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Solvent influence on the thermodynamics for hydride transfer from bis(diphosphine) complexes of nickel[†]

Samantha J. Connelly Robinson,‡ Christopher M. Zall, Deanna L. Miller, John C. Linehan and Aaron M. Appel*

The thermodynamic hydricity of a metal hydride can vary considerably between solvents. This parameter can be used to determine the favourability of a hydride-transfer reaction, such as the reaction between a metal hydride and CO_2 to produce formate. Because the hydricities of these species do not vary consistently between solvents, reactions that are thermodynamically unfavourable in one solvent can be favourable in others. The hydricity of a water-soluble, bis-phosphine nickel hydride complex was compared to the hydricity of formate in water and in acetonitrile. Formate is a better hydride donor than $[HNi(dmpe)_2]^+$ by 7 kcal mol⁻¹ in acetonitrile, and no hydride transfer from $[HNi(dmpe)_2]^+$ to CO_2 occurs in this solvent. The hydricity of $[HNi(dmpe)_2]^+$ is greatly improved in water relative to acetonitrile, in that reduction of CO_2 to formate by $[HNi(dmpe)_2]^+$ was found to be thermodynamically downhill by 8 kcal mol⁻¹. Catalysis for the hydrogenation of CO_2 was pursued, but the regeneration of $[HNi(dmpe)_2]$ under catalytic conditions was unfavourable. However, the present results demonstrate that the solvent dependence of thermodynamic parameters such as hydricity and acidity can be exploited in order to produce systems with balanced or favourable overall thermodynamics. This approach should be advantageous for the design of future water-soluble catalysts.

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Introduction

While CO_2 is a byproduct of fossil fuel consumption, it is also an attractive starting material for chemical transformations.^{1–6} For energy applications, designing a synthetic carbon cycle involving efficient and sustainable reduction of CO_2 to a liquid fuel is an enticing prospect that could provide renewable fuels for transportation.^{7–10} The reduction of CO_2 is thermodynamically and kinetically challenging, requiring the development of efficient catalysts. In the design of new catalytic cycles, many different reaction parameters can be tuned, both for the catalyst (ligands, metal, oxidation state) and for the reaction conditions (temperature, pressure, solvent choice, addition of a base). These changes can lead to the production of reduced species from CO_2 , such as formate^{11–16} or methanol.^{17–20} However, understanding and predicting the influence of reaction conditions, such as choice of solvent, will require thermodynamic data in multiple solvents for the same catalysts and catalytic intermediates. For complexes relevant to the reduction of CO_2 , there have been few reports of thermodynamic data for the same system in multiple solvents.^{21–24}

The hydrogenation of CO₂ with one equivalent of molecular hydrogen produces formic acid, which is a thermodynamically unfavourable reaction in aqueous solution under standard state conditions of 1 atm. pressure of gases and 1 M formate. Increasing the solution pH, however, changes the thermodynamic bias and can make the reaction thermodynamically favourable (Scheme 1). The effect of non-standard state concentrations of solutes and pressures of gases can be determined using the equations in the right column, noting that $-RT \ln K$ equals $-1.364 \log K$ by conversion to kcal mol⁻¹ at 25 °C and using base-10 log rather than natural log. More specifically, the effect of pH upon the reaction free energy can be calculated using the last term in Scheme 1. This term can be simplified to $\Delta G_{rxn}^{\circ} - 1.364 \times pH$, for which ΔG_{rxn}° is the free energy at standard state (1 atm. for gases, 1 M formate). Using this equation, it can be shown that hydrogenation of CO_2 to formate is favourable above a pH of 7.4.

The reaction of CO_2 with a metal hydride is a key step in the catalytic reduction of CO_2 to formate. As such, the hetero-



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Pacific Northwest National Laboratory, P.O. Box 999, MS K2-57, Richland, Washington 99352, USA. E-mail: aaron.appel@pnnl.gov

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[‡] Current address: Eaton Hall, Seattle Pacific University, Seattle, WA 98119, USA.

