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Activation of Water, Ammonia, and Other Small Molecules by $\mathrm{PC_{carbene}P}$ Nickel Pincer Complexes

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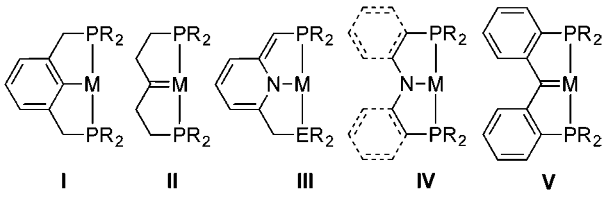
Supporting Information

ABSTRACT: Nickel complexes of a $\mathrm{PC_{carbene}P}$ pincer ligand framework are described. Dehydrobromination of the precursor $(\mathrm{PC_{sp^3}P})\mathrm{NiBr}$ in the presence of a donor ($\mathrm{PPh_3}$ or $\mathrm{NC^tBu}$) leads to the title complexes, which feature a rare nickel−carbene linkage as the pincer ligand anchor point. This strongly donating, nucleophilic carbene center engages in a variety of E−H bond activations (E = H, C, N, O), some of which are reversible. This represents a new mode of bond activation by ligand cooperativity in nickel pincer complexes.

The direct utilization of ammonia or water in catalytic cycles that activate and functionalize the E−H bonds (E = N, O) is a longstanding challenge in catalytic chemistry.[1,2] One step in addressing this challenge lies in the discovery of systems that selectively activate the bonds of these EH_n substrates, but N−H activations for hydroaminations or C−N bond formation[1,3,4] and O−H activations for water splitting[2,5,6] remain limited, largely because of the tendency of these molecules to coordinate metals rather than undergo E−H cleavage processes.

One successful strategy for encouraging bond activation over Werner coordination in these substrates is the incorporation of strongly σ-donating ligands into pincer ligand[7] frameworks. For example, second- and third-row transition-metal complexes of the classic Shaw PCP systems **I**[8] and **II**[9,10] shown in Chart 1 (and related PSiP ligands[11]) have been shown to activate the bonds of $\mathrm{NH_3}$[12] and $\mathrm{H_2O}$[13] via oxidative addition.[5] A second promising strategy for activating and functionalizing these bonds involves metal−ligand cooperation[14−16] for the heterolytic splitting of the E−H bonds. A variety of small molecules, including $\mathrm{NH_3}$ and $\mathrm{H_2O}$, can be activated via an aromatization/dearomatization sequence associated with the noninnocent PNP pincer ligand **III** in complexes of Ir and Ru.[17] This mode of E−H activation has been incorporated into catalytic transformations,[18−20] but analogous first-row transition-metal complexes[15,21] were found to be less reactive. Alternatively, in pincer frameworks where the anchoring donor can accept electrophiles, as in the $\mathrm{PN_{amido}P}$ pincer complexes **IV**,[22,23] activation of several E−H bonds (E = H, C, S, B) via 1,2-addition across the central M−N bond has also been demonstrated.[24−28]

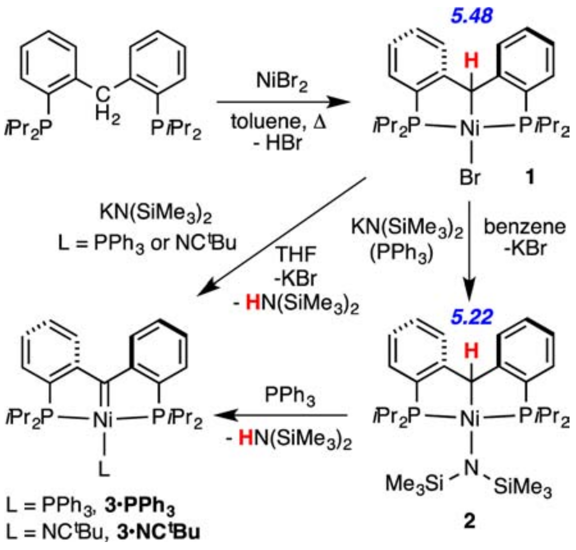
Chart 1



In light of these studies, we combined design elements of ligand types **II** and **IV** to develop "β-hydrogen elimination immune" $\mathrm{PC_{carbene}P}$ ligands **V** (Chart 1),[29] where the central donor atom is both strongly σ-donating *and* capable of accepting electrophiles. When these ligands were incorporated into iridium complexes, reversible $\mathrm{H_2}$ activation across the Ir=C bond was observed,[29] but other E−H bonds were not activated. Here we report the synthesis of nickel complexes supported by this pincer ligand system and the activation of various small molecules via heterolytic splitting of their E−H (E = C, N, O) bonds.

