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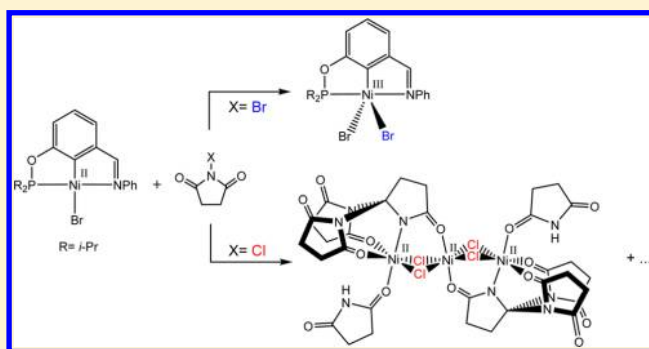
# Synthesis, Characterization, and Oxidation of New POCN<sub>imine</sub>-Type Pincer Complexes of Nickel

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**S** Supporting Information

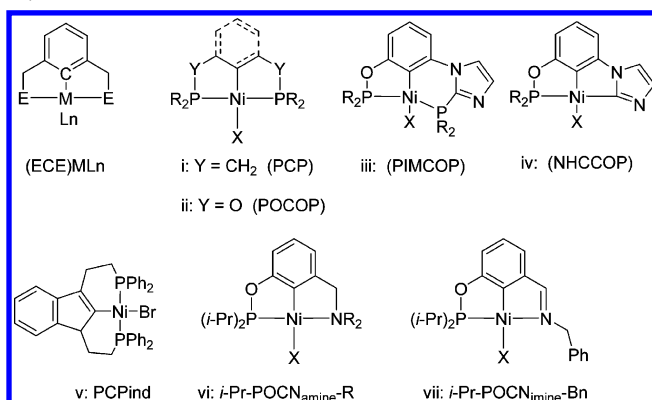
**ABSTRACT:** This report describes the synthesis and characterization of new pincer-type complexes of divalent and trivalent nickel. Refluxing toluene mixtures of  $\text{NiBr}_2(\text{CH}_3\text{CN})_n$  and the unsymmetrical pincer-type ligands  $\text{Ph-POCN}_{\text{imine}}\text{-R}$  gave  $(\text{Ph-POCN}_{\text{imine}}\text{-R})\text{Ni(II)Br}$  in good yields ( $\text{Ph-POCN}_{\text{imine}}\text{-R} = 1\text{-(Ph}_2\text{PO)}_2\text{3-(CHNR)}\text{C}_6\text{H}_4$ ;  $\text{R} = \text{Bn}$ , **1**;  $\text{Ph}$ , **2**;  $t\text{-Bu}$ , **3**;  $\text{Cy}$ , **4**). The C–H nickelation step involved in these syntheses is facilitated in the presence of  $\text{NEt}_3$ . Treating compounds **1–4** with  $\text{Br}_2$ ,  $\text{I}_2$ ,  $N$ -bromosuccinimide (NBS) and  $N$ -chlorosuccinimide appears to bring about the desired one-electron oxidation of the  $\text{Ni(II)}$  center in these complexes, but the putative trivalent species decompose over time and could not be isolated. One of the decomposition products obtained in the  $\text{Br}_2$  reaction was identified as the zwitterionic compound  $[\text{Br}_3\text{Ni(II)}\{\kappa^{\text{O}}\text{-(E)-N-(3-((diphenylphosphoryl)oxy)benzylidene)benzenaminium}\}]$ , **5**. To identify the factors that are important for isolation of stable trivalent derivatives, we prepared the divalent precursors  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{NiX}$  ( $\text{X} = \text{Br}$ , **6**, and  $\text{NCS}$ , **9**) and studied their reactions with various oxidants. Whereas treatment of **6** with  $\text{Br}_2$  or NBS gave the target 17-electron complex  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni(III)Br}_2$  (**7**), no mixed-ligand trivalent complexes of the type  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni(III)Br(X)}$  could be isolated from reactions of  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni(NCS)}$  (**9**) with NBS or of **6** with  $N$ -chlorosuccinimide. The latter reaction gave a complex mixture from which was isolated a paramagnetic, trinuclear compound (**8**) composed of octahedral  $\text{Ni(II)}$  units featuring  $\mu^2\text{-Cl}$  and  $\mu^2, \kappa^{\text{O}}, \kappa^{\text{N}}$ -succinimide fragments. The solid state structures of all new complexes **2–9** have been elucidated by X-ray crystallography.



## INTRODUCTION

Most of the early ECE-type pincer complexes reported in the 1970s by the groups of Shaw<sup>1</sup> and van Koten<sup>2</sup> had the general formula  $\{2,6\text{-(ECH}_2)_2\text{C}_6\text{H}_3\}\text{ML}_n$  wherein E represented a neutral donor moiety such as  $\text{PR}_2$  or  $\text{NR}_2$  (Chart 1). Over the last four decades, the molecular architecture of ECE-type pincer ligands has evolved from the prototypical symmetrical structure

