ORGANOMETALLICS

Effects of Phosphine–Carbene Substitutions on the Electrochemical and Thermodynamic Properties of Nickel Complexes

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Supporting Information

ABSTRACT: Nickel(II) complexes containing chelating Nheterocyclic carbene—phosphine ligands ($[NiL_2](BPh_4)_2$, for which L = $[MeIm(CH_2)_2PR_2]$, MeIm = 1-methylimidizolylidene, and R = Ph or Et) have been synthesized for the purpose of studying how this class of ligand affects the electrochemical and thermodynamic properties compared to the nickel bisdiphosphine analogues. The nickel complexes were synthesized and then characterized by X-ray crystallography, electrochemical methods, and thermodynamic studies, including DFT calculations. On the basis of the reduction potentials



 (E°) , substitution of an NHC for one of the phosphines in a diphoshine ligand resulted in negative shifts in potential by 0.6 to 1.2 V relative to the corresponding nickel bis-diphosphine complexes. From computational studies of the nickel hydride complex of the phenyl-substituted phosphine—carbene ligand, the hydride donor ability was determined to improve by 32 kcal/mol relative to the estimated hydride donor ability for the analogous nickel complex of the chelating diphosphine ligand 1,3-bis(diphenylphosphino)propane. The free energy for addition of H₂ is presented, and the implications for catalysis are discussed. These quantitative results highlight the substantial effect that NHC ligands can have on the electronic properties of the metal complexes.

■ INTRODUCTION

The application of N-heterocyclic carbenes (NHCs) in organometallic and coordination chemistry has undergone a renaissance¹ since the isolation of the first stable, "free" carbene by Arduengo in 1991,² despite metal NHC complexes being known since the late 1960s.^{3,4} Due to their strong σ -donating properties, NHCs typically form stronger bonds to transition metal centers than the corresponding tertiary phosphine analogues, resulting in more robust complexes, which are less prone to decomposition via ligand dissociation.^{5–7} As such, ongoing research has been dedicated to the modification of the NHC ligands and quantifying the *electronic* properties imparted by NHCs to transition metal complexes.^{1,5,7–11}

Numerous studies, both experimental and theoretical, have been reported for the use of techniques to quantify the electron-donating ability of various NHC–transition metal complexes.^{6,8,9,11–13} The most common method is observing the ν (CO) of various [Ni(CO)₃(NHC)] and [MCl(CO)-(NHC)] (M = Ir or Rh) by IR spectroscopy, as reported by Nolan,^{7,11} Crabtree,¹⁴ and others.^{6,15,16} Direct measurement of the redox potentials using electrochemical methods, though reported, has been underutilized in determining the electrondonating ability of NHCs to transition metal centers. Roberts et al. have recently shown that replacement of a PMe₃ with IMes (1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) in CpW-(CO₂)₂(L)H shifts the W^{•/-} couple more negative, from -1.12 V to -1.65 V versus ferrocene, resulting in a lower BDFE of the W–H bond and increase in the pK_a(MH) of the hydride.¹⁷ Several studies of ruthenium–NHC complexes have also been reported.¹⁸ Demonceau et al. correlated the reduction potentials of $\operatorname{RuCl}_2(p$ -cymene)(NHC) complexes to the efficacy for atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA).¹⁹ Electrochemical studies performed by Xie et al. show that the potentials of the Ru(III/II) couple for bridged carboranyl–cyclopentadienyl ruthenium complexes are more negative when NHCs are employed as ancillary ligands then when compared to traditional nitrogen and phosphorus donors.²⁰ Finally, Plenio reported redox couples for a variety of NHC-modified secondgeneration Grubbs and Hoveyda–Blechert metathesis catalysts.^{21,22}

In more recent publications, there has been an effort in synthesizing and studying mixed ligand systems, ligands that contain both NHC and heteroatom donor functionalities, particularly phosphine.^{23–36} One of the goals of our research is developing an understanding of how to control thermochemical properties of metal complexes through ligand variation, and therefore the thermochemical effect of substitution of a diphosphine ligand with a mixed ligand containing an NHC is of great interest. In particular, nickel hydride complexes of diphosphine ligands are insufficiently hydridic^{37,38} to convert CO_2 to formate,^{39–41} unlike the cobalt analogues.⁴² The replacement of phosphines with NHC donors (Scheme 1) is

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Scheme 1. Nickel Complexes of Diphosphine Ligands and Newly Prepared Analogues Containing NHC Donors.



expected to improve the hydride donor abilities of metal complexes,¹⁷ but the extent to which the hydride donor abilities of Ni–H complexes can be improved relative to nickel bisdisphosphine complexes has not been previously determined.

We report the synthesis and characterization of two new nickel(II) complexes with chelating ligands that contain both a phosphine and an NHC. Electrochemical studies of these complexes have been used to measure the effect of substitution of diphosphine ligands with the chelating phosphine–carbene ligands. To explain the reactivity of these new complexes, DFT studies have been used to quantify the heterolytic and homolytic bond strengths for one of the hydride complexes, as well as free energy for H_2 addition to the corresponding Ni(II) complex.

