Solvent dependent C–H Bond Strength in a Nickel Pincer Complex

Felix Schneck,[a] Markus Finger,[a] Inke Siewert,[a] and Sven Schneider*[a]

Metal coordination can substantially weaken the bond strength of X–H bonds in coordinated ligands. Despite the importance for redox catalysis, this phenomenon is surprisingly scarcely examined for C–H bonds of organometallic compounds. We here report a nickel(l) pincer complex with a remote methylene group in the ligand backbone that exhibits an unusually solvent dependent C–H bond dissociation free energy (BDFE_{C–H}). Structural and thermochemical characterization in MeCN and THF indicates that the BDFE_{C–H} strongly depends on solvent binding to the metal within the Ni^{II}/Ni^{I} redox couple.

Introduction

Proton-coupled-electron transfer (PCET) is of pivotal importance in biological redox reactions, (electro-)chemical energy conversion, and organic transformations.[1] For example, the thermochemical coupling of proton and electron transfer can be utilized to facilitate and control X–H bond activation by coordination of redox active metal ions.[2] Several methods for experimental determination of bond dissociation free energies (BDFEs) of H+/e− donor and acceptor sites are known. Besides calorimetry,[3] the most common approach for experimental BDFE determination of X–H bonds is the potential-pK_a method introduced by Bordwell et al. and later refined by Tilset and Parker (Scheme 1).[4] The BDFE_{X–H} is determined via an isodesmic Hess cycle from pK_a and reduction potentials vs. the reduction potential of H^+/H^+ in the respective solvent.[4] The conceptual importance to redox catalysis led to a large number of BDFEs of organometallic compounds were reported despite the relevance for catalysis.[5]

Bordwell et al. showed that π-bonding of M(CO)_3[6] fragments to fluorene has little effect on the BDFE_{C–H} of the benzylic methylene group (Figure 1).[6] This can be rationalized as a result of two opposing effects: On one hand, the C–H pK_a value decreases upon coordination of Cr(CO)_3 (|ΔpK_a| = 4.4) or Mn(CO)_3[7] (|ΔpK_a| = 16.9), respectively. At the same time, this is compensated by large positive shifts of the oxidation potentials of the conjugate bases. Notably, as judged from comparison

Scheme 1. Thermochemical cycle for the determination of BDFE_{X–H} in metal complexes in solution (C_G = E^0(H^+ / H)^+).[6]

Figure 1. Experimental and computational (in brackets) C–H BDFEs of metalorganic compounds in kcal mol$^{-1}$.[6] Bond Dissociation Enthalpy (BDE).[6]
partially compensated by the $p_K$ shift of metal binding to hexamethylbenzene. Bruno examined a Niobium methoxide complex (Figure 1) with a BDE$_{C-H}$ that is about 22 kcal mol$^{-1}$ compared with free methanol, which was attributed to the $\eta_2$ coordination of formaldehyde in the PCET product.\textsuperscript{[46]} Chirik and co-workers computationally determined the bond dissociation energy for a series of Co complexes with a PNP pincer ligand (Figure 1).\textsuperscript{[20]} The low BDE$_{C-H}$ that are reduced by 30–35 kcal mol$^{-1}$ with respect to the free ligand were attributed to the facile, metal centred oxidation of the Co compounds. More recently, the same group reported unusually large C–H bond weakening for the $\beta$-H of a molybdenum ethyl complex.\textsuperscript{[46]}
Overall, the limited amount of data suggests that the weakening of C–H bonds even in remote ligand positions can be controlled by the separation of $\text{H}^+$ and $\text{e}^-$ donation from the ligand and metal, respectively.