**Chart 1. Structures and Acronyms for Various Pincer Systems**



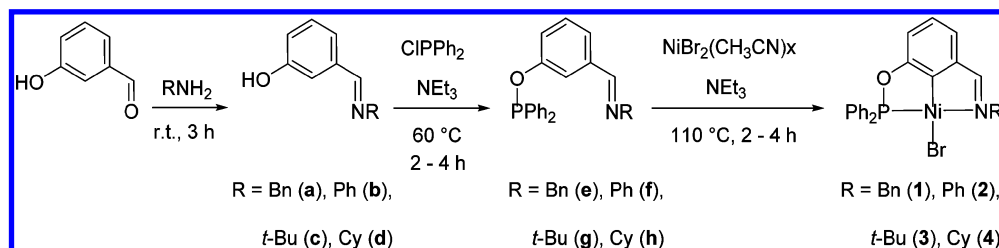
based on a 2,6-disubstituted phenylene backbone to encompass a large variety of terdentate, monoanionic ligands featuring N-, P-, O-, S-, or C-based donor moieties and different backbones (aliphatic,<sup>3</sup> aromatic,<sup>4</sup> symmetrical,<sup>3a,4a–h,5</sup> unsymmetrical<sup>6</sup>). Rigid, planar backbones generally give thermally robust metal complexes that often display interesting catalytic,<sup>7</sup> materials,<sup>8</sup> and photophysical properties.<sup>7b,9</sup> A combination of such functional properties and the relative ease with which the steric and electronic properties of pincer complexes can be modified have contributed to the growing popularity of ECE-type pincer complexes.<sup>10</sup>

In this context, the reactivities of organonickel complexes featuring symmetrical PCP and POCOP ligands based on aromatic as well as aliphatic backbones (i and ii in Chart 1) have received much attention over the past two decades.<sup>3i–m,11</sup> Our group has also introduced nickel complexes of unsymmetrical pincer ligands featuring 2,6-disubstituted phenylene<sup>12</sup> and 1,3-indenylene<sup>13</sup> backbones (iii, iv, and v in Chart 1). We have also described the synthesis via C–H nickelation of a first series of  $\text{POCN}_{\text{imine}}$ -type complexes (vi in Chart 1) and briefly explored their reactivities in hydroalkoxylation and Kharasch

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Scheme 1. Synthesis of Ligands e–h and Complexes 1–4



additions.<sup>14</sup> Studies conducted on the latter complexes showed that the *N*-substituents influence the redox behavior of the Ni center, and attempted oxidation of the benzylamine derivative {2-OP(*i*-Pr<sub>2</sub>),6-CH<sub>2</sub>NH(Bn)-C<sub>6</sub>H<sub>3</sub>}NiBr (Bn = CH<sub>2</sub>Ph) gave instead the first example of a POCN<sub>imine</sub>-type complex<sup>14c</sup> (vii in Chart 1).

Whereas the influence of some structural variations on reactivities of PCP–Ni and POCOP–Ni complexes has been studied extensively,<sup>3j,l,11</sup> very few studies have explored the impact of *N*- and *P*-substituents on the structures and reactivities of POCN–Ni complexes. Thus, we have reported on the syntheses and reactivities of (*i*-Pr-POCN<sub>imine</sub>)NiBr complexes featuring four different amine moieties (NMe<sub>2</sub>, NEt<sub>2</sub>, morpholino, and N(H)Bn).<sup>14a,b</sup> We have also reported the preparation and oxidation of one POCN<sub>imine</sub>–Ni complex, (*i*-Pr-POCN<sub>imine</sub>-Bn)NiBr,<sup>14c</sup> whereas Xia's group has reported the syntheses and Kumada coupling activities of (R-POCN<sub>imine</sub>-Ar)Ni(II) complexes (R = Ph, and *i*-Pr; Ar = 2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>).<sup>15</sup> This paucity of studies/data prompted us to prepare a new series of (R-POCN<sub>imine</sub>)Ni(II)Br complexes bearing different *P*- and *N*-substituents and explore their structures, reactivities, and oxidation potentials.

Presented herein are the synthesis and characterization of the new complexes (Ph-POCN<sub>imine</sub>-R)NiBr (R = Bn (1); Ph (2); *t*-Bu (3); Cy (4)) and (*i*-Pr-POCN<sub>imine</sub>-Ph)NiX (X = Br (6), NCS (9)). This report also describes the successful isolation of the trivalent complex (*i*-Pr-POCN<sub>imine</sub>-Ph)NiBr<sub>2</sub> (7) as well as various unsuccessful oxidation attempts that led to isolation of two unusual Ni(II) compounds, the zwitterionic tetrahedral species [Br<sub>3</sub>Ni(II){κ<sup>O</sup>-(*E*)-*N*-(3-((diphenylphosphoryl)oxy)-benzylidene)benzenaminium}], 5, and the trinuclear species composed of octahedral Ni(II) units featuring μ<sup>2</sup>-Cl and μ<sup>2</sup>,κ<sup>O</sup>,κ<sup>N</sup>-succinimide fragments. Our interest in trivalent nickel complexes stems from the important role that species bearing Ni(III)–C bonds are believed to play in hydrocarbon oxidation<sup>16</sup> and coupling reactions.<sup>17,18</sup> Mechanistic proposals for the latter transformations often invoke five-coordinate alkyl- or aryl-bound di- or trivalent intermediates. While many pentacoordinated organometallic Ni(II) species are known,<sup>19</sup> far fewer examples of their trivalent counterparts have been reported. Indeed, until very recently, most examples of fully characterized organometallic Ni(III) species were based on NCN-type pincer ligands popularized by van Koten's group,<sup>20</sup> but a number of recent reports have introduced trivalent complexes based on different ligand frames.<sup>17,21,22</sup> Therefore, the isolation and characterization of Ni<sup>III</sup> species bearing one or more Ni–C bonds is critical in efforts to expand organonickel chemistry.