Reaction	ΔG° (kcal/mol)	ΔG (kcal/mol)
$CO_{2(g)} + 2H_{(aq)} + 2e^{-} + HCO_{2}H_{(aq)}$	-nF(-0.108 V) = +5.0	$-nFE^{\circ} + 1.364 \log \left(\frac{[\text{HCO}_2\text{H}]}{P_{\text{CO2}} [\text{H}^+]^2}\right)$
$HCO_2H_{(aq)} \longrightarrow HCO_2^{-}_{(aq)} + H^{+}_{(aq)}$	1.364 p $K_a = +5.1$	1.364 pK _a + 1.364 log $\left(\frac{[H^+][HCO_2^-]}{[HCO_2H]}\right)$
H _{2(g)} ~ 2 H ⁺ _(aq) + 2 e ⁻	nF(0.00 V) = 0.0	nFE° + 1.364 $\log\left(\frac{[H^+]^2}{P_{H2}}\right)$
$CO_{2(g)} + H_{2(g)} = H^{+}_{(aq)} + HCO_{2^{-}(aq)}$	$\Delta G^{\circ}_{\rm rxn}$ = +10.1	$\Delta G^{\circ}_{rxn} + 1.364 \log \left(\frac{[\text{H}^+][\text{HCO}_2^-]}{P_{\text{CO2}}P_{\text{H2}}} \right)$

Scheme 1 Determination of the pH requirement for the favourable reduction of CO₂ to formate

lytic bond strength to cleave H- from metal hydrides (discussed here as the hydricity) has been studied extensively in organic solvents.25-29 The hydricity of formate has been reported in acetonitrile to be 44 kcal mol⁻¹,^{30,31} as corrected by Bercaw et al.32 The favourability of the reaction between a metal hydride and carbon dioxide can be predicted by comparing the hydricities of formate and the metal hydride: the reaction will be thermodynamically favoured if the hydricity value $(\Delta G_{\mu^{-}}^{\circ})$ of the M–H species is smaller than 44 kcal mol⁻¹. In acetonitrile, hydride transfer from $[HNi(dmpe)_2]^+$ (dmpe = 1,2bis(dimethylphosphino)ethane) to CO2 was reported to be thermodynamically uphill by 7 kcal mol⁻¹,^{31,32} as illustrated in Scheme 2. The favourability of this reaction can be modified using reaction additives. Bercaw et al. have established that the reaction between $[HNi(dmpe)_2]^+$ and CO₂ in organic solvent can be made more favourable in the presence of boranes.³²

The favourability of a reaction also depends strongly on solvent, due to factors such as the solvent dependence of the acidity of a species. Noting the variation of pK_a scales between solvents, Creutz et al. first showed that the hydricities of metal hydrides can also vary considerably with solvent.21 Recent reports by Berben et al.^{23,24} and Yang et al.²² have also shown significant differences between the hydricities of metal hydrides in organic vs. aqueous solutions. Recently, we proposed revised thermodynamic parameters for the aqueousphase reactions of fundamental species such as H⁺, H⁻, H⁻, and H2.33 When used appropriately and consistently, these values enable quantifying the favourability of many important chemical reactions. For instance, the hydricity of formate is increased ($\Delta {\cal G}^{^{\!\!\!o}}_{H^-}$ is decreased) in water relative to acetonitrile $(\Delta G_{H^-}^{\circ} = 24 \text{ kcal mol}^{-1} \text{ vs. } 44 \text{ kcal mol}^{-1}, \text{ respect-}$ ively). In water, the Ru complexes reported by Creutz et al. undergo an even greater improvement in the hydricity than is observed for formate.²¹ Due to the discrepancy in the magni-

Scheme 2 Hydride transfer from formate to generate $[HNi(dmpe)_2]^+$ in acetonitrile.

tude of change in hydricity between metal hydrides and formate, the choice of solvent can be used to control the spontaneity of the hydride transfer reaction.

