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Electrocatalytic H$_2$ production with a turnover frequency >10^7 s^{-1}: The medium provides an increase in rate but not overpotential

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Broader Context: Hydrogen is an excellent storage medium for energy derived from renewable sources such as solar and wind. Fast, efficient catalytic formation of H$_2$ by molecular catalysts will require the development of catalysts based on inexpensive, earth-abundant metals that precisely control proton movement and their coupling to electron transfers. Such catalysts will need to operate at very fast rates and high efficiencies (low overpotentials) to be attractive for practical applications. Here we report the dramatic effect of changing medium on rates of electrocatalytic production of H$_2$ by nickel bis(diphosphine) complexes that contain pendant amines to control proton movement. The remarkable increases in rate observed in aqueous ionic liquid media are obtained without an increase in overpotentials, illustrating the ability of the reaction medium to influence catalysis.

Rapid proton movement results in exceptionally fast electrocatalytic H$_2$ production (up to 3 × 10^7 s^{-1}) at overpotentials of ~400 mV when catalysed by [Ni(P$^{Ph}_2$N$^{C6H4X}_2$)$_2$]$^{2+}$ complexes in an acidic ionic liquid - water medium ([(DMF)H]NTf$_2$-H$_2$O, χ$_{H2O}$ = 0.71).

Catalyst systems that convert electrical energy to chemical fuels offer a method of storing this energy, a key element in grid-level load balancing and a prerequisite to the broader use of intermittent power sources such as wind and solar.[1] To approach this goal, molecular electrocatalysts for H$_2$ production and oxidation are being developed in our laboratory[2, 3] with a focus on optimizing reactivity through the use of bio-inspired proton relays, like that in the [FeFe]-hydrogenase active site.[4, 5] The [Ni(P$^R_2$N$^{R'}_2$)$_2$]$^{2+}$ family of complexes (P$^R_2$N$^{R'}_2$ = 1,5-R'-3,7-R-1,5-diaza-3,7-diphosphacyclooctane, e.g. Fig. 1) are active catalysts for H$_2$ production and oxidation that employ positioned pendant amines functioning as proton relays in the second coordination sphere to facilitate the movement of protons between the Ni center and the reaction medium. Within this series, varying the R and R' substituents of the P$^R_2$N$^{R'}_2$ ligand can modulate H$_2$ production turnover frequencies (TOFs) from 4 s^{-1} to 1,500 s^{-1} in dry MeCN, with overpotentials ranging from 114-765 mV.[6-8] Modifications of the P$^R_2$N$^{R'}_2$ ligand architecture have produced more substantial increases: two related series of catalysts with *P,N*-heterocyclic ligands having only one pendant amine per ligand (7P$^R_2$N$^{R'}$, with seven atoms in the heterocycle backbone, and 8P$^R_2$N$^{R'}$, with eight) afford TOF values ranging up to 10^5 s^{-1}, though these systems operate at larger overpotentials (>640 mV).[9, 10]

The effect of water on TOFs has proven to be as substantial as modification of the ligand architecture.[11] Proton reduction electrocatalysis with the [Ni(P$^R_2$N$^{R'}_2$)$_2$]$^{2+}$, [Ni(7P$^R_2$N$^{R'}$)$_2$]$^{2+}$,

and [Ni(8P$^R_2$N$^{R'}_2$)$_2$]$^{2+}$ complexes in MeCN electrolyte demonstrate up to 50-fold increases in TOFs when small quantities of water are added, with little or no change in overpotential.[9-10,12] An increase in TOF by a particular catalyst, without a corresponding increase in overpotential, may be indicative of lowering a kinetic barrier in the catalytic pathway without significantly changing the free energies of the reaction intermediates. These results motivated the pursuit of water-soluble [Ni(P$^R_2$N$^{R'}_2$)$_2$]$^{2+}$ complexes, leading to a phenol-substituted P$^R_2$N$^{R'}_2$ variant (R = Ph, R' = *p*-C$_6$H$_4$OH) that has a turnover frequency of 35 s^{-1} in anhydrous MeCN and more than 10^5 s^{-1} in MeCN-H$_2$O mixtures (mole fraction water, χ$_{H2O}$, of 0.9). This catalyst operates at overpotentials of 310-470 mV, demonstrating that rates of catalysis can be significantly improved without negatively impacting their energy efficiency.[13]
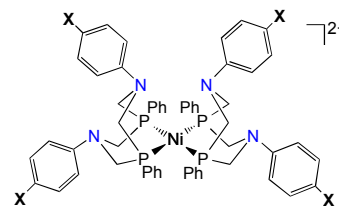

Figure 1: Structure of [Ni(P$^{Ph}_2$N$^{C6H4X}_2$)$_2$]$^{2+}$, (**1^X**) with X = n-hexyl (**1^{hex}**), X = Br (**1^{Br}**), X = H (**1^H**) and X = OMe (**1^{OMe}**).

