Anion control of tautomeric equilibria: Fe–H vs. N–H influenced by NH···F hydrogen bonding†

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Counterions can play an active role in chemical reactivity, modulating reaction pathways, energetics and selectivity. We investigated the tautomeric equilibrium resulting from protonation of Fe(P(EtNMePET)(CO)3 (P(EtNMePET) = (Et2PCH2)2NMe) at Fe or N. Protonation of Fe(P(EtNMePET)(CO)3 by [Et2O2H]+[B(C6F5)4]− occurs at the metal to give the iron hydride [Fe(P(EtNMePET)(CO)3H]−[B(C6F5)4]−. In contrast, treatment with HBF4·OEt2 gives protonation at the iron and at the pendant amine. Both the FeH and NH tautomers were characterized by single crystal X-ray diffraction. Addition of excess BF4− to the equilibrium mixture leads to the NH tautomer being exclusively observed, due to NH···F hydrogen bonding. A quantum chemical analysis of the bonding properties of these systems provided a quantification of hydrogen bonding of the NH to BF4− and to OTf−. Treatment of Fe(P(EtNMePET)(CO)3 with excess HOTf gives a dicaticonic complex where both the iron and nitrogen are protonated. Isomerization of the dicaticonic complex was studied by NOESY NMR spectroscopy.

Introduction

Tautomerization has been extensively studied, the archetypal example being the keto–enol equilibrium of ketones and aldehydes.1–3 Hydrogen bonding and other non-covalent interactions can profoundly influence tautomeric equilibria, and consequently, affect the selectivity of catalytic reactions.4 Tautomers play a key role in the structure and reactivity of transition metal complexes. Tautomeric equilibria between dihydrogen and dihydride complexes (eqn (1)) were identified early in the history of H2 complexes.5–11 Subsequent studies examined more deeply the properties of elongated dihydrogen complexes,12,13 and the relationship between dihydrogen and dihydride tautomers.14,15 Tautomeric equilibria between M(η5-SiH4) and M(H)(SiH3) complexes have also been observed.16

Proton transfers play a prominent role in catalysis. Studies on the kinetic and thermodynamic acidity of metal hydrides17–19 and dihydrogen complexes20 provide a foundation for understanding catalytic reactions that require proton transfers. Pendent amines in diphosphine ligands can function as proton relays,21 leading to electrocatalysts for production of H2 [ref. 22 and 23] and oxidation of H2.24,25 Studies of the intramolecular26 and intermolecular27 proton transfers in these systems has provided insight into the mechanisms of catalysis. Proton transfer between a pendant amine and a metal is often rapid, a feature that enhances catalytic rates. It has seldom been possible to separately observe or characterize the two tautomers.

Ion pairing can influence the thermodynamics and kinetics of transition metal chemistry, particularly those involving proton transfer reactions of metal hydrides.28–31 Bifurcated hydrogen bonding of BF4− to two NH bonds was observed in a crystal structure of a di-iron complex.32 Rauchfuss and co-workers found that excess BF4− shifted the equilibrium between Fe–H and N–H tautomers in a synthetic [FeFe]−hydrogenase model complex, increasing the amount of the ammonium tautomer.33 The role of counterions on reactivity has been studied computationally,34 with much of the work focusing on the influence of counterions on transition states and how they lower kinetic barriers35 or change the regioselectivity in catalysis.36,37 Poli, Shubina and co-workers reported computations showing how specific hydrogen bonding interactions between Mo dihydride complexes and BF4− could be altered by solvent choice, which ultimately determined the...
thermodynamic equilibrium between Mo dihydrides and dihydrogen complexes.\textsuperscript{36} Dub and Gordon suggested that hydrogen bonding between BF\textsubscript{4}\textsuperscript{−} and H\textsubscript{2} ligands may influence enantioselective ketone hydrogenations.\textsuperscript{38} Computations from Heinze and co-workers showed that non-covalent interactions between NO\textsubscript{2}-substituted gold tetraarylporphyrins and PF\textsubscript{6}\textsuperscript{−} counterion change the electronic structure from a metal-centered to a ligand-centered radical.\textsuperscript{39}

