 (±0.1) MHz.²¹ For the distal nitrogen, ¹⁴N₂, field-dependent ¹⁴N₂ simulations of 4-pulse HYSCORE provide A(¹⁴N₂) = 4.4 MHz (seen in ESI, Fig. S7†). A clearly-resolved quadrupole interaction of ¹⁴N₂ reveals a very small asymmetry η = 0, which compares well with sp-hybridized ¹⁴N found in N=≡N and [C≡C]-¹⁸ For the ¹⁴N₁ (red in Fig. 3), it was found that K = 0.9 MHz. In the case of the ¹⁴N₁, the data was insufficient for a more precise determination, and the quadrupole values of ¹⁴N₁ were used as an approximation. For ligand atoms directly bonded with covalent character, a point-
dipole model can be inaccurate; for $^{14}$N$_D$ $T = 1.2$ MHz, and for $^{14}$N$_B$ the simulation value was $T = 0.6$ MHz. To confirm that both $^{14}$N signals derive from the same molecule (considering that no large $^{14}$N hyperfine coupling was observed) close examination of the dq, dq peaks at 3471 G reveals weak multi-nuclear combination frequency peaks such as $N_p$[dq], $N_p$[dq], $N_p$[dq] (seen in Fig. S7†), a signal class previously reported by Stich et al. for Mn$_4$(m/n) Catalase. It is notable that no ‘half-field’ resonance ($g = 4$) was observed in the CW-ESR experiments, which would be expected for the hypothetical triplet ($S = 1$) $[\text{Fe(depe)}_2]\mu_2-\text{(H)}_2$ due to a formally forbidden $\Delta M_s = 2$ transition, as has been documented for other transition metal diradicals. Collectively alongside other spectroscopic data, these observations strongly support the solution-phase assignment of $[1\cdot\text{N}_2]^-$ as $[\text{Fe(depe)}_2(\eta^1-\text{N}==\text{N})][\text{BArF}_3^-]$.

Given that $\{\text{TM}(\sigma\text{-N}_2)\}$ and $\{\text{TM}(\sigma\cdot\text{H}_2)\}$ fragments are related by the same VE count, numerous diamagnetic metal–ligand platforms have been shown to interconvert these species under N$_2$ and H$_2$ mixtures; however, analogous open-shell examples are extremely rare. Furthermore, only two thoroughly characterised paramagnetic dihydrogen ligand complexes have been reported to date: $(\text{P}_3\text{Si})\text{Fe}(\text{H})_2$ and $(\text{P}_3\text{Si})\text{Fe}(\text{H})_2$; both of these are idealised $C_4$ symmetric, trigonal bipyramidal $S = 1/2$ complexes. In spite of the different coordination geometry and cationic charge, admission of H$_2$ (1 atm.) to DFB or THF solutions of $[1\cdot\text{BArF}_3^-]$ demonstrated clear reaction (Fig. 4(a)), as evidenced by an immediate colour change to pale green ($\Delta_{\text{max}} = 850$ nm, $\varepsilon_{\text{max}} \approx 19$ m$^2$ mol$^{-1}$) and the appearance of a new near-axial ESR signal (X-band, PhMe/DFB, 40 K; $g = 2.000, 2.085, 2.160$, $g_{\text{iso}} = 2.08$, Fig. S6†), which displays more pronounced hyperfine splitting for $g_2$ and $g_3$ than seen for $[1\cdot\text{N}_2]^-$ [BArF$_3^-$]. The most plausible identities of this species are the Fe(ii) adduct $[\text{Fe(depe)}_2(\sigma\cdot\text{H}_2)]$ [1-H$_2$] or the Fe(iii) oxidative addition product $[\text{Fe(depe)}_2(\eta^1\cdot\text{H})_2]$ [1-H$_2$]. Using the DFT-optimised structures of [1-H$_2$] and [1-H$_2$] (vide infra), the angle ($\beta$) between the $g_1$ principal axis and the Fe–H vectors was calculated to be 16° and 31°, respectively.