We recently reported electrocatalytic H$_2$ formation using [Ni(P$^{Ph}_2$N$^{C6H4X}_2$)$_2$]$^{2+}$ complexes (**1^X**, Fig. 1) in the protic ionic liquid [(DBF)H]NTf$_2$, prepared by protonation of dibutylformamide using the superacid bis(trifluoromethanesulfonyl)amine.[14] In this case, the medium serves as solvent, electrolyte and proton source. In the absence of water, catalysis in this medium is very slow (≤ 10 s^{-1}), but once again, increasing the water content produces a striking increase

in the catalytic current, resulting in TOF increases of as much as three orders of magnitude.[14] In the case of 1^X (X = *n*-hexyl, 1^{hex}), rates exceeding 10^4 s^{-1} were observed. This rate was postulated to be the result of interactions between the butyl substituents of the DBF and $[(DBF)H]^+$ and the hexyl tail of the catalyst facilitating proton delivery to the metal center.[14]

To test this hypothesis, we investigated the impact of a, less hydrophobic and less sterically bulky ionic liquid on the catalytic rates of 1^X with X = *n*-hexyl (1^{hex}), Br (1^{Br}), H (1^H) and OMe (1^{OMe}) in dimethylformamide bis(trifluoromethanesulfonyl)amine/water mixtures ($[(DMF)H]NTf_2$-H_2O) compared with those in $[(DBF)H]NTf_2$-H_2O. Unexpectedly, this small change in the structure of the ionic liquid cation results in a dramatic increase (up to two orders of magnitude) in TOFs for all four catalysts without increasing the overpotential. As with $[(DBF)H]NTf_2$-H_2O, the TOFs observed in $[(DMF)H]NTf_2$-H_2O are strongly dependent on the water content (χ_{H2O}), and the resulting analysis suggests that rapid proton movement and the steric bulk,of the cation rather than hydrophobic interactions, are the dominant factors controlling the catalytic rates.

The $[(DMF)H]NTf_2$ ionic liquid was prepared by the method reported for $[(DBF)H]NTf_2$.[14] Nickel complexes were also prepared by literature methods, and their spectroscopic data (*Fig. S1-S3*) are in agreement with the reported complexes.[12, 14] Electrocatalytic responses were measured in $[(DMF)H]NTf_2$-H_2O with χ_{H2O} ranging from 0.46 to 0.71. The cyclic voltammogram traces (Fig 2) of the family of 1^X compounds collected at a scan rate (v) of 1 V s^{-1}, catalyst concentrations of 10 μM and χ_{H2O} = 0.71, show current enhancements indicative of catalytic production of H_2. In each case, the TOF increased with increasing water concentration. Aqueous ionic liquid media with $\chi_{H2O} > 0.71$ were not studied due to precipitation of the catalyst. Bulk electrolysis with complex 1^{hex} produced H_2 with 96% current efficiency as determined by analysis of the headspace by gas chromatography.
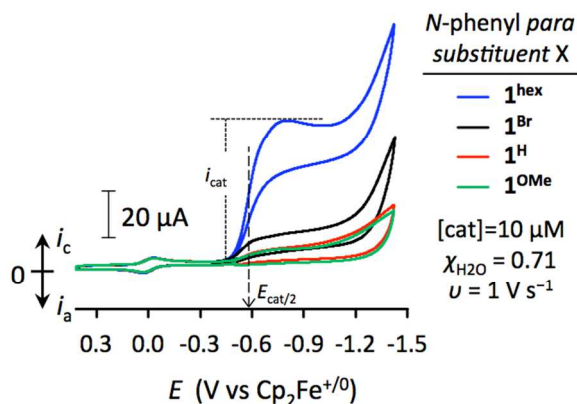

Figure 2: Cyclic voltammograms of 10 μM 1^X in $[(DMF)H]NTf_2$-H_2O (χ_{H2O} = 0.71) and a scan rate of 1 V s^{-1} showing that all complexes are H_2 production catalysts, with 1^{hex} exhibiting the fastest TOF under these conditions.