## RESULTS AND DISCUSSION

**Synthesis and Spectroscopic Characterization of (Ph-POCN<sub>imine</sub>-R)Ni(II)Br Complexes 1–4.** The synthetic route

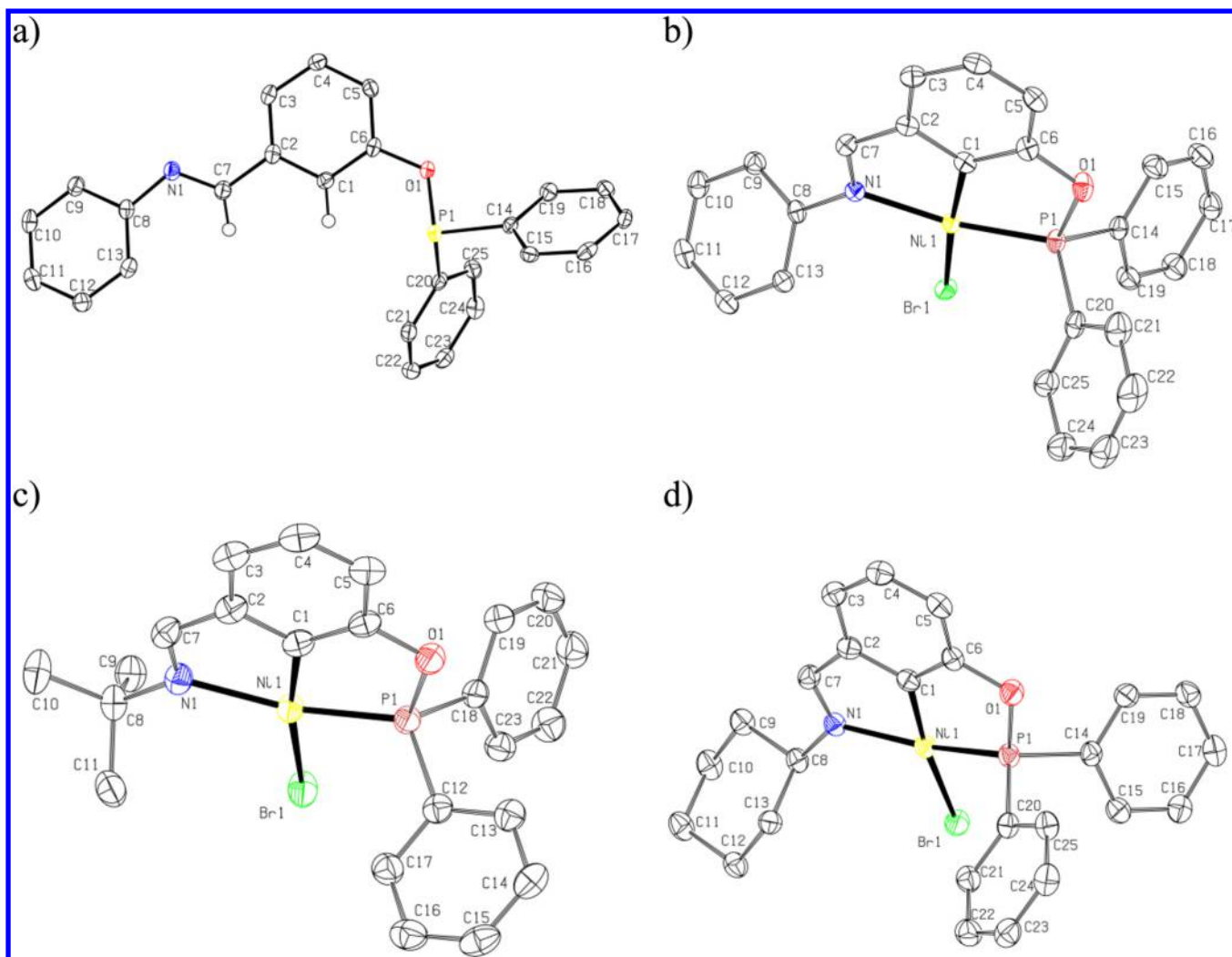
leading to the new complexes 1–4 is shown in Scheme 1. The iminophenol preligands a–d were prepared by condensation of 3-hydroxybenzaldehyde with the corresponding primary amines.<sup>14c,23</sup> The preligands were isolated in good yields as powders that were white (a), brown (b), yellow (c), or beige (d), and their identities were established by elemental analysis and NMR spectroscopy. The most characteristic signals were those of the imine and phenol protons (ca. 8.2–8.3 and 5.0–5.1 ppm, respectively) and the imine carbon (ca. 162–163 ppm).

Phosphination of a–d with ClPPh<sub>2</sub> and NEt<sub>3</sub> gave the corresponding Ph-POCN<sub>imine</sub> ligands e–h, which were isolated in high yields as colorless (e), brown (f), or yellowish (g, h) oils and characterized by NMR spectroscopy (e.g., <sup>31</sup>P δ: 110–112). It is important to note that all of these ligands are air sensitive and must be stored under inert atmosphere. A PARATONE oil coated single crystal of f proved sufficiently stable to be subjected to X-ray diffraction analysis; the ORTEP diagram for this compound is shown in Figure 1 and will be discussed below along with the solid state structures of 2–4.