Orientation-selective ENDOR has previously been used to differentiate between Fe(H$_2$) and Fe(H)$_2$ formulations using electron–$^1$H dipolar hyperfine coupling interactions, where only small $\beta$ angles ($<15^\circ$; see Fig. 4(b)) were able to reproduce the observed experimental lineshape. The 1 : 2 : 1 hyperfine seen at the five negative $^{31}$P peaks of $g_{\text{min}}$ in CW-ESR of Fig. S6† was interrogated more closely with H$_2$/D$_2$-saturated solutions of [1][BArF$_3^-$] using $^1$H Davies ENDOR (Electron-Nuclear Double Resonance) and both $^1$H & $^1$H HYSCORE experiments (see Fig. 5). Fits to data from both techniques used two $^1$H hyperfine interaction values, for $^1$H $A[{^1}\text{H}] = [-17.99, -19.93, 26.58]$ MHz, while the values were scaled by the nuclear $g$-factor ratio $g_{\text{Fe}}^2 / g_{\text{H}}$ was 0.1535 for the $^1$H HYSCORE simulation, revealing a dipolar component of $T = 15.2$ MHz. The Fe–H distance, $r_{\text{Fe-H}}$ (Å), can thus be obtained from $r_{\text{Fe-H}} = \sqrt{(r_{\text{Fe-H}})^2 - 0.06}$, using a spin density of $\rho_{\text{Fe-H}}$ = 0.83 as remainder of the large isotropic $^{31}$P hyperfine interactions. This coupling is consistent with an Fe–H bond distance of 1.64 Å. Considering the spin density at Fe and the coordinating ligand atoms and DFT coordinates (vide infra), eqn (3) was used to fit an angle of $2\beta = \text{H–Fe–H} = 5.5^\circ$, using the empirical principal dipolar values [$-14.2, -16.2, 30.4$] MHz (written as $[-7(1 - \delta), -7(1 + \delta), 27]$ with $\delta$ as the rhombicity parameter); this value is in excellent agreement with that found for $(\text{P}_3\text{Si})\text{Fe(H)}_2$ ($\beta = 6^\circ$) which was interpreted as indicative of partial rotational averaging of the dipolar interaction. However, the angle $\beta = 5.5^\circ$ includes spin density on opposing $^1$H, and Morris et al., has shown that rotational motion can reduce H–H dipolar interactions by up to a factor of four, implying that $\beta = 5.5^\circ$ should be considered an upper limit.

Simulations of ENDOR data for [1-H$_2$] in Fig. 6 are consistent with the DFT structure (vide infra), in having two classes of
$^3\text{P}$ hyperfine interaction, $a_{\text{iso}}(^{31}\text{P}) = 69.3$ MHz of P in-plane orthogonal to the Fe(II)-H$_2$ bond and $a_{\text{iso}}(^{31}\text{P}) = 66.3$ MHz for the P bent out-of-plane; furthermore the P-Fe-P depe ligand angle of 85.5° suggests that the symmetry lies closer to 2-fold than 4-fold. Correspondingly, these results provide strong evidence that [1-H$_2$]$^+$ is best described as a non-classical o-H$_2$ adduct.

Freshly-prepared solutions of [1-H$_2$]$^+$ are sufficiently stable for detailed in situ characterisation and, as with solutions under N$_2$, vacuum/Ar-degassing resulted in regeneration of spectroscopic signals attributed to [1]$^+$, demonstrating reversible coordination of H$_2$. Nevertheless, attempts to obtain thermo-chemical information for H$_2$ binding were unfortunately frustrated by slow and irreversible formation of the Fe(II) trishydrate trans-[Fe(depe)$_2$(H)(H$_2$)]$^+$, [2]$^{31}$. Appreciating that ligation of N$_2$ or H$_2$ to [1]$^+$ results in minimal deformation of the [Fe(depe)$_2$]$^+$ core,$^{32}$ we speculated that binding of these gases might also be reversible in the solid state, as in solution. Gratifyingly, admission of either N$_2$ or H$_2$ to powdered samples of [1]$^+$[BArF$_4$]$^-$ led to comparable colour changes (deep blue to yellow or green, respectively), consistent with clean conversion to [1·(N$_2$/H$_2$)]$^+$[BArF$_4$]$^-$. ESR spectra closely matched those obtained in solution, strongly suggesting that the geometry of the [Fe(depe)$_2$]$^+$ core is preserved in both phases upon N$_2$ and or H$_2$ coordination. Crucially, removal of N$_2$/H$_2$ from these samples under vacuum led to complete restoration of the original ESR signal of [1]$^+$ (Fig. 7 and S2†), confirming that binding is fully reversible (over multiple cycles) in the solid state; importantly, no loss in signal intensity was observed (which would be expected from formation of diamagnetic [2]$^+$) under H$_2$. Furthermore, ready exchange of the N$_2$ ligand for H$_2$ is achieved via simple evacuation of N$_2$ and replacing with H$_2$, and vice versa.

