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A Wacker-Type Strategy for the Synthesis of Unsymmetrical POC_{sp}³E-Nickel Pincer Complexes

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ABSTRACT: ECE-type pincer complexes have evolved into a diverse family of compounds possessing interesting structural/bonding features, reactivities, and practical applications. An important factor promoting the growth of pincer chemistry is the availability of versatile synthetic pathways that give access to everdiverse pincer complexes. This report describes the synthesis of pincer–Ni complexes possessing the following features: a central Ni–C_{sp}³ linkage, two different peripheral donor moieties, and two differently sized metallacycles. The synthetic methodology reported herein is based on the reactivity of a phosphinite derived from 2-vinylphenol. Stirring the substrate $2-CH_2=CH-C_6H_4-OP(i-Pr)_2$, 1, with the Ni^{II} precursor {(*i*-PrCN)NiBr₂}_n and Et₃N



at room temperature gave the 6,5-POC_{sp}³PO-type pincer complex { $\kappa^{O}, \kappa^{C}, \kappa^{P}-2-[(i-Pr)_2P(\underline{O})CH_2\underline{C}H]-C_6H_4-O\underline{P}(i-Pr)_2$ }NiBr, **2**. Conducting this reaction in the presence of an excess of **1** hinders the formation of **2**, giving instead the nickelacyclopropane complex { $\kappa^{C}, \kappa, \kappa^{P}-2-[(2-CH_2=CH-C_6H_4O)P(i-Pr)_2\underline{C}H\underline{C}H]-C_6H_4-O\underline{P}(i-Pr)_2$ }NiBr, **3**, whereas introducing a second, stronger nucleophile into the reaction mixture leads to the formation of pincer complexes featuring rare 4-membered metallacycles. For instance, using HNR(R') as nucleophile gave the 6,4-POC_{sp}³N-type pincer complexes { $\kappa^{N}, \kappa^{C}, \kappa^{P}-2-[R(R')\underline{N}CH_2\underline{C}H]-C_6H_4-O\underline{P}(i-Pr)_2$ }NiBr (NR(R') = *N*-morpholyl, **4**; NPh(Et), **5**; NH(*i*-Pr), **6**; NH(Ph), **7**; NH(Cy), **8**; NH(*t*-Bu), **9**), whereas using HPR₂ as nucleophile led to the 6,4-POC_{sp}³P-type pincer complexes { $\kappa^{P}, \kappa^{C}, \kappa^{P'}-2-[R_2\underline{P}CH_2\underline{C}H]-C_6H_4-O\underline{P}(i-Pr)_2$ }NiBr (R = *i*-Pr, **10**; *i*Ph, **11**). Single crystal diffraction studies have established the solid-state structures of complexes **2**–**11**. All the pincer complexes reported here feature 6-membered metallacycles defined by the phosphinite moiety, while the phosphine-oxide moiety in **2** defines a 5membered metallacycle and 4-membered metallacycles form by the coordination of the amine moieties in **4**–**9** and the phosphines in **10** and **11**. Cyclic voltammetry measurements on complexes **2**, **4**–**6**, **10**, and **11** have shown that these pincer–Ni complexes undergo facile one-electron oxidation.

INTRODUCTION

Since its inception more than four decades ago,^{1,2} the field of pincer chemistry has evolved rapidly to make major contributions in diverse areas of application, including catalysis³ and preparation of functional materials.⁴ A key element in the rapid development of pincer chemistry has been the successful elaboration of efficient synthetic strategies that have paved the way to a diverse array of ligand platforms based on aromatic or aliphatic backbones. These synthetic methodologies have thus provided access to a variety of classical or novel pincer complexes featuring symmetrical and unsymmetrical architectures, different peripheral and central donor moieties, and (less frequently) different metallacycle sizes. This diversity has, in turn, led to the discovery of unique reactivities and properties that are the general hallmarks of pincer complexes today.⁵

By and large, the most commonly used synthetic strategies for the preparation of ECE-type tridentate, monoanionic pincer ligands rely on (a) the activation/metalation of C-H bonds in EC(H)E-type proligands and (b) the oxidative addition or transmetalation of C–X bonds in EC(X)E-type proligands. These classical strategies are exemplified by Shaw's¹ and van Koten's⁶ landmark studies on the synthesis of (PCP)ML_n and (NCN)ML_n, respectively (Scheme 1).

The success of synthetic routes based on activation/ metalation of C–H bonds depends on many factors, including the nature of the donor moieties, the ligand backbone, and the type of metal precursor used. For instance, PCP-type pincer complexes of nickel are accessible via relatively facile C–H nickelation reactions with *m*-phenylene type proligands mentioned above.⁷ In contrast, analogous proligands featuring

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Scheme 1. Classical Synthetic Strategies for Preparation of ECE-Type Pincer Complexes



two amine moieties are much less amenable to pincer formation via C–H nickelation. 8

C–H nickelation is also more difficult with aliphatic proligands, even when they feature phosphine- or phosphinite-type donor groups. For instance, the aliphatic proligands 1,3-(R₂PO)₂-(CH₂)₃ and 1,5-(R₂P)₂-(CH₂)₅ require more forcing conditions to undergo C_{sp}^{3} -H metalation in comparison to their counterparts based on *m*-phenylene backbones.⁹ Although these limitations have not hindered the advance of pincer chemistry,¹⁰ it would be advantageous to develop a new synthetic strategy that sidesteps the (often-significant) barriers to C_{sp}^{3} -H activation/metalation steps.

This report describes one such strategy based on net addition of nucleophiles to an olefin moiety coordinated to a divalent nickel precursor. This new Wacker-type¹¹ synthetic methodology was discovered during our investigations on the C-H nickelation of phenyl and naphthyl phosphinites. Earlier studies had shown that in most cases nickelation of aryl phosphinites occurs regioselectivity at the unsubstituted C-H moiety *ortho* to the OPR₂ position, as illustrated in Scheme 2

Scheme 2. Cyclonickelation of Phosphinites Derived from Phenols and Naphthols (R = i-Pr)



(reaction A).¹² In other words, ring substituents were found to be largely inert to nickelation.¹³ The only exception to this regioselectivity was observed with 2-allyl-1-naphthyl-OP(*i*-Pr)₂ (Scheme 2, reaction B).¹⁴ This observation was quite unexpected as the normally less facile nickelation of a *substituent* C_{sp}^{3} -H moiety proceeded in preference over reactivity at the ring C-H. Indeed, the α C-H moiety in the allyl substituent of this substrate was nickelated at room temperature, which is in stark contrast to the requirement of high temperatures (80–160 °C) for the nickelation of the aromatic C-H moieties in most aryl phosphinites.¹⁵

This discovery prompted us to examine the reactivity of alkenyl-substituted aryl phosphinites to determine whether C-

H nickelation would occur on the alkenyl substituent or the aryl ring. As will be described herein, studying the reactivities of the vinyl-substituted phenyl phosphinite $2\text{-CHCH}_2\text{-C}_6\text{H}_4\text{-}$ OP $(i\text{-Pr})_2$, 1, led to the development of a new synthetic route that allows facile formation of novel families of unsymmetrical pincer complexes without going through a C–H activation/ metalation step.

RESULTS AND DISCUSSION

Initial Exploration of the Reactivity of 2-Vinyl-Phenylphosphinite. This study began by preparation of the target substrate 1 and examination of its reactivity under the conditions used for our previous nickelation studies.^{13,14} Thus, 1 was treated in acetonitrile with $\{(i-PrCN)NiBr_2\}_n$ and Et₃N (molar ratio of 1.0:1.2:1.2), and the reaction progress was monitored by NMR spectroscopy. ³¹P NMR spectral analysis of the greenish mixture obtained after 2 h of stirring at room temperature showed that the initial signal for 1 had been replaced almost completely by two new ³¹P resonances at 103 and 202 ppm. The chemical shift of the latter signal was close to that observed for the π -allyl complex shown in Scheme 2 (**B**, 201 ppm), thus hinting that nickelation might have occurred at the vinyl C-H moiety. However, the 1:1 intensity ratio of the new peaks suggested the formation of a complex featuring two different P-bearing moieties.

In order to isolate the reaction product and characterize it unambiguously, we worked-up the reaction mixture by evaporating the solvent and extracting the residues with toluene. The resulting orange solution displayed two ³¹P peaks at 94 and 205 ppm in a 1:1 ratio; this mixture also contained 15-20% of the unreacted bis-phosphinite complex (1)₂NiBr₂.¹⁶ Evaporation and recrystallization from Et₂O afforded deep red crystals that displayed two very weakly coupled ³¹P doublets at 94 and 206 ppm (CDCl₃: $J_{PP'} \approx 3$ Hz). XRD analysis of a single crystal revealed the unsymmetrical ECE'-type pincer complex **2** shown in Scheme **3**.





The main structural parameters for the unexpected product 2 (and all the other solid-state structures presented herein) will be presented and discussed fully in the last section of this report. For now, it is worth noting that this complex features two different metallacycles, a 6-membered ring formed by the coordination of the original phosphinite moiety in 1, and a 5-membered ring defined by the chelation of the in situ formed phosphine oxide moiety. The latter originates from a second equivalent of 1 via a rearrangement that results in the expulsion of its aryl fragment. The overall transformation of 1 into 2 also

converts the sp²-hybridized α -C of the vinyl substituent in **1** into the sp³-hybridized central carbon moiety of the new 6,4-POC_{sp}³P(O)-type pincer complex. Thus, no net C–H nickelation takes place during the formation of the unsymmetrical pincer complex **2**.

The above considerations allowed us to envisage the following speculative scenario for the formation of **2**. First, π -coordination of the vinyl moiety in **1** to the Ni^{II} center would give an intermediate complex featuring a chelating phosphinite/vinyl ligand, as shown in Scheme 4 (step A). The

Scheme 4. Proposed Mechanism for the Formation of Complex 2



coordinated vinyl moiety would thus become susceptible to an outer-sphere nucleophilic attack, and then a second equivalent of 1 would add to the β -C of the vinyl moiety to generate a new P–C bond and a new Ni–C bond (step B in Scheme 4). A subsequent SN_{Ar}-type nucleophilic attack by a bromide anion on the *ipso* carbon of the aryl ring in the newly generated phosphonium moiety would break the Ar–O bond to generate the P=O moiety (step C in Scheme 4).