We have recently examined the bond strength of the methylene group in the backbone of nickel(II) pincer complex [NiBr(PNP)]$^{-}$ (PNP = N(CH$_3$)$_2$P(Bu)$_2$) (Figure 1).\textsuperscript{[13]} The relatively high BDE$_{C-H}$ (76.3 kcal mol$^{-1}$) is in line with a predominantly ligand centered redox event, which is supported by X-ray absorption spectroscopy and DFT. We here extend our efforts to examine ligand centered C–H PCET reactions by expansion to the Ni$^2$/Ni$^0$ redox couple. Thermochemical characterization of [Ni(L)(PNP)]$^{-}$ (L = MeCN, none) indicates a distinct dependence of the remote backbone BDE$_{C-H}$ on L, which is mainly attributed to stabilization of [Ni(L)(PNP)]$^{-}$ (PNP = N(CH$_2$CH$_2$P(Bu)$_2$)). In consequence, the methylene BDE$_{C-H}$ exhibits an unusually large solvent dependence in MeCN vs. THF.

### Experimental Section

**Synthetic and Analytical Details.** All experiments were performed under inert conditions using standard Schlenk and box techniques (argon atmosphere). Dichloromethane, n-pentane, and THF were purchased in HPLC quality (Sigma Aldrich) and dried using a MBraun Solvent Purification System. Acetonitrile (Sigma Aldrich) was degassed and used without further purification. Deuterated solvents were obtained from Deutero GmbH. THF-d$_8$ was dried over CaH$_2$ and stored over molecular sieves (3 Å). [(Et$_2$O)H]BF$_4$ was purchased from Deutero GmbH, NaBF$_4$ (n-hex)NiBr, Cp$_3$Co, Cp$_2$FeP$_2$F$_2$ and NaBAR$_4$ (BAR$_4$ = B(C$_6$H$_5$)$_3$: 3.5-(CF$_3$)$_2$) were purchased from Sigma Aldrich and used without further purification. 2,4,6-tris(tert-butyl)phenoxyl, [(Et$_2$O)H]BAR$_4$, [NiBr(NiCH$_2$CH$_2$P(Bu)$_2$)]$_2$, and [Ni(PNP)] were prepared according to previously published procedures.\textsuperscript{[10,21]} NMR spectra were recorded on Bruker Avance III 300, Avance III 400 or Avance 500 spectrometer with a Prodigy broadband cryoprobe. Spectra were calibrated to the residual solvent signals (CD$_2$Cl$_2$: $\delta_C = 5.32$ ppm, $\delta_H = 54.0$ ppm; THF-d$_8$: $\delta_C = 3.58$ ppm, $\delta_H = 67.21$ ppm; MeCN-d$_3$: $\delta_C = 1.94$ ppm, $\delta_H = 1.32$ ppm).\textsuperscript{[20]} NMR data was referenced externally to phosphoric acid ($\delta = 0.0$ ppm). The following abbreviations were used for signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), vt (virtual triplet). LFID (Linden CMS) mass spectra were measured by the Zentrale Massenabteilung, Fakultät für Chemie, Georg-August-Universität. Elemental analyses were obtained from the Analytisches Labor, Georg-August-Universität using an Elementar Vario EL 3 analyzer. IR spectra were obtained as KBr pellets on a Thermo Science Nicolet iZ10, or as powder on a Bruker ALPHA FT-IR spectrometer with Platinum ATR module. UV/Vis spectra were obtained on an Agilent Cary 300 spectrometer. Gas phase analysis was performed by a Shimadzu GC-2014 equipped with a TCD detector and a molecular sieve 5 Å, 80/100 column. Cyclic voltammetry was performed in an argon filled glovebox (WE: glassy carbon, CE: Pt wire, RE: Ag wire). EPR spectra were measured using a Bruker ELEXSYS E500 spectrometer, equipped with the digital temperature control system ER 4131VT using nitrogen as coolant. All spectra at 150 K were recorded at about 9.4 GHz microwave frequency and 4 G field modulation amplitude, 100 kHz field modulation frequency, and around 10 mW microwave power. Simulation of EPR spectra was performed using the Easyspin software package.\textsuperscript{[12]}

**Crystallographic Details.** Suitable single crystals for X-ray structure determination were selected from the mother liquor under an inert gas atmosphere and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream on the diffractometer. The diffraction data were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-K$_\alpha$, radiation, $\lambda = 0.71073$ Å). The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structure was solved and refined using the Bruker SHELX 2014 software package.\textsuperscript{[14]} All non-hydrogen atoms were refined with anisotropic displacement parameters. All C–H hydrogen atoms were refined isotropically on calculated positions by using a riding model with their Us$_{iso}$ values constrained to 1.5 Us$_{iso}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other atoms.