Heating the ligands e–h with NiBr<sub>2</sub>(MeCN)<sub>n</sub> in the presence of NEt<sub>3</sub> (toluene, 110 °C, 2–4 h) led to ligand nickelation and furnished the new complexes as brick-red (2) or orange (1, 3, and 4) solids in 72–95% yields (Scheme 1). It is worth emphasizing that the nickelation step does proceed in the absence of added base, but using NEt<sub>3</sub> maximizes the reaction yield in all cases since it quenches the HBr generated during the cyclometalation step, thus preventing it from protonating the donor moieties of the ligands.<sup>24</sup>

All derivatives (Ph-POCN<sub>imine</sub>)NiX are air stable: indefinitely in the solid state and over short time periods in solution. Indeed, some derivatives were purified by extracting their solutions briefly with water to remove residual traces of salts. The bromo derivatives 1–4 also show good thermal stabilities in the solid state, melting or decomposing above 220 °C, whereas their solutions in hexane, toluene, benzene, acetonitrile, or dichloromethane are stable at rt over several hours.

The diamagnetic complexes 1–4 were fully characterized by NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, COSY, HSQC, and HMBC). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra showed singlet resonances at 141–150 ppm, 30–40 ppm downfield of the resonances for the corresponding ligands (ca. 110–112 ppm). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 1–4 were quite complex due to the presence in these molecules of multiple aromatic moieties, but most signals were assigned thanks to <sup>1</sup>H–COSY, HSQC, and HMBC correlation experiments. The CH=NR proton was most distinctive both for its characteristic chemical shift (ca. 8.0–8.5 ppm) and its multiplicity due to a 4-bond coupling to the <sup>31</sup>P nucleus. For example, a doublet is observed for this proton (<sup>4</sup>J<sub>P–H</sub> = 4 Hz) in complexes 2 (CHNPh) and 3 (CHNBu<sup>t</sup>), whereas broadened or more complex multiplicities were observed in NCH<sub>2</sub>Ph derivatives due to additional



**Figure 1.** ORTEP diagrams for ligand **f** (a) and complexes **2** (b), **3** (c), and **4** (d). Thermal ellipsoids are set at the 50% probability level. Most hydrogen atoms are omitted for clarity. A selection of structural parameters is listed in Table 1. Selected bond distances (Å) and angles (deg) for ligand **f**: P–O = 1.671(1); P1–C14 = 1.826(2); P1–C20 = 1.846(2); N–C7 = 1.276(3); N–C8 = 1.424(3); P1–O1–C2 = 120.2(1); O1–P1–C14 = 96.35(8); O1–P1–C20 = 100.93(8); P1–O1–C2–C1 = 150.1(1); C1–C6–C7–N1 = 169.0(2).

coupling to the benzylic protons. Similar observations were made in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for the imine carbon nucleus.

**Solid State Structures of Ligand **f** and Complexes **2–4**.** Figure 1 shows the ORTEP diagrams for ligand **f** and complexes **2–4**, and selected structural parameters are listed in the figure caption (for **f**) and Table 1 (**2–4**); Table S1 in the Supporting Information provides the crystal data. Comparison of structural parameters in **f** and **2** reveals the impact of complexation to Ni. For instance: the phosphinite and imine moieties adopt a transoid disposition in **f** but are cisoid in **2**; orientation of the *N*-Ph ring with respect to the central aryl moiety is  $14^\circ$  in **f** and  $49^\circ$  in **2**; there is a tightening in the angles P–O–Ar (ca.  $120^\circ$  vs  $109^\circ$ ) and N–C–Ar (ca.  $122^\circ$  vs  $116^\circ$ ); the P–O distance shrinks (1.671(1) vs 1.645(1) Å) while the N–C7 lengthens (1.276(3) vs 1.293(2) Å).

The overall geometry around the nickel center in **2–4** is a distorted square planar arrangement as defined by the atoms C1, P1, N1, and Br. The carbon atoms C7 and C8 bonded to the imine N atom are also in the main plane due to the  $\pi$ -delocalization in the POCN ligand. The main source of structural distortions is the small bite angle of the pincer ligand

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for Complexes **2–4**

parameter	2	3	4
Ni–C(1)	1.856(1)	1.859(2)	1.863(2)
Ni–P(1)	2.1099(5)	2.1231(5)	2.1192(6)
Ni–N(1)	1.994(1)	2.050(1)	1.988(2)
Ni–X(1)	2.3358(3)	2.3705(3)	2.3518(4)
P(1)–O(1)	1.645(1)	1.657(1)	1.658(2)
C(7)=N(1)	1.293(2)	1.292(2)	1.278(3)
C(8)–N(1)	1.433(2)	1.497(2)	1.477(3)
C(1)–Ni–P(1)	80.20(5)	79.97(5)	80.04(6)
C(1)–Ni–N(1)	82.55(6)	82.47(6)	82.23(8)
C(1)–Ni–X(1)	171.57(5)	170.30(5)	173.37(6)
N(1)–Ni–P(1)	162.25(4)	162.27(4)	160.73(5)
N(1)–Ni–X(1)	101.61(4)	106.87(4)	101.70(5)
P(1)–Ni–X(1)	96.03(1)	90.78(2)	96.69(2)

(N1–Ni–P1  $\sim 161$ – $163^\circ$ ) that is also responsible for the smaller- and larger-than- $90^\circ$  cis angles (e.g., C1–Ni–P1  $\sim 80^\circ$ ; N1–Ni–X  $\sim 102$ – $107^\circ$ ). The Ni–C1 bond lengths of 1.86–1.87 Å are comparable to the corresponding distances observed



in the complex  $i\text{-Pr-POCN}_{\text{imine}}$  (1.86 Å for R = Bn),<sup>14c</sup> but shorter than those of  $\text{POCN}_{\text{amine}}$ -type complexes (2.03 Å).<sup>14a</sup>