Although the sequence of steps illustrated in Scheme 4 seemed feasible at first, subsequent tests generated a number of observations that cast doubt on the validity of step C in this transformation. First, the proposed SN_{Ar} -type nucleophilic attack by Br^- resulting in the P==O moiety should have led to the concomitant formation of 2-Br-styrene, but GC-MS analysis of the final reaction mixture showed no trace of this byproduct. Second, the proposed mechanism envisages no role for Et_3N , and yet a few experiments helped establish that a stoichiometric amount of Et_3N is necessary for the formation of 2. For instance, treating 1 with 1.2 equiv of $\{(i-PrCN)NiBr_2\}_n$ in the absence of Et_3N failed to give any conversion to 2, even after 20 h, whereas the analogous reaction in the presence of 0.10 equiv of base led to partial conversion.

One more observation regarding the role of the base was made in the aftermath of the reaction of 1 with $\{(i \text{PrCN})\text{NiBr}_2\}_n$ and Et_3N (1:1.2:1) in acetonitrile. ESI-MS analysis of the crude reaction mixture after 2 h indicated the formation of the ammonium species $[(2\text{-vinylphenyl})\text{NEt}_3]\text{Br}$ at M⁺ and $[(2\text{-vinyl-phenyl})\text{NEt}_3]_2\text{Br}$ at $[M - 1]^+$ (see Figures S1 and S2). Evidently, a stoichiometric amount of base is required for the reaction under discussion. We believe that the role of Et_3N is to promote the cleavage of the Ar–O bond required for the formation of the P=O moiety (step D in Scheme 4).

Another aspect of the mechanism proposed in Scheme 4 was puzzling at first: although the mechanism requires 2.0 equiv of substrate 1 relative to the metal precursor and Et_3N , tests showed that using more than 1.0 equiv of substrate slows down the formation of 2. For instance, monitoring a reaction mixture containing 2.0 equiv of 1 (acetonitrile, room temperature) by ³¹P NMR spectroscopy showed a much slower conversion of 1 to 2. Similarly, a much slower reaction was observed when the reaction of 1 with the nickel precursor and Et_3N was conducted in THF instead of acetonitrile, either with 1.0 or 2.0 equiv of substrate.

Interestingly, allowing the above-noted 2:1:1 (1: Ni: Et₃N) reactions to proceed over extended periods led to the formation of a new species that over time (>48 h) became the major product of the reaction besides complex 2. That this new species is structurally similar to complex 2 was indicated by the emergence of a second set of ³¹P resonances fairly close to those of 2 (i.e., around 97 and 210 ppm vs 103 and 202 ppm for 2 in MeCN). Workup of the reaction mixture in Et₂O followed by cooling gave two sets of crystals: deep-red crystals that were identified as the expected product 2, and bright orange crystals that turned out to be a new zwitterionic complex 3 cocrystallized with 2 (Scheme 5).





The structural discussion presented later on in this report will address the contributions of the three canonical representations of complex 3 illustrated in Scheme 5. The resonance structure γ featuring an ylide moiety is in theory possible, but the distance between the phosphorus and the metal center of >3 Å in 3 rules out any P–Ni interaction. We conclude, therefore, that the zwitterionic species α and β give more accurate descriptions of this complex. The ¹H and ¹³C NMR spectra of 3 (Figures S29–S41) indicate that the α form shown in Scheme 5 and featuring a nickelacyclopropane moiety is the prevalent resonance structure of compound 3 in solution. Thus, the two C–H moieties bound to the metal center gave signals in the aliphatic region: δ ¹H at 2.04 and 2.95 ppm; δ ¹³C at 18.63 and 37.17 ppm.

We propose that both complexes 2 and 3 form via the intermediate species arising from the nucleophilic attack by 1 on the complex bearing the chelating ligand (shown in Scheme 4 and Scheme 5). The pathway that gives 3 instead of 2 involves a subsequent deprotonation of the proton adjacent to the phosphonium site. It is worth noting that 2 is the main

product during the early stages of the reaction of substrate 1 with the Ni^{II} precursor and Et₃N, whereas complex 3 forms more gradually but becomes the predominant product over time (Figures S126-S127). For this reason, preparation of reasonably pure samples of 3 required long reaction times (>3 days).

Nucleophilic Amines Lead to 6,4-POCN-NiBr Pincers. The previous section established that coordination of the vinyl moiety in substrate 1 to the Ni^{II} center renders it susceptible to attack by even a weak nucleophile such as the phosphinite moiety in 1. This attack generates a phosphonium-bearing intermediate that undergoes subsequent transformations to give either the 5,6-POCPO-type pincer complex 2 (without going through a C–H metalation step) or the zwitterionic nickelacyclopropane 3. On the basis of these observations, we surmised that conducting the reaction of 1 with the Ni^{II} precursor in the presence of a protic nucleophile might lead to new pincer complexes featuring a 4-membered nickelacycle, as illustrated in Scheme 6.¹⁷

Scheme 6. Proposed Wacker-Type Strategy Leading to (6,4-POC_{sp}³E)NiBr Pincer Complexes



Morpholine was selected as nucleophile of choice for testing the above hypothesis, because our previous experience with the synthesis of 5,5-POCN-type pincer complexes of nickel had shown this amine to be a viable donor for preparing stable pincer complexes.¹⁸ Thus, treating 1 in acetonitrile for 1 h with 1.2 equiv of $\{(i\text{-PrCN})\text{NiBr}_2\}_n$ and 2.0 equiv of morpholine (as both nucleophile and base) led to complete disappearance of the ³¹P signal for (1)₂NiBr₂ and emergence of a minor signal for complex **2** and a new signal at 204 ppm. Conducting this reaction in THF with 1.2 equiv of Et₃N slowed the rate (16 h at room temperature), but led to a cleaner conversion, with barely any byproducts being detected (Figure S128). The orange powder isolated from this mixture showed NMR spectra consistent with the formation of the expected (6,4-POCN^{morph})NiBr complex **4** (Scheme 7). For example, the ¹H

Scheme 7. Synthesis of the 6,4-POCN Pincer Complex Arising from Morpholine (4) and Its Molecular Diagram



NMR spectrum displayed signals at 1.59 for Ni–*CH* and at 3.42 and 3.68 ppm for Ni–*CH*–*CH*₂, with the corresponding ¹³C signals at -1.12 and 64.72 ppm, respectively.

Recrystallization of the orange powder and XRD analysis of the obtained single crystals allowed us to confirm the identity of the product as the monomeric complex 4. Inspection of the molecular diagram shown in Scheme 7 reveals that this compound features the aforementioned unusual 4-membered ring metallacycle incorporating the amine moiety. It also has a 6-membered metallacycle incorporating the phosphinite moiety, similarly to what was observed in **2**.

Having established the competence of morpholine to intercept the formation of 2, we moved next to test this new reactivity with a less nucleophilic secondary amine in order to determine the lower threshold of nucleophilicity required for hindering the formation of 2. Substrate 1 was thus treated at room temperature with 2.0 equiv of N-ethylaniline and 1.2 equiv each of Et₃N and the Ni^{II} precursor, in THF or acetonitrile. As before, the reaction proceeded more slowly in THF (16 h), but gave a somewhat cleaner conversion (Figure S129). ³¹P NMR spectral analysis of these crystals showed two singlets at 207 and 204 ppm in a 7:1 ratio (Figure S74), suggesting the existence of two isomers of the target complex. The nucleophilic moiety N(Et)(Ph) being nonsymmetrical, we infer that these isomers could arise from different orientations of the N-substituents relative to the aromatic cycle of the pincer ligand backbone (Scheme 8).

Scheme 8. Synthesis of Complex 5



Workup of the above reaction mixture followed by recrystallization gave single crystals of the target complex 5. XRD analysis of a single crystal revealed one isomer of complex 5 featuring the Ph moiety pointing away from the aromatic cycle of the backbone (Scheme 8). Full NMR spectral analysis revealed that this isomer is the major product in solution in a 7:1 ratio. An NOE analysis also showed magnetization transfer cross peaks resulting from dynamic exchange between the two isomers, indicating that both isomers are in equilibrium at room temperature.

Next, we tested the reactivity of primary amines to see if the presence of a second N–H can hinder the formation of a 6,4-POCN pincer complex. Treating our usual Ni^{II} precursor with Et₃N and *i*-PrNH₂ as nucleophile showed the formation of the target 6,4-POCN^{iPr,H} complex as two diastereoisomers **6** and **6'** (³¹P δ : 200.6 and 200.9 ppm), as well as <5% of by-products. Recrystallization afforded single crystals of **6**, the isomer with the *i*-Pr substituent of the amine moiety pointing away from the aromatic cycle of the backbone (Scheme 9).

As mentioned in the case of complex 5, magnetization transfer cross peaks in the NOE spectrum indicated that complex 6 was involved in a dynamic exchange process in





https://dx.doi.org/10.1021/acs.organomet.0c00590 Organometallics XXXX, XXX, XXX–XXX solution, at room temperature. This conclusion was corroborated by the following experiment. Analysis of a batch of crystals by powder XRD (Figure S133) confirmed the presence of only the one diastereoisomer of **6** previously identified by single crystal XRD analysis. Redissolution of the powder in C_6D_6 and analysis by ³¹P NMR spectroscopy showed again the presence of two isomers in a close to 1:1 ratio. This finding establishes that the isomerization process occurs in solution at room temperature, likely owing to the hemilability of the amine arm. That the dissociation of the amine moiety is accessible at room temperature is presumably because it releases the strain in the 4-membered nickelacycle.

Repeating the reaction shown in Scheme 9 with the less nucleophilic PhNH₂ led to a less clean reaction as evidenced by the appearance of several peaks in the 198–206 ppm region, none being dominant (Figure S131). Nevertheless, since the starting material had completely disappeared, we undertook the workup as before and obtained some crystals of the target complex (6,4-POCN^{Ph,H})NiBr (7 in Scheme 10). XRD analysis

Scheme 10. Formation of (6,4-POCN^{R',H})NiBr Pincer Complexes 7–9 from Primary Amines



of one of these crystals showed it to be the isomer with the Ph substituent of the amine moiety pointing away from the aromatic ring of the pincer backbone (see the Supporting Information for the structural diagram).

Similar reactions conducted with $CyNH_2$ and t-BuNH₂ proved not as clean as the reaction with *i*-PrNH₂, but still much cleaner than that with PhNH₂. Thus, the ³¹P NMR spectra of the crude mixtures of these reactions indicated a similar outcome, displaying two major peaks in each case, at 200.7 and 201.0 ppm for the reaction with $CyNH_2$ and at 198.5 and 200.0 ppm for the reaction with *t*-BuNH₂. The intensities of these peaks were in a nearly 1:1 ratio, suggesting the coexistence of two isomers close in energy.