**Computational Details.** Structure and energy calculations were performed within the ORCA 4.1.1 program suite.\textsuperscript{[15]} The optimization of the molecular structures was carried out using the PBE0 functional, Grimme’s dispersion correction with Becke-Johnson damping (D3(BJ))\textsuperscript{[16]} and the resolution of identity (RI)\textsuperscript{[17]} approximation to minimize computational costs. Ahlrichs’ revised de2-SVP all electron basis set and the corresponding auxiliary basis set were used for all elements.\textsuperscript{[18]} Tight convergence criteria in the SCF procedure and structure optimization and a fine integration grid (Grid5) were applied and the optimized (gas phase) structures were defined as minima by analytical vibrational analyses. The electronic energies were evaluated by single point calculations applying the PBEO\textsuperscript{[19]} functional, Ahlrichs’ de2-TZVP basis set and Truhlar’s SMD solvation model (THF and CH$_3$CN).\textsuperscript{[20]} Finally, thermodynamic data were computed by applying Grimme’s quasi-RHOO approach.\textsuperscript{[21]} All free energies were further corrected for standard solution conditions (1 mol L$^{-1}$, 298.15 K) by adding 1.89 kcal mol$^{-1}$. In case of THF and CH$_3$CN, 3.38 and 3.64 kcal mol$^{-1}$ were added instead, accounting for their actual concentrations in the pure solvent. The free energy correction of H$^+$ was obtained from the translational and electronic partition function and corrected for standard solution conditions:

$$G(H^+) = -RT (lnq_{\text{trans}} + lnq_{\text{el}}) + 1.89 \text{ kcal mol}^{-1} = -4.78 \text{ kcal mol}^{-1}$$

Redox potentials were evaluated against the ferrocene/ferrocerium redox couple.\textsuperscript{[22]} EPR data was obtained\textsuperscript{[23]} with the ADF program\textsuperscript{[24]} employing the two-component ZORA formalism implemented in ADF.\textsuperscript{[25]} The PBEO hybrid functional and the TZP Slater type orbital basis set.\textsuperscript{[26]}

