The hydricity ($\Delta G_H$) of a newly synthesized nickel hydride was experimentally determined in acetonitrile (50.6 kcal mol$^{-1}$), dimethyl sulfoxide (47.1 kcal mol$^{-1}$), and water (22.8 kcal mol$^{-1}$). The hydricity values indicate hydride transfer from $[\text{HNi(TMEPE)}_2][\text{BF}_4]$ (TMEPE = 1,2-bis[di(methoxyethyl)phosphino]ethane) to CO$_2$ is exergonic in water and endergonic in the organic solvents.

The reduction of CO$_2$ to formate is a convenient path to a carbon-neutral renewable fuel that can be transported as a liquid.$^1$ Formate can be produced from CO$_2$ through hydrogenation$^{1a,b,2}$ or direct electrochemical reduction.$^3$ Conversely, formate can be utilized through dehydrogenation to liberate dihydrogen$^{3c,2a,4}$ or used directly in a formate oxidation fuel cell to generate electricity.$^5$ All of these routes for formate production and consumption require catalysts. For homogeneous catalysts, these reactions proceed through transition metal hydride intermediates.

The thermodynamic cycle for hydride transfer to CO$_2$ or from formate is outlined in Scheme 1. Comparison of the hydride transfer energy of a transition metal hydride (eqn (1), $\Delta G_H$ (MH), or hydricity) to the hydride transfer energy of formate (eqn (2)), $\Delta G_H$ (HCO$_2^-$) indicates whether CO$_2$ reduction or formate oxidation is exergonic or endergonic (eqn (3)). Values for $\Delta G_H$ (HCO$_2^-$) have been measured or estimated in several solvents.$^6$ To develop a thermodynamic framework to guide catalyst design for the interconversion of CO$_2$ to formate, our group$^6a$ and others$^{3b,3a,b,6b,7}$ have been quantifying hydricity values for transition metal hydrides.

We previously measured the hydricity ($\Delta G_H$) of $[\text{HNi(DHMPE)}_2]^+$ (DMPE = 1,2-bis[di{hydroxymethyl}phosphino]ethane, Chart 1) versus dihydrogen in acetonitrile (CH$_3$CN), dimethylsulfoxide (DMSO), and water. In solvents with higher polarity, the hydricity of $[\text{HNi(DHMPE)}_2]^+$ shifts to lower values, or becomes a better hydride donor (see Scheme 3).$^6a$ In aqueous solutions, the decrease of $\Delta G_H$ for $[\text{HNi(DHMPE)}_2]^+$ is greater in magnitude than the decrease in $\Delta G_H$ for formate. The change in free energy for CO$_2$ reduction to formate in water was initially observed by Creutz and coworkers with $[\text{HRu}(\eta^5-C_6\text{Me}_6)(\text{bpy})]^+$, $^{7,8}$ and subsequent studies show a similar trend among transition metal hydrides.$^{1a,b,7,8}$ However, with only a few exceptions,$^{1b,7,8,9}$ the ultimate reactivity remains the same across solvents (i.e. the magnitude of the free energy changes, but not the sign). This is true of $[\text{HNi(DHMPE)}_2]^+$; the free energy for hydride transfer to CO$_2$ (eqn (3)) decreases from 13.5 and 13.4 kcal mol$^{-1}$ in DMSO and CH$_3$CN, respectively, to 5.9 kcal mol$^{-1}$ in water, but the reaction is still endergonic in all three solvents.

We sought to modify $[\text{HNi(DHMPE)}_2]^+$ to increase the metal hydride donor strength (or decrease $\Delta G_H$) in order to favor aqueous CO$_2$ reduction to formate. To increase the donor strength of the ligand while maintaining water solubility, we replaced DHMPE with TMEPE (TMEPE = 1,2-bis[di{methoxyethyl}phosphino]ethane), shown in Scheme 1. In TMEPE, the electron-withdrawing oxygen heteroatom is further extended from the phosphine ligand by an additional methylene group. Additionally, we had previously observed that DHMPE was unstable to alkaline conditions, which we attributed to deprotonation of the distal alcohols. To circumvent this issue, the alcohols were replaced with methoxide substituents in TMEPE.

As expected, the experimentally measured hydricity values for $[\text{HNi(TMEPE)}_2]^+$ are lower, or more hydric, than $[\text{HNi(DHMPE)}_2]^+$ in CH$_3$CN, DMSO, and water. While hydride transfer from $[\text{HNi(TMEPE)}_2]^+$ is still endergonic in CH$_3$CN and DMSO, it is now exergonic in water. The hydricities of over 100 transition metal complexes have been measured in CH$_3$CN, water, or both; this is only the fifth complex known to exhibit solvent-dependent reactivity.