The Ni(II) $\mathrm{PC_{sp^3}P}$ bromide complex **1** was obtained by reaction of $\mathrm{NiBr_2}$ with the ligand bis[2-(diisopropylphosphino)-phenyl]methane in refluxing toluene (Scheme 1). The reaction was accompanied by evolution of HBr, and brown crystals of **2** were isolated in 61% yield by crystallization from a toluene/hexanes mixture at −30 °C. The lower yield was a result of the concomitant formation of unidentified blue-green paramagnetic nickel products.[30−32]

Scheme 1



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The diamagnetic Ni(II) complex **1** is characterized by a broad ^{1}H NMR signal at 5.48 ppm integrating to one proton, corresponding to the benzylic proton, that correlates to a triplet ($^2J_{CP}$ = 8.5 Hz) at 45.3 ppm in the ^{13}C NMR spectrum. X-ray crystallographic structure determination (see Figure S1 in the Supporting Information for a depiction of the molecular structure) revealed a slightly distorted square-planar geometry at the Ni center. The Ni−C$_{benzyl}$ distance of 1.973(3) Å is comparable to those found in related PC$_{sp^3}$P complexes and slightly longer than those in PC$_{sp^2}$P compounds.[30,33]

PC$_{sp^3}$P-ligated nickel bromide **1** could be further dehydrobrominated as shown in Scheme 1. Treatment with KN(SiMe$_3$)$_2$ in benzene solvent in the presence (or absence) of PPh$_3$ resulted in salt metathesis and formation of the bis(trimethylsilyl)amido complex **2**, as indicated by retention of a resonance for the ligand benzylic proton at 5.22 ppm in the ^{1}H NMR spectrum. However, when the reaction solvent was changed to tetrahydrofuran (THF), clean formation of the PC$_{carbene}$P nickel complex **3·PPh$_3$** was observed; PPh$_3$ served to complete the coordination sphere of the nickel center upon loss of KBr and HN(SiMe$_3$)$_2$. Interestingly, when amido complex **2** was treated with PPh$_3$ in THF, slow conversion to **3·PPh$_3$** with elimination of amine was observed. In the ^{1}H NMR spectrum of **3·PPh$_3$**, no benzylic proton resonance is present, and in the ^{13}C spectrum, a doublet at 181.8 ppm ($^2J_{CPtrans}$ = 35.8 Hz) is assignable to the carbene carbon at the ligand anchor point.[29] Two mutually coupled resonances were observed in ^{31}P NMR spectrum, a doublet at 48.5 ppm ($^2J_{PP}$ = 13.1 Hz) and a triplet at 40.2 ppm, corresponding to the pincer phosphorus and PPh$_3$ atoms, respectively. Except for N-heterocyclic carbenes, nickel carbene complexes are rare, the only other example being Hillhouse's three-coordinate diphenylcarbene, whose carbene carbon resonates at 222 ppm.[34]