**Syntheses.** [Ni(NCMe)$_2$(PNP)]$X$ (1$^+$). $^{1}$H NMR, [NiBr(PNP)]$^+$ (50 mg, 0.10 mmol, 1.00 eq) and NaBAR$_4$ (89 mg, 0.10 mmol, 1.0 eq) are dissolved in 5 mL of acetonitrile and stirred at room temperature overnight. After evaporation of the solvent the violet residue is
dissolved in dichloromethane and filtered. The volume of the solution is reduced to 1 mL and the product is precipitated by addition of n-pentane. Decantation of the solvent and drying of the residue in vacuo gives the product as a violet powder. Yield: 114 mg (86%). Anal. Calcd. for C₉₀H₇₀BF₅N₅P₈ (1323.49): C, 49.01; H, 4.49; N, 2.12%. Found: C, 49.04 H, 4.27; N, 2.03%. 31P{1H} NMR (122 MHz, CDCl₃) δ = -93.3 ppm. 1H NMR (300 MHz, CDCl₃) δ = 7.73 (br, 8H, BArF'), 7.57 (br, 4H, BArF), 2.48 (Ar₂BCXX'C'B'A'B'C') ppm. \( \text{[Ni(NCMe)}(\text{PNN})\text{]}(\text{BArF})\) (23 mg, 0.023 mmol, 1.0 eq) are dissolved in 5 mL of dichloromethane. The solution is stirred for 30 min at room temperature and filtered. Evaporation of the solvent and washing with 2 x 1 mL of n-pentane, followed by drying in vacuo gives the product as a yellow solid. Yield: 43 mg (86%). Anal. Calcd. for C₉₀H₇₀BF₅N₅P₈ (2182.68): C, 47.32; H, 3.09; N, 1.28%. Found: C, 47.23 H, 3.00; N, 1.29%. 31P{1H} NMR (121 MHz, CDCl₃) δ = -87.0 (d, \( \text{J}_{2pF} = 216 \text{ Hz} \), 84.8 (d, \( \text{J}_{2pF} = 216 \text{ Hz} \) ppm). 1H NMR (300 MHz, CDCl₃) δ = 8.14 (dt, \( \text{J}_{2pF} = 25.8 \text{ Hz} \), \( \text{J}_{2pF} = 2.4 \text{ Hz} \), 1H, NCHCF), 7.73 (m, 16H, BArF), 7.57 - 7.46 (br, 8H, BArF), 2.08 (dd, \( \text{J}_{2pF} = 33.0 \text{ Hz} \), \( \text{J}_{2pF} = 6.0 \text{ Hz} \), 1H, NCH), 6.16 - 6.09 (dd, \( \text{J}_{2pF} = 3.7 \text{ Hz} \), \( \text{J}_{2pF} = 5.9 \text{ Hz} \), 1H, PCH), 3.32 (dd, \( \text{J}_{2pF} = 8.2 \text{ Hz} \), \( \text{J}_{2pF} = 2.4 \text{ Hz} \), 2H, PCH), 2.60 (t, \( \text{J}_{2pF} = 2.0 \text{ Hz} \), 3H, NCHCF), 1.48 (m, 18H, PCH), 1.58 (d, \( \text{J}_{2pF} = 2.7 \text{ Hz} \), 1H, NCHCF), 143.0 (s, NCHCF), 135.2 (br, BArF), 129.5 (q, \( \text{J}_{2pF} = 2.9 \text{ Hz} \), 2H, BArF), 125.0 (q, \( \text{J}_{2pF} = 272.5 \text{ Hz} \), BArF), 117.9 (p, \( \text{J}_{2pF} = 4.2 \text{ Hz} \), 6.19 (vt, \( \text{J}_{2pF} = 4.2 \text{ Hz} \), NCHCF), 36.5 (vt, \( \text{J}_{2pF} = 7.3 \text{ Hz} \), PCMe)), 29.2 (vt, \( \text{J}_{2pF} = 2.1 \text{ Hz} \), PCMe), 22.6 (vt, \( \text{J}_{2pF} = 11.1 \text{ Hz} \), PCH) ppm. MS (LIFDI, CH₂Cl₂): m/z = 419.2 (100%, [C₉₀H₇₀BF₅N₅P₈]⁺).
Synthesis and characterization of nickel(II) complexes. As a starting point to examine the thermochromic properties of the [Ni\(^{II}\)](L)(PNP)\(^{+}\)/[Ni\(^{II}\)](PNP)\(^{+}\) PCET couples, nickel(II) complexes of the type [Ni\(^{II}\)](L)(PNP)\(^{+}\) and [Ni\(^{II}\)](L)(PNP)\(^{+}\) were synthesized. The divinyl amide complex [Ni(\(\text{NCMe}\))(PNP)]BAr\(_4\)\(^{{2\text{BAF}}}\); BAr\(_4\)\(^{{2\text{BAF}}}\) = B(C\(_6\)H\(_5\)3,5-C\(_6\)F\(_3\))\(_{14}\) was obtained in two steps from the previously reported precursor [Ni\(\text{Br}(\text{Ni}(\text{NCMe})(\text{PNP}))\)BAr\(_4\)\(^{{2\text{BAF}}}\), which is isolated as a purple solid (\(\lambda_{\text{max}} = 93.4\) ppm). A triplet \(^{1}\)H NMR resonance at \(\delta(\text{CDCl}_{3}) = 2.20\) ppm is assigned to the acetonitrile ligand and shows weak coupling to phosphorus (\(J_{\text{PNP}} = 2.0\) Hz). MeCN coordination is further confirmed by IR spectroscopy (\(\nu(\text{KBr}) = 2360, 2340\) cm\(^{-1}\)).