Catalytic currents (i_{cat}, Fig. 2) increased linearly with catalyst concentration ([cat]; *Fig. S4*) over 1-2 orders of magnitude, and all four 1^X complexes produced current responses that were independent of scan rate above 1 V s^{-1} (*Fig. S5*), demonstrating that catalysis is first-order in the Ni complex and at steady state. Under these conditions, the TOF is related to i_{cat} by eq. 1,[15] with n redox equivalents passed per turnover ($n = 2$ for H_2 production/oxidation), electrode area A (0.00785 cm^2), Faraday constant F, and catalyst diffusion coefficient D_{cat}.† Values of D_{cat} were determined for each

$$i_{cat} = nFA[cat](D_{cat})^{1/2}(TOF)^{1/2} \qquad (1)$$

catalyst by pulsed-field gradient (PFG) NMR spectroscopy (see the ESI for experimental details).[16] The high analyte concentrations required prevented the direct measurement of D_{cat} in $[(DMF)H]NTf_2$-H_2O (χ_{H2O} = 0.71). However, the diffusion coefficients of the NTf_2^- anion (D_{NTf2-}) and H_2O/H_3O^+ (D_{H+}), measurable in both media, were three times larger in $[(DMF)H]NTf_2$-H_2O than in $[(DBF)H]NTf_2$-H_2O at all water contents (*Fig. S6-S9*). As such, D_{cat} values were assumed to scale by the same factor and were estimated for $[(DMF)H]NTf_2$-H_2O (χ_{H2O} = 0.71) from values measured in $[(DBF)H]NTf_2$-H_2O (χ_{H2O} = 0.71) (Table S1).

The TOFs for the family of 1^X compounds in $[(DMF)H]NTf_2$-H_2O and $[(DBF)H]NTf_2$-H_2O were calculated from the slope of the best fit line from the plots of i_{cat} vs [cat] (eq. 1, *Fig. S4*).† As in previous work and detailed in the Electronic Supplementary Information,[14, 17] open circuit potential measurements were used to determine the equilibrium potentials for the interconversion of protons and electrons with H_2 (E_{H+}). The overpotentials are then easily calculated as the difference between E_{H+} and the half-peak potentials, $E_{cat/2}$, of the catalytic waves (defined as the potential at half of the catalytic current used to calculate the TOF, i.e. $i_{cat/2}$, data found in Figure *S10* and Table *S2*).[18] The catalytic TOFs and overpotentials for the 1^X family of catalysts operating in $[(DMF)H]NTf_2$-H_2O, $[(DBF)H]NTf_2$-H_2O and MeCN-H_2O using $[(DMF)H]OTf$ as the proton source, are reported in Table 1.

Table 1. Turnover frequencies and overpotentials at $E_{cat/2}$ for complexes 1^X in ionic liquid-H_2O and MeCN-H_2O mixtures.

Cmpd	$[(DMF)H]NTf_2$ χ_{H2O} = 0.71 E_{H+}: -0.180 V TOF (s^{-1})	η (V)	$[(DBF)H]NTf_2$[a] χ_{H2O} = 0.71[a] E_{H+}: -0.207 V TOF[a] (s^{-1})	η (V)	MeCN χ_{H2O} = 0.002-0.01[b] E_{H+}: -0.262 V TOF (s^{-1})	η (V)
1^{hex}	3×10^7	0.41	6×10^5	0.40	7.4×10^2	0.38
1^{Br}	1×10^6	0.38	2×10^4	0.44	1.0×10^3	0.46
1^H	5×10^5	0.40	2×10^4	0.42	7.2×10^2	0.53
1^{OMe}	4×10^5	0.40	5×10^3	0.37	4.8×10^2	0.51

[a]TOFs and overpotentials (η) determined in this work under identical conditions as $[(DMF)H]NTf_2$-H_2O (*Fig. S11-S12*).
[b]See ref 14 for 1^{hex} and ref. 7 for 1^{Br}, 1^H, 1^{OMe}; overpotentials are corrected from literature values based on recently published work.[17]