RESULTS

Synthesis of Ligand Precursors and Ni(II) Complexes. The ligand precursors $[MeIm(CH_2)_2PR_2](BPh_4)$ were prepared in good yield using a slightly modified literature procedure previously reported by Field et al.²⁴ Alkylation of 1-methylimidizole with the appropriate dihaloalkane yielded the desired 3-(2-bromoethyl)-1-methylimidazolium and 3-(2-chloroethyl)-1-methylimidazolium salts (Scheme 2). Substitution of

Scheme 2. Synthesis of Phosphine-Carbene Ligand Precursors.



the 3-(2-bromoethyl)-1-methylimidazolium bromide with lithium diphenylphosphide in THF at room temperature followed by anion exchange with sodium tetraphenylborate (NaBPh₄) gave the carbene precursor $HL^{Ph}(BPh_4)$.

When 3-(2-bromoethyl)-1-methylimidazolium bromide was treated with LiPEt₂, a significant amount of 1-methyl-3-vinylimidazolium was observed as a major byproduct via an elimination pathway. To avoid this elimination pathway, the chloro-substituted equivalent was used (structure shown in Figure S1). The treatment of 3-(2-chloroethyl)-1-methylimidazolium bromide with LiPEt₂ followed by anion exchange with NaBPh₄ resulted in the clean isolation of the desired substitution product HL^{Et}(BPh₄).

Synthesis and Characterization of Ni(II) Complexes $[NiL_2^R](BPh_4)_2$. The metalation of the $HL^R(BPh_4)$ ligands was performed using a one-pot procedure analogous to that reported by Lee et al.,²⁷ as shown in Scheme 3. A 2:1:2





molar ratio of $HL^{Ph}(BPh_4)$ or $HL^{Et}(BPh_4)$, $NiCl_2 \cdot 6H_2O$, and $NaOAc \cdot 2H_2O$ was combined in DMSO and heated to 70 °C for 3 h. Removal of the DMSO by distillation followed by washing the residue with distilled water and methanol afforded pure $[NiL_2^R](BPh_4)_2$ as pale yellow, air stable solids.

The ¹H and ³¹P{¹H} NMR spectra of [NiL^{Ph}₂]²⁺ and $[NiL_{2}^{Et}]^{2+}$ are typical of diamagnetic, low-spin, Ni(II) complexes. Diastereotopic proton resonances corresponding to the ethylene bridge are observed as multiplets with ranges of 4.2–4.8 ppm for the methylene adjacent to the C_3 -nitrogen of the imidizolylidene and 1.9-2.2 ppm for the methylene adjacent to the phosphorus atom. The ethylene bridging protons for $[NiL_{2}^{ph}]^{2+}$ are shifted further downfield compared to $[NiL^{Et}_{2}]^{2+}$, consistent with the more electron-withdrawing nature of the phosphine substituent. Each complex exhibits a single resonance in the ${}^{31}P{}^{1}H$ spectrum with values of 22.5 and 23.1 ppm for the Ph and Et complexes, respectively. The observation of a singlet in the ${}^{31}P{}^{1}H{}$ NMR spectrum of each complex suggests that only one of the two possible isomers is formed, specifically that the phosphorus atoms of both chelating ligands occupy sites either cis or trans to one another.

X-ray Diffraction Studies. Single crystals of $[NiL_{2}^{Ph}]_{2}$ (BPh₄)₂ suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether into a saturated solution of $[NiL_{2}^{Ph}](BPh_{4})_{2}$ in acetonitrile. X-ray quality crystals of $[NiL_{2}^{Et}](BPh_{4})_{2}$ were grown by slow cooling of a hot, saturated acetonitrile solution of $[NiL_{2}^{Et}](BPh_{4})_{2}$ to room temperature. The corresponding structures are shown in Figures 1 and 2, along with selected bond distances and angles.

Both structures show a slightly distorted square planar geometry around the nickel(II) center. In each complex, ligands



Figure 1. Thermal ellipsoid plot of the crystal structure of $[NiL^{Ph}_2](BPh_4)_2$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and the $(BPh_4)^-$ anions are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ni1–P1 2.1935(5), Ni1–P2 2.2019(5), Ni1–C15 1.9038(19), Ni–C33 1.9035(19); P1–Ni1–P2 168.43(3), C15–Ni1–P1 86.95(6), C15–Ni1–P2 98.27(6), C33–Ni1–P1 93.61(6), C33–Ni1–P2 80.66(6), C33–Ni1–C15 176.99(8).



Figure 2. Thermal ellipsoid plot of the crystal structure of $[NiL_{2}^{Et}](BPh_{4})_{2}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and the $(BPh_{4})^{-}$ anions are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ni1–P1 2.1988(9), Ni1–P2 2.1931(9), Ni1–C1 1.872(3), Ni1–C11 1.889(3); P2–Ni1–P1 164.74(4), C1–Ni1–P1 84.61(10), C1–Ni1–P2 93.36(9), C1–Ni1–C11 178.48(13), C11–Ni1–P1 95.95(9), C11–Ni1–P2 86.48(9).

derived from $\text{HL}^{\text{Ph}}(\text{BPh}_4)$ and $\text{HL}^{\text{Et}}(\text{BPh}_4)$ are coordinated to nickel(II) by the phosphorus and carbene donor atoms, where like donors are oriented *trans* to one another, consistent with the observation of a single isomer in the ${}^{31}\text{P}\{{}^{1}\text{H}\}$ NMR spectra. Deviations from an ideal square planar geometry occur along the P–Ni–P bond angle. In complex $[\text{NiL}^{\text{Ph}}_2]^{2+}$, the P1–Ni1– P2 angle is 168.43(3)°, and in $[\text{NiL}^{\text{Et}}_2]^{2+}$ the P1–Ni1–P2 angle is 164.74(4)°. Similar deviations have been observed in analogous nickel complexes.²⁷