Subsequent pincer oxidation with a slight excess of 2,4,6-tris(tert-butyl)phenoxyl (2,4,6-TTBP) at 50 °C affords the divinyl amide complex 2\(^{\text{BAF}}\) in 61% isolated yield. Backbone oxidation is evident from the olefinic resonances in the \(^{1}\)H NMR spectrum (\(\delta = 6.84, 4.18\) ppm) and MeCN coordination by IR spectroscopy (\(\nu(\text{KBr}) = 2361, 2338\) cm\(^{-1}\)). Anion exchange with NaBAr\(_4\) enabled crystallographic characterization as 2\(^{\text{BAF}}\) (Figure 2). The molecular structure reveals the acetonitrile coordination in the solid state, and the C–C bond distances in the ligand backbone (1.340(2) and 1.342(2) Å) confirm the dehydrogenation of the pincer framework. 2\(^{\text{BAF}}\) can be alternatively synthesized upon oxidation of the previously reported nickel(II) complex [Ni\(^{II}\)](PNP)] with [CP\(_3\)Fe]BAr\(_4\)\(^{+}\) in MeCN.\(^{[11]}\)

Next, pincer backbone protonation was carried out to install a proton for PCET reactivity. The vinylcyclic anions in β-position to nitrogen are often the basic sites of complexes with this ligand.\(^{[27,28]}\) A wide variation of \(pK_a\) values for the conjugate C–H acids of nickel(II) complexes was reported, as of [Ni\(^{II}\)](H\(^{+}\))\(^{[\text{PNP}]}\)^{+} (\(pK_a(\text{MeCN}) = 18.4\)) and [Ni\(^{II}\)](Br\(^{+}\))\(^{[\text{PNP}]}\)^{+} (\(pK_a(\text{MeCN}) = 0.9\)).\(^{[27,28]}\) Protonation of 2\(^{\text{BAF}}\) with Brookhart’s acid, [H(\text{Et}_2\text{O})\(_2\)]BAr\(_4\), in CH\(_2\)Cl\(_2\) gives the dicationic enimine complex [Ni\(^{II}\)](NCMe)(\(\text{PNP}\))](\(\text{BArF}^2\); Scheme 2). Carbon-centered backbone protonation is confirmed by pincer asymmetrization, giving two \(^{13}\)P NMR signals in CD\(_2\)Cl\(_2\) (\(\delta = 87.3, 84.7\) ppm) with typical trans-coupling (\(J_{\text{PD}} = 215.8\) Hz). \(^{1}\)H and \(^{13}\)C NMR characterizations further confirm the structural assignment with overall C\(_3\) symmetry. In \(d_{1}\)-MeCN, the two \(^{31}\)P signals were not resolved, but the \(^{1}\)H NMR spectrum confirms formation of the enimine tautomer. The C–H acidity of 3\(^{\text{BAF}}\) was quantified by NMR titration with PPh\(_3\) as base, giving \(pK_a(\text{MeCN}) = 8.9\). The higher acidity as compared with the monocatic hydride complex [Ni\(^{II}\)(\(\text{PNP}\))](BAr\(_4\)\(^{+}\))\(_{-}\) (\(pK_a(\text{MeCN}) = 18.4\))\(^{[27]}\) is attributed to the additional charge and the weaker donor properties of MeCN vs. the hydride ligand.