Hydrogen bonding involving metal hydrides is especially interesting, as the M–H bond can engage in two different types of hydrogen bonding, as discussed in reviews by Shubina and co-workers.\textsuperscript{40–42} Crabtree\textsuperscript{43} and Brammer.\textsuperscript{44} Intramolecular Ir–H···H–N interactions were discovered independently and reported in 1994 by Morris\textsuperscript{45} and by Crabtree.\textsuperscript{46,47} In these examples, the M-H bond serves as the weak base (hydrogen bond acceptor). The protic-hydridic attraction (H\textsuperscript{−}···H\textsuperscript{3+}) in the "dihydrogen bond"\textsuperscript{48} has been studied in many examples since these interactions were recognized. Intermolecular M–H···H–O interactions of metal hydrides have been characterized by extensive spectroscopic studies,\textsuperscript{49} particularly in the interaction of metal hydrides with acidic alcohols. Studies of these dihydrogen bonds provide insights into details of hydrogen bonding preceding proton transfer reactions.\textsuperscript{50–52} A Ru–H···H–N interaction is cleaved in reaction with CO\textsubscript{2}, leading to a ruthenium formate complex.\textsuperscript{53} In iron electrocatalysts for oxidation of H\textsubscript{2}, an Fe–H···H–N dihydrogen bond was characterized by neutron diffraction, providing precise structural characterization.\textsuperscript{54} NMR spectroscopy can provide evidence for dihydrogen bond formation; Manor and Rauchfuss found that the dihydrogen bond formed by addition of HNMe\textsubscript{3} to a hydride bridging Fe and Ni led to a change of about 2 ppm in the \textsuperscript{1}H NMR chemical shift.\textsuperscript{55}

Metal hydrides exhibit versatile reactivity patterns; in addition to the hydrogen bonds described above, metal hydrides engage in hydrogen bonding where the M–H bond is the weak acid, or hydrogen bond donor. Early examples were reported for hydrogen bonding between cationic metal hydrides and the P=O bonds of phosphine oxides, such as Ph\textsubscript{3}P=O.\textsuperscript{56,57} Subsequent detailed studies showed that neutral metal hydrides engage in intermolecular hydrogen bonding with phosphine oxides or amines.\textsuperscript{58} Hydrogen bonding has been found between dihydrogen ligands and BF\textsubscript{4}\textsuperscript{−} (ref. 59) or OTF\textsuperscript{−} anions.\textsuperscript{60}

We report here that protonation of Fe(P\textsuperscript{EtNMePEt})(CO)\textsubscript{3} \((P\textsuperscript{EtNMePEt} = (Et\textsubscript{2}PCH\textsubscript{2})\textsubscript{2}NMe)\) can occur at either the N, or the Fe, or both. Singly protonated N–H and Fe–H tautomers were isolated, and their structures were characterized by X-ray diffraction. The preference for protonation at N or Fe is strongly influenced by the counterion; addition of BF\textsubscript{4}\textsuperscript{−} to Fe–H tautomer converts it to the N–H tautomer. Computational studies provide insights into the N–H···F hydrogen bonding that strongly influences the tautomeric equilibria. The doubly protonated complex resulting from protonation at both N and Fe has been characterized by spectroscopic and crystallographic studies, and is shown to exist as an interconverting mixture of isomers.

**Results and discussion**

**Synthesis and characterization of Fe(diphosphine)(CO)\textsubscript{3} complexes**

The iron complex Fe(P\textsuperscript{EtNMePEt})(CO)\textsubscript{3} (Fe\textsuperscript{0}) is prepared by heating toluene solutions of Fe(COT)(CO)\textsubscript{3} [COT = cyclooctatetraene] and P\textsuperscript{EtNMePEt} to 110 °C (eqn (2)). It is purified by chromatography and isolated in 78% yield as a pale yellow, mildly air-sensitive microcrystalline crystalline solid. The aniline derivative Fe(P\textsuperscript{EtNPhPPEt})(CO)\textsubscript{3} \((P\textsuperscript{EtNPhPPEt} = (Et\textsubscript{2}PCH\textsubscript{2})\textsubscript{2}NPh)\) was prepared in a similar manner. The solid state structure of Fe\textsuperscript{0} was determined by single crystal X-ray diffraction (Fig. 1). The iron adopts a trigonal bipyramidal geometry with the diphosphine spanning an axial and equatorial site.