Nickel bis(diphosphine) complexes have been used extensively in catalytic reactions, especially in electrocatalytic production and oxidation of hydrogen,^{25,34} oxidation of formate,^{35,36} and oxidation of alcohols.³⁷ Catalyst development using these complexes has been greatly aided by an understanding of their hydricity values, which have been well characterized in organic solvents. Recently, Yang et al. determined the hydricity values of a nickel bis(diphosphine) complex, [HNi(DHMPE)₂]⁺ in acetonitrile, DMSO, and water.²² Compared to the hydricity of formate, the nickel hydride complex was a weaker donor by more than 12 kcal mol⁻¹ in acetonitrile and DMSO, but only ~6 kcal mol⁻¹ in water. Catalytic CO_2 reduction with this complex is therefore unfavourable in all three solvents, but the reaction is closer to favourable in water. The hydricities of Ni complexes can be tuned by variation of the phosphine ligand, and we hypothesized that a strong hydride donor such as $[HNi(dmpe)_2]^+$, which has the lowest hydricity of bis-diphosphine nickel complexes in acetonitrile, might promote favourable hydride transfer to CO₂ in water. Herein, we determine the hydricity $(\Delta G^{\circ}_{H^{-}})$ of $[HNi(dmpe)_2]^+$ in aqueous solution. Based on the relative hydricities of [HNi(dmpe)₂]⁺ and formate, hydride transfer from $[HNi(dmpe)_2]^+$ to CO₂ is predicted to be ~8 kcal downhill. Consistent with this prediction, we observed the stoichiometric transfer of a hydride from $[HNi(dmpe)_2]^+$ to CO₂ to produce formate in water. The catalytic conversion of CO₂ to formate was investigated; however, only stoichiometric reactions were observed due to inadequate solution basicity to regenerate the hydride complex in the presence of CO2. As a potential pathway toward catalytic turnover, the related complex [HNi (dmpbz)₂]⁺ (dmpbz = 1,2-bis(dimethylphosphino)benzene) was investigated, but the limited solubility of this complex in water impeded catalysis.

Results

The complexes $[Ni(dmpe)_2](BF_4)_2$ and $[HNi(dmpe)_2](BF_4)$ were synthesised as previously described,^{38,39} and they were used for reactivity and thermochemical studies, as described below.

Table 1 Measured equilibrium constants for eqn (1) and the resulting hydricity of $[\text{HNi}(\text{dmpe})_2]^+$

Entry #	Base	$P(H_2)$ (atm.)	$K_{\rm eq.}~({\rm atm.}^{-1})$	$-\Delta G^{^{\mathrm{o}}}_{\mathrm{H}^{-}}$ (kcal mol $^{-1}$)
1	$[CO_3]^{2-}$ buffer	1.1	4.4×10^{-4} 5.4 × 10^{-4}	15.6
3	$[CO_3]^{2-}$ buffer	20.4	3.4×10^{-3} 2.3×10^{-3}	16.6
4 5	Et₃N Et₂N	$1.4 \\ 40.8$	8.2×10^{-3} 3.3×10^{-3}	16.7 16.1
5	Et ₃ N	40.8	3.3×10^{-3}	16.1

Average aqueous	hydricity =	16.2 ± 1.0	kcal mol ⁻¹
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The equilibrium involving the interconversion of $[Ni(dmpe)_2]^{2+}$ and $[HNi(dmpe)_2]^+$ was studied by combining aqueous solutions of $[Ni(dmpe)_2]^{2+}$ with bases under various pressures of hydrogen gas, as shown in eqn (1) and Table 1. Sodium carbonate was used as a base under 1.1, 1.7, and 20.4 atm. of H₂. Triethylamine was employed as a base at 1.4 atm. and 40.8 atm. of H₂. The reaction free energy was determined from the K_{eq} values measured by NMR spectroscopy.

$$Ni(dmpe)_2^{2+} + Base + H_{2(g)} \rightleftharpoons HNi(dmpe)_2^{+} + HBase^+$$
 (1)

As shown in Scheme 3, the equilibrium data for the overall reaction (eqn (2)) was combined with the pK_a for the conjugate acid of the base employed (eqn (3)) and the heterolytic cleavage free energy for hydrogen in water (eqn (4))³³ to determine the hydricity (eqn (5), $\Delta G_{H^-}^{\circ}$) of [HNi(dmpe)₂]⁺. The individual measurements and the average value of 16 ± 1 kcal mol⁻¹ are shown in Table 1. The data and detailed calculations are included in the ESI.[†]