The THF analogue of the MeCN complex 2\(^{\text{BAF}}\) was synthesized through the nickel(II) route. UV/vis spectroelectrochemistry suggests selective oxidation of [Ni\(^{II}\)](PNP)] in THF, as indicated by an isosbestic point (see ESI). Accordingly, chemical oxidation with [CP\(_3\)Fe]BAr\(_4\) in THF gave a single diamagnetic product (\(\delta_{\text{THF}} = 63.7\) ppm), which is assigned to the THF adduct [Ni(\(\text{x-O-THF}\))\(^{[\text{PNP}]}\)]BAr\(_4\)\(^{2\text{BAF}}\) (Scheme 3). Crystallographic characterization as 4\(^{\text{BAF}}\) confirmed the molecular structure (Figure 2). However, high electrophilicity is indicated by slow polymerization of THF solutions of 4\(^{+}\) at room temperature, which also prevented isolation as analytically pure product. The enhanced reactivity of 4\(^{\text{BAF}}\) compared to 2\(^{\text{BAF}}\) is attributed to weaker binding of THF, which is supported by DFT computa-
The redox chemistry of the nickel(II) complexes was first examined by cyclic voltammetry (CV). Due to the low chemical stability of 4+, we focused on the MeCN substituted platform. The CV of 2+ in MeCN exhibits two reversible redox events, an oxidation at $E_{1/2} = +0.52$ V vs Fe$^{3+}$ and a reduction at $E_{1/2} = -1.78$ V (Figure 3). In THF, the reversible oxidation process is observed at $E_{1/2} = +0.66$ V. The anodic shift with respect to $[\text{Ni}^2+\text{Br}^{-}\text{PNP}]]$ ($E_{1/2} = +0.19$ V) is in line with the positive charge of 2+. Note, that the oxidation of $[\text{Ni}^3+\text{Br}^2\text{PNP}]]$ which is also confirmed for 2+ by DFT computations (ESI, Figure S29). Interestingly, the reduction of 2+ in THF exhibits a broad and irreversible feature at $E_{p,c} = -1.9$ V (Figure S22, $\nu = 100$ mV/s), which might be attributed to MeCN dissociation and formation of the previously reported T-shaped nickel(I) complex $[\text{Ni}^2\text{PNP}]]$.[11]

The CV data of complex 3+ in acetonitrile showed no oxidative event within the electrochemical window, while a reversible $\text{Ni}^2+/\text{Ni}^3-$ wave was found at $E_{1/2} = -0.96$ V (Figure 3). The substantial anodic shift vs. parent 2+ ($\Delta E = 0.82$ V) is attributed to the additional positive charge that arises from pincer protonation. Notably, the reverse scan after reduction features an oxidation wave at $E_{pa} = +0.56$ V, which coincides with the oxidation of parent 2+ (Figure 3), suggesting slow hydrogen atom loss after reduction. Chemical reduction of $[\text{Ni}^2\text{Br}^2\text{PNP}]]$ with cobaltocene at room temperature confirmed the selective formation of 2+ by $^1\text{H}$ NMR spectroscopy (Scheme 4).[30] Furthermore, $^2\text{H}$ evolution was detected by gas chromatography.

The immediate reduction product of $[\text{Ni}^2\text{Br}^2\text{PNP}]]$ was examined by EPR spectroscopy upon in situ reduction of $[\text{Ni}^2\text{Br}^2\text{PNP}]]$ in MeCN and rapid freezing. The spectrum at 140 K could be simulated best as a rhombic signal ($g_1 = 2.027$, $g_2 = 2.089$, $g_3 = 2.192$) with large, anisotropic $^{31}\text{P}$ hyperfine interaction (HFI) that is slightly different for the two $^{31}\text{P}$ nuclei (Figure 4). The distinct $^{31}\text{P}$ HFI resembles the EPR spectrum of the carbonyl complex $[\text{Ni}^{\text{II}}(\text{CO})(\text{PNP})]]$ ($A_{\text{iso}}(\text{P}) = 278$ MHz).[31] This compound is four-coordinate, yet with strong distortion from square-planar geometry, which is destabilized due to population of the $d_{x^2-y^2}$ orbital in nickel(I).[31] DFT modeling of the 4-coordinate acetonitrile complex $[\text{Ni}^{\text{II}}(\text{NCMe})(\text{PNP})]]^{5+}$ indicated that MeCN binding is about thermoneutral (Scheme 6). Importantly, the computa-

**Figure 3.** Top: Scan rate dependent CVs of the oxidation (left) and reduction (right) of 2+ in MeCN. Bottom: CV data of 3+ (black) and 2+ (red) in MeCN ($\nu = 100$ mV/s) and scan rate dependent reduction of 3+ (1 mM [Ni], 0.1 M [(n-Bu)3NPF6]).