The reaction conditions for the synthesis of these complexes and the workup processes have not been optimized, but XRD analyses were performed on crystals obtained from these reactions for the sole purpose of structural comparison. These analyses showed once again the formation of (6,4-POCN)NiBr complexes (8 and 9, Scheme 10); the isomers obtained were those wherein the *N*-alkyl substituent was pointing away from the arene ring of the pincer backbone.

To gain some insight into the mechanism of the reactions with amine nucleophiles, we carried out a competition experiment between the two nucleophiles PhN(Et)H and *i*-PrNH₂. ³¹P NMR spectral monitoring of the reaction of **1** with 1.2 equiv each of the Ni^{II} precursor, *i*-PrNH₂, PhN(Et)H and Et₃N gave a surprising result. After 1 h of reaction in THF at room temperature, the ratio of the two complexes **5**:6 was found to be 57:43, indicating that the less nucleophilic PhN(Et)H produces the (6,4-POCN)NiBr product slightly faster (Scheme 11).

The above seemingly counterintuitive observation can be rationalized if we recall that the more nucleophilic amine binds Scheme 11. Competitive Formation of 6,4-POCN Pincer Complexes 5 and 6



more readily to the Ni center.¹⁹ Thus, a higher proportion of the less nucleophilic amine would be expected to remain uncoordinated in the reaction mixture. For this reason, and at least in the early stages of the reaction, the less nucleophilic amine would be more likely to participate in the outer-sphere attack on the Ni-bound vinyl moiety group to give the anticipated product. Indeed, when the above competition experiment was conducted over longer reaction times, the ratio of **5**:6 reversed to 47:53 after 7 h and then 33:67 after 24 h (Scheme 11).²⁰ This indicates that the formation of **6** is thermodynamically more favored than that of **5**, and that **6** can be converted to **5** in the reaction medium.

6,4-POCP-Type Pincer Complexes from *P***-Based Nucleophiles.** Having developed a relatively facile protocol for the synthesis of the above-discussed rare 6,4-POCN-type pincer complexes of Ni prompted us to test this approach for the synthesis of the corresponding compounds based on 6,4-POCP ligands that are also quite rare.²¹ As a proof of concept for this idea, we stirred 1 in THF at room temperature with a 1.2:1.2:1.0 ratio of the Ni precursor, Et₃N and an Et₂O solution of *i*-Pr₂PH.²²

Analysis of the above reaction mixture (after 4 h) by ³¹P NMR spectroscopy showed a major set of two AB doublets at 192 and -57 ppm. The large coupling constants of this set of signals ($J_{PP} = 310$ Hz) is characteristic of *trans* phosphines, allowing us to conclude that they represent the expected complex **10** (Scheme 12). The remaining minor resonances

Scheme 12. Synthesis of the (6,4-POCP)NiBr Complexes 10 and 11 Arising from R'_2PH



included the signals for complex **2**, the known complex $(i - Pr_2PH)_2NiBr_2$,¹⁴ and other unidentified resonances. Orange crystals obtained from workup of this reaction mixture were identified as the desired (6,4-POCP^{iPr2})NiBr complex **10** by NMR spectroscopy and XRD analysis (Scheme 12).

To limit the formation of byproduct **2** in the above approach, we changed the source of nucleophile from free *i*- Pr_2PH to the complex $(i-Pr_2PH)_2NiBr_2$. Thus, treating **1** with 1.2 equiv of Et_3N , 0.7 equiv of the usual Ni^{II} precursor, and 0.5 equiv of $(i-Pr_2PH)_2NiBr_2$ gave complex **10** in 76% yield, along with minor amounts of **2**; the formation of the latter side-product could not be suppressed completely.

The formation of even minor quantities of complex 2 in the above reaction with *i*-Pr₂PH was somewhat surprising, because

this side-product was known to form much more slowly (16 h in THF). It occurred to us that in this case **2** might well arise from the reaction with small amounts of *i*-Pr₂P(O)H impurities generated during the synthesis of *i*-Pr₂PH.²³ To validate this hypothesis, we prepared *i*-Pr₂P(O)H²⁴ and used it in a reaction with 1.0 equiv of **1** and 1.2 equiv of both Et₃N and the Ni^{II} precursor in THF. This mixture showed complete disappearance of the starting material after 3 h and we detected a sharp resonance at 205 ppm and a broad one at 96 ppm attributed to the (6,5-POCPO)NiBr complex **2** (Scheme 13).

Scheme 13. Direct Preparation of Complex 2 from *i*-Pr₂P(O)H



It is noteworthy that this reaction was much cleaner than the synthetic approach described earlier with 1 only (Scheme 3). Applying this new synthetic route allowed us to isolate 2 in high yields and uncontaminated by the side-product 3.

Finally, we studied the reaction of 1 with Ph₂PH as shown in Scheme 12. ³¹P NMR spectral analysis of the crude reaction mixture (deep red) obtained after 4 h confirmed the formation of the target complex: the resonance for the starting material had been replaced by AB doublets at 197 and -78 ppm with a $J_{PP'}$ of 320 Hz. Workup of the reaction mixture followed by crystallization of the resulting brown solids from hot acetonitrile afforded deep red crystals of the target product (6,4-POCP^{Ph})NiBr, 11, in only 35% yields. Unfortunately, conducting the reaction in acetonitrile did not result in improved yields. XRD analyses and full NMR spectroscopic characterization confirmed its identity.

It is noteworthy that the above reaction also generated a mass of brick-red solid that remained insoluble in either polar or nonpolar solvents (acetonitrile, THF, Et_2O , or toluene). One clue for this side reaction is the observation of minor resonances attributed to complex **10** in the crude reaction mixture, which suggests an exchange reaction between the nucleophile used, Ph₂PH, and substrate **1**, as shown in eq 1. Such an exchange equilibrium would also rationalize the poor isolated yield for complex **11**, if Ni complexes generated from the competitive Ph₂P–OAr ligand are less soluble.

$$i - \Pr_2 P - OAr + \Pr_2 P - H \rightleftharpoons i - \Pr_2 P - H + \Pr_2 P - OAr$$
 (1)

Electrochemical Analysis. To the best of our knowledge, the pincer-type compounds described in the above sections represent new families of pincer–Ni complexes. Indeed, Scifinder and CCCD searches have revealed no previous example of POCN-Ni complexes featuring an aliphatic backbone, nor pincer-type Ni complexes based on POCP ligands (phosphinite/phosphine donor moieties) or POCP(O) ligands (phosphinite/phosphine oxide donor moieties) with either aliphatic or aromatic linking groups. The access to these unprecedented pincer-type Ni complexes led us, naturally, to investigate their structures and other properties relevant to reactivities. Our long-standing interest in the synthesis and reactivities of high-valent Ni complexes^{10a,25} prompted us to use cyclic voltammetry (CV) to measure the one-electron oxidation potentials of the above-mentioned $POC_{sp}{}^{3}N$ and $POC_{sp}{}^{3}P$ complexes. The main objective of this exercise was to study the variations in redox potentials as a function of different structural features, and use any insight gleaned from such studies to prepare thermally stable high-valent derivatives.

Although solid samples of the new complexes proved stable in air over a few hours, exposing their solutions to air led to quick decomposition as evidenced by the quick disappearance of the yellow/orange colors of the complexes. For this reason, the samples for CV measurements were prepared in the glovebox. The CV measurements began with CH_2Cl_2 solutions of 4 using $[n-Bu_4N]PF_6$ as supporting electrolyte. These showed a distinct but irreversible oxidation wave attributed to Ni^{II}/Ni^{III} (Figure S3). That this one-electron oxidation is irreversible implies that the in situ generated 15-electron species $[(6,4-POCN^{morph})Ni^{III}Br]^+$ is unstable. Thus, we switched to using acetonitrile solution to see if the greater binding ability of this solvent might stabilize the in situ formed trivalent cationic species and favor reversibility of the redox events.

The CV trace obtained at a scan rate of 100 mV/s in acetonitrile was much cleaner, but the difference between the anodic and cathodic peak potentials in this trace was 270 mV, which is much greater than the ideal value of 59 mV for $|E_{p,a} E_{\rm p,c}$ of a fully reversible single electron redox process.²⁶ This larger-than-ideal potential difference is attributed to the likelihood that the redox process in question involves different species; in other words, the oxidation occurs with complex 4, whereas the reduction likely occurs with the in situ generated penta- or hexacoordinate cationic MeCN adducts $[\{\kappa^{N}, \kappa^{C}, \kappa^{P}, 2 [(morphol-N-yl)CH_2CH]-C_6H_4-OP(i-Pr)_2$ NiBr(NCMe)_n]⁺ (n = 1 or 2). For this reason, we have opted to base our analysis of the CV data on the anodic peak potentials $E_{p,a}$. The values for all the compounds investigated here have been referenced to the $E_{1/2}$ for ferrocene (Fc/Fc⁺), which is used as the standard complex for calibrating our measurements.

Analogous CV measurements were also conducted on acetonitrile samples of 6,4-POCN complexes 5 and 6, and representative CV traces for 4-6 are shown in Figure 1. Examination of the CV data presented in this figure allows us to comment on the impact of various structural features on



Figure 1. Cyclic voltammograms of complexes 4–6 (1 mM) in the presence of $[n-Bu_4N]PF_6$ (100 mM) in MeCN at a glassy carbon electrode. Potentials are referenced against the $E_{1/2}$ of the Fc/Fc⁺ redox couple.

electrochemical oxidation potentials. For instance, the $E_{\rm p,a}$ values for 4 (-13 mV), 5 (+89 mV), and 6 (+57 mV) confirm that the morpholine moiety bestows a greater electron density to Ni relative to N(*i*-Pr)H and N(Ph)Et. It is also worth noting here that the CV traces for these complexes were all quasi-reversible; nevertheless, decomposition of the Ni^{III} species is evident, implying that the presence/absence of an N–H moiety has no major influence on this phenomenon.

It is also instructive to compare the above data for the 6,4-POC_{sp}³N complexes **4–6** to the $E_{p,a}$ values we have obtained for the 6,4-POC_{sp}³P pincer complexes **10** and **11** that feature a phosphine donor moiety instead of an amine moiety. Curiously, the CV traces (Figure 2) show anodic potentials



Figure 2. Cyclic voltammograms of complexes **9**, **10**, and **2** (1 mM) in the presence of $[n-Bu_4N]PF_6$ (100 mM) in MeCN at a glassy carbon electrode. Potentials are referenced against the $E_{1/2}$ of the Fc/Fc⁺ redox couple.

that are quite comparable to the 6,4-POC_{sp}³N-type complex 4: -8 mV (10) and +14 mV (11) vs -13 mV (4). These findings were somewhat surprising, because we had anticipated that replacing a "hard" amine moiety in 4 by a "soft" phosphine moiety should be unfavorable to oxidation. We were also surprised that the $E_{p,a}$ values for these 6,4-POC_{sp}³P-type complexes did not seem to follow the anticipated order: complex 10, the one bearing the presumed better σ -donor $CH_2P(i-Pr)_2$ moiety, was found slightly more difficult to oxidize than its CH_2PPh_2 counterpart. This said, the difference is not large.