The impact of different *N*-substituents R in (Ph- $\text{POCN}_{\text{imine}}$ -R)NiBr is evident when we compare the structures of **3** (N-*t*-Bu), **2** (N-Ph), and **4** (N-Cy): complex **3** displays the longest Ni–Br distance (2.37 vs 2.34–2.35 Å) and the largest N–Ni–Br angle (107° vs 102°), presumably due to the greater steric demands of the *t*-Bu-N moiety. The same factor might also explain the much longer Ni–N distance in **3** vs **2** and **4**: ca. 2.05 vs 1.99 Å. Curiously, the Ni–P bond distances also increase with the increasing steric bulk of the *N*-substituent, 2.1099(5) Å for N-Ph < 2.1192(6) Å for N-Cy < 2.1231(5) Å for N-*t*-Bu, which seems counterintuitive, because we would expect that the longer (and presumably weaker) Ni–N bond should lead to stronger and shorter Ni–P bonds. This anomalous observation can be rationalized by considering that the greater steric bulk at the imine moiety displaces the Br atom toward the phosphinite moiety, which would in turn lengthen/weaken the Ni–P bond. Indeed, the N–Ni–Br and P–Ni–Br angles bear witness to this phenomenon: N–Ni–Br is largest and P–Ni–Br is smallest for the *t*-BuN derivative **3** (Table 1).

### Synthesis and Characterization of Trivalent Species.

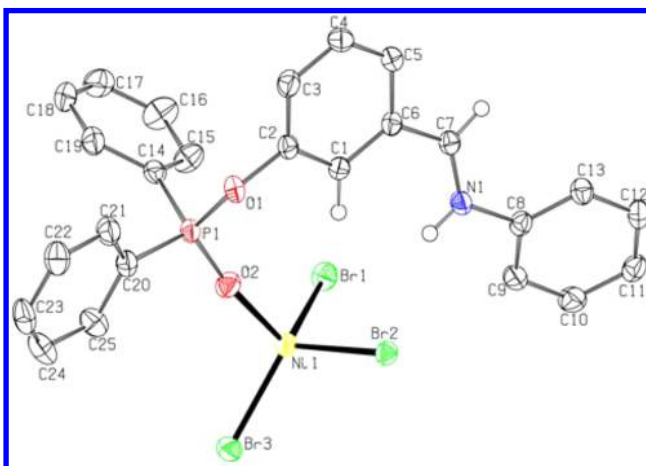
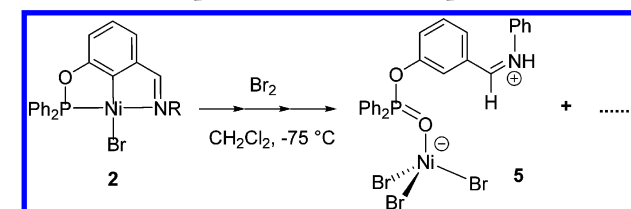
Cyclic voltammetry measurements conducted on previously reported (*i*-Pr- $\text{POCN}_{\text{amine}}$ )NiBr complexes have shown that these complexes undergo reversible or quasi-reversible redox behavior ( $E_{\text{ox}}^{1/2} \sim 500\text{--}600$  mV with respect to the ferrocene/ferrocenium redox couple).<sup>14a</sup> CV measurements conducted on our (Ph- $\text{POCN}_{\text{imine}}$ )NiBr complexes showed one-electron oxidations at comparable potentials (see Figure S18 in the Supporting Information), but only complex **4** showed reversible oxidation. This might imply that the putative, electrochemically generated trivalent species [(Ph- $\text{POCN}_{\text{imine}}$ -R)NiBr]<sup>+</sup> are less stable in comparison to [(*i*-Pr- $\text{POCN}_{\text{amine}}$ )NiBr]<sup>+</sup>. Nevertheless, we set out to investigate the preparation of stable and isolable trivalent derivatives based on Ph- $\text{POCN}_{\text{imine}}$  ligands.

Several attempts were made to oxidize complexes **1–4** using chemical oxidants such as Br<sub>2</sub>, I<sub>2</sub>, *N*-bromosuccinimide (NBS), and *N*-chlorosuccinimide; these oxidation attempts were performed under reaction conditions that had proved favorable for the previous syntheses of (*i*-Pr- $\text{POCN}_{\text{amine}}$ )NiBr<sub>2</sub><sup>14a</sup> and (*i*-Pr- $\text{POCN}_{\text{imine}}$ -Bn)NiBr<sub>2</sub>.<sup>14c</sup> Our initial observations were consistent with the anticipated oxidation reaction: the original yellow/orange color of the reaction mixtures containing (Ph- $\text{POCN}_{\text{imine}}$ )NiBr darkened upon addition of the oxidant, and NMR spectroscopy indicated conversion of the diamagnetic Ni(II) precursors to NMR-silent species. The in situ generated products were found to be fairly soluble in dichloromethane but less so in toluene or hexane; regardless of solvent, however, the reaction mixtures decomposed gradually at room temperature to give yellow (**1**, **3**, **4**) or reddish (**2**) solutions of new species that were also NMR-silent.