**Figure 4.** Top left: X-band EPR spectrum of 5+ from in situ reduction of $[\text{Ni}^2\text{Br}^2\text{PNP}]]$ in MeCN at 140 K (9.422584 GHz). Top right: DFT computed spin density plot of 5+. Bottom left: X-band EPR spectrum of isolated 6+ in THF at 154 K (9.428423 GHz). Bottom right: DFT computed spin density plot of 6+. DFT computed spectra of 5+ and 6+ are shown in blue with computed parameters in parentheses.

**Scheme 3.** Synthesis of complexes $4\text{BAF}$ and $6\text{BAF}$.

**Scheme 4.** Hydrogen evolution upon in situ formation of $[\text{Ni}^2(\text{NCMe})(\text{PNP})]]^{5+}$. 
Notably, dissolving isolated $\text{[Ni(NCMe)\text{PNP}]Br}_2$ (BDFE$_2$, Scheme 3) was synthesized by protonation of [Ni(PNP)] with lutidinium in THF in high yield. The T-shaped coordination of 6+ was confirmed in the solid state by X-ray diffraction (Figure 2), showing typical bond metrics for the enmine moiety and a slightly elongated Ni–N bond distance (1.9604(18) Å) with respect to parent amide complex [Ni(PNP)] (1.9337(12) Å). EPR spectroscopic characterization in frozen THF supports the T-shaped structure (Figure 4); a broad, near axial signal was obtained with resolved $^{14}$N hyperfine interaction (HFI) in one direction, as in parent [Ni(PNP)]. DFT computations confirmed endergonic THF coordination to 3-coordinate 6+ (Scheme 6) and nicely reproduced the EPR data (Figure 4). Notably, dissolving isolated 6BDFE in MeCN gave identical EPR spectra as in situ reduction of 3BDFE (see ESI).

Thermochemical analysis of C–H PCET. The EPR characterization revealed that the protonated nickel(II) platform is 3-coordinate in THF (6+) and 4-coordinate in MeCN (5+). The speculation correlates with drastically different chemical stability in these solvents: While the three coordinate complex 6BDFE is stable in THF over several days, reduction of 3BDFE in MeCN results in rapid formation of 2+, suggesting hydrogen atom transfer reactivity upon MeCN coordination. Accordingly, dissolving isolated 6BDFE in MeCN also results in the selective formation of 2+ (Scheme 4).

To rationalize these observations, C–H PCET from [Ni\((1^\text{PNP})\text{PNP}\)] was analyzed by a thermochemical cycle using the data reported above. The pK$_\Lambda$ value (8.9) and the reduction potential of 3+ ($E_{1/2} = -0.96$ V) allow for estimating the C–H bond strength of the methylene group. The obtained value (BDFE$_{\text{C−H}}$ = 42.6 kcal mol$^{-1}$) is in excellent agreement with DFT computations (Scheme 5). This result is in line with the decay of 5+ by homolysis of the weak C–H bonds and the evolution of dihydrogen (0.5BDFE$_{\text{C−H}}$ = 52.0 kcal mol$^{-1}$). In comparison, PCET of the formal Ni/$^{1^\text{PNP}}$/Ni$^{3^+}$ couple [Ni(NCMe)(1$^\text{PNP}$)]$^{3+}$/Ni(NCMe)(PNP)$^{2+}$, which is thermochemically defined by the same pK$_\Lambda$ value and the oxidation potential of 2+, is about 34 kcal mol$^{-1}$ higher in free energy (Scheme 5). Note, that DFT computations indicate predominantly ligand centred oxidation of 2+ (ESI, Scheme S29) as was previously confirmed spectroscopically for [NiBr(PNP)]$^{3+}$.[8] Furthermore, an almost identical methylene BDFE$_{\text{C−H}}$ was found for [NiBr(1$^\text{PNP}$)]$^{3+}$ (76.3 kcal mol$^{-1}$ in dmso). We therefore associate the distinct weakening of the C–H bond in the Ni$^{3+}$ complex 5+ with respect to 3$^{3+}$ with the metal centred redox process.