ESR spectra of [1]$^+$[BArF$_4$]$^-$ obtained in the presence of a single equivalent of N$_2$ or H$_2$ allow for a quantitative comparison of the binding affinities of the two gases; the ratio [1-L]$^+$/[1]$^+$ (L = N$_2$ or H$_2$; determined by signal intensity at 303 K) is significantly larger for H$_2$ (44) than N$_2$ (0.15), revealing that binding of the former is almost 300 times more favourable at ambient temperature.$^{33}$ For comparison, (P$_3$B)Co(L) (L = N$_2$, H$_2$) are in rapid dissociative equilibrium in solution under similar conditions, whereas (P$_3$Si)Fe(L) species require several days to interconvert (proposed to proceed via an associative mechanism involving partial dechelation of the P$_3$Si ligand);$^{7,14}$ both demonstrate a preference for H$_2$ binding, albeit to differing degrees ($K_{H_2}/K_{N_2} \approx 2$ and 50 for Co and Fe, respectively). This difference in exchange kinetics was postulated to result from the poorer π-backbonding capability of Co vs. Fe which leads to weaker M-L interactions. Hence it is plausible that the ready reversibility of N$_2$ and H$_2$ exchange for [1]$^+$ relative to (P$_3$Si)Fe could also be due (in part) to poorer π-donation from the former, by virtue of its cationic charge, which is also manifest in the higher $\nu_{NN}$ stretch value of the former (2067 vs. 2003 cm$^{-1}$).

**Computational calculations**

In order to probe the structure and electronic properties of [1]$^+$, [1·N$_2$]$^+$, and [1·H$_2$]$^+$, density functional calculations were
carried out using the ADF program suite version 2014.1. The Slater-type orbital (STO) basis sets were of triple-$\zeta$ quality augmented with a one polarization function (ADF basis TZP). Core electrons were frozen (C, N 1s; Fe 2p) in our model of the electronic configuration for each atom. The local density approximation (LDA) by Vosko, Wilk and Nusair (VWN) was used together with the exchange correlation corrections of Becke and Perdew (BP86).

Optimized geometries were ascertained as local minima via frequency calculations. Geometry optimisation of base-free $[1]^+$ with $S = 1/2$ resulted in a $D_2$ structure consistent with X-ray crystallographic data, with an angle of approximately 7° between the two iron-ligand Fe(PP) coordination planes (Fig. 8(a)); fixing the spin state to $S = 3/2$ showed the alternative high-spin structure to be some 0.77 eV (approximately 17.8 kcal mol$^{-1}$) higher in energy. Geometry optimisation of $[1\cdot N_2]^+$ results in a structure of $C_2$ symmetry with a slightly increased angle between the two Fe(PP) planes of 19° (Fig. 8(b)). The coordination geometry around Fe is square-based pyramidal with P–Fe–N$^a$ angles of 94.8° and 95.6°. The calculated stretching frequency for the bound N$_2$ ligand was 2059 cm$^{-1}$, which is in good agreement with experiment (2067 cm$^{-1}$). Geometry optimisation of $[1\cdot H_2]^+$ (Fig. 8(c)) gave an α-complex with a H–H bond length of 0.899 Å (cf. free H$_2$: 0.74 Å)$^a$ and an average Fe–H distance of 1.61 Å, which correlates well with 2D-ESR data. An alternative $[1\cdot (H) _2]^+$ isomer (Fig. 8(d)), corresponding to the product of H$_2$ oxidative addition and containing two well-separated hydride ligands (H···H = 1.57 Å and Fe–H distances of 1.51 Å), could also be located, albeit 12 kcal mol$^{-1}$ higher in energy than $[1\cdot H_2]^+$ (see Table S2 in ESI for further details$^\dagger$).