Next, we undertook an oxidation experiment at low temperature in an attempt to slow down and arrest the putative trivalent species. Complex **2** was treated with Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at  $-78^\circ\text{C}$ , and the resulting dark reaction mixture was kept at ca.  $-75^\circ\text{C}$  to give a yellowish precipitate over a period of days. Closer inspection of this precipitate showed that it consisted of an amorphous, NMR-silent yellow solid as well as small quantities of NMR-silent green crystals. X-ray diffraction analysis conducted on the latter identified it as [Br<sub>3</sub>Ni<sup>II</sup>(κ<sup>−</sup>(*E*)-N-(3-((diphenylphosphoryl)oxy)benzylidene)-

benzenaminium}], **5**, a zwitterionic tetrahedral complex composed of a nicklate anion and an iminium cation (Scheme 2, Figure 2). Thus, instead of the intended single-electron

### Scheme 2. Attempted Oxidation of Complex **2**

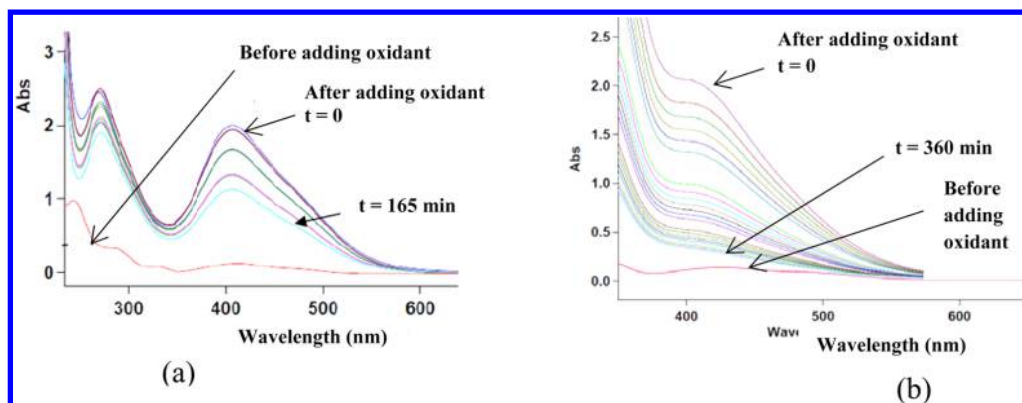


**Figure 2.** ORTEP diagram for complex **5**. Thermal ellipsoids are set at the 50% probability level. Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Br1 = 2.3702(5); Ni1–Br2 = 2.4113(6); Ni1–Br3 = 2.3591(7); Ni1–O2 = 1.963(2); P1–O1 = 1.598(2); P1–O2 = 1.481(2); N1–C7 = 1.295(4); N1–C8 = 1.434(3); P1–C14 = 1.792(2); P1–C20 = 1.776(2); Br1–Ni1–Br2 = 101.81(2); Br1–Ni1–Br3 = 128.82(2); Br2–Ni1–Br3 = 111.01(2); Br1–Ni1–O2 = 103.66(7); Br2–Ni1–O2 = 103.26(7); Br3–Ni1–O2 = 105.55(7); O1–P1–O2 = 114.1(1); C7–N1–C8 = 125.3(2); C6–C7–N1 = 124.8(2).

oxidation by addition of a Br atom to Ni, the observed transformation of **2** consists of a two-electron oxidation of the phosphinite moiety and a net addition of two HBr to the Ni–C and Ni–N moieties. We speculate that this unusual transformation is the result of a hydrolytic decomposition of the putative, thermally unstable trivalent intermediate.

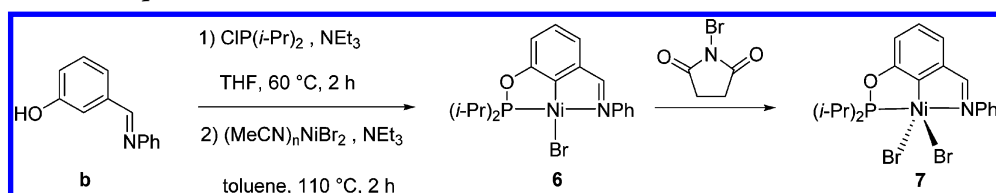
The structural parameters for **5** (Figure 2) confirm that P–O2 < P–O1 (ca. 1.48 vs 1.60 Å) and N–C7 < N–C8 (ca. 1.30 vs 1.43 Å). The Ni center adopts a distorted tetrahedral geometry with fairly uniform Br–Ni–O angles (103–106°) but quite different Br–Ni–Br angles (101–129°); one of the Ni–Br bonds is also significantly longer than the others (2.41 vs 2.36–2.37 Å). Comparison of these parameters to literature values for related species indicates that the observed nonuniform Ni–Br distances and Br–Ni–Br angles might be due to the proximity of the NiBr<sub>3</sub> moiety to the positively charged fragment inside the unit cell.<sup>25</sup>

The failure to isolate the target trivalent species (Ph- $\text{POCN}_{\text{imine}}$ -R)NiX<sub>2</sub> prompted us to monitor the oxidation reaction and measure thermal stabilities of the products by UV–vis spectroscopy, as had been done previously for the fully characterized trivalent complex (*i*-Pr- $\text{POCN}_{\text{imine}}$ -Bn)NiBr<sub>2</sub>.<sup>14a</sup> We found that addition of 0.6 equiv of Br<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>,



**Figure 3.** UV-vis spectra of nickel complexes before and after addition of 3 equiv of  $\text{Br}_2$ : (a) **1** ( $10^{-3}$  M in DCM) at 25 °C; (b) **2** ( $10^{-3}$  M in toluene) at 70 °C).