**Protonation and tautomerization studies**

Protonation of Fe\textsuperscript{0} with [(Et\textsubscript{2}O)\textsubscript{2}H\textsuperscript{+}]\textsubscript{−} \([B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\) occurs at the metal to give a cationic iron hydride complex (Scheme 1). After crystallization from Et\textsubscript{2}O/n-pentane, the hydrides \([Fe(P\textsuperscript{EtNMePEt})(CO)\textsubscript{3}H]\) \([B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\) \([FeH]\) \([B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\) and \([Fe(P\textsuperscript{EtNPhPPEt})(CO)\textsubscript{3}H]\) \([B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\) were isolated as white solids. The structure of \([FeH]\) \([B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\) was determined by X-ray
Overall positive charge of ≈ 0.25 was determined by IR spectroscopy (Fig. 3) showing protonation at both the Fe and the pendant amine. Monitoring the reaction by IR spectroscopy (Fig. 3) shows ν_{CO} bands at 1920, 1894 cm⁻¹ assigned to the amine-protonated isomer [FeNH]⁺, along with bands for [FeH]⁺. The shift in the ν_{CO} bands to higher energy in [FeNH]⁺ compared to Fe⁰ is consistent with the overall positive charge of [FeNH]⁺, and the relatively lower energy of the ν_{CO} bands compared to [FeH]⁺ is consistent with the difference in formal oxidation state between the two tautomers.

Crystals of the protonated amine tautomer, [FeNH]⁺BF₄⁻, were obtained from the reaction mixture from MeCN/Et₂O solutions, and its structure was determined by X-ray crystallography (Fig. 4). The NH···F distance was found to be 1.93(1) Å, consistent with the presence of NH···F hydrogen bonding of the protonated amine to an F of the BF₄⁻ anion. Structural studies of organic compounds with protonated amines with BF₄⁻ counterions show NH···F hydrogen bonding. Infrared spectroscopy (KBr) of the crystallized [FeNH]⁺BF₄⁻ gave IR bands similar to those assigned to [FeNH]⁺ in the solution spectra shown in Fig. 3. The trflate derivate was also prepared by protonation of Fe⁰ with HOTf, and [FeNH]⁺OTf⁻ was also characterized crystallographically (Fig. 5).

To determine the influence of the anion BF₄⁻ on the equilibrium between [FeH]⁺ and [FeNH]⁺, solutions of [FeH]⁺[B(C₆F₅)₄]⁻ were treated with [Et₄N]⁺[BF₄]⁻. Treatment of CH₂Cl₂ solutions of [FeH]⁺[B(C₆F₅)₄]⁻ with less than 1 equiv. of [Et₄N]⁺[BF₄]⁻ gives IR spectra indicating a preference for [FeH]⁺. As more [Et₄N]⁺[BF₄]⁻ is added, [FeNH]⁺ becomes the preferred tautomer. At high concentrations of [Et₄N]⁺[BF₄]⁻, the Fe–H isomer is no longer detected (Fig. 6). These results suggest that hydrogen bonding of N–H to BF₄⁻ dramatically influences the equilibrium because of the formation of an NH···F hydrogen bond. When monitored by H NMR spectroscopy, isolated single crystals of [FeNH]⁺BF₄⁻ in CD₂Cl₂/THF-d₈ (95 : 5) solution treated with K[B(C₆F₅)₄] give [FeH]⁺, as determined by H NMR spectroscopy, concomitant with precipitation of KBF₄ (Fig. S11†). Similarly, the hydride resonance in CD₂Cl₂ solutions of [FeH]⁺[B(C₆F₅)₄]⁻ is no longer observed following treatment with [Et₄N]⁺[BF₄]⁻ (Fig. S12†).

Recognizing the precedents cited above for hydrogen bonding involving metal hydrides, we considered whether...
a BF$_4^-$ counterion. The structure$^3$ of [FeH[P(CH$_2$CH$_2$PPh$_2$)$_3$]]$^{+}$BF$_4^-$ reveals a Fe–H⋯F separation of 2.91 Å, and an Fe–H⋯F separation of 3.40 Å was found$^4$ in [FeH(CO)$_3$(dppf)]$^{+}$BF$_4^-$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene). The location of the hydride ligand is usually subject to uncertainty when determined by X-ray diffraction, so that will potentially make these comparisons less precise. Compared to the sum of the van der Waals radii of H and F (about 2.67 Å), these structures indicate that any Fe–H⋯F interactions are, at most, weak. The shortest H⋯F distance in the cationic molybdenum hydride, [Cp*MoH(PMe$_3$)$_3$]$_3$PF$_6^-$, is 3.33 Å.$^5$ While that distance is longer than would normally be considered a hydrogen bond, a computational study provided evidence for a weak interaction.