Electrochemical Studies. Cyclic voltammograms were obtained for both $[NiL_2^R]^{2+}$ complexes in acetonitrile and are shown in Figure 3. Both of the complexes $[NiL^{Ph}_2]^{2+}$ and $[NiL^{Et}_2]^{2+}$ display two distinct and reversible reduction waves assigned to the Ni(II/I) and Ni(I/0) couples with peak-to-peak separations, ΔE_p , ranging from 60 to 70 mV, consistent with the ΔE_p value for the ferrocenium/ferrocene couple (66 mV) under identical conditions, as shown in Table 1. The analogous ΔE_p values for the complexes and the internal reference suggest that the couples for the complexes are electrochemically reversible one-electron processes. A comparison of the Ni(II/I) and Ni(I/0) couples is contained in Table 1, for the new carbene-containing complexes as well as the analogous bis-diphosphine complexes. ^{40,41,43} Due to the strong electron-donating abilities of the NHC moiety, the Ni(II/I) and Ni(I/0) potentials have shifted to much more negative potentials.

Thermodynamic Studies. To evaluate the possible use of the $[NiL^{Ph}_2]^{2+}$ complexes for the catalytic hydrogenation of CO₂, the complexes were reacted with H₂ in the presences of a base to observe and quantify the generation of the hydride complex, $[HNiL^{Ph}_2]^+$. At one atmosphere of H₂ in the presence of 10 equivalents of triethylamine (pK_a of 18.8 in MeCN),⁴⁴ hydride formation was not observed. When using stronger bases, such as DBU (pK_a of 24.3 in MeCN),⁴⁴ the predominant observed reaction was the formation of unidentified paramagnetic species. This reactivity is distinct from that observed for nickel bis-diphosphine complexes, for which the reaction with H₂ and a base produces the nickel hydride complex and a protonated base.⁴¹

To understand this reactivity, DFT calculations were performed for nickel complexes of the phenyl-substituted



Potential (V vs Cp₂Fe^{+/0})

Figure 3. Cyclic voltammograms of $[NiL^{Ph}_2]^{2+}$ (top) and $[NiL^{Et}_2]^{2+}$ (bottom) in 0.2 M $[NBu_4](PF_6)$ supporting electrolyte in acetonitrile, glassy carbon working electrode, and scan rate of 50 mV/s. Potentials referenced with respect to the ferrocenium/ferrocene couple.

Table 1. Electrochemical Data for $[NiL_{2}^{Ph}]^{2+}$ and $[NiL_{2}^{Et}]^{2+}$, as Well as Literature Values for Related Complexes

complex	$E_{1/2}(\mathrm{II}/\mathrm{I})^a$	$E_{1/2}({\rm I}/{\rm 0})^a$
$[Ni(dppp)_2]^{2+b}$	-0.19 (-)	-0.91 (-)
$[Ni(depp)_2]^{2+b}$	-0.61 (74)	-1.34 (71)
$[NiL_{2}^{Ph}]^{2+}$	-1.38 (70)	-1.69 (65)
$[NiL_{2}^{Et}]^{2+}$	-1.62 (60)	-1.96 (65)

^{*a*}Values in parentheses are ΔE_p . Values in CH₃CN with potentials reported to the Cp₂Fe⁺⁷⁰ couple. ^{*b*}dppp is 1,3-bis-(diphenylphosphino)propane, and depp is 1,3-bis(diethylphosphino)-propane. Potentials reported by Berning et al.⁴⁰ and Curtis et al.⁴³

ligand \mathbf{L}^{Ph} using the methods previously reported for bisdiphosphine complexes of nickel.³⁸ An isodesmic reaction was constructed for hydride transfer from $[\text{HNiL}^{Ph}_2]^+$ to $[\text{Ni-}(\text{dmpp})_2]^{2+}$ (eq 1, where dmpp is 1,3-bis(dimethylphosphino)propane) using a computational protocol that has been shown to predict thermodynamic properties of $[\text{HNi}(\text{diphosphine})_2]^+$ complexes within 2 kcal mol⁻¹.³⁸ By combining the reaction free energy computed for eq 1 (-20.1 kcal/mol) and the experimentally measured $\Delta G^{\circ}_{H^-}$ of $[\text{HNi}(\text{dmpp})_2]^+$ (61.2 kcal mol⁻¹),⁴⁰ a $\Delta G_{\text{H}-}$ of 41.1 kcal mol⁻¹ was calculated for [HNiL^{Ph}₂]⁺.

$$[\text{HNi}\mathbf{L}^{\mathbf{Ph}}_{2}]^{+} + [\text{Ni}(\text{dmpp})_{2}]^{2+}$$

$$\approx [\text{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{2+} + [\text{HNi}(\text{dmpp})_{2}]^{+}$$
(1)

This computed hydride donor ability and the experimentally measured $E_{1/2}(II/I)$ and $E_{1/2}(I/0)$ values can be used in known thermochemical cycles^{45–49} to calculate the solution homolytic bond dissociation free energy ($\Delta G^{\circ}_{H^{\bullet}} = 46.9 \text{ kcal mol}^{-1}$) and the p K_a value (23.7) for [HNiL^{Ph}_2]⁺. The sum of eqs 2–4 is eq 5, which gives the homolytic bond dissociation free energy for [HNiL^{Ph}_2]⁺.