The free energy for the reaction of $[\text{HNi}(\text{dmpe})_2]^+$ with CO₂ was calculated using the hydricity of $[\text{HNi}(\text{dmpe})_2]^+$ in conjunction with the hydride acceptor ability $(-\Delta G^{\circ}_{\text{H}^-})$ of formate, as illustrated in Scheme 4. Consistent with this predicted free energy, the addition of 1 atm. CO₂ to a solution containing $[\text{HNi}(\text{dmpe})_2]^+$ in water resulted in formation of $[\text{Ni}(\text{dmpe})_2]^{2+}$ and formate, as observed by ¹H NMR spectroscopy. Scheme 5 shows a proposed catalytic cycle for hydrogenation of CO₂ to

$HNi(dmpe)_2^* + HBase^* \longrightarrow Ni(dmpe)_2^{2+} + Base + H_{2(g)}$	(2)	-1.364 log(1/K _{eq})
Base + H+ HBase+	(3)	–1.364 p <i>K</i> a
H _{2(g)} → H++ H ⁻	(4)	+34.2 kcal/mol
$HNi(dmpe)_2^+ \longrightarrow H^- + Ni(dmpe)_2^{2+}$	(5)	ΔG°_{H-}

Scheme 3 Reactions and equations to determine hydricity of [HNi $(dmpe)_2$]⁺.

$HNi(dmpe)_2^+ \longrightarrow H^- + Ni(dmpe)_2^{2+}$	(5)	16.1 kcal/mol
$CO_{2(g)} + H^- \longrightarrow HCO_2^-$	(6)	-24.1 kcal/mol
$HNi(dmpe)_{2}^{+} + CO_{2(g)} + HCO_{2}^{-} + Ni(dmpe)_{2}^{2+}$	(7)	-8.0 kcal/mol

Scheme 4 Free energy for H^- transfer in aqueous solution from [HNi (dmpe)_2]^+ to $\text{CO}_2.$



 $\label{eq:scheme 5} \begin{array}{l} \mbox{Proposed catalytic cycle for reduction of CO_2 to formate in aqueous solution.} \end{array}$

formate in aqueous solution, in which the hydride transfer step is shown as Step 1.

Metal hydrides can be regenerated using heterolysis of H_2 as a source of a hydride, but this reaction also produces a proton. The driving force for heterolysis of H_2 is provided by the sum of the hydride acceptor ability of the metal and the basicity of the proton acceptor. To determine the feasibility for regenerating the hydride (Step 2 in Scheme 5), the pH at which the hydride generation is favourable was considered. The reaction shown in eqn (8) has a free energy of +18 kcal mol⁻¹ under standard state conditions (eqn (4) minus eqn (5)). Therefore, nickel hydride generation will only be favourable above pH ~ 13, and below this pH, protonation of the hydride to eliminate H_2 will be favourable (calculations shown in the ESI†).

$$Ni(dmpe)_{2}^{2^{+}} + H_{2(g)} \rightleftharpoons HNi(dmpe)_{2}^{+} + H^{+}$$
(8)

Phosphate and carbonate buffers were utilised to help control the pH of the solution by mitigating acidification by CO_2 , but no catalytic turnover was observed. In phosphate buffers, the pH of the solution could be monitored by ${}^{31}P{}^{1}H{}^{1}$ NMR spectroscopy, and could be observed to drop from pH 12 to pH 8 upon addition of CO_2 at 1 atm. The calibration curve relating the solution pH with the chemical shift of the phosphate buffer at room temperature in the ${}^{31}P{}^{1}H{}^{1}$ NMR spectrum is included in the ESI.†

 $[Ni(dmpbz)_2](BF_4)_2$ the corresponding hydride and $[HNi(dmpbz)_2](BF_4)$ were synthesised using methods analogous to those employed for $[Ni(dmpe)_2](BF_4)_2$ and [HNi(dmpe)₂](BF₄). The complexes of dmpbz were originally prepared with different anions by Warren & Bennett.^{40 31}P and ¹H NMR spectroscopy data for $[Ni(dmpbz)_2]^{2+}$ and $[HNi(dmpbz)_2]^+$ are included in the Experimental section, † as this spectroscopy data has not been reported previously. The crystal structures of the BF_4^- salts of both $[Ni(dmpbz)_2]^{2+}$ and $[HNi(dmpbz)_2]^+$ are included as Fig. 1 and 2, with detailed information available in the ESI.† By X-ray diffraction, the structure for [HNi(dmpbz)₂][BF₄] is nearly tetrahedral around nickel, with no obvious coordination site for the hydride



Fig. 1 X-ray crystallographic structure of [Ni(dmpbz)₂][BF₄]₂. Thermal ellipsoid probability set at 30%. BF_4^- anions and hydrogen atoms omitted for clarity.