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with CO₂. These results demonstrate how hydricity can be tuned through ligand design to impart favorable reactivity for the conversion between CO₂ and formate. We also discuss how hydricity can be used to determine pH conditions where the metal hydride is stable to protonation as a method to promote selective hydride transfer to CO₂. 1,2-Bis[di(methoxymethyl)phosphino]ethane (TMEPE) was synthesized from methyl vinyl ether in 63% yield according to a modified preparation (see Experimental section in ESI†). The 1H and 31P{1H} NMR spectra (Fig. S1 and S2, ESI†) were consistent with the original preparation.11

The Ni(n) complex [Ni(TMEPE)_2][BF_4]_2 (2) was synthesized by the addition of two equivalents of TMEPE to Ni(COD)_2 in THF at -35 °C, resulting in an immediate color change from yellow to dark orange-brown. The solution was warmed to room temperature and stirred overnight to give 3 in 95% yield. Complex 3 was characterized by 1H and 31P{1H} NMR spectroscopy (Fig. S3 and S4, ESI†). Single crystals suitable for analysis by X-ray crystallography were grown by vapor diffusion of diethyl ether into a THF/toluene solution; the solid-state structure is shown in Fig. 1. The nickel ion lies on an inversion center and the asymmetric unit contains only one TMEPE ligand; the other half of the molecule is generated by symmetry, resulting in a square planar geometry around the metal center.

The Ni(0) complex, Ni(TMEPE)_2 (3), was prepared by adding two equivalents of TMEPE to Ni(COD)_2 in THF at -35 °C, resulting in an immediate color change from yellow to dark orange-brown. The solution was warmed to room temperature and stirred overnight to give 3 in 95% yield. Complex 3 was characterized by 1H and 31P{1H} NMR spectroscopy (Fig. S5 and S6, ESI†).

The nickel hydride complex [HNi(TMEPE)_2][BF_4] (1, Chart 1), was generated by in situ protonation of 3 by the addition of one equivalent of acid in either H_2O, DMSO, or CH_3CN. The 1H and 31P{1H} NMR spectra for 1 are shown in Fig. S7–S12 (ESI†).

Despite extensive purification attempts using a variety of solvent systems, we were unable to obtain acceptable elemental analyses on 1, 2, and 3 as they are isolated as oils in larger scale preparations. (Bulk recrystallization of 2 under the same conditions used to grow single crystals for X-ray analysis was also unsuccessful.) In the following experiments, the purity and concentration of each complex was determined using quantitative 1H and 31P{1H} NMR experiments relative to a PPh_3 standard in solution.

The hydricity values were measured using the thermodynamic cycle shown in Scheme 2. The equilibrium constant (K_{eq}) associated with the formation of complex 1 from 2 using H_2 in the presence of a base (eqn (4)) was measured in CH_3CN, DMSO, and H_2O. With this method, the estimated hydricity is benchmarked to the heterolytic bond cleavage energy of H_2 (ΔG^0_H2) and the pK_a values of the conjugate acids in the solvent of interest. The values for the previously studied [HNi(DHMPE)]⁺ were measured using the same method, so they are self-consistent.

In each solvent, the reaction shown in eqn (4) was monitored by 1H and 31P{1H} NMR spectroscopy. The relative integration for [HNi(TMEPE)_2][BF_4] (1) and [Ni(TMEPE)_2][BF_4] (2) were compared to an internal capillary reference containing 0.5 M H_3PO_4 in D_2O (eqn (4)). To ensure that equilibrium was achieved, K_{eq} was measured when the relative amounts of 1 to 2 remained constant for 3 days.

Hydricity values for 1 in non-aqueous and aqueous solvents are listed in Table 1 and shown in Scheme 3. In CH_3CN, the base Et_3N (pK_a of [HNEt_3]^+ = 18)13 was used to establish an equilibrium between 1 and 2. Coordination of NEt_3 to 2 was not observed. The relative 31P{1H} NMR integrations at equilibrium resulted in a hydricity of 1 for 50.6 kcal mol⁻¹ in CH_3CN. The hydricity of 1 in DMSO was determined using 1,8-diazabicyclocoundec-7-ene (DBU) as a base [pK_a of [HDBU]^+] = 12.14 Again, no coordination of DBU was observed. The reaction reached equilibrium after 6 days, and the measured K_{eq} resulted in a hydricity of 47.1 kcal mol⁻¹. In water, H_2 heterolysis was conducted in phosphate buffered solutions at pH 7, 7.5, and 8 with no added base. Equilibrium was achieved at pH 8 after 15 days and leads to a ΔG_H2 (1) of 22.8 kcal mol⁻¹ (see ESI† for more details on hydricity measurements).

Hydride donor strength increases with increasing solvent polarity, as shown in Table 1 and Scheme 3. By comparing the relative hydricities of 1 (22.8 kcal mol⁻¹) to formate (24.1 kcal mol⁻¹), we note that the free energy of hydride transfer to CO₂ is still endergonic in organic solvents, but is now exergonic by 1.2 kcal mol⁻¹ in water.

We experimentally validated our measurements by examining the oxidation of lithium formate by 2. There is clean hydride formation in basic solution, as shown in Scheme 3. By comparing the relative hydricities of 1 (22.8 kcal mol⁻¹) to formate (24.1 kcal mol⁻¹), we note that the free energy of hydride transfer to CO₂ is still endergonic in organic solvents, but is now exergonic by 1.2 kcal mol⁻¹ in water.

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Notes and references