$$[\mathrm{HNi}\mathbf{L}^{\mathbf{Ph}}_{2}]^{+} \rightleftharpoons [\mathrm{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{2+} + \mathrm{H}^{-} + 41.1 \text{ kcal/mol}$$
(2)

$$[\operatorname{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{2+} + e^{-} \rightleftharpoons [\operatorname{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{+}$$
$$-1.38 \text{ V} (+31.8 \text{ kcal/mol})$$
(3)

$$H^{-} \rightleftharpoons H^{\bullet} + e^{-} -26.0 \text{ kcal/mol}$$
(4)

$$[\text{HNiL}^{\text{Ph}}_{2}]^{+} \rightleftharpoons [\text{NiL}^{\text{Ph}}_{2}]^{+} + \text{H}^{\bullet} + 46.9 \text{ kcal/mol}$$
(5)

Similarly, the sum of eqs 6–9 is eq 10, which gives the pK_a value for $[HNiL^{Ph}_2]^+$.

$$\left[\mathrm{HNiL}^{\mathrm{Ph}}_{2}\right]^{+} \rightleftharpoons \left[\mathrm{NiL}^{\mathrm{Ph}}_{2}\right]^{2+} + \mathrm{H}^{-} + 41.1 \text{ kcal/mol} \qquad (6)$$

$$[\operatorname{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{2+} + e^{-} \rightleftharpoons [\operatorname{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{+}$$
$$-1.38 \text{ V} (+31.8 \text{ kcal/mol})$$
(7)

 $[\operatorname{NiL}^{\operatorname{Ph}}_{2}]^{+} + e^{-} \rightleftharpoons \operatorname{NiL}^{\operatorname{Ph}}_{2} -1.69 \operatorname{V}(+39.0 \operatorname{kcal/mol})$ (8)

$$H^{-} \rightleftharpoons H^{+} + 2e^{-} -79.6 \text{ kcal/mol}$$
(9)

$$[\mathrm{HNiL}^{\mathrm{Ph}}_{2}]^{+} \rightleftharpoons \mathrm{NiL}^{\mathrm{Ph}}_{2} + \mathrm{H}^{+} \quad 23.7 \ (+32.3 \ \mathrm{kcal/mol})$$
(10)

An isodesmic reaction was also constructed for proton transfer from $[\text{HNiL}^{\text{Ph}}_2]^+$ to Ni(dmpp)₂ (eq 2) as a secondary check on the computed bond energies. A pK_a value of 23.1 was calculated for $[\text{HNiL}^{\text{Ph}}_2]^+$ by combining the reaction free energy computed for eq 11 (-1.11 kcal mol⁻¹) and the experimentally measured pK_a of $[\text{HNi}(\text{dmpp})_2]^+$ (23.9).⁴⁰ The pK_a values of $[\text{HNiL}^{\text{Ph}}_2]^+$ obtained by direct computation and by thermochemical cycles employing the computed $\Delta G_{\text{H-}}$ value differed by only 0.6 pK_a units (0.8 kcal mol⁻¹), which is consistent with the previously observed accuracy of this computational protocol.³⁸

$$[\text{HNiL}^{\mathbf{Ph}}_{\mathbf{2}}]^{+} + \text{Ni}(\text{dmpp})_{2} \rightleftharpoons \text{NiL}^{\mathbf{Ph}}_{\mathbf{2}} + [\text{HNi}(\text{dmpp})_{2}]^{+}$$
(11)

A third isodesmic reaction was constructed for proton transfer from $[(H)_2\text{NiL}^{Ph}_2]^{2+}$, a formally Ni(IV) dihydride complex, to $[\text{HNi}(\text{dmpp})_2]^+$ (eq 12). Combination of the reaction free energy for eq 12 (7.7 kcal mol⁻¹) with the previously computed pK_a of $[(H)_2\text{Ni}(\text{dmpp})_2]^{2+}$ $(-0.8)^{38}$ affords a pK_a of 4.8 for $[(H)_2\text{NiL}^{Ph}_2]^{2+}$.

$$[(H)_{2}NiL^{Ph}{}_{2}]^{2+} + [HNi(dmpp)_{2}]^{+}$$

$$\approx [HNiL^{Ph}{}_{2}]^{+} + [(H)_{2}Ni(dmpp)_{2}]^{2+}$$
(12)

From the hydride donor ability of $[\text{HNiL}^{\text{Ph}}_2]^+$, the p K_a value for $[(\text{H})_2\text{NiL}^{\text{Ph}}_2]^{2+}$, and the free energy for heterolytic cleavage

of H_2 ,^{45,46} a thermochemical cycle can be used to determine the free energy for the addition of H_2 to $[NiL^{Ph}_2]^{2+}$, as shown through adding eqs 13–15 to give eq 16. The resulting value of +28.4 kcal/mol at one atmosphere of H_2 is consistent with the addition of H_2 being remarkably endergonic at any attainable pressure.