The last complex studied by CV was the 6,5-POCP(O) compound **2**. The analysis of the data is complicated in this case owing to the flatness of the anodic wave: an oxidation event is evident, but a clear anodic peak is not revealed (i.e., dI/dE never reaches 0 around the oxidation event). Thus, we used the first derivative dI/dE = f(E) to approximate the $E_{p,a}$ closer to the inflection point, which turned out to be between +25 and +50 mV vs Fc/Fc⁺. This uncertainty in the precise value of $E_{p,a}$ notwithstanding, we conclude that the P(O) donor moiety does not diminish the electrochemical oxidation prospects for the Ni center relative to the 6,4-POC_{sp}³N complex bearing the strong σ -donor NH(*i*-Pr). This is presumably due to a strongly polarized phosphine oxide moiety in which the R₃P⁺-O⁻ resonance form is prevalent.

Overall, the CV measurements presented above allow us to conclude that the new pincer complexes studied herein are much easier to oxidize relative to the classical pincer-type complexes (5,5-POC_{sp}²N)NiBr and (5,5-POC_{sp}²OP)NiBr^{29a,b} that we have studied previously (see Figure S5). It appears, therefore, that a C_{sp}^{3} –Ni moiety bestows a great deal of electron density to the Ni center. On the other hand, van Koten's (NC_{sp}²N)NiBr system is much easier to oxidize (-390 mV in acetone)² in spite of its aromatic backbone, establishing the superior oxidation prospects for pincer systems with two amine donor moieties.

Structural Characterization of the New Complexes. Single crystal diffraction analyses have been performed for all the new complexes prepared in this study. This section presents the most pertinent parameters for all structures (Table 1) along with molecular diagrams and brief descriptions for the structures of complexes 2-6, 10, and 11. Complete listings of the crystal data as well as the molecular diagrams for complexes 7-9 are presented in the Supporting Information.

All the complexes under discussion display a square planar geometry, the Ni center being located on or near the mean coordination plane defined by the four atoms bound to it. The 6-membered nickelacycle forces the aromatic ring originating from ligand 1 to lift off the mean coordination plane by about

Table 1. Selected Bonds	(Å)	and Angles	(deg) for	Complexes	2 - 11	
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	Ni-C7	Ni-P1	Ni-Br	Ni-E ^a	P-Ni-C	E-Ni-C	P-Ni-E	C-Ni-Br
2 ^b	1.9979(17)	2.1104(5)	2.3743(3)	1.9477(12)	90.41(5)	90.74(6)	165.08(4)	171.10(6)
	1.9978(15)	2.1106(4)	2.3785(3)	1.9317(10)	88.39(5)	91.11(6)	177.47(4)	171.85(5)
3 ^c	1.9101(16)	2.1103(5)	2.3479(3)	2.0103(16)	92.46(5)	43.18(6)	135.02(5)	157.10(5)
	1.9051(14)	2.1058(4)	2.3479(3)	2.0148(14)	90.47(4)	43.33(6)	133.61(4)	155.99(4)
4	1.9436(16)	2.1095(5)	2.3524(3)	2.0250(14)	90.22(5)	72.95(6)	158.13(4)	172.07(5)
5	1.943(2)	2.0967(7)	3.3533(4)	2.026(2)	90.06(7)	72.36(9)	156.80(6)	168.82(7)
6	1.9433(15)	2.1141(4)	2.3734(3)	1.9884(13)	90.70(5)	73.91(6)	164.39(4)	175.64(5)
7	1.938(2)	2.1065(5)	2.3608(3)	1.9884(15)	89.14(6)	74.07(7)	162.41(5)	173.25(5)
8	1.945(2)	2.1154(6)	2.3727(4)	1.9828(18)	89.54(7)	73.83(8)	163.98(6)	175.25(7)
	1.951(2)	2.1130(6)	2.3864(4)	1.9836(18)	89.69(6)	73.69(8)	162.78(6)	174.41(6)
9	1.939(2)	2.1175(7)	2.3689(4)	2.004(2)	88.17(7)	73.68(9)	159.91(6)	173.95(8)
	1.942(2)	2.1214(6)	2.3753(4)	2.008(2)	89.19(7)	73.53(9)	161.45(6)	175.77(7)
10	1.991(3)	2.1501(8)	2.3562(5)	2.1762(8)	89.79(8)	73.07(8)	161.47(3)	174.89(8)
	1.998(3)	2.1509(8)	2.3604(5)	2.1650(8)	90.37(8)	73.44(8)	163.59(3)	173.42(8)
11	2.001(3)	2.1541(8)	2.3472(6)	2.1897(8)	90.30(8)	71.65(8)	155.44(4)	174.19(8)

^{*a*}E refers to O2 in complex 2, C8 in complex 3, N1 in complexes 4-9, and P2 in complexes 10-11. ^{*b*}The first row corresponds to value found in the structure of 2 only, and the second row to values found in cocrystals of 2 and 3. ^{*c*}The first row corresponds to value found in the structure of 3 only, and the second row to values found in cocrystals of 2 and 3.

51–66° (Figures 3–5). Perhaps the most noteworthy feature of the 6,4-POCN complexes 4-9 and 6,4-POCP complexes 10



Figure 3. Side views of the molecular diagrams for complexes 2 (left) and 4 (right). Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms refined via the riding model and terminal Me substituents of $P(i-Pr)_2$ moleties are omitted for clarity.



Figure 4. Molecular diagrams for complexes 5 (left) and 6 (right) that crystallized as R,R and S,S isomers. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms refined via the riding model are omitted for clarity.



Figure 5. Molecular diagrams for complexes 10 (left) and 11 (right). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms refined via the riding model are omitted for clarity.

and **11** is the 4-membered nickelacycle. The acute *cis* angles C7–Ni1–N1 and C7–Ni1–P2 defining these 4- membered rings range from 71° to 74°, whereas the C7–Ni1–P1 angles defining the 6-membered nickelacycles are closer to the ideal right angles (88° –91°). By comparison, the C7–Ni1–O2 angle of 91° defining the 5-membered nickelacycle in complex **2** is also close to the ideal value expected for a square planar geometry, whereas the corresponding *cis* angles in the analogous 5,5-aromatic-pincer-Ni complexes reported previously²⁸ range from 83° to 85°.

As was alluded earlier (see for example Scheme 10), the solution isomerization displayed by our POCN complexes 5-9 likely results from the hemilabile N \rightarrow Ni interactions present in the 4-membered metallacycles of these complexes. Interestingly, the solid state data do not show any indication that the acute *cis* angles inside the 4-membered metallacycles cause unusually long Ni–N bond distances. Indeed, comparison of the Ni–N and Ni–P bond distances in 4-11 to the corresponding values in the analogous 5,5-POCN,^{18,27} 5,5-

POCOP,^{9a,28} 5,5-PCP,^{9b,29} and PCN³⁰ complexes does not reveal significant differences: 1.983(2)-2.026(2) vs 1.97-2.05 Å for Ni–N distances; 2.17-2.19 vs 2.16-2.21 Å for Ni–P distances.

One remarkable feature of the 6,4- and 6,5-pincer complexes described here is the relative insensitivity of the 6-membered metallacycle to the size of the adjoining metallacycle, as well as to the identity of the donor moiety contained in it. This is reflected in the P1–Ni1–C7 angles that are in the narrow range of $88-91^{\circ}$ over complexes 2 and 4-11. In contrast, the P–Ni–C *cis* angles of typical 5,5-pincer-Ni complexes are more acute ($80-85^{\circ}$),³¹ whereas (5,6-POCOP)NiBr displays a wider *cis* angle of 93° for its 5-membered nickelacycle.^{21b}

The *trans* C7–Ni1–Br1 angles are greater than 169° in all complexes except in the more distorted compound **3** wherein it is much smaller (156°). Among the 6,4-POCN complexes **4–9**, those featuring a N–H amine moiety show C7–Ni1–Br1 angles that are fairly close to the ideal value of 180°, whereas the corresponding angles in the analogous complexes with tertiary amine are somewhat narrower (174–176° vs 169–172°).

Other Ni-ligand bond distances were also found to be nearly constant, with only minor variations noted in certain cases. Thus, the Ni–Br distances range from 2.345 to 2.388 Å, which is in the same range as observed for the analogous POCOP, PCP, POCN, and PIMCOP complexes bearing $P(i-Pr)_2$ phosphinites. Among the 6,4-POCN complexes, those featuring a primary amine moiety display significantly longer Ni–Br distances (2.361–2.388 Å vs 2.352–2.353). Only small variations were observed among the Ni1–C7 bond distances in the 6,4-POCN complexes **4–9**, (1.938(2) to 1.951(2) Å). This is similar to the range of Ni–C distances reported for aliphatic 5,5-POCOP (1.94–1.96 Å); in contrast, significantly larger values were obtained for complexes **2**, **10**, and **11** (ranging 1.991(3)–2.001(3) Å). For compound **3**, the Ni1–C7 bond distance is significantly shorter with a value of 1.91 Å.

The Ni1–P1 bond distances found in complexes 2-9 are also in the same range as in the analogous 5,5-POCN-Ni complexes reported previously (2.11-2.12 vs 2.10-2.11 Å). The somewhat longer Ni1–P1 bond distances of 2.150(1)-2.154(1) Å observed in complexes 10 and 11 are likely due to the greater *trans* influence of the phosphine moieties. Consistent with this assertion, similar Ni–P bond distances (2.14-2.16 Å) have been reported in the analogous aliphatic and aromatic 5,5-POCOP^{*i*-Pr} complexes reported previously, whereas even longer Ni–P bond distances were found in the 6membered nickelacycle of the 6,5-POCOP^{*i*-Pr} (>2.17 Å).

The Ni1–O2 bond distances of 1.932(1)-1.948(1) Å and P2–O2 of 1.523(1) Å in our 6,5-POCPO complex 2 are similar to those observed in PCP(O) pincer–Ni complexes featuring a R(*i*-Pr)₂P=O \rightarrow Ni interaction (1.93–1.96 Å for Ni–O and 1.50–1.53 Å for P–O).³² It is also worth noting that the P=O bond distance displayed in 2 is clearly longer than in reported free *i*-Pr₂P(O)–CH₂–R molecules (with P–O bonds ranging 1.48–1.50 Å),³³ indicating a bond order close to unity and thus strong polarization of the R₃P⁺–O⁻ bond, which gives this arm an almost X-ligand character.