### Computational studies of the influence of the anion

Structures of [FeH]$^+$, [FeNH]$^+$, [FeNH]$^+$/BF$_4^-$, and [FeNH]$^+$/OTf$^-$ were optimized computationally, and the bonding properties were analyzed in the natural bond orbital (NBO)$^6$ theory framework, as discussed below. Both anions have a similar overall effect on the structure of [FeNH]$^+$. Without any anion, the N–H bond of [FeNH]$^+$ tucks in towards the Fe, with an Fe⋯H distance of 2.51 Å (Fig. S32f). When the counterion is added, the N–H bond moves away from the Fe. For comparison, the Fe⋯H distance is 3.59 Å in [FeNH]$^+$/BF$_4^-$ and 3.69 Å in [FeNH]$^+$/OTf$^-$. The computed N⋯F distance of 2.60 Å in [FeNH]$^+$/BF$_4^-$ is nearly identical to the computed N⋯O distance of 2.59 Å in [FeNH]$^+$/OTf$^-$(Fig. 7). However, the N–H bond length in [FeNH]$^+$/BF$_4^-$ (1.07 Å) is shorter than in [FeNH]$^+$/OTf$^-$(1.10 Å), suggesting a stronger N–H⋯X interaction in the latter.

Our calculations clearly show that anions can provide energetic stabilization of the N-protonated ligand. The calculated [FeH]$^+ \rightarrow [FeNH]^+$ isomerization free energy of $\Delta E^0 = -2.5$ kcal mol$^{-1}$ shifts to $-2.0$ kcal mol$^{-1}$ and $-8.2$ kcal mol$^{-1}$, when BF$_4^-$ or OTf$^-$ are added. The nearly isoergic formation of [FeNH]$^+$/BF$_4^-$ is consistent with the experimental observation of both tautomers being present at a 1 : 1 ratio of the iron complex to BF$_4^-$.

The strength of hydrogen bonds between the anion and the protonated amine was calculated in the NBO framework.$^6$ From an electronic standpoint, the formation of a hydrogen bond is accompanied by a sizeable charge transfer from the lone pair $n(X)$ of the hydrogen bond acceptor to the $\sigma^*$[N–H] anti-bonding orbital of the donor. The energy stabilization due to the hydrogen bond between [FeNH]$^+$ and the counterion is given by the ratio of the off-diagonal components of the Fock matrix and the difference in energy between the two orbitals.$^6$ This analysis also gives an estimate of the amount of charge transferred, $q_{CT}$, from the donor orbital to the acceptor orbital using eqn (3), wherein $\Delta E^{(2)}_{CT}$ is the energy lowering, and the denominator represents the difference in orbital energies.$^6$

$$q_{CT} \equiv \frac{\Delta E^{(2)}_{CT}}{\epsilon_{\sigma^*} - \epsilon_n}$$

For comparison, the interaction between N–H and one CI of dichloromethane solvent was calculated. The calculated
between an electronegative atom and the N–H bond. Further
details of the contributing interactions are provided in the ESI.†
In contrast to the results with the protonated pendant
amine, there is no donation from the lone pair of F to the Fe–H.
This is not surprising, in view of the hydridic nature of the Fe–
H, compared to the protic nature of the N–H. The atomic charge
of the H of the ammonium was calculated to be +0.46, which
contrasts greatly with the calculated value of −0.05 when bound
to iron. Thus, the interaction between the hydride and the
counterion will be repulsive, which is indicated by the ener-
getics (ΔG = 7.9 kcal mol⁻¹) shown in Fig. S33.† Indeed, the
small stabilization due to the interaction between the iron
hydride bonding orbital, σ(Fe–H), and the four F–B antibonding
orbitals, σ*(B–F), does not compensate for the overall elec-
tric static repulsion. The delocalized nature of the σ(Fe–H)-to-σ*(B–
F) interaction is indicated by the geometry, wherein the BF₄⁻
anion is close to the hydride, with three fluorine atoms oriented
toward the hydride, rather than the directed interaction seen in
the geometry of the protonated amine complex. It is important
to note that the σ(Fe–H)-to-σ*(B–F) interaction is much smaller
than the σ(N–H)-to-σ*(B–F) interaction. Summing all of the
stabilization energies gives ΔE[n=2]* = 3.0 kcal mol⁻¹, for the Fe–H
BF₄⁻ interaction, which is far less than the ΔE[n=1]* =
15 kcal mol⁻¹ exhibited by the interaction with between the
N–H and BF₄⁻.