In addition to the increase in catalytic performance observed with the family of 1^X compounds in $[(DMF)H]NTf_2$-H_2O, 1^{hex} also shows enhanced stability in this medium. No observable decrease in i_{cat} was observed with 1^{hex} in $[(DMF)H]NTf_2$-H_2O over a period of 14 days (*Fig. S14*). In contrast, 1^H shows 75% loss of activity after six days under identical conditions. In $[(DBF)H]NTf_2$-H_2O medium with identical water content, complex 1^{hex} exhibits decomposition with $t_{1/2}$ of $\approx$ 1 week.[14] Although the mechanism of decomposition has not been studied, this finding also illustrates the profound effect of medium-catalyst interactions on chemical reactivity.

Understanding the nature of the stunning differences in the catalytic performance of the 1^X family of compounds in the three different media is important for continued development and improvement of these molecular catalysts. Diffusion studies conducted on $[(DMF)H]NTf_2$-H_2O and $[(DBF)H]NTf_2$-H_2O indicate water plays a key role in accelerating proton movement, (i.e. facilitating exchange from the ion pair), and increasing the observed rates of catalysis (i.e. Fig. 3, blue and red circles; Fig. S8,S9).

Without added water, the catalytic activities in the ionic liquids are marginal (i.e. Fig. 3, *S15* green squares).‡ In both ionic liquid-H_2O mixtures, the rate of diffusion of H_3O^+/H_2O increases significantly more than any other component (i.e. Cp_2Fe, NTf_2^-) with increasing χ_{H2O}.* The increase in TOF with increasing χ_{H2O} accelerates dramatically at $\chi_{H2O} > 0.5$ (Fig. 3, *S15* green squares). This trend correlates with the increase in D_{H+}, which also accelerates sharply as χ_{H2O} reaches ~0.5 for both [(DBF)H]NTf$_2$-H_2O and [(DMF)H]NTf$_2$-H_2O (Fig. 3, blue and red circles). The correlation between the TOFs and the proton transport, when coupled to water content, further suggests water plays a key role in delivering the protons to the active site of the catalyst.
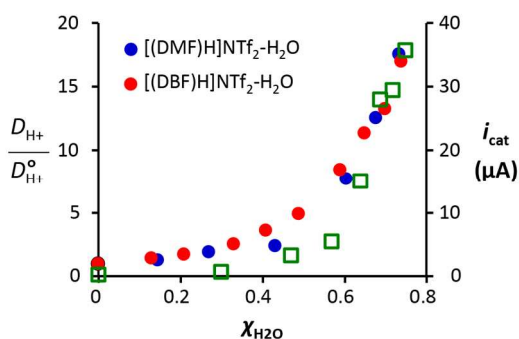

Figure 3: Proton diffusion coefficients vs. χ_{H2O} (left ordinate; normalized by dividing D_{H+} by D_{H+}°, the value with no added water) for [(DMF)H]NTf$_2$-H_2O (red circles) and [(DBF)H]NTf$_2$-H_2O (blue circles); i_{cat} measured with $\mathbf{1^{hex}}$ in [(DBF)H]NTf$_2$-H_2O vs χ_{H2O} (green squares, right ordinate). A dramatic increase is observed for both processes after a critical concentration of $\chi_{H2O} \approx$ 0.6 is reached. Similar comparison of proton diffusion coefficients and i_{cat} measured in [(DMF)H]NTf$_2$-H_2O is found in Fig. *S15*.

The enhanced electrocatalytic formation of H_2 by the family of $\mathbf{1^X}$ compounds is 3-5 orders of magnitude faster in the aqueous ionic liquid medium compared to MeCN-H_2O, without a concomitant increase in overpotential (Fig. 4). For example, in the case of catalysis by $\mathbf{1^{hex}}$ in [(DMF)H]NTf$_2$-H_2O the overpotential increases by only 10 mV compared to the overpotential in [(DBF)H]NTf$_2$-H_2O and 30 mV compared to the overpotential observed in MeCN-H_2O. Increasing the rate of catalysis without adversely impacting the overpotential was previously demonstrated in catalysis by [Ni(P$^{Ph}_2$N$^{C6H4OH}_2$)$_2$]$^{2+}$ in CH_3CN with $\chi_{H2O} > 0.9$ and attributed to increased rates of proton delivery and removal to and from the catalyst by H_3O^+/H_2O.[13] The increase in TOFs in the ionic liquid-H_2O media, without a corresponding increase in overpotentials, strengthens this hypothesis; proton transport, and hence the rate of proton delivery to the catalyst, strongly influences the catalytic TOFs without significantly changing free energies of the catalytic intermediates.