Fig. 2 X-ray crystallographic structure of $[HNi(dmpbz)_2][BF_4]$. Thermal ellipsoid probability set at 30%. BF_4^- anion and hydrogen atoms omitted for clarity. Disorder in the location of the Ni metal centre is shown and likely leads to the difficulty in locating the hydride ligand in the electron density map.

ligand. The Ni centre is disordered over a special position, and we anticipate that the hydride ligand induces this disorder. The presence of the hydride ligand was confirmed by dissolving the crystalline material in CD_3CN . Only one ³¹P-containing species is observed, and the resonance for the hydride ligand integrates appropriately in the ¹H NMR spectrum (ESI[†]).

The synthesis of $[Ni(dmpbz)_2]^{2^+}$ and $[HNi(dmpbz)_2]^+$ was driven by the expectation that the hydricity of $[HNi(dmpbz)_2]^+$ would be lower, and therefore regeneration of the hydride would be more feasible in spite of solution acidification by CO_2 (see discussion). However, thermochemical, reactivity, and catalytic studies of $[Ni(dmpbz)_2]^{2^+}$ were limited by the

insolubility of $[HNi(dmpbz)_2]^+$ in aqueous solution. The hydricity as well as reactivity towards CO_2 could not be determined.

Discussion

Whether hydride transfer occurs between a metal hydride and CO_2 to give formate depends on the hydricity of the metal complex relative to that of formate. Previously, it has been determined that the hydricity of $[HNi(dmpe)_2]^+$ in acetonitrile is insufficient to promote hydride transfer to carbon dioxide.³² In fact, the hydride transfer reaction proceeds in the opposite direction: formate reacts with $[Ni(dmpe)_2]^{2+}$ in acetonitrile to generate the nickel hydride complex (Scheme 2).³¹ In contrast to the observed hydride transfer from formate to the dicationic metal complex in acetonitrile, dissolution of $[Ni(dmpe)_2]^{2+}$ and HCO_2^- in water resulted in no observable reaction over a period of days.

To estimate the hydricity of $[HNi(dmpe)_2]^+$ in water, a thermochemical cycle can be established using measured equilibria, as well as previously reported constants.³³ By determining the hydricity of $[HNi(dmpe)_2]^+$, as shown in Scheme 3 and Table 1, the free energy for transferring a hydride from $[HNi(dmpe)_2]^+$ to CO₂ can be estimated, as shown in Scheme 4. While the hydricity of $[HNi(dmpe)_2]^+$ is inadequate in acetonitrile to transfer a hydride to CO_2 ,³² the hydricity is greatly improved in water relative to that of formate. While this reaction is 7 kcal mol⁻¹ unfavourable in acetonitrile,³² the reaction was determined to be 8 kcal mol⁻¹ favourable in aqueous solution.

The primary factor that enables the change in relative hydricities is that the hydricity values reported here and those reported previously by Creutz²¹ do not change consistently between acetonitrile and water. This variable change between solvents is expected to enable catalysis in water that was disfavoured thermodynamically in organic solvents. For the present report, $[HNi(dmpe)_2]^+$ becomes a better hydride donor by 35 kcal mol⁻¹ (from 51 to 16 kcal mol⁻¹) when moved from acetonitrile to water, whereas the hydricity value of formate changes by only 20 kcal mol⁻¹ (from 44 to 24 kcal mol⁻¹). As such, the hydricity of formate is surpassed by that of $[HNi(dmpe)_2]^+$, and hydride transfer to generate formate is favoured.