Protonation at both Fe and N to give a dication
When Fe⁰ is treated with excess HBF₄·OEt₂ or HOTf, protona-
tion at both Fe and N is observed, giving a dication (Scheme 2).
The doubly protonated complex, [FeHNH]²⁺[OTf]⁻, was char-
acterized crystallographically (Fig. 8), showing one OTf⁻ that is
hydrogen bonded to the N–H, and one OTf⁻ counterion that is
not interacting. This dicaticonic complex exhibits a notably
shorter NH–O distance (1.80(3) Å) relative to the monoproto-
nated complex [FeNH][OTf]⁻ (1.89(3) Å), suggesting a stronger
hydrogen bonding interaction. The IR spectra of the doubly
protonated [FeHNH]²⁺[BF₄]⁻ and [FeHNH]²⁺[OTf]⁻ complexes feature
νCO bands shifted to higher energy relative to [FeH]⁺; the
difference is similar to that observed between Fe⁰ and [FeNH]⁺.

Table 1  Computed charge transfer and stabilization energies in
[FeNH]⁺

<table>
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<tr>
<th>Interaction</th>
<th>Total charge transfer, q_CT</th>
<th>Stabilization energy, ΔE[n]* (kcal mol⁻¹)</th>
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<tr>
<td>N–H···ClCH₂Cl</td>
<td>0.0004</td>
<td>0.2</td>
</tr>
<tr>
<td>N–H···BF₄</td>
<td>0.0220</td>
<td>14.8</td>
</tr>
<tr>
<td>N–H···OTf</td>
<td>0.0399</td>
<td>20.3</td>
</tr>
</tbody>
</table>

ΔE[n]* and q_CT values are reported in Table 1. The magnitude
of the charge transfer from both anions is comparable to values
calculated for hydrogen bonding interactions between anions and
water.⁷⁷ The second-order stabilization energy between the
complex and BF₄⁻ and OTf⁻ is ΔE[2]* = 14.8 and 20.3 kcal mol⁻¹, respectively. The charge transfer and stabilization
energy from both anions is orders of magnitude larger than the
negligible stabilization energy from dichloromethane
solvent. This result implies that the hydrogen bonding inter-
action is significant, and not merely the result of an interaction

![Image](image-url)

**Fig. 7** The tautomer with a protonated amine ligand is favored with
an OTf⁻ or BF₄⁻ counterion, as shown by DFT calculations. The
computed structures of [FeHNH]⁺[OTf]⁻ and [FeNH]⁺[BF₄]⁻ are shown in
the lower part of the figure. Hydrogen atoms have been omitted,
except for the protonated ammonium.
NH resonance of one isomer, proposed to be the syn isomer. An additional exchange correlation is observed between the NH resonances of the two isomers, consistent with interconversion between syn (chair) and anti isomers.

At $\delta +0.40$, a broad resonance observed at $\delta 7.11$ is proposed to arise from a third isomer in which the FeH and NH are syn and the six-membered ligand ring adopts a boat conformation, bringing the FeH and NH in close proximity. The FeH and NH in the syn (boat) isomer are likely stabilized to some extent by dihydrogen bonding.\textsuperscript{48} Computational analysis shows $\Delta E_{\text{syn}}^\text{calc} = 2.9$ kcal mol$^{-1}$ in the presence of counterion. A more detailed discussion of this dihydrogen bonding is provided in the ESI.\textsuperscript{†}

The NOESY spectrum at $\delta +0.40$ shows an exchange correlation of the FeH only with the NH resonance of the syn (boat) isomer, presumably occurring through an unobserved Fe(H$_2$)+ intermediate.\textsuperscript{54,68}