Comparing the differences in TOFs across the $\mathbf{1^X}$ family of catalysts in the three media reveals trends in the ionic liquids that are not observed in MeCN-H_2O (Fig. 4), suggesting that the interactions between the catalyst and the medium play a significant role in determining the rates. The TOF of complex $\mathbf{1^{hex}}$ is two orders of magnitude faster than that of $\mathbf{1^H}$ in each ionic liquid; however, the two catalysts have identical TOFs in MeCN-H_2O. Hydrophobic interactions between the hexyl tail of the catalyst and butyl chain of the [(DBF)H]$^+$ cation were previously postulated to facilitate increased rates through enabling proton delivery to the catalytically productive protonation site.[14] The increase in TOFs in catalysis by

$\mathbf{1^{hex}}$ observed with the less hydrophobic [(DMF)H]$^+$ compared to [(DBF)H]$^+$, however, does not support this hypothesis. On the contrary, the observed trends in TOFs in the three media suggest two alternative theories for the rate enhancement; the size of the acid/conjugate base (e.g methyl vs. butyl groups in the ionic liquids) and/or catalyst structure/medium interactions (e.g. $\mathbf{1^X}$, hexyl vs. H) play an important role in determining the rate of catalysis.
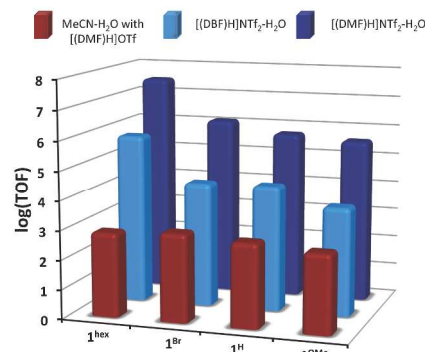

Figure 4: Plot of the log(TOF) as a function of the reaction medium for catalysts $\mathbf{1^X}$, with water added to afford maximum rates. The identity of the **X** substituent significantly affects TOFs in the ionic liquid-H_2O media but not in MeCN-H_2O with [(DMF)H]OTf as the proton source.

Productive protonation of the catalyst has been proposed to be a major factor in determining the overall rate of electrocatalytic H_2 production by the [Ni(P$^R_2$N$^{R'}_2$)$_2$]$^{2+}$ family of compounds.[6, 19, 20] In these catalysts, access to the active *endo* site of protonation is sterically disfavored, resulting in kinetically preferential *exo* protonation (Fig. 5).[19] Interconversion between the *endo* and *exo* isomers has been shown to be accompanied by chair/boat isomerization, as shown in Figure 5. The steric bulk of the acid has also been shown to affect the relative rates of *exo* and *endo* protonation, and thus TOF.[7] In MeCN, the [Ni(P$^{Ph}_2$N$^{C6H4X}_2$)$_2$]$^{2+}$ catalysts show faster turnover with [(DMF)H]OTf as the acid than with larger anilinium acids of similar strength;[7] in both cases, the TOFs increase when water is added in limited amounts, with a larger enhancement observed for the larger acid. These results have been attributed to an increase in proton transfer rates resulting from the significantly reduced steric penalty for H_3O^+ to enter the active site, compared to anilinium or [(DMF)H]$^+$. The 30- to 80-fold increase in TOF observed in [(DMF)H]NTf$_2$-H_2O compared to [(DBF)H]NTf$_2$-H_2O suggests that there is also a persistent steric effect related to the size of the dialkylformamides. The H_2O:H_3O^+ and H_2O:dialkylformamide molar ratio in the ionic liquids is 2.5:1 at $\chi_{H2O} = 0.71$, precluding proton solvation solely by H_2O. As a result, proton-dialkylformamide interactions likely remain present to aid in proton solvation, continuing to influence proton delivery to the active catalytic site.
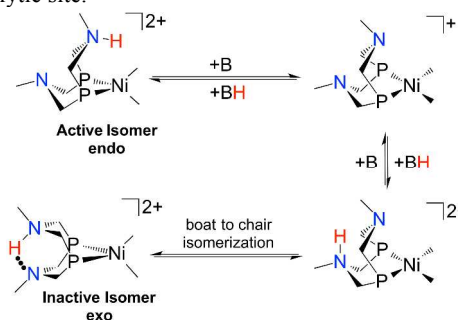

Figure 4: Catalytically productive protonation at *endo* sites

compared to *exo* sites. Only one of the two $P^R_2N^{R'}_2$ ligands is shown, and the R and R′ groups have been omitted for clarity.