The majority of the change in the relative hydricities of formate and the metal complexes is likely due to stabilization of formate by hydrogen bonding in water. This explanation is consistent with the much larger than average change in the acidities of carboxylic acids than for other protic species in moving between water and acetonitrile, such as the nearly 19 unit change in p_{K_a} value for acetic acid (from 4.7 to 23.5), rather than the more typical change by 7–8 units.⁴¹ This ~11 unit discrepancy for carboxylic acids is within error of the 15 kcal mol⁻¹ change in the relative hydricities of formate and [HNi(dmpe)₂]⁺ in MeCN and water (using 1.364 as the conversion³³ from a difference in p_{K_a} values to a difference in free energy in kcal mol⁻¹). The change in hydricity for

 $[HNi(dmpe)_2]^+$ is also considerably smaller than the change reported for the analogous complex with a hydroxy substituent at each methyl group,²² as this previously reported complex had a change in hydricity of 27.4 kcal mol⁻¹ between acetonitrile and water. The difference in change between these complexes may be the result of hydrogen bonding effects for the hydroxy substituents in water,²² similar to the difference observed for formate, as discussed above.

Consistent with the favourable free energy for transfer of a hydride from $[HNi(dmpe)_2]^+$ to CO_2 , the stoichiometric reaction is spontaneous, and therefore the first step in the catalytic cycle illustrated in Scheme 5 is feasible. To ensure that the reaction of the hydride with CO_2 is more favourable than its protonation to generate H_2 , a high pH is required. Even at pH 11.8, the solution is acidic enough to protonate most of the $[HNi(dmpe)_2]^+$, forming $[Ni(dmpe)_2]^{2+}$ and hydrogen gas. The protonation reaction to lose H_2 and the hydride transfer to CO_2 to produce formate occur on competing kinetic time scales (spectra are included in the ESI[†]).

While the individual steps of the catalytic cycle can be made favourable, catalytic turnover was not achieved with $[Ni(dmpe)_2]^{2+}$. Turnover was impeded by acidification of the reaction solution upon addition of CO₂, preventing hydride regeneration. Under CO₂ pressure with a phosphate buffer, the solution pH equilibrated near 8, lower than the pH required to regenerate the hydride.

To increase the favourability of Step 2 of the catalytic cycle, a nickel hydride complex with a more electron-withdrawing ligand was used, thereby increasing the stability of the metal hydride against protonation and loss of hydrogen. The hydricity of [HNi(dmpbz)₂]⁺ in acetonitrile has been calculated to be 55.9 kcal mol⁻¹, making it more stable than $[HNi(dmpe)_2]^+$ (50.9 kcal mol⁻¹) by ~5 kcal mol⁻¹.⁴² Assuming a similar difference in aqueous solution, this increase in stability should result in lower reactivity towards protonation as well as CO₂ hydrogenation. The free energy of hydride transfer to CO₂ in water should still be favourable, with a change in driving force from -8 to -3 kcal mol⁻¹. The greater stability against protonation and loss of hydrogen should allow catalysis near pН of the CO_2/HCO_3^{-} buffer. Unfortunately, the $[HNi(dmpbz)_2]^+$ was insoluble in aqueous solutions, so aqueous hydride transfers could not be studied.

Summary and conclusions

The hydricities of metal hydrides are highly solvent dependent, especially in comparison to the hydricity of formate. Although hydride transfer from $[\text{HNi}(\text{dmpe})_2]^+$ to CO₂ is unfavourable in acetonitrile ($\Delta G^\circ = +7$ kcal mol⁻¹), this same reaction proceeds spontaneously in water, resulting in the generation of formate. Thermodynamic measurements were performed to determine that the transfer of a hydride from $[\text{HNi}(\text{dmpe})_2]^+$ to CO₂ is favourable by 8 kcal mol⁻¹ in water. The observed dependence of the relative hydricities on the solvent can enable catalytic reactions in water that are not thermodynamically favourable in organic solvents. Studies of catalytic CO_2 hydrogenation in aqueous solution with complexes of first row transition metals are in progress in our laboratory.