In view of the diamagnetic nature of the compound, a formally Ni(II) square-planar structure was anticipated. X-ray-quality crystals of **3·PPh$_3$** were obtained from a toluene/hexanes solution at −30 °C, and Figure 1 shows the molecular structure and selected metrical data. As can be seen, the geometry is highly distorted from ideal square planarity in that the carbene carbon C1 is located 1.62 Å above the plane defined by the three P atoms and the Ni center; the P3−Ni1−C1 angle is 141.82°. This distortion was modeled well utilizing DFT computations (B3LYP/LANL2DZ) and is likely due to steric interactions between the pincer ligand isopropyl groups and the PPh$_3$ ligand rather than a tendency toward a tetrahedral geometry in which the ligand serves as an overall neutral donor to a Ni(0) center, although this is a viable alternative view. To support the former view, we also prepared **3·NC^{t}Bu** incorporating the sterically less demanding *tert*-butylcyanide ligand. As can be seen in Figure 1, this complex assumes a nearly ideal square-planar geometry. This illustrates the fact that despite the anticipated rigidity associated with this PCP pincer system, the ligand does feature some geometrical flexibility. The Ni1−C1 bond lengths in **3·PPh$_3$** [1.908(5) Å] and **3·NC^{t}Bu** [1.927(4) Å] are shorter than the Ni−C bond in **1** [1.973(3) Å] but somewhat longer than that in the Hillhouse nickel carbene, in which the Ni═C bond length is 1.836(2) Å.[34]

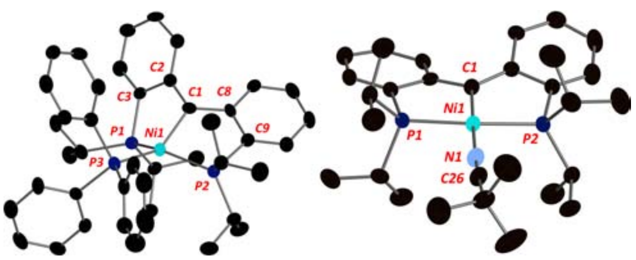

Figure 1. Molecular structures of **3·PPh$_3$** and **3·NC^{t}Bu**. H atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **3·PPh$_3$**: Ni1−C1, 1.908(5); Ni1−P1, 2.1925(16); Ni1−P2, 2.2270(15); Ni1−P3, 2.2081(15); C1−Ni1−P3, 141.81(17); P1−Ni1−P2, 139.58(6). Selected bond lengths (Å) and angles (deg) for **3·NC^{t}Bu**: Ni1−C1, 1.927(4); Ni1−P1, 2.1648(11); Ni1−P2, 2.1584(11); Ni1−N1, 1.890(4); C1−Ni1−N1, 177. 36(17); P1−Ni1−P2, 170.58(5).

In contrast to the PC$_{carbene}$P iridium compounds we previously reported, where the ligand formally functions as a neutral donor to an Ir(I) center,[29,35] the ligands in compounds **3·L** are formally "Schrock-type" doubly negative ligands supporting a Ni(II) center. Therefore, as in the Hillhouse Ni carbene,[34,36,37] it was expected that the carbene anchors in compounds **3·L** should be more nucleophilic than in the Ir(I) compounds and function as electrophilic sites for ligand cooperativity in bond activation reactions.

As shown in Figure 2, this expectation was borne out in a variety of E−H bond additions across the Ni═C bond in **3·PPh$_3$** to generate a range of PC$_{sp^3}$P compounds. These reactions were rapid (occurring essentially upon mixing of reagents) and accompanied by the loss of PPh$_3$.[38] In each case, the reappearance of a signal for the benzylic proton of the ligand in the ^{1}H NMR spectrum was diagnostic; the chemical shifts are noted in blue in Figure 2. For example, exposure of a solution of **3·PPh$_3$** to 1 atm H$_2$ resulted in rapid conversion to hydride complex **4**, as indicated by a doublet of triplets at −11.99 ppm ($^2J_{PP}$ = 59 Hz; $^3J_{HH}$ = 3.6 Hz) in the ^{1}H NMR spectrum for the terminal hydride ligand. A slow reaction between **4** and the eliminated PPh$_3$ ligand resulted in reductive elimination to the three-coordinate Ni(0) complex shown. Spectroscopically identical samples could be generated from **1** and NaHBEt$_3$, and X-ray-quality crystals were obtained from these phosphine-free samples, confirming the identity of this compound (Figure 2, upper left). This addition of H$_2$ to **3·PPh$_3$** appeared to be reversible, since exposure of solutions of **4** to D$_2$ resulted in deuterium incorporation into the benzylic position as determined by ^{2}H NMR spectroscopy. The addition of H$_2$ across the Ir═C bonds of the Ir(I) PC$_{carbene}$P complexes was also observed.[29]