Since all compounds had unpaired spins the DFT calculations were unrestricted, with different orbitals for $\alpha$ and $\beta$ spins. The energies of the $\alpha$ spin electrons, of which there are more, tended to be lower than those of the $\beta$ spin electrons in corresponding orbitals because of exchange stabilization (Fig. 9).

The unpaired electron in the three cases, $[1]^+$, $[1\cdot N_2]^+$, and $[1\cdot H_2]^+$, occupies an orbital of primarily d($z^2$) character; in the case of $[1\cdot N_2]^+$ and $[1\cdot H_2]^+$ this is also hybridized with the Fe 4p($z$) orbital (Fig. 10), and is antibonding with respect to the coordinated N$_2$ or H$_2$, thus explaining the weak association of these ligands to the [Fe(depe)$_2$]$^+$ core. Of particular interest is the virtual orbital ($z$) of [Fe(depe)$_2$]$^+$, the isosurface of which is shown in Fig. 10; its AO composition is predominantly Fe 4p($z$) and P 3p.

Time-dependent DFT (TDDFT) was used to calculate the electronic absorption spectra of $[1]^+$, $[1\cdot N_2]^+$ and $[1\cdot H_2]^+$ (see...
metal catalysts for N2 reduction, mediated by H+/e\(^{-}\)¼ \([\text{H}^+]/\text{e}^{-}\) is absent as a consequence of ligand binding along the axis, hence their respective absorption spectra have no analogous feature. Thus, in spite of the lack of numerical agreement for the d\(^{5}\) bands, many features of the calculated spectra give a good account of those observed.

### Conclusions

In conclusion, we have synthesised and fully characterised an open-shell, cationic Fe(i) complex, \([\text{I}^+]\text{[BAR}_{4}\text{F}^{-}]\), and demonstrated the readily reversible coordination of N\(_2\) and H\(_2\) to the S = 1/2 Fe centre. Remarkably, this facile exchange between N\(_2\) and H\(_2\) coordination occurs in either solution or solid states under ambient conditions, likely due to the very small structural change in transitioning between square planar \([\text{I}^+]\) and square-based pyramidal \([\text{I}^+\text{[N}_2\text{H}_6\text{]}\] species. Furthermore, \([\text{I}^+\text{[H}_2\text{]}\text{[BAR}_{4}\text{F}^{-}]\) is a rare example of a well-defined paramagnetic \(\text{H}_2\) complex, as corroborated by ESR spectroscopy and DFT calculations. These results reveal that reversible coordination of these small molecules to open-shell complexes is neither restricted to neutral compounds nor \(\text{C}_3\) molecular symmetries, which until now, have been the only known examples. Given the importance of Fe in catalytic N\(_2\) fixation, this work is of significant relevance to the ongoing development and investigation of well-defined transition metal catalysts for N\(_2\) reduction, mediated by H\(^{+}\)/e\(^{-}\) sources or (ideally) H\(_2\) as the terminal reductant.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references


13. The synthesis of a ‘light blue’ salt \(\text{[I}^+\text{[BAR}_4\text{F}^{-}]\) was briefly described in a recent publication; however only limited characterisation data (under N\(_2\)) were provided. In light of the comprehensive study reported herein, we believe that this salt in fact likely comprises a mixture of predominantly \(\text{[I}^+\text{[BAR}_4\text{F}^{-}]\) and \([\text{I}^+\text{[N}_2\text{H}_6\text{]}\text{[BAR}_4\text{F}^{-}]\). See: J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, 139, 5952, and related ESI†.

14. The disorder arises due to a mismatch between the lower symmetry of the cation (\(\text{D}_3\)) and the site symmetry of its location in the crystal (\(\text{S}_3\)), hence only the Fe atom (which sits directly on the latter) is strictly ordered. See ESI† for full crystallographic details.