Additional structural analysis is required for complex 3 (Figure 6), in particular regarding what the structural parameters of this compound might reveal regarding the interactions between the Ni center and the carbons C7 and C8 arising from the vinyl moiety of ligand 1. We had argued earlier on the basis of NMR spectral data that the α and β forms of



Figure 6. Molecular diagram for complex **3**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms refined via the riding model and cocrystallized complex **2** are omitted for clarity.

compound 3 shown in Scheme 5 and featuring a nickelacyclopropane moiety are the prevalent resonance structures. Comparison of solid-state parameters to previously reported analogous complexes supports this argument. A CCDC search of complexes regarded as Ni(0) species featuring one alkene or *trans*-stillbene revealed that their C–C bond distances span the range of 1.395(4)-1.428(4) Å in spite of the presence of strong σ donors such as phosphines or NHC ligands. Surprisingly, in our 6,3-POCC complex 3 that bears only moderate σ donors (phosphinite, bromide), the C7–C8 bond distance is significantly longer, 1.446(2)-1.451(2) Å. This C-C distance is consistent with a metalacyclopropane It is not clear to us on what basis you write metalacyclopropane with a single "l" but metallacycle is written with double"l". moiety or an olefin moiety bearing an electron-withdrawing substituent (phosphonium) and coordinated to a formally anionic Ni(0) center. Closely analogous nickel complexes reported by Carmona's and Li's groups and bearing phosphonium substituents show very similar C-C bond lengths (1.44(2) and 1.458(5) Å).35,36

Another important consideration pertains to the Ni-C bond distances in complex 3. In mono-olefin-Ni(0) complexes, the Ni-C distances span the range of 1.96-2.01 Å, whereas much shorter distances of 1.88–1.91 Å are reported for the highly π acidic Ni-polyfluoroalkenes, which are regarded as essentially nickelacyclopropanes bound to Ni^{II.37} Given that the average Ni1-C7 bond length of 1.91 Å found in complex 3 is much shorter than C-Ni bonds in Ni-olefin complexes, the metalacyclopropane description for this moiety seems more reasonable. Indeed, the Ni1-C7 distance is even shorter than the corresponding distances in Ni–C $_{\rm benzyl}$ complexes (1.95– 2.02 Å),³⁸ in the 6,4 pincer compounds 4-11 reported here (1.93-2.01 Å), and also in previously reported aromatic/ aliphatic pincer-NiX complexes (1.94-1.96 Å).9,29 It should be acknowledged, however, that the second Ni-C distance in the putative metalacyclopropane moiety of complex 3 is much longer (Ni1-C8 = 2.010(2)-2.015(2) Å); we believe that the greater steric bulk of the phosphonium substituent on C8 might be at least partially responsible for this lengthening.

CONCLUSION

The study presented herein has led to the development of a new synthetic strategy for the preparation of unsymmetrical ECE'-Ni pincer complexes that are unprecedented. The key step in this synthetic route likely involves an outer-sphere nucleophilic addition onto the olefin moiety of the phosphinite 1; chelation of an electrophilic Ni^{II} center by this substrate activates the olefin moiety toward the requisite nucleophilic attack. This approach works with readily available precursors and proceeds at room temperature to give products that would be otherwise difficult to access without more elaborate starting materials such as zerovalent Ni precursors and proligands bearing one or more C-halide moieties. Thus, the new synthetic strategy under discussion obviates the need for C– H or C–X addition/metalation, frequently difficult steps that can constitute important obstacles for the synthesis of ECE'type pincer complexes.

An interesting and somewhat unexpected feature of the pincer—Ni complexes synthesized in the current study is the observed thermal stability of the 4-membered metallacycles. The observed solution isomerization that these complexes undergo underlines the hemilability of the N \rightarrow Ni coordination bond; this hemilability bodes well for potential reactivities and catalytic applications of these complexes.

Another interesting aspect of the pincer complexes described in this report touches on the ligand/complex features that render the Ni^{II} center prone to relatively facile electrochemical oxidation. The CV measurements we have reported demonstrate the important impact of a C_{sp}^3 -Ni moiety for facilitating single electron oxidation of the Ni centers in these complexes. Future efforts will be directed at exploiting the insights gleaned from these studies to prepare thermally stable high-valent analogues of these pincer complexes. We will also pursue the possibility of extending this synthetic strategy for the preparation of analogous pincer complexes with other metals, as well as to other ligand platforms such as phosphinites derived from homoallylic alcohols.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00590.

Synthetic procedures, NMR spectra, crystal structure data, and additional figures (PDF)

Accession Codes

CCDC 2006809–2006820 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Moulton, C. J.; Shaw, B. L. Transition metal-carbon bonds. Part XLII. Complexes of nickel, palladium, platinum, rhodium and iridium with the tridentate ligand 2,6-bis[(di-t-butylphosphino)methyl]phenyl. J. Chem. Soc., Dalton Trans. 1976, No. 11, 1020– 1024. (b) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. Formation of large chelate rings and cyclometallated products from diphosphines of type But2P(CH2)nPBut2(n= 5-8) and Ph2P(CH2)SPPh2 with palladium and platinum chlorides: factors affecting the stability and conformation of large chelate rings. J. Chem. Soc., Dalton Trans. 1979, No. 12, 1972–1982. (c) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. Large-ring and cyclometallated rhodium complexes from some medium-chain.alpha.,.omega.-diphosphines. J. Am. Chem. Soc. 1980, 102 (13), 4373–4379.

(2) (a) Grove, D. M.; Van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. Unique stable organometallic nickel(III) complexes; syntheses and the molecular structure of [Ni[C6H3(CH2NMe2)2– 2,6]I2]. J. Am. Chem. Soc. **1983**, 105 (5), 1379–1380. (b) Grove, D. M.; Van Koten, G.; Mul, P.; Zoet, R.; Van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. Syntheses and characterization of unique organometallic nickel(III) aryl species. ESR and electrochemical studies and the x-ray molecular study of squarepyramidal [Ni{C6H3(CH2NMe2)2-0,0'}I2]. *Inorg. Chem.* **1988**, 27 (14), 2466–2473.

(3) (a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. Highly Active Pd(II) PCP-Type Catalysts for the Heck Reaction. J. Am. Chem. Soc. 1997, 119 (48), 11687-11688. (b) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. The synthesis of a new palladacycle catalyst. Development of a high performance catalyst for Heck reactions. Tetrahedron Lett. 1999, 40 (41), 7379-7383. (c) Bedford, R. B.; Draper, S. M.; Noelle Scully, P.; Welch, S. L. Palladium bis(phosphinite) 'PCP'-pincer complexes and their application as catalysts in the Suzuki reaction. New J. Chem. 2000, 24 (10), 745-747. (d) Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Canty, A. J.; van Koten, G. Design and Performance of Rigid Nanosize Multimetallic Cartwheel Pincer Compounds as Lewis-Acid Catalysts. Organometallics 2001, 20 (14), 3159-3168. (e) Sebelius, S.; Olsson, V. J.; Szabó, K. J. Palladium Pincer Complex Catalyzed Substitution of Vinyl Cyclopropanes, Vinyl Aziridines, and Allyl Acetates with Tetrahydroxydiboron. An Efficient Route to Functionalized Allylboronic Acids and Potassium Trifluoro-(allyl)borates. J. Am. Chem. Soc. 2005, 127 (30), 10478-10479. (f) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. Catalytic Alkane Metathesis by Tandem Alkane Dehydrogenation-Olefin Metathesis. Science 2006, 312 (5771), 257-261. (g) Naghipour, A.; Sabounchei, S. J.; Morales-Morales, D.; Canseco-González, D.; Jensen, C. M. A highly active two sixmembered phosphinite palladium PCP pincer complex [PdCl{C6H3-(CH2OPPri)2-2,6}]. Polyhedron 2007, 26 (7), 1445-1448. (h) Gunanathan, C.; Ben-David, Y.; Milstein, D. Direct Synthesis of Amides from Alcohols and Amines with Liberation of H2. Science 2007, 317 (5839), 790-792. (i) Bernskoetter, W. H.; Brookhart, M. Kinetics and Mechanism of Iridium-Catalyzed Dehydrogenation of Primary Amines to Nitriles. Organometallics 2008, 27 (9), 2036-2045. (j) Zweifel, T.; Naubron, J.-V.; Grützmacher, H. Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines. Angew. Chem., Int. Ed. 2009, 48 (3), 559-563. (4) (a) Batema, G. D.; Lutz, M.; Spek, A. L.; van Walree, C. A.; Donegá, C. d. M.; Meijerink, A.; Havenith, R. W. A.; Pérez-Moreno, J.; Clays, K.; Büchel, M.; Dijken, A. v.; Bryce, D. L.; van Klink, G. P. M.; Koten, G. v. Substituted 4,4'-Stilbenoid NCN-Pincer Platinum-(II) Complexes. Luminescence and Tuning of the Electronic and NLO Properties and the Application in an OLED. Organometallics 2008, 27 (8), 1690-1701. (b) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. Organoplatinum crystals for gas-triggered switches. Nature 2000, 406 (6799), 970-974. (c) Rivera, E. J.; Figueroa, C.; Colón, J. L.; Grove, L.; Connick, W. B. Room-Temperature Emission from Platinum(II) Complexes Intercalated into Zirconium Phosphate-Layered Materials. Inorg. Chem. 2007, 46 (21), 8569-8576. (d) Tastan, S.; Krause, J. A.; Connick, W. B. Synthesis, structures and spectroscopic properties of palladium(II) complexes with tridentate piperidyl-containing pincer ligands. Inorg. Chim. Acta 2006, 359 (6), 1889-1898.