In contrast to the iridium chemistry, however, rapid addition of C−H, N−H, and O−H bonds to **3·PPh$_3$** was facile. The nickel acetylide complex **5** was produced upon addition of phenylacetylene; no reactivity with less acidic C−H bonds has been observed to date. Treatment of **5** with DCCPh did not result in deuterium exchange, suggesting that this reaction is irreversible. Reaction of **3·PPh$_3$** with an excess of ammonia was also rapid, producing the monomeric amido complex **6** as the kinetic product.[39,40] The amido protons appear at −1.16 ppm as a triplet ($^3J_{HP}$ = 7.0 Hz) in the ^{1}H NMR spectrum. Subsequent to generation of **6**, the NMR spectra became progressively more complex, and when attempts to grow crystals of the brown monomer **6** were made, yellow crystals of the dimer [**6**]$_2$ were deposited and analyzed by X-ray crystallography (Figure 2, lower right). In this dimer, one of the phosphine arms of the PC$_{sp^3}$P ligand is detached, and the terminal NH$_2$ group bridges the two nickel centers of the dimer. This behavior is not apparent in

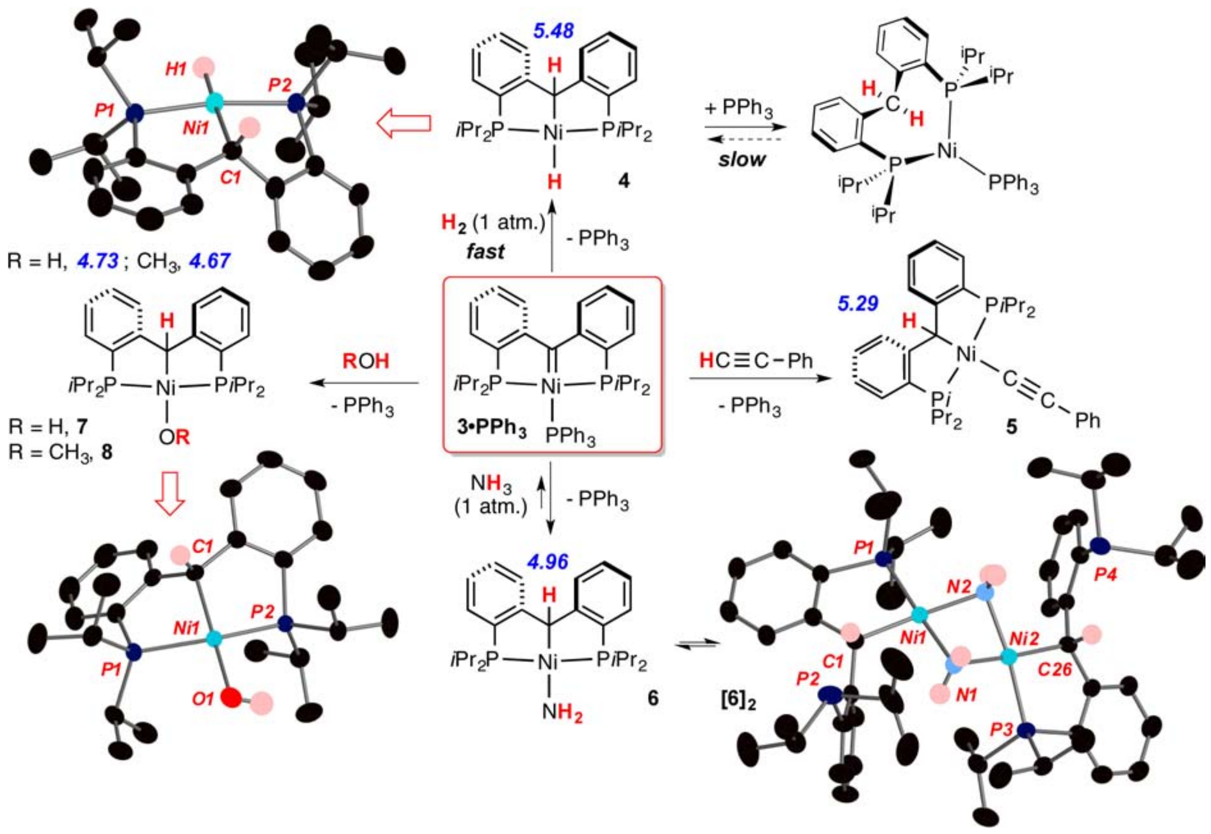

Figure 2. E−H bond activation reactions of $PC_{carbene}P$ nickel complex **3·PPh$_3$**. For the X-ray structures shown, displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg) for **4**: Ni1−C1, 2.000(3); Ni1−P1, 2.1315(7); Ni1−P2, 2.1122(7); Ni1−H1, 1.37(3); P1−Ni1−P2, 172.20(3). Selected bond distances (Å) for [**6**]$_2$: Ni1−C1, 1.981(3); Ni2−C26, 1.989(3); Ni1−N1, 1.912(3); Ni1−N2, 1.938(3); Ni2−N1, 1.932(3); Ni2−N2, 1.915(3), Ni1−Ni2, 2.7510(5). Selected bond distances (Å) and angles (deg) for **7**: Ni1−C1, 1.978(2); Ni1−O1, 1.9082(15); C1−Ni1−O1, 170.15(8).

related Ni−NH$_2$ complexes of ligands **I**[41,42] or **II**,[43] which suggests that the $PC_{sp^3}P$ ligand here is more strongly donating at the carbon anchor point. The carbon centers C1 and C26 are asymmetric, and it is conceivable that the ligated phosphorus centers P1 and P3, which are trans-disposed in the analyzed structure, could be cis-oriented across the Ni_2N_2 core. Thus, the C_2-symmetric dimer that selectively crystallized is one of six possible stereoisomers of [**6**]$_2$ (see Figure S5 for an analysis), which accounts for the observed complexity of the thermodynamic mixture that eventually results in this