### Scheme 3. Synthesis of Complexes **6** and **7**



acetonitrile, toluene, or THF solutions of the bromo derivatives **1–4** caused an immediate and significant increase in the intensities of the absorptions at ca. 400 nm, and weak-intensity absorptions emerged in the 480–520 nm region (Figure 3); these observations are comparable to what has been observed previously during the oxidation of  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Bn})\text{NiBr}$ . For the latter complex, it had been noted that slow decomposition of the oxidized species led to regeneration of the initial divalent species, as confirmed by monitoring the time profile of the UV-vis spectra.<sup>14c</sup> In contrast, the UV-vis spectra of the putative  $(\text{Ph-POCN}_{\text{imine}}\text{-R})\text{NiBr}_2$  complexes studied here indicated a much faster decomposition process that did *not* regenerate the initial divalent precursors via a simple unimolecular dissociation of a bromine radical. We conclude, therefore, that the chemical oxidation of  $(\text{Ph-POCN}_{\text{imine}}\text{-R})\text{NiBr}$  is not reversible as the thermally unstable trivalent species undergo ligand degradation (*vide infra*).

Altogether, the above observations indicated that trivalent species supported by  $\text{Ph-POCN}_{\text{imine}}$  might be inherently too unstable to be isolated. In order to confirm the crucial importance of *P*-substituents for the thermal stability of trivalent species based on  $\text{POCN}_{\text{imine}}$  ligands, we set out to prepare the *i*-Pr<sub>2</sub>P-analogue of **2** and attempt its oxidation, as described below.

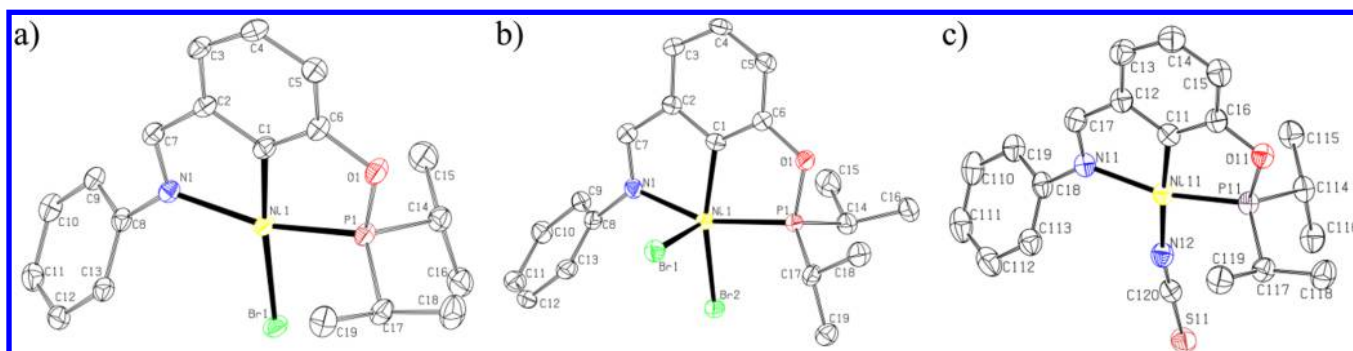
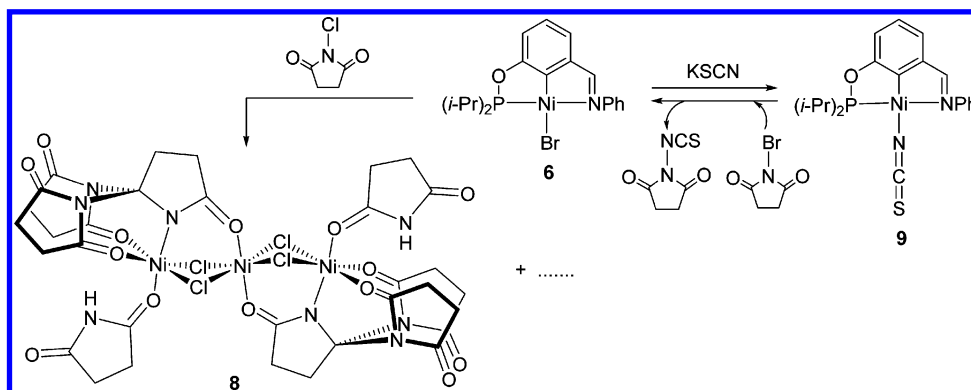
**Preparation and Chemical Oxidation of  $(i\text{-Pr-POC- N}_{\text{imine}}\text{-Ph})\text{NiBr}$ , **6**.** Compound **6** was prepared in a straightforward, one-pot procedure as follows: a THF mixture of the preligand **b**,  $\text{CIP}(i\text{-Pr})_2$ , and  $\text{NEt}_3$  was refluxed for 2 h, and then evaporated to dryness; to the residue was added a toluene suspension of  $\text{NiBr}_2(\text{MeCN})_n$  and  $\text{NEt}_3$ , and the resulting mixture was refluxed for 2 h (Scheme 3). The target product **6** was obtained in 75% yield after standard workup and chromatography, and fully characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography (*vide infra*).

With the new complex **6** in hand, we attempted its oxidation by treatment with  $\text{Br}_2$  or NBS, which proved successful and allowed us to isolate the target trivalent species (*i*-Pr-