$$[\operatorname{Ni}\mathbf{L}^{\mathbf{Ph}}_{\mathbf{2}}]^{2+} + \mathrm{H}^{-} \rightleftharpoons [\operatorname{HNi}\mathbf{L}^{\mathbf{Ph}}_{\mathbf{2}}]^{+} -41.1 \text{ kcal/mol} \quad (13)$$

$$[\mathrm{HNi}\mathbf{L}^{\mathbf{Ph}}_{2}]^{+} + \mathrm{H}^{+} \rightleftharpoons [(\mathrm{H})_{2}\mathrm{Ni}\mathbf{L}^{\mathbf{Ph}}_{2}]^{2+}$$

$$4.8 (-6.5 \text{ kcal/mol}) \tag{14}$$

$$H_2 \rightleftharpoons H^+ + H^- \quad 76.0 \text{ kcal/mol} \tag{15}$$

$$[\text{NiL}^{\text{Ph}}_{2}]^{2+} + \text{H}_{2} \rightleftharpoons [(\text{H})_{2}\text{NiL}^{\text{Ph}}_{2}]^{2+} + 28.4 \text{ kcal/mol}$$
(16)

The hydride donor ability, homolytic bond dissociation free energy, pK_a values, electrochemical potentials, and the free energy for H_2 addition were combined into the thermochemical scheme shown in Scheme 4.

Scheme 4. Thermochemical Scheme for $[NiL_{2}^{Ph}]^{2+}$ and Related Complexes^{*a*}



^aValues in parentheses were determined computationally. Values in brackets were determined using thermochemical cycles.

DISCUSSION

Through the synthesis of $[NiL^{Ph}_2]^{2+}$ and $[NiL^{Et}_2]^{2+}$, a comparison of nickel complexes of different chelating ligands can be made, specifically for the purpose of quantifying the effect of NHC ligands relative to phosphine ligands. These two NHC-containing complexes both have a three-atom bridge between the donor atoms and are thereby analogous to $[Ni(dppp)_2]^{2+}$ and $[Ni(depp)_2]^{2+}$, respectively (where dppp is 1,3-bis(diphenylphosphino)propane and depp is 1,3-bis(diethylphosphino)propane; see Scheme 1). While the solid-state structures of $[Ni(dppp)_2]^{2+}$ and $[Ni(depp)_2]^{2+}$ have not been reported, the analogous structure for $[Ni(dmpp)_2]^{2+}$ has been reported, both with acetonitrile bound and in the absence of acetonitrile⁴⁰ (where dmpp is 1,3-bis(dimethylphosphino)-propane). Similar structures are observed for $[NiL^{Ph}_2]^{2+}$

 $[\operatorname{NiL}_{2}^{\operatorname{Et}}]^{2+}$, but acetonitrile is not observed to bind in either structure, even though the crystals for each were grown in the presence of acetonitrile. These results are consistent with a complex of more strongly σ -donating ligands, which may result in weaker binding of acetonitrile to the metal complexes.

The reduction potentials for the complexes containing NHCs were found to be substantially more negative than the diphosphine counterparts, as shown in Table 1. The Ni(II/I) couples were observed to be 1.2 and 1.0 V more negative for the complexes with phenyl substituents and ethyl substituents, respectively, at phosphorus. Similarly, the Ni(I/0) couples were observed to be 0.8 V more negative for the complexes with phenyl substituents and 0.6 V more negative for the complexes with ethyl substituents. The larger effect of the substitution on the Ni(II/I) couple than the Ni(I/0) couple may be the result of steric effects, as previously suggested for varying bis-diphosphine complexes of nickel.^{40,50} Consistent with this previous suggestion, steric effects appear to result in small differences in the structures of $[NiL^{Ph}_2]^{2+}$ and $[NiL^{Et}_2]^{2+}$. The Ni-C bond length is actually slightly shorter for the ethylsubstituted complex than for the phenyl-substituted complex, which is the reverse of the expected trend based on a purely electronic argument.

In addition to the effects on the redox potentials, the substitution of the phosphines for NHC ligands was expected to have a substantial influence on the bond dissociation free energies of the corresponding Ni-H complexes, especially for the heterolytic bond cleavage reactions. Due to a lack of reactivity of these complexes with H₂, DFT calculations were used in combination with experimental data to estimate the heterolytic and homolytic bond dissociation free energies, as shown in Scheme 4. These studies revealed that the incorporation of NHC donors led to a remarkable improvement in hydricity, with this heterolytic bond strength decreasing by \sim 32 kcal/mol relative to estimates for the analogous $[HNi(dppp)_2]^+$ complex. This increase in the ability of this complex to transfer a hydride was countered by a very unfavorable free energy for the addition of H_2 of +28.4 kcal/ mol at 1.0 atm. The extent to which this reaction is endergonic is consistent with an inability of this complex to perform hydrogenation reactions, as H₂ addition will not occur at an appreciable rate, even in the presence of a strong base.

Surprisingly, in addition to the influence of the NHC on the hydride donor ability and the free energy for H_2 addition, the homolytic bond dissociation free energy for $[HNiL^{Ph}_2]^+$ was estimated to be 47.1 kcal/mol, which is significantly lower than typical nickel hydrides with diphosphine ligands. The relatively weak homolytic bond dissociation free energy for the carbene-containing complex is expected to result in bimolecular homolytic loss of H_2 from two equivalents of $[HNiL^{Ph}_2]^+$ in solution. Given the inability to heterolytically cleave H_2 due to the large and unfavorable free energy for H_2 addition as well as the thermodynamic instability of $[HNiL^{Ph}_2]^+$ due to the weak homolytic bond dissociation free energy, these complexes are not expected to be effective catalysts for ionic hydrogenations, such as the conversion of CO₂ to formate.