reaction. Despite the complexity, van't Hoff analysis (Figure S7) showed that monomer **6** and the various dimers [**6**]$_2$ are in equilibrium [$\Delta H° = -13.3(2)$ kcal mol^{-1}; $\Delta S° = -27(1)$ cal mol^{-1} K^{-1}; $\Delta G°_{298} = -5.2(1)$ kcal mol^{-1}]. Furthermore, treatment of this thermodynamic mixture with ND_3 resulted in slow incorporation of deuterium into the ligand benzylic position (as well as the amido positions) over the course of several hours, suggesting that N−H addition across the Ni═C bond in **3·PPh$_3$** is reversible.

Finally, the additions of the O−H bonds of H_2O and CH_3OH to yield hydroxo complex **7** and methoxide compound **8** were also facile. In the former instance at least, the reaction was not reversible; treatment of **7** with an excess of D_2O led to deuteration of the OH position but *not* the benzylic proton.[44] Compound **7** was characterized by X-ray crystallography (Figure 2, lower left). In comparison to related compounds supported by ligands **I**,[42,45] **II**,[43] or **IV**[46] which have Ni−O bond distances in the range 1.8634−1.8793 Å, the Ni1−O1 bond length of 1.9082(15)Å in **7** is the longest in the series. This again speaks to the high donor character of the present PCP ligand framework, a potentially exploitable phenomenon for further use of these compounds in catalytic transformations.

In summary, we have utilized a $PC_{carbene}P$ ligand framework recently reported by our group to prepare new nickel pincer complexes that feature a rare nickel carbene moiety. In these complexes, the nickel carbene donor is noninnocent and capable of activation of a variety of E−H bonds by addition across the Ni═C bond. In some instances, this is reversible, a feature potentially exploitable in catalysis. Furthermore, the high σ-donating character of the central carbon moiety labilizes the ligand in the trans position, another attractive feature for development of catalytic reactions using this system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details for the syntheses and characterization of all new complexes and tables and CIFs giving details of the crystallographic data for compounds **1**, **3·PPh$_3$**, **3·NC^{t}Bu**, **4**, [**6**]$_2$, and **7**. 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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