As judged from electronic structure considerations, the BDFE$_{\text{C−H}}$ of the [Ni(1$^\text{PNP}$)]$^{3+}$ framework might be sensitive to solvent coordination: Binding of a fourth ligand should shift the oxidation potential cathodically due to destabilization of the high-lying, metal centered SOMO that is located in the pincer plane. At the same time, the LS-Ni$^{3+}$ state strongly prefers square-planar geometry, which will further affect the Ni$^{3+}$ redox couple. We therefore aimed at examining PCET from the 3-coordinate complex 6+. Unfortunately, the thermal instability of 4+ and lack of electrochemical reversibility for the oxidation of [Ni(1$^\text{PNP}$)] in THF prevented quantitative thermochemical analysis.

Motivated by the excellent agreement of experimental and computational thermochemical data in MeCN, the methylene BDFE$_{\text{C−H}}$ in THF was evaluated computationally (Scheme 6). The PCET couple defined by 3-coordinate nickel(II) complex 6+ and square-planar nickel(II) product 4+ exhibits a remarkably

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Scheme 5. Thermodynamic data for C–H PCET in MeCN (BDFEs in kcal mol$^{-1}$). Computational values are given in parentheses.

Scheme 6. Computed thermochemical data in MeCN (red) and THF (green), respectively.
stronger C–H bond (BDFE C–H = 58.1 kcal mol⁻¹) than in MeCN. This value reveals that the stability of 6⁺ vs. H₂ evolution is of thermodynamic and not only kinetic origin. A thermochemical cycle that connects the spectroscopically observed PCET couples by solvent association equilibria to Ni²⁺ and Ni⁰, respectively, and H transfer (Scheme 6) reveals the origin of the distinct C–H bond weakening in MeCN: The all 3-coordinate PCET couple [Ni²⁺(PNP)]⁺/²⁻(Ni⁰(PNP)) exhibits a considerably higher and solvent independent BDFE C–H around 69 kcal mol⁻¹. The C–H bond strength is reduced by stabilization of nickel(II) as solvent adduct [Ni²⁺(PNP)]⁺, which is however more pronounced for binding of the stronger donor MeCN vs. THF (ΔΔG ≈ 15.9 kcal mol⁻¹). In turn, Ni⁰ is effectively not further stabilized by solvent coordination, which can be attributed to the location of the SOMO within the plane defined by the pincer ligand.

Conclusions

In summary, the solvent dependence of the thermal stability of [Ni²⁺(L)²⁺(PNP)]⁺ with respect to hydrogen evolution from the remote methylene group was rationalized by thermochemical analysis of the PCET couples [Ni²⁺(L)²⁺(PNP)]⁺/²⁻[Ni⁰(L)²⁺(PNP)]⁺ (L = MeCN, THF/none). In comparison, the dicaticonic complex [Ni⁰(MeCN)²⁺(PNP)]⁺ exhibits a considerably higher BDFE of H bond which is almost identical with the previously reported nickel(II) complex [Ni⁰(Br)²⁺(PNP)]⁺.[9] In these cases, the redox processes are predominantly pincer ligand centered, resulting in decoupling of the metal redox potential and the the C–H bond strength. The high BDFEs are in line with Bordwell’s previous work.[4] The metal redox potential and the C–H bond strength are predominantly pincer ligand centered, resulting in decoupling of the metal redox potential and the the C–H bond strength. This study exemplifies that metal solvation can have a large impact on ligand C–H bond activation even in remote sites.

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