SUMMARY AND CONCLUSIONS

To probe the effects of NHCs on the redox properties of nickel complexes, we synthesized and characterized nickel complexes of chelating phosphine—carbene ligands that have not previously been reported. The cyclic voltammetry data for these complexes show redox potentials that are shifted negative by 0.6-1.2 V relative to the analogous bis-diphosphine nickel complexes. These results indicate that through systematic functionalization, the thermochemical properties of nickel complexes of chelating ligands can be controlled to a remarkable extent, with a change of up to 1.4 V by exchanging one phosphine of each ligand for an NHC donor as well as the variation of the substituents at phosphorus. However, thermodynamic studies of these complexes suggest that, while the heterolytic bond strengths can be greatly influenced by incorporating NHC donors, the effects on the free energy for H₂ addition as well as the homolytic bond dissociation free energy will impede the use of these complexes as catalysts for hydrogenation reactions.

MATERIALS AND METHODS

General Experimental Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen. All reagents were purchased from commercial sources and used as received unless specified. Unless noted otherwise, solvents were purified by passage through neutral alumina using an Innovative Technology, Inc., PureSolv solvent purification system. The imidazolium precursor (3-(2-bromoethyl)-1-methylimidazolium bromide)²⁴ and lithium reagents LiPPh₂⁵¹ and LiPEt₂⁵² were synthesized according to literature procedures. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA, USA).

Instrumentation. All electrochemical experiments were performed under an atmosphere of nitrogen in a 0.2 M tetrabutylammonium hexafluorophosphate solution, [NBu4](PF6), in benzonitrile using a CH Instruments 600 or 1100 series three-electrode potentiostat. The working electrode was a glassy carbon disk (1 mm diameter), and the counter electrode was a glassy carbon rod. The pseudoreference electrode was a silver wire in electrolyte solution separated from the working compartment by a Vycor (4 mm, BAS) frit. All potentials were measured using Cp₂Fe (ferrocene, 0 V) as an internal reference, with all potentials reported vs the $Cp_2Fe^{+/0}$ couple. ¹H and ³¹P NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer. The ¹H spectra were referenced using residual solvent, and the ³¹P spectra with respect to an 85% H₃PO₄ external standard. Crystals of $[NiL_{2}^{Ph}](BPh_{4})_{2}$ and $[NiL_{2}^{Et}](BPh_{4})_{2}$ suitable for X-ray structural determinations were mounted in polybutene oil on a glass fiber and transferred on the goniometer head to the precooled instrument. Crystallographic measurements were carried out on a Bruker SMART CCD 1K area detector diffractometer using Mo Ka radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares procedures using SHELXL-97.53 All non-hydrogen atoms are anisotropically refined unless otherwise reported; the hydrogen atoms were included in calculated positions as riding models in the refinement. Crystallographic data collection and refinement information can be found in the Supporting Information.

Synthesis of [Melm(CH₂)₂PPh₂](BPh₄) (HL^{Ph}(BPh₄)). A slurry of [MeIm(CH₂)₂Br](Br) (402 mg, 1.5 mmol) in 10 mL of THF was treated dropwise with a yellow solution of LiPPh₂ (315 mg, 1.6 mmol) dissolved in 5 mL of THF. The resulting pale yellow solution was stirred for 20 min at room temperature, after which the solvent was removed by vacuum. The residue was dissolved in 20 mL of anhydrous ethanol, and a NaBPh₄ solution (513 mg, 1.5 mmol) in 10 mL of EtOH was added. A white precipitate immediately formed, and the slurry was stirred for 10 min, vacuum filtered, washed with EtOH (2 × 5 mL) and ether (2 × 10 mL), and then dried under vacuum to give the desired product (755 mg, 82%). Spectroscopic data were identical to those reported by Messerle²⁴ (see the Supporting Information). **Synthesis of [Melm(CH₂)₂CI](Br).** A mixture of 1-methylimida-

Synthesis of [Melm(CH₂)₂Cl](Br). A mixture of 1-methylimidazole (4.0 mL, 50 mmol) and 1-bromo-2-chloroethane (4.2 mL, 50 mmol) in 50 mL of THF was stirred at 60 °C under nitrogen for 48 h. The resulting white precipitate was vacuum filtered, washed with ether (2 × 10 mL), and dried under vacuum to give the desired compound (6.89 g, 62% yield). The product may be recrystallized from hot acetonitrile. ¹H NMR (DMSO- d_6 , 20 °C): δ (ppm) 9.12 (1H, s, N-CH=N), 7.82 (1H, s, C_{im}-H_{backbone}), 7.75 (1H, s, C_{im}-H_{backbone}), 4.56 (2H, t, J = 5.5 Hz, N-CH₂-CH₂-Cl), 4.08 (2H, t, J = 5.5 Hz, N-CH₂-CH₂-Cl), 3.89 (3H, s, N-CH₃). ¹³C{¹H}NMR (DMSO- d_6 , 20 °C): δ (ppm) 137.1 (s, N-CH=N), 123.6 (s, C_{im}=C_{im}), 122.4 (s, C_{im}=C_{im}), 50.2 (s, N-CH₂-CL), 43.2 (s, N-CH₂-CL), 31.96; H, 4.47; N, 12.42. Found C, 31.85; H, 4.52; N, 12.44.