17 THF was selected for these experiments as the solubility of 
N₂ is known in this medium, in contrast to DFB. See: 
2012, 134, 14158.
19 The solution-phase free energy of N₂ binding to 
a [P₄(amine)]²⁻ Fe(i)-tetraphosphine complex has been 
recently disclosed (see: D. E. Prokopchuk, E. S. Wiedner,
E. D. Walter, C. V. Popescu, N. A. Piro, W. S. Kassel,
R. M. Bullock and M. T. Mock, J. Am. Chem. Soc., 2017,
139, 9291). In contrast to [1]⁺, N₂ binding was found to be 
endoergic (ΔG₂₉₈ = +0.4(5) kcal mol⁻¹), which may arise 
from their use of poorer aryl-phosphine donors vs. alkyl-
phosphines in [1]⁺, translating to a weaker Fe–N₂ bond.
20 C. G. Balesdent, J. L. Crossland, D. T. Regan, C. T. López and 
21 D. Goldfarb, V. Kofman, J. Libman, A. Shanzer, 
R. Rahmatouline, S. Van Doorslaer and A. Schweiger, J. 
22 R. D. Britt, J. L. Zimmermann, K. Sauer and M. P. Klein, J. 
B, 2010, 114, 14178; (b) Simultaneous simulations of both 
¹⁴N in Fig. S7† are important for a full description of the 
signal in Fig. 3, yet these are beyond the scope of the 
present work.
2010, 46, 1013.
27 Use of D₂ in place of H₂ did not lead to any change in the ¹H 
NMR spectrum, nor did any new resonances appear in the 
³¹P NMR spectrum (other than ¹H NMR spectrum (other than D₂ itself). These data are 
consistent with H/D being directly bound to the 
paramagnetic Fe centre.
28 Yellow/green crystals form upon cooling (~35 °C) saturated solutions of [1]⁻[BArF₄]⁻ in Et₂O under N₂/H₂, respectively.
However, attempts to obtain structural data from these 
( presumable of [1-N₂/H₂][BArF₄]⁻) were thwarted by a rapid 
loss in crystallinity during handling.
29 W. A. Gunderson, D. L. M. Suess, H. Fong, X. Wang, 
C. M. Hoffmann, G. E. Cutsail III, J. C. Peters and 
30 O. M. Usov, P. S.-T. Choi, J. P. Shapleigh and C. P. Scholes, J. 
31 Exact determination of the fraction of spin on the central 
Fe(i) ion and the fractions of spin on ligating ³¹P nuclei is 
non-trivial due to the nature of the particular s-orbital and 
p-orbital character of the molecular orbital, and these 
differ by a factor 36.5 for implications of ligand spin 
35, 243; (b) G. A. Facey, T. P. Fong, D. Gusev, 
33 Diamagnetic trans-[Fe(depe)₂(H)₂][BArF₄]⁻ was identified by 
³H and ³¹P NMR spectroscopy. See: M. Bautista, 
1987, 109, 3780; M. V. Baker, L. D. Field and D. J. Young, J. 
conversion was observed to be somewhat variable 
(depending on solvent, trace impurities etc.), and 
promoted by elevated temperatures and/or extended 
periods. The mechanism is currently under investigation.
34 Computational data for [1-H₂]⁺ predict a similar dihedral 
angle between Fe(PP) planes (16.9°) as that for [1-N₂]⁺ 
(18.9°). DFT calculations on [1]⁻ and [1-N₂]⁻ were in good 
agreement with experimental X-ray crystallographic data 
(see ESI†).
35 Unfortunately the difficulty of ensuring a consistent 
temperature throughout the headspace of the sample tube, 
and the inability to accurately deconvolute the overlapping 
ESR signals of [1]⁺, [1-N₂]⁻ and [1-H₂]⁻ (which become 
increasingly isotropic at elevated temperatures, likely due 
the phase change behaviour), precluded a solid-state 
thermodynamic analysis of binding.
36 Theoretical Chemistry, ADF2016, SCM, Vrije Universiteit, 
1200.