(5) (a) Albrecht, M.; van Koten, G. Platinum Group Organometallics Based on "Pincer" Complexes: Sensors, Switches, and Catalysts. Angew. Chem., Int. Ed. 2001, 40 (20), 3750-3781. (b) van der Boom, M. E.; Milstein, D. Cyclometalated Phosphine-Based Pincer Complexes: Mechanistic Insight in Catalysis, Coordination, and Bond Activation. Chem. Rev. 2003, 103 (5), 1759-1792. (c) Singleton, J. T. The uses of pincer complexes in organic synthesis. Tetrahedron 2003, 59 (11), 1837-1857. (d) Slagt, M. Q.; Zwieten, D. A. P. v.; Moerkerk, A. J. C. M.; Gebbink, R. J. M. K.; Koten, G. v. NCN-pincer palladium complexes with multiple anchoring points for functional groups. Coord. Chem. Rev. 2004, 248 (21), 2275-2282. (e) Liang, L.-C. Metal complexes of chelating diarylamido phosphine ligands. Coord. Chem. Rev. 2006, 250 (9), 1152-1177. (f) Nishiyama, H. Synthesis and use of bisoxazolinyl-phenyl pincers. Chem. Soc. Rev. 2007, 36 (7), 1133-1141. (g) Benito-Garagorri, D.; Kirchner, K. Modularly Designed Transition Metal PNP and PCP Pincer Complexes based on Aminophosphines: Synthesis and Catalytic Applications. Acc. Chem. Res. 2008, 41 (2), 201-213. (h) Leis, W.; Mayer, H. A.; Kaska, W. C. Cycloheptatrienyl, alkyl and aryl PCPpincer complexes: Ligand backbone effects and metal reactivity. Coord. Chem. Rev. 2008, 252 (15), 1787-1797. (i) Selander, N.; Szabó, K. J. Catalysis by Palladium Pincer Complexes. Chem. Rev. 2011, 111 (3), 2048–2076.

(6) (a) Grove, D. M.; Van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. Organonickel(II) complexes of the tridentate monoanionic ligand 0,0'-bis[(dimethylamino)methylphenyl (N-C-N). Syntheses and the x-ray crystal structure of the stable nickel(II) formate [Ni(N-C-N)O2CH]. Organometallics 1984, 3 (7), 1003-1009. (b) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. Electronic tuning of arylnickel(II) complexes by para substitution of the terdentate monoanionic 2,6-bis-[(dimethylamino)methyl]phenyl ligand. Organometallics 1994, 13 (2), 468-477. (c) Kleij, A. W.; Gossage, R. A.; Klein Gebbink, R. J. M.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. A "Dendritic Effect" in Homogeneous Catalysis with Carbosilane-Supported Arylnickel(II) Catalysts: Observation of Active-Site Proximity Effects in Atom-Transfer Radical Addition. J. Am. Chem. Soc. 2000, 122 (49), 12112-12124. (d) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. A Bis(ortho-amine)aryl-Gold(I) Compound as an Efficient, Nontoxic, Arylating Reagent. Organometallics 2002, 21 (21), 4556-4559.

(7) Other examples of pincer-type nickel complexes easily accessible through C-H metalation include POCOP- and POCN-type pincer complexes of nickel featuring two phosphinite or one phosphinite and one amine donor moieties. For representative reports of this type of complexes, see: (a) Gómez-Benítez, V.; Baldovino-Pantaleón, O.; Herrera-Álvarez, C.; Toscano, R. A.; Morales-Morales, D. High yield thiolation of iodobenzene catalyzed by the phosphinite nickel PCP pincer complex: [NiCl{C6H3-2,6-(OPPh2)2}]. Tetrahe-

dron Lett. 2006, 47, 5059-5062. (b) Benito-Garagorri, D.; Bocokić, V.; Mereiter, K.; Kirchner, K. A Modular Approach to Achiral and Chiral Nickel(II), Palladium(II), and Platinum(II) PCP Pincer Complexes Based on Diaminobenzenes. Organometallics 2006, 25 (16), 3817-3823. (c) Chakraborty, S.; Krause, J. A.; Guan, H. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes. Organometallics 2009, 28, 582-586. (d) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. An Efficient Nickel Catalyst for the Reduction of Carbon Dioxide with a Borane. J. Am. Chem. Soc. 2010, 132, 8872-8873. (e) Vabre, B.; Lindeperg, F.; Zargarian, D. Direct, one-pot synthesis of POCOP-type pincer complexes from metallic nickel. Green Chem. 2013, 15 (11), 3188-3194. (f) Mougang-Soumé, B.; Belanger-Gariépy, F.; Zargarian, D. Synthesis, Characterization, and Oxidation of New POCNimine-Type Pincer Complexes of Nickel. Organometallics 2014, 33 (21), 5990-6002. (g) For a recent review on ECE-type pincer complexes of nickel, see: Zargarian, D.; Castonguay, A.; Spasyuk, D. M. ECE-Type Pincer Complexes of Nickel. In Organometallic Pincer Chemistry; van Koten, G., Milstein, D., Eds.; Springer: Berlin, Heidelberg, 2013; pp 131-173.

(8) (a) Cloutier, J.-P.; Vabre, B.; Moungang-Soumé, B.; Zargarian, D. Synthesis and Reactivities of New NCN-Type Pincer Complexes of Nickel. *Organometallics* **2015**, *34* (1), 133–145. (b) Shao, D.-D.; Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. Neutral and cationic chiral NCN pincer nickel(ii) complexes with 1,3-bis(2'-imidazolinyl)-benzenes: synthesis and characterization. *Dalton Trans.* **2011**, *40* (35), 9012–9019.

(9) (a) Pandarus, V.; Zargarian, D. New Pincer-Type Diphosphinito (POCOP) Complexes of Nickel. *Organometallics* 2007, 26 (17), 4321–4334. (b) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. Preparation and Reactivities of PCP-Type Pincer Complexes of Nickel. Impact of Different Ligand Skeletons and Phosphine Substituents. *Organometallics* 2008, 27 (21), 5723–5732. (c) Pandarus, V.; Castonguay, A.; Zargarian, D. Ni(II) complexes featuring non-metallated pincer-type ligands. *Dalton Trans.* 2008, No. 35, 4756–4761.

(10) For selected reports of PCP-type pincer complexes featuring a M-Csp3 linkage, see: (a) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. Palladium and rhodium complexes of a chiral pincer ligand derived from 1,3-trans disubstituted cyclohexane. Inorg. Chim. Acta 2006, 359 (9), 2806-2811. (b) Arunachalampillai, A.; Olsson, D.; Wendt, O. F. Synthesis and characterisation of PCsp3P phosphine and phosphinite iridium complexes. Cyclometallation and dehydrogenation of a cyclohexyl ring. Dalton Trans. 2009, No. 40, 8626-8630. (c) Olsson, D.; Arunachalampillai, A.; Wendt, O. F. Synthesis and characterisation of PCsp3P phosphine and phosphinite platinum(ii) complexes. Cyclometallation and simple coordination. Dalton Trans. 2007, No. 46, 5427-5433. (d) Nilsson, P.; Wendt, O. F. Kinetic investigation of a PC(sp3)P pincer palladium (II) complex in the Heck reaction. J. Organomet. Chem. 2005, 690 (18), 4197-4202. (e) Olsson, D.; Wendt, O. F. Suzuki reaction catalysed by a PCsp3P pincer Pd(II) complex: Evidence for a mechanism involving molecular species. J. Organomet. Chem. 2009, 694 (19), 3112-3115. (f) Zhao, J.; Goldman, A. S.; Hartwig, J. F. Oxidative Addition of Ammonia to Form a Stable Monomeric Amido Hydride Complex. Science 2005, 307 (5712), 1080-1082. (g) Jonasson, K. J.; Polukeev, A. V.; Marcos, R.; Ahlquist, M. S. G.; Wendt, O. F. Reversible α -Hydrogen and α -Alkyl Elimination in PC(sp3)P Pincer Complexes of Iridium. Angew. Chem., Int. Ed. 2015, 54 (32), 9372-9375.

(11) Addition of nucleophiles on unsaturated hydrocarbons (including ethylene and other olefins) coordinated to transition metal-based electrophiles is well-precedented and has a long history. In the case of olefins, the reversal of polarity (Umpolung) resulting from coordination to electrophilic metal centers is often referred to as Wacker-type reactivity. For reviews and primary reports on Pd(II)-catalyzed Wacker-type reactions, see: (a) Henry, P. M. Palladium(ll)-Catalyzed Exchange and Isomerization Reactions. *Acc. Chem. Res.* **1973**, 6 (1), 16–24. (b) Keith, J. A.; Nielsen, R. J.; Oxgaard, J.; Goddard, W. A. Unraveling the Wacker Oxidation Mechanisms. *J. Am.*

Chem. Soc. 2007, 129 (41), 12342–12343. (c) Åkermark, B.; Bäckvall, J. E.; Hegedus, L. S.; Zetterberg, K.; Siirala-Hansén, K.; Sjöberg, K. Palladium-promoted addition of amines to isolated double bonds. J. Organomet. Chem. 1974, 72 (1), 127–138. (d) Majima, T.; Kurosawa, H. Isolation of stable β -alkoxyethylpalladium complexes and the first direct evidence for trans alkoxypalladation of ethylene. J. Chem. Soc., Chem. Commun. 1977, No. 17, 610–611. (e) Holton, R. A.; Kjonaas, R. A. Carbopalladation-depalladation of homoallylic amines and sulfides. J. Organomet. Chem. 1977, 142 (1), C15–C18. (f) Kurosawa, H.; Asada, N. The first direct evidence for trans addition of β -diketo anions and palladium to ethylene. Tetrahedron Lett. 1979, 20 (3), 255–256.

(12) Mangin, L. P.; Zargarian, D. C-H Nickelation of Aryl Phosphinites: Mechanistic Aspects. *Organometallics* **2019**, *38* (7), 1479–1492.

(13) Mangin, L. P.; Zargarian, D. C-H nickellation of phenolderived phosphinites: regioselectivity and structures of cyclonickelated complexes. *Dalton Trans.* **2017**, *46* (46), 16159–16170.

(14) Mangin, L. P.; Zargarian, D. C–H Nickelation of Naphthyl Phosphinites: Electronic and Steric Limitations, Regioselectivity, and Tandem C–P Functionalization. *Organometallics* **2019**, *38* (24), 4687–4700.

(15) (a) Estudiante-Negrete, F.; Hernández-Ortega, S.; Morales-Morales, D. Ni(II)–POCOP pincer compound [NiCl{C10H5–2,10-(OPPh2)2}] an efficient and robust nickel catalyst for the Suzuki– Miyaura coupling reactions. *Inorg. Chim. Acta* 2012, 387, 58–63. (b) Lefèvre, X.; Spasyuk, D. M.; Zargarian, D. New POCOP-type pincer complexes of Nickel(II). *J. Organomet. Chem.* 2011, 696 (4), 864–870. (c) Vabre, B.; Petiot, P.; Declercque, R.; Zargarian, D. Fluoro and Trifluoromethyl Derivatives of POCOP-Type Pincer Complexes of Nickel: Preparation and Reactivities in S(N)2 Fluorination and Direct Benzylation of Unactivated Arenes. *Organometallics* 2014, 33, 5173–5184.

(16) It should be noted that the amount of this adduct is a rough estimate based on the integration of the broad peak at 135 ppm against that of the product.