Experimental section

Syntheses and reactivity studies were carried out in air-free conditions using a N₂ glove box or Schlenk techniques. NMR spectra were recorded on Varian 500 MHz spectrometers. High pressure reactions involving CO_2^{43} were carried out in poly-ethyletherketone (PEEK) NMR tubes capable of withstanding the high pressures used in these experiments.^{44,45} Safety warning: operators of high-pressure equipment such as that required for these experiments should take proper precautions to minimise the risk of personal injury.

The metal starting material, $[Ni(CH_3CN)_6][BF_4]_2$, was synthesised according to literature procedure.⁴⁶ Ligand dmpe (bis-1,2-dimethylphosphinoethane) was used as received, and ligand dmpbz (bis-1,2-dimethylphosphinobenzene) was synthesised according to a previously reported method.⁴⁷ Full experimental details for all compounds are included in the ESI.[†]

Synthesis of [Ni(dmpe)₂][BF₄]₂

The dmpe complex of nickel(π) was synthesised and purified similarly to the previously published procedure.³⁸ Characterization data in aqueous solution: ¹H NMR spectrum (500 MHz, 298 K, D₂O): 2.07 ppm (CH₂, vt, 8H), 1.62 ppm (P(CH₃)₂, vt, 24H). ³¹P{¹H} NMR spectrum (202 MHz, 298 K, D₂O): 43.3 ppm (s).

Synthesis of [HNi(dmpe)₂][BF₄]

In previous reports, $[HNi(dmpe)_2]^+$ was obtained by protonation of Ni(dmpe)_2 (synthesised from a Ni(0) precursor).³⁹ For this study, the material was obtained from reaction of $[Ni(dmpe)_2][BF_4]_2$ with excess CsHCO₂ in acetonitrile. Over the course of several minutes, the stirring suspension changes from yellow to orange in colour. The excess CsHCO₂ can be removed by filtration. Characterization data in aqueous solution: ¹H NMR spectrum (500 MHz, 298 K, D₂O): 1.83 ppm (CH₂, vt, 8H), 1.45 ppm (P(CH₃)₂, vt, 24H), -13.6 ppm (NiH, br) (signal disappears following exchange with the deuterated solvent). ³¹P{¹H} NMR spectrum (202 MHz, 298 K, D₂O): 24.9 ppm (s) (NiD); 25.0 ppm (s) (NiH).

Synthesis of [Ni(dmpbz)₂][BF₄]₂

The dmpbz complex of nickel(π) was prepared by a method modified from the procedure reported by Warren & Bennett.⁴⁰ [Ni(CH₃CN)₆][BF₄]₂ was employed as a Ni(π) precursor, and stirred with the dmpbz ligand to generate the desired complex. The product was precipitated by layering the solution with diethylether. [Ni(dmpbz)₂]²⁺ was originally characterised only by UV-vis spectroscopy and elemental analysis, so the NMR spectroscopic data are reported here in both water and acetonitrile.

¹H NMR Spectroscopy (500 MHz, 298 K, D₂O): 2.05 ppm (P(CH₃)₂ vt, 24 H), 7.90 ppm (Ph, 4H), 8.08 ppm (Ph, 4H) (500 MHz, 298 K, CD₃CN): 1.97 ppm (P(CH₃)₂ vt, 24 H), 7.88 ppm (Ph, 4H), 8.05 ppm (Ph, 4H) $^{31}P{^{1}H}$ NMR spectroscopy (202 MHz, 298 K, D₂O): 39.2 ppm (s) (202 MHz, 298 K, CD₃CN): 41.8 ppm (s).

Synthesis of [HNi(dmpbz)₂][BF₄]

 $[Ni(dmpbz)_2][BF_4]_2$ was reacted with CsHCO₂ in acetonitrile to produce the nickel hydride species by the same procedure as used for $[HNi(dmpe)_2][BF_4]$. ¹H NMR spectroscopy (500 MHz, 298 K, CD₃CN): 1.69 ppm (P(CH₃)₂, vt, 24 H), -13.15 ppm (NiH, p, 1H), 7.66 ppm (Ph, 4H), 7.90 ppm (Ph, 4H). ³¹P{¹H} NMR Spectroscopy (202 MHz, 298 K, CD₃CN): 26.7 ppm (s). This species was completely insoluble in water such that no aqueous NMR spectroscopy data could be obtained.

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