Synthesis of [Melm(CH₂)₂CI](BPh₄). An aqueous solution of [MeIm(CH₂)₂Cl](Br) (1.03 g, 4.6 mmol) in 10 mL of degassed water was treated with 5 mL of aqueous NaBPh₄ (1.56 g, 4.6 mmol). The resulting white precipitate was stirred for 15 min, vacuum filtered, washed with degassed water (2 × 10 mL), methanol (2 × 5 mL), and ether (1 × 10 mL), and dried under vacuum to give the desired compound as a fluffy white solid (1.73 g, 80%). X-ray quality crystals were grown from vapor diffusion of ether into a saturated acetonitrile solution. ¹H NMR (DMSO-*d*₆, 20 °C): δ (ppm) 9.12 (1H, s, N-CH=N), 7.78 (1H, m, C_{im}-H_{backbone}), 7.71 (1H, m, C_{im}-H_{backbone}), 7.16 (8H, br s, B-Ph-H), 6.90 (8H, t, *J* = 7.5 Hz, B-Ph-H), 6.77 (4H, t, *J* = 7.0 Hz, B-Ph-H), 4.52 (2H, t, *J* = 5.5 Hz, N-CH₂-CH₂-Cl), 4.04 (2H, t, *J* = 5.0 Hz, N-CH₂-CH₂-Cl), 3.85 (3H, s, N-CH₃). ¹³C{¹H}NMR (DMSO-*d*₆, 20 °C): δ (ppm) 163.4 (q, *J*_{B-C} = 49.0 Hz, B-C_{Ph}), 123.7 (s, *C*_{im}=C_{im}), 132.5 (s, B-C_{Ph}), 123.5 (s, B-C_{Ph}), 50.3 (s, N-CH₂-CH₂-Cl), 43.1 (s, N-CH₂-CH₂-Cl), 3.88 (s, N-CH₃). **Synthesis of [Melm(CH₂)₂PEt₂](BPh₄) (HL^{Et}(BPh₄)).** A slurry of

[MeIm(CH₂)₂Cl](Br) (491 mg, 2.2 mmol) in 10 mL of THF was treated dropwise with a yellow solution of LiPEt₂ (419 mg, 2.2 mmol) dissolved in 10 mL of THF and stirred for 1 h. The solvent was then removed by vacuum, leaving a tacky, pale yellow solid that was dissolved in 10 mL of degassed, distilled water. This solution was treated with 10 mL of an aqueous solution of NaBPh₄ (752 mg, 2.2 mmol), which immediately formed a white precipitate. The precipitate was collected by vacuum filtration and dried under vacuum. The crude product was recrystallized by diffusion of diethyl ether into a saturated dichloromethane solution. The resulting fluffy white solid (909 mg) was isolated by vacuum filtration and washed with diethyl ether (2×5) mL). A second crop of product was obtained (174 mg) from the filtrate to give a total of 1.08 g (98%) of purified product. ¹H NMR (DMSO-d₆): δ 9.08 (1H, s, N-CH=N), 7.77 (1H, s, C_{im}-H_{backbone}), 7.64 (1H, s, C_{im}-H_{backbone}), 7.16 (8H, br s, B-Ph-H), 6.91 (8H, t, J = 7.3 Hz, B-Ph-H), 6.77 (4H, t, J = 7.1 Hz, B-Ph-H), 4.23 (2H, m, N-CH2-CH2-P), 3.80 (3H, s, N-CH2), 1.96-1.86 (2H, m, N-CH2-CH2-P), 1.42 (4H, q, J = 7.5 Hz, P-CH₂-CH₃), 0.99 (6H, m, P-CH₂-CH₃). ³¹P{¹H}NMR (DMSO- d_{6} 20 °C): δ (ppm) –28.4 (s). ¹³C{¹H}NMR (DMSO- $d_{6\prime}$ 20 °C): δ (ppm) 163.3 (q, J_{B-C} = 49.4 Hz, B- C_{Ph}), 136.3 (s, N-CH=N), 135.5 (s, B-C_{Ph}), 125.3 (q, J_{B-C} = 2.9 Hz, B-C_{Ph}), 123.5 (s, $C_{im} = C_{im}$), 122.2 (s, $C_{im} = C_{im}$), 121.5 (s, B- C_{Ph}), 46.5 (d, J = 22.4Hz, N-CH₂-CH₂-P), 35.7 (s, N-CH₃), 26.3 (d, J = 17.3 Hz, N-CH₂-CH₂-P), 17.6 (d, J = 11.6 Hz, P-CH₂-CH₃), 9.8 (d, J = 12.5 Hz, P-CH₂-CH₃). Anal. Calcd for C₃₄H₄₀BN₂P: C, 78.76; H, 7.78; N, 5.40. Found: C, 79.01; H, 7.76; N, 5.39.