(17) One of the reviewers of this manuscript has pointed out that an inner-sphere insertion-type mechanism might also be viable for rationalizing the reactivities observed in our system. The following reports document pertinent precedents in a Pd(II) system: (a) Hanley, P. S.; Marković, D.; Hartwig, J. F. Intermolecular Insertion of Ethylene and Octene into a Palladium–Amide Bond. Spectroscopic Evidence for an Ethylene Amido Intermediate. J. Am. Chem. Soc. **2010**, 132 (18), 6302–6303. (b) Hanley, P. S.; Hartwig, J. F. Intermolecular Migratory Insertion of Unactivated Olefins into Palladium–Nitrogen Bonds. Steric and Electronic Effects on the Rate of Migratory Insertion. J. Am. Chem. Soc. **2011**, 133 (39), 15661–15673.

(18) Spasyuk, D. M.; Zargarian, D.; van der Est, A. New POCN-Type Pincer Complexes of Nickel(II) and Nickel(III). *Organometallics* **2009**, *28* (22), 6531–6540.

(19) Consistent with this assertion, during the synthesis of complex 8 in THF at 60 °C, we isolated colorless crystals of the compound $(CyNH_2)_4NiBr_2$ (Figure S144 for its molecular diagram). For a recent report of analogous $(RNH_2)_4NiBr_2$ complexes, see: Kudisch, M.; Lim, C.-H.; Thordarson, P.; Miyake, G. M. Energy Transfer to Ni-Amine Complexes in Dual Catalytic, Light-Driven C–N Cross-Coupling Reactions. J. Am. Chem. Soc. **2019**, 141 (49), 19479–19486.

(20) It is worth noting here that quantification by ³¹P NMR against $[n-Bu_4N][PF_6]$ as the internal standard confirmed that complex **5** was not simply decomposing in the medium.

(21) (a) For a previously reported 6,4-system see: Gwynne, E. A.; Stephan, D. W. Nickel(II) and Palladium(II) Bis-Aminophosphine Pincer Complexes. *Organometallics* **2011**, *30* (15), 4128–4135. (b) For a previously reported 6,5-system see: Salah, A.; Corpet, M.; ul-Hassan Khan, N.; Zargarian, D.; Spasyuk, D. M. Synthesis of unsymmetrical 5,6-POCOP'-type pincer complexes of nickel(ii): impact of nickelacycle size on structures and spectroscopic properties. *New J. Chem.* **2015**, *39* (8), 6649–6658. (22) *i*-Pr₂PH was prepared from *i*-Pr₂PCl and LiAlH₄ followed by H_2O quenching. See Supporting Information for details.

(23) Indeed, NMR analysis of the reaction mixture from the synthesis of *i*- Pr_2PH showed about 8% *i*- $Pr_2P(OH)$. See Supporting Information.

(24) This was prepared by the reaction *i*- Pr_2PCl with H_2O , followed by the addition of the base. See Supporting Information for details.

(25) (a) Cloutier, J.-P.; Zargarian, D. Functionalization of the Aryl Moiety in the Pincer Complex (NCN)NiIIIBr2: Insights on NiIII-Promoted Carbon-Heteroatom Coupling. *Organometallics* **2018**, 37 (9), 1446–1455. (b) Cloutier, J.-P.; Rechignat, L.; Canac, Y.; Ess, D. H.; Zargarian, D. C-O and C-N Functionalization of Cationic, NCN-Type Pincer Complexes of Trivalent Nickel: Mechanism, Selectivity, and Kinetic Isotope Effect. *Inorg. Chem.* **2019**, 58 (6), 3861–3874.

(26) Note that by comparison, the Fc/Fc+ couple used under the same conditions as the reference in these measurements gives a $|E_{p,a} - E_{p,c}|$ value of 68–72 mV, which is close to the ideal values.

(27) (a) Spasyuk, D. M.; Zargarian, D. Monomeric and Dimeric Nickel Complexes Derived from a Pincer Ligand Featuring a Secondary Amine Donor Moiety. Inorg. Chem. 2010, 49 (13), 6203-6213. (b) Sanford, J.; Dent, C.; Masuda, J. D.; Xia, A. Synthesis, characterization and application of pincer-type nickel iminophosphinite complexes. Polyhedron 2011, 30 (6), 1091-1094. (c) Smith, J. B.; Miller, A. J. M. Connecting Neutral and Cationic Pathways in Nickel-Catalyzed Insertion of Benzaldehyde into a C-H Bond of Acetonitrile. Organometallics 2015, 34 (19), 4669-4677. (d) Smith, J. B.; Kerr, S. H.; White, P. S.; Miller, A. J. M. Thermodynamic Studies of Cation-Macrocycle Interactions in Nickel Pincer-Crown Ether Complexes Enable Switchable Ligation. Organometallics 2017, 36 (16), 3094-3103. (e) Gudun, K. A.; Segizbayev, M.; Adamov, A.; Plessow, P. N.; Lyssenko, K. A.; Balanay, M. P.; Khalimon, A. Y. POCN Ni(ii) pincer complexes: synthesis, characterization and evaluation of catalytic hydrosilylation and hydroboration activities. Dalton Trans. 2019, 48 (5), 1732-1746.

(28) (a) Pandarus, V.; Zargarian, D. New pincer-type diphosphinito (POCOP) complexes of NiII and NiIII. Chem. Commun. 2007, No. 9, 978-980. (b) Vabre, B.; Spasyuk, D. M.; Zargarian, D. Impact of Backbone Substituents on POCOP-Ni Pincer Complexes: A Structural, Spectroscopic, and Electrochemical Study. Organometallics 2012, 31 (24), 8561-8570. (c) Chen, T.; Yang, L.; Li, L.; Huang, K.-W. Homocoupling of benzyl halides catalyzed by POCOP-nickel pincer complexes. Tetrahedron 2012, 68 (31), 6152-6157. (d) Wellala, N. P. N.; Dong, H. T.; Krause, J. A.; Guan, H. Janus POCOP Pincer Complexes of Nickel. Organometallics 2018, 37 (21), 4031-4039. (e) Adhikary, A.; Krause, J. A.; Guan, H. Configurational Stability and Stereochemistry of P-Stereogenic Nickel POCOP-Pincer Complexes. Organometallics 2015, 34 (14), 3603-3610. (f) García-Eleno, M. A.; Padilla-Mata, E.; Estudiante-Negrete, F.; Pichal-Cerda, F.; Hernández-Ortega, S.; Toscano, R. A.; Morales-Morales, D. Single step, high yield synthesis of para-hydroxy functionalized POCOP ligands and their Ni(II) pincer derivatives. New J. Chem. 2015, 39 (5), 3361-3365. (g) Lapointe, S.; Vabre, B.; Zargarian, D. POCOP-Type Pincer Complexes of Nickel: Synthesis, Characterization, and Ligand Exchange Reactivities of New Cationic Acetonitrile Adducts. Organometallics 2015, 34 (14), 3520-3531. (h) Li, H.; Meng, W.; Adhikary, A.; Li, S.; Ma, N.; Zhao, Q.; Yang, Q.; Eberhardt, N. A.; Leahy, K. M.; Krause, J. A.; Zhang, J.; Chen, X.; Guan, H. Metathesis reactivity of bis(phosphinite) pincer ligated nickel chloride, isothiocyanate and azide complexes. J. Organomet. Chem. 2016, 804, 132-141. (i) Joksch, M.; Haak, J.; Spannenberg, A.; Beweries, T. Synthesis, Characterisation and Hydrogen Bonding of Isostructural Group 10 Metal Halido Complexes Bearing a POCOP Ligand. Eur. J. Inorg. Chem. 2017, 2017 (32), 3815-3822. (j) Salomón-Flores, M. K.; Bazany-Rodríguez, I. J.; Martínez-Otero, D.; García-Eleno, M. A.; Guerra-García, J. J.; Morales-Morales, D.; Dorazco-González, A. Bifunctional colorimetric chemosensing of fluoride and cyanide ions by nickel-POCOP pincer receptors. Dalton Trans. 2017, 46 (15), 4950-4959.

(29) (a) Bachechi, F. X-Ray Structural Analysis of NiII, PdII, and PtII Complexes with the Potentially Tridentate Ligand 1,3-Bis-(diphenylphosphinomethyl)benzene, 1,3-C6H4(CH2PPh2)2. Struct. Chem. 2003, 14 (3), 263-269. (b) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. Nickel promoted C-H, C-C and C-O bond activation in solution. Inorg. Chim. Acta 2004, 357 (13), 4015-4023. (c) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. Syntheses and Reactivities of New PCsp3P Pincer Complexes of Nickel. Organometallics 2006, 25 (3), 602-608. (d) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. New Derivatives of PCP-Type Pincer Complexes of Nickel. Inorg. Chem. 2009, 48, 3177-3184. (e) Rossin, A.; Peruzzini, M.; Zanobini, F. Nickel(ii) hydride and fluoride pincer complexes and their reactivity with Lewis acids BX3·L (X = H, L = thf; X = F, L = Et2O). Dalton Trans. 2011, 40 (17), 4447-4452. (f) Duncan, D.; Hope, E. G.; Singh, K.; Stuart, A. M. A recyclable perfluoroalkylated PCP pincer palladium complex. Dalton Trans. 2011, 40 (9), 1998-2005. (g) Schmeier, T. J.; Nova, A.; Hazari, N.; Maseras, F. Synthesis of PCP-Supported Nickel Complexes and their Reactivity with Carbon Dioxide. Chem. - Eur. J. 2012, 18 (22), 6915-6927. (h) Jonasson, K. J.; Wendt, O. F. Synthesis and characterisation of new PCsp3P-supported nickel complexes. J. Organomet. Chem. 2014, 759, 15-18. (i) Yang, Z.; Liu, D.; Liu, Y.; Sugiya, M.; Imamoto, T.; Zhang, W. Synthesis and Structural Characterization of Nickel Complexes Possessing P-Stereogenic Pincer Scaffolds and Their Application in Asymmetric Aza-Michael Reactions. Organometallics 2015, 34 (7), 1228-1237. (j) Yang, X.-Y.; Tay, W. S.; Li, Y.; Pullarkat, S. A.; Leung, P.-H. Versatile Syntheses of Optically Pure PCE Pincer Ligands: Facile Modifications of the Pendant Arms and Ligand Backbones. Organometallics 2015, 34 (8), 1582-1588. (k) Gibbons, S. K.; Xu, Z.; Hughes, R. P.; Glueck, D. S.; Rheingold, A. L. Chiral Bis(Phospholane) PCP Pincer Complexes: Synthesis, Structure, and Nickel-Catalyzed Asymmetric Phosphine Alkylation. Organometallics 2018, 37 (13), 2159-2166. (1) Zhang, J.; Liu, T.; Wei, C.; Chang, J.; Ma, Q.-Q.; Li, S.; Ma, N.; Chen, X. The Reactivity of Mercapto Groups against Boron Hydrides in Pincer Ligated Nickel Mercapto Complexes. Chem. - Asian J. 2018, 13 (21), 3231-3238.