Preparation, isolation and reactions of stable 17e Fe cations

The cyclic voltammogram of Fe$^0$ (Fig. 9) in fluorobenzene shows a reversible one-electron oxidation at $E_{1/2} = 0.37$ V vs. Cp$_2$Fe$^{0/+}$. Oxidation of Fe$^0$ by [Cp$_2$Fe][BARF$_4$]\textsuperscript{−} (1 equiv.; ArF = 3,5-bis(trifluoromethyl)phenyl) resulted in an immediate color change of the solution from yellow to dark green. The paramagnetic complex [Fe(P$^{\delta+}$NMe$_2$P$^{\delta-}$)(CO)$_3$][BARF$_4$]$^-$, [Fe$^{II}$]$^+$, was isolated as air-sensitive dark green crystals. X-Band EPR spectroscopy of [Fe$^{II}$]$^+$ at $22^\circ$C gives $g_{\text{iso}} = 2.05$ and a phosphorus hyperfine coupling $A_{\text{iso}} = 63$ MHz (see ESI), similar to spectra reported for related complexes.\textsuperscript{64,69} The 17-electron iron center adopts a square pyramidal geometry, as indicated by X-ray crystallography (Fig. 10). The carbonyl stretching frequencies ($\nu_{\text{CO}} = 2069$, 2007, 1999 cm$^{-1}$) shift to higher energies compared to 1, consistent with reduced backbonding in the cationic iron complex.
Solutions of \([\text{FeH}]^{+}\) treated with TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) immediately become dark green, converting the hydride to \([\text{Fe}^1]^+\), as confirmed by IR spectroscopy (eqn (4)). Rauchfuss and co-workers reported similar reaction proceeding through a proton-coupled electron transfer reaction in studies of \([\text{FeFe}]\)-hydrogenase model complexes with pendant amines, in which the protonated amine form is strongly favored.78

Reactions of \(\text{Fe}^3\) complexes with \(\text{H}_2\) are seldom reported, but Peters and co-workers reported a \(\text{Fe}^3\) complex that reacts with \(\text{H}_2\) to generate a rare \(\text{Fe}^3(\text{H}_2)\) complex.79 We found that dark green solutions of \([\text{Fe}^1]^+\) react slowly with \(\text{H}_2\) (1 atm) to give pale yellow solutions of the hydride \([\text{FeH}]^+\), but the reaction is slow, occurring over a few days. When monitored by \(^1\text{H}\) NMR spectroscopy, the broad resonances of the paramagnetic complex \([\text{Fe}^1]^+\) decrease, and new resonances appear, corresponding to the iron hydride \([\text{FeH}]^+\), but unidentified side products are observed. The yield of \([\text{FeH}]^+\) was determined to be approximately 60% by integration against an internal standard. Camara and Rauchfuss reported that the reaction of a \([\text{FeFe}]\)-hydrogenase complex with \(\text{H}_2\) is accelerated by a one-electron oxidation, even though that oxidant is not capable of oxidizing the complex. We carried out the reaction of \([\text{Fe}^1]^+\) with \(\text{H}_2\) with added \([\text{Cp}_2\text{Fe}]^+\), but the reaction rate and yield were similar to that observed with no oxidant added. The very slow reaction with \(\text{H}_2\) and the low yield of the iron hydride preclude using \([\text{Fe}^1]^+\) as a competent electrocatalyst for \(\text{H}_2\) oxidation.

**Conclusion**

Protonation of the iron diphosphine complex \(\text{Fe}^{[\text{P}^{9}\text{N}^{4}\text{Me}^{2}\text{Fe}^{3}]}^{+}\)(CO)\(_3\)) occurs at Fe and the amine, generating tautomers. The iron hydride complex \(\text{Fe}^{[\text{P}^{9}\text{N}^{4}\text{Me}^{2}\text{Fe}^{3}]}^{+}\)(CO)\(_3\)-H\(^\text{+}\)[B(C\(_{6}\)F\(_5\))\(_3\)]\(^-\) is converted to the N-H tautomer, with a protonated amine, by addition of excess \([\text{Et}_2\text{N}]^+\)BF\(_4^-\). Both isomers were characterized by spectroscopy and X-ray crystallography. Control of the tautomeric equilibrium occurs because of the favorable formation of an NH-·-F hydrogen bonding interaction between the protonated amine and the BF\(_4^-\) anion. Quantum chemical calculations quantified the strength of hydrogen bonding and its influence on the equilibrium. Protonation of \(\text{Fe}^{[\text{P}^{9}\text{N}^{4}\text{Me}^{2}\text{Fe}^{3}]}^{+}\)(CO)\(_3\)) with an excess of HOTf gives a doubly protonated dication with Fe-H and N-H bonds. The dication exists as interconverting isomers in solution, as determined by 2D NMR spectroscopic studies.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**References**