While the steric difference between the [(DMF)H]NTf$_2$–H$_2$O and [(DBF)H]NTf$_2$–H$_2$O systems can explain the increase in TOFs between these two media, the steric difference does not explain the extraordinary increase in TOFs observed between $\mathbf{1^{hex}}$ and the other $\mathbf{1^X}$ catalysts (Fig. 3). As such, the large TOFs observed for catalysis with $\mathbf{1^{hex}}$ could be related to the selectivity of *endo/exo* protonation sites and catalyst dynamics in the ionic liquid-H$_2$O media. Previous studies have shown that the energy of the *endo* protonation isomer is similar to that of the *exo* protonation isomer that is stablilized by a "pinched" N-H-N hydrogen bond.[20] The *n*-hexyl tail may improve *endo* site proton delivery by disfavouring formation of the *exo* "pinched" N-H-N species in the ionic liquid-water mixtures through a mechanism that is not accessible in MeCN-H$_2$O. For example, the size of the hexyl substituent, solvation of the hydrophobic tail, and the viscosity of the reaction medium could slow chair/boat isomerization for $\mathbf{1^{hex}}$ significantly more than for the other catalysts in this study, kinetically disfavouring the formation of the *exo* species. Studies investigating these structural effects and their influence on TOFs are in progress.

In summary, relative rates of proton movement and protonation site selectivity play a central role in determining the turnover frequency and energy efficiency of electrocatalytic H$_2$ production complexes. The enhanced performance observed with all the $\mathbf{1^X}$ catalysts in ionic liquid-H$_2$O media suggests that the large turnover frequencies arise predominantly from rapid proton movement facilitated by the high water content in the reaction medium. The lack of change in overpotential from low rates in MeCN-H$_2$O to the 3-5 orders of magnitude faster rates in ionic liquid-H$_2$O mixtures also reflects the important role of the catalyst medium in enhancing catalytic performance. The extraordinary catalytic performance and stability demonstrated by $\mathbf{1^{hex}}$ in the ionic liquid-H$_2$O mixtures relative to the other $\mathbf{1^X}$ catalysts indicate medium-induced catalyst dynamics may play an important role for fast catalysis. The overall catalytic rates and efficiencies reported represent a significant advancement in understanding of these catalysts and demonstrates the importance of proton movement in optimizing catalyst efficiency.

Notes and references

† TOF values for molecular electrocatalysts are often determined from the ratio of maximum currents obtained in the absence and presence of substrate; however, the ionic liquid solvent is itself the substrate, so that method cannot be used here. The TOFs in [(DBF)H]NTf$_2$-H$_2$O determined in this work differ from those previously published due to more accurate determination of D_{cat} in this medium, among other factors.

‡ Prior ^{31}P NMR studies of **1** in [(DBF)H]NTf$_2$-H$_2$O indicate why this is the case.[14] The catalyst is doubly protonated in the Ni(II) state (i.e. prior to electroreduction) and the protons are stabilized in a bridging interaction that spans the two P atoms of each ligand (see Fig. 4 showing the 'unproductive exo isomer'; this species is catalytically unproductive since the protons cannot be transferred directly to Ni from these sites). Increasing the water content produces a negative shift in the equilibrium potential for H$_2$ production, indicating a decrease in solution acidity. The doubly-protonated Ni(II) complex is not detected by ^{31}P NMR beyond $\chi_{H2O} = 0.47$, and at $\chi_{H2O} > 0.64$ the ^{31}P chemical shift becomes identical to that of the unprotonated Ni(II) complex in neutral dibutylformamide,

suggesting that this species predominates in [(DMF)H]NTf$_2$-H$_2$O at high water content.

* The PFG NMR method detects the physical displacement of protons (vehicular diffusion) but not the movement of proton equivalents by the Grotthuss mechanism (structural diffusion),[21-23] which may be relevant for proton transfer reactions between catalytic species.

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