(30) Mousa, A. H.; Bendix, J.; Wendi, O. F. Synthesis, Characterization, and Reactivity of PCN Pincer Nickel Complexes. *Organometallics* **2018**, 37 (15), 2581–2593.

(31) The bite angles for the 5,5-pincer-Ni complexes bearing at least one phosphinite moiety are as follows: 81–83° for the POCOP complexes based on aromatic or aliphatic backbones; 80–82° for the POCNimine, POCNamine, and NHCCOP systems featuring aromatic backbones; and 83–85° for PIMCOP systems. See refs 11a and 29 for POCOP and ref 19 POCN systems, and the following reports for NHCCOP and PIMCOP systems: (a) Vabre, B.; Canac, Y.; Duhayon, C.; Chauvin, R.; Zargarian, D. Nickel(II) complexes of the new pincer-type unsymmetrical ligands PIMCOP, PIMIOCOP, and NHCCOP: versatile binding motifs. *Chem. Commun.* 2012, 48 (84), 10446–10448. (b) Vabre, B.; Canac, Y.; Lepetit, C.; Duhayon, C.; Chauvin, R.; Zargarian, D. Charge Effects in PCP Pincer Complexes of NiII bearing Phosphinite and Imidazol(i)ophosphine Coordinating Jaws: From Synthesis to Catalysis through Bonding Analysis. *Chem. - Eur. J.* 2015, 21 (48), 17403–17414.

(32) LaPierre, E. A.; Clapson, M. L.; Piers, W. E.; Maron, L.; Spasyuk, D. M.; Gendy, C. Oxygen Atom Transfer to Cationic PCPNi(II) Complexes Using Amine-N-Oxides. *Inorg. Chem.* **2018**, *57* (1), 495–506.

(33) (a) Cermak, J.; Kvicalova, M.; Sabata, S.; Blechta, V.; Vojtisek, P.; Podlaha, J.; Shaw, B. L Diphosphinoazines (Z,Z)-R2PCH2C-(But)-NN-C(But)CH2PR2 with R groups of various sizes and complexes {[(Z,Z)-R2PCH2C(But)-NN-C(But)CH2PR2]-[η 3-CH2C(CH3)-CH2PdCl]2}. *Inorg. Chim. Acta* 2001, 313 (1), 77-86. (b) Matsumoto, K.; Toda, M.; Iida, H.; Hamana, H. Is There Any Effect of Pressure on Metal Cation Extraction Properties of 7,13-Bis(2'-Thiazoyl)-1,4,10-Trioxa-7,13-Diaza-Cyclopentadecane? *Heterocycl. Commun.* 2007, 13 (1), 13. (c) Rieckborn, T. P.; Karakoc, E.; He, J.; Prosenc, M. H. Chlorido{[2-(dicyclohexylphosphanoyl)ethyl]bis-

[2-(dicyclohexylphosphanyl)ethyl]phosphane}platinum(II) chloride dichloromethane hemisolvate tetrahydrate. Acta Crystallogr., Sect. E: Struct. Rep. Online 2009, 65 (1), m57-m58. (d) Martinez-Prieto, L. M.; Melero, C.; del R10, D.; Palma, P.; Campora, J.; Alvarez, E. Synthesis and Reactivity of Nickel and Palladium Fluoride Complexes with PCP Pincer Ligands. NMR-Based Assessment of Electron-Donating Properties of Fluoride and Other Monoanionic Ligands. Organometallics 2012, 31 (4), 1425-1438. (e) Morales-Becerril, I.; Flores-Álamo, M.; Tlahuext-Aca, A.; Arévalo, A.; García, J. J. Synthesis of Low-Valent Nickel Complexes in Aqueous Media, Mechanistic Insights, and Selected Applications. Organometallics 2014, 33 (23), 6796-6802. (f) Hao, J.; Vabre, B.; Mougang-Soumé, B.; Zargarian, D. Small Molecule Activation by POCOP-Nickel Complexes. Chem. -Eur. J. 2014, 20 (39), 12544-12552. (g) Kovács, T.; Fülöp, L. S.; Mucsi, Z.; Karaghiosoff, K.; Czugler, M.; Keglevich, G. Revisiting the 7-Phospanorbornene Family: New P-Alkyl Derivatives. Heteroat. Chem. 2015, 26 (5), 335-347.

(34) (a) Brunker, T. J.; Blank, N. F.; Moncarz, J. R.; Scriban, C.; Anderson, B. J.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Sommer, R. D.; Incarvito, C. D.; Rheingold, A. L. Chiral Palladium(0) trans-Stilbene Complexes: Synthesis, Structure, and Oxidative Addition of Phenyl Iodide. Organometallics 2005, 24 (11), 2730-2746. (b) Schaub, T.; Radius, U. Efficient C-F and C-C Activation by a Novel N-Heterocyclic Carbene-Nickel(0) Complex. Chem. - Eur. J. 2005, 11 (17), 5024-5030. (c) Barrios-Francisco, R.; García, J. J. Stereoselective Hydrogenation of Aromatic Alkynes Using Water, Triethylsilane, or Methanol, Mediated and Catalyzed by Ni(0) Complexes. Inorg. Chem. 2009, 48 (1), 386-393. (d) Harrold, N. D.; Hillhouse, G. L. Strongly bent nickel imides supported by a chelating bis(N-heterocyclic carbene) ligand. Chem. Sci. 2013, 4 (10), 4011-4015. (e) Kruckenberg, A.; Wadepohl, H.; Gade, L. H. Bis-(diisopropylphosphinomethyl)amine Nickel(II) and Nickel(0) Complexes: Coordination Chemistry, Reactivity, and Catalytic Decarbonylative C-H Arylation of Benzoxazole. Organometallics 2013, 32 (18), 5153-5170. (f) Brendel, M.; Braun, C.; Rominger, F.; Hofmann, P. Bis-NHC Chelate Complexes of Nickel(0) and Platinum(0). Angew. Chem., Int. Ed. 2014, 53 (33), 8741-8745. (g) Barrett, B. J.; Iluc, V. M. Group 10 Metal Complexes Supported by Pincer Ligands with an Olefinic Backbone. Organometallics 2014, 33 (10), 2565-2574. (h) Gendy, C.; Mansikkamäki, A.; Valjus, J.; Heidebrecht, J.; Hui, P. C.-Y.; Bernard, G. M.; Tuononen, H. M.; Wasylishen, R. E.; Michaelis, V. K.; Roesler, R. Nickel as a Lewis Base in a T-Shaped Nickel(0) Germylene Complex Incorporating a Flexible Bis(NHC) Ligand. Angew. Chem., Int. Ed. 2019, 58 (1), 154-158. (i) Nattmann, L.; Saeb, R.; Nöthling, N.; Cornella, J. An air-stable binary Ni(0)olefin catalyst. Nat. Catal. 2020, 3 (1), 6-13.

(35) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. Alkyne insertion reactions in nickel acyl complexes. Occurrence of a 1,2-trimethylphosphine shift and the x-ray structures of [cyclic] Ni[C(Ph):C(H)(COCH2SiMe3)]Cl(PMe3)2 and [cyclic] Ni[C(Ph)(PMe3)C(H)(COCH2CMe2Ph)]Cl(PMe3)6. *Organometallics* **1984**, 3 (9), 1438–1440.

(36) Zhou, H.; Sun, H.; Zheng, T.; Zhang, S.; Li, X. Synthesis of Vinylnickel and Nickelacyclopropane Complexes Containing a Chelate [P,Se]-Ligand. *Eur. J. Inorg. Chem.* **2015**, 2015 (19), 3139–3145.

(37) (a) Ohashi, M.; Saijo, H.; Shibata, M.; Ogoshi, S. Palladium-Catalyzed Base-Free Suzuki-Miyaura Coupling Reactions of Fluorinated Alkenes and Arenes via a Palladium Fluoride Key Intermediate. *Eur. J. Org. Chem.* **2013**, 2013 (3), 443-447. (b) Ohashi, M.; Shibata, M.; Saijo, H.; Kambara, T.; Ogoshi, S. Carbon-Fluorine Bond Activation of Tetrafluoroethylene on Palladium(0) and Nickel(0): Heat or Lewis Acidic Additive Promoted Oxidative Addition. *Organometallics* **2013**, 32 (13), 3631-3639. (c) Xu, W.; Sun, H.; Xiong, Z.; Li, X. Acid-Promoted Selective Carbon-Fluorine Bond Activation and Functionalization of Hexafluoropropene by Nickel Complexes Supported with Phosphine Ligands. *Organometallics* **2013**, 32 (23), 7122-7132. (d) Giffin, K. A.; Pua, L. A.; Piotrkowski, S.; Gabidullin, B. M.; Korobkov, I.; Hughes, R. P.; Baker, R. T. Generation of Hydrofluoronickelacycles from Trifluoroethylene and Ni(0): Ligand Effects on Regio-/Stereo-selectivity and Reactivity. *J. Am. Chem. Soc.* **2017**, *139* (11), 4075–4086.

(38) (a) Sujith, S.; Noh, E. K.; Lee, B. Y.; Han, J. W. Synthesis, characterization, and norbornene polymerization of η 3-benzylnickel-(II) complexes of N-heterocyclic carbenes. J. Organomet. Chem. 2008, 693 (12), 2171-2176. (b) Azerraf, C.; Shpruhman, A.; Gelman, D. Diels-Alder cycloaddition as a new approach toward stable PC(sp3)P-metalated compounds. Chem. Commun. 2009, No. 4, 466-468. (c) Gutsulvak, D. V.; Piers, W. E.; Borau-Garcia, J.; Parvez, M. Activation of Water, Ammonia, and Other Small Molecules by PCcarbeneP Nickel Pincer Complexes. J. Am. Chem. Soc. 2013, 135 (32), 11776-11779. (d) Borau-Garcia, J.; Gutsulvak, D. V.; Burford, R. J.; Piers, W. E. Selective hydration of nitriles to amides catalysed by PCP pincer supported nickel(ii) complexes. Dalton Trans. 2015, 44 (27), 12082-12085. (e) LaPierre, E. A.; Piers, W. E.; Gendy, C. Divergent Reactivity of CO2, CO, and Related Substrates at the Nickel Carbon Double Bond of (PCcarbeneP)Ni(II) Pincer Complexes. Organometallics 2018, 37 (20), 3394-3398.