General Synthesis of [NiLPh2](BPh4). A mixture of [MeIm- $(CH_2)_2PPh_2)(BPh_4)(HL^{Ph})$ (627 mg, 1.02 mmol), NiCl₂·6H₂O (121 mg, 0.51 mmol), NaOAc·2H₂O (138 mg, 1.02 mmol), and 5 mL of DMSO was heated in a Schlenk flask at 70 °C for 2.5 h. The solution began as pale green but became yellow at the end of the reaction time. The solvent was distilled under vacuum at 70 °C to give a thick yellow paste. The residue was washed with 25 mL of distilled water in air, vacuum filtered, washed with distilled water $(2 \times 10 \text{ mL})$, methanol (2 \times 10 mL), and ether (1 \times 10 mL), and then dried under vacuum to give the product as a pale yellow powder (511 mg, 78%). ¹H NMR (CD₃CN, 20 °C): δ (ppm) 7.84 (4H, m, P-Ph-H), 7.69-7.60 (6H, m, P-Ph-H), 7.42 (4H, m, P-Ph-H), 7.31-7.24 (20H, m, P-Ph-H and B-Ph-H), 7.01 (16H, t, J = 7.4 Hz, B-Ph-H), 6.94 (6H, m, B-Ph-H and C_{im} - $H_{backbone}$), 6.86 (8H, tt, J = 7.4 Hz, 1.4 Hz, B-Ph-H), 6.40 (2H, J = 1.8 Hz, C_{im}-H_{backbone}), 4.89 (2H, m, N-CH₂-CH₂-P), 4.68 (2H, m, N-CH2-CH2-P), 3.26 (6H, s, N-CH3), 3.06-2.93 (4H, m, N-CH2-CH2-P). ³¹P{¹H}NMR (CD₃CN, 20 °C): δ (ppm) 22.5 (s). Anal. Calcd for

 $C_{84}H_{78}B_2N_4NiP_2:$ C, 78.46; H, 6.11; N, 4.49. Found: C, 78.33; H, 6.28; N, 4.49.

[NiL^{ft}₂](**BPh**₄)₂. A similar procedure to that above was followed to yield a bright yellow powder in 66% yield. ¹H NMR (CD₃CN, 20 °C): δ (ppm) 7.31 (18H, m, Ci_m-H_{backbone} and B-Ph-H), 7.22 (2H, d, J = 1.8 Hz, C_{im}-H_{backbone}), 7.02 (16H, t, J = 7.4 Hz, B-Ph-H), 6.87 (8H, t, J = 7.2 Hz, B-Ph-H), 4.46 (2H, m, N-CH₂-CH₂-P-), 4.21 (2H, m, N-CH₂-CH₂-P), 2.21 (2H, m, N-CH₂-CH₂-P), 2.15 (6H, s, N-CH₃), 1.91 (2H, m, N-CH₂-CH₂-P), 1.59–1.27 (8H, m, P-CH₂-CH₃), 0.82–0.75 (12H, m, P-CH₂-CH₃). ³¹P{¹H}NMR (CD₃CN, 20 °C): δ (ppm) 23.1 (s). Anal. Calcd for C₆₈H₇₈B₂N₄NiP₂: C, 74.68; H, 7.19; N, 5.12. Found: C, 74.25; H, 7.19; N, 5.19.

General Procedure for the Heterolytic Cleavage of H_2 Using $[NiL^{Ph}_2]^{2+}$. A J. Young NMR tube containing a solution of $[NiL^{Ph}_2](BPh_4)_2$ (16.3 mg, 0.0127 mmol) and triethylamine (12.8 mg, 17.6 uL, 0.127 mmol) in 0.5 mL of CD₃CN was degassed and backfilled with one atmosphere of hydrogen gas. The reaction was monitored over several days using ¹H and ³¹P NMR spectroscopy; however no $[HNiL^{Ph}_2]^+$ was observed during this time or even after several months. A similar reaction was carried out using DBU as a base but led to observation of unidentified paramagnetic products and a limited amount of a hydride (<5%). Decomposition was observed with stronger phosphine bases such as Verkade's base.

COMPUTATIONAL DETAILS

All structures were optimized without symmetry constraints using the B3P86 functional.^{54,55} The Stuttgart basis set with effective core potential (ECP)⁵⁶ was used for the Ni atom, whereas the 6-31G* basis set^{57,58} was used for all other atoms with one additional p polarization funtion $[\xi(p) = 1.1]$ for the hydride atoms. Each structure was confirmed by a frequency calculation at the same level of theory to be a real local minimum on the potential energy surface without an imaginary frequency. For each optimized geometry, harmonic vibrational frequencies were calculated to obtain the zero-point energy (ZPE) and thermal contributions (298 K and 1 atm) to the gas-phase free energy. Solvation free energies in acetonitrile were calculated by using the polarizabile continuum model (C-PCM)^{59,60} using Bondi⁶¹ atomic radii. Several conformations of $[HNiL^{Ph}_{2}]^{+}$ and $[(H)_{2}NiL^{Ph}_{2}]^{2+}$ were generated as a starting structure for geometry optimization, and the lowest energy conformer was used in the isodesmic calculations. The computed half-reaction free energies for hydride and proton transfer from $[HNi(dmpp)_2]^+$ were previously reported,³⁸ and the half-reaction free energy for proton transfer from $[(H)_2Ni(dmpp)_2]^+$ is given in the Supporting Information. All of the calculations were carried out with the program Gaussian 09.62

ASSOCIATED CONTENT

S Supporting Information

Crystallographic cif files, a text file of all computed molecule Cartesian coordinates in a format for convenient visualization, thermal ellipsoid plot of the crystal structure of 3-(2-chloroethyl)-1-methylimidazolium tetraphenylborate, a table of computed energies, and spectroscopic data for HL^{Ph}(BPh₄). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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