$\text{POCN}_{\text{imine}}\text{-Bn})\text{NiBr}_2$ , **7**, as a black paramagnetic solid in 63% yield; characterization of this compound will be described below. The successful preparation and isolation of **7** allowed us to conclude that the choice of *P*-substituent is very crucial for stabilizing Ni(III) species. This finding also encouraged us to further probe the stabilities of  $\text{POCN}_{\text{imine}}$ -based trivalent derivatives as a function of other factors, including the nature of the anionic ligands *X*. The latter was suspected to be an important factor because our previous studies on PCP-, POCOP-, and POCN-based Ni(III) complexes had indicated that the dibromo derivatives are by far more stable than their dichloro and diiodo analogues; moreover, mixed-halogen species have also proven to be unstable to isolation. Indeed, nearly all known examples of such complexes feature identical *X* ligands, i.e.,  $(\text{pincer})\text{NiX}_2$  or  $(\text{pincer})\text{NiX}_2(\text{L})$  (*X* = halide or NCS), the only confirmed example of a “heteroleptic”  $(\text{pincer})\text{Ni(III)}$  species being  $(\text{NCN})\text{NiBr}(\text{Cl})$ , reported in 2009 by Kozhanov et al.<sup>20d,26</sup> It appeared, therefore, that “heteroleptic” complexes of the type  $(\text{pincer})\text{NiX}(\text{Y})$  might be inherently unstable. In an effort to further investigate this phenomenon with  $\text{POCN}_{\text{imine}}$ -type ligands, we carried out the experiments described below to test the feasibility of isolating trivalent, 17-electron  $(\text{POCN}_{\text{imine}})\text{NiXY}$ .

In the first experiment, the bromo derivative **6** was treated with *N*-chlorosuccinimide with the objective of preparing  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni}^{\text{III}}(\text{Br})\text{Cl}$ . In contrast to the relatively straightforward preparation and isolation of **7**, we found that oxidation of **6** with *N*-chlorosuccinimide proved much more complicated. Evaporation of the dark-brown solution obtained from this reaction gave solid residues, which were washed with hexane and recrystallized from  $\text{CH}_2\text{Cl}_2$  to give a deep-brown powder containing some red crystals. The latter were physically separated from the bulk material, and both components were subjected to recrystallization attempts. These attempts having proven unsuccessful, we undertook a column chromatography of the mixture (80/20, hexane/DCM) and obtained two reddish bands, which were characterized as follows.

Scheme 4. Synthesis of Complex 9 and Attempted Oxidation of Complexes 6 and 9



**Figure 4.** ORTEP diagrams for complexes 6 (a), 7 (b), and 9 (c). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. A selection of structural parameters is listed in Table 2.

The first band consisted of a diamagnetic compound showing a  $^{31}\text{P}$  singlet resonance similar but not identical to that of the starting material 6 (200.6 ppm vs 201.2 ppm). This band yielded small quantities of reddish crystals that appeared to be a new derivative of 6 in which the *N*-Ph moiety had been brominated at the *para* position; unfortunately, however, an unequivocal assignment was not possible owing to the low quality of the data obtained.<sup>27,28</sup> The second band consisted of an NMR-silent compound that could be identified unequivocally as the trinuclear complex 8 featuring Ni(II) units bridged by chloride and succinimide ligands (Scheme 4), to be discussed below.

The above-described unsuccessful attempt to prepare a "heteroleptic" trivalent species  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni}^{\text{III}}(\text{Br})\text{X}$  by oxidation of the bromo derivative prompted us to attempt oxidation of another divalent derivative  $(i\text{-Pr-POCN}_{\text{imine}}\text{-Ph})\text{Ni}^{\text{II}}(\text{X})$  with NBS, which in our hands had proven to be the most reliable oxidant for the preparation of trivalent species. We selected the thiocyanate derivative ( $\text{X} = \text{NCS}$ ) as a suitable candidate for this purpose because of the anticipated ease in its characterization by X-ray crystallography.<sup>29</sup> Thus, the Ni-NCS derivative of 6 was prepared by treating it with KNCS in dichloromethane (Scheme 4); the complete characterization of the new derivative 9 will be described below. Unfortunately, oxidation of the latter proved unsuccessful: treatment of 9 with *N*-bromosuccinimide led to regeneration of 6 and formation of a side product that was identified (by X-ray diffraction studies) as the known compound *N*-thiocyanatosuccinimide<sup>30</sup> (Scheme 4).

**Characterization of Complexes 6–9.** The NMR features of complex 6 are fairly similar to those of its *N*-Bn analogue reported previously,<sup>14c</sup> including the  $^{31}\text{P}$  singlet (200 vs 201

ppm) and the  $^{13}\text{C}$  doublet for the imine carbon (174 vs 172 ppm;  $^3J_{\text{P-C}} = 2\text{--}3\text{ Hz}$ ). One notable difference is the chemical shift of the imine proton, which resonates at 8.43 ppm in 6 ( $d, ^4J_{\text{HP}} = 4$ ) compared to ca. 7.3 ppm in its *N*-Bn analogue. The structural analysis of a single crystal of 6 (Figure 4a, Table 2) allowed us to compare its solid state structure to that of its  $\text{PPh}_2$  analogue 2. The overall structures of these complexes are quite similar, as are most of the analogous distances. For instance, the Ni–P distance is insignificantly shorter in 6 (2.1067(8) vs 2.1099(5) Å) and the Ni–N distances are nearly equivalent (2.003(2) vs 1.9994(1) Å). These observations imply comparable trans influences for *i*-Pr<sub>2</sub>P and Ph<sub>2</sub>P moieties.

X-ray diffraction analysis of the trivalent complex 7 revealed a pentacoordinated geometry (Figure 4b), which is best described as distorted square pyramidal based on the small value of the  $\tau$  parameter calculated for this structure (ca. 0.023).<sup>31</sup> This is comparable to the  $\tau$  values observed for analogous trivalent complexes  $(i\text{-Pr-POCN}_{\text{amine}})\text{NiBr}_2$  (ca. 0.032),<sup>14a</sup>  $(i\text{-Pr-POCN}_{\text{imine-Bn}})\text{NiBr}_2$  (ca. 0.05),<sup>14c</sup>  $(\text{POC}_{\text{sp}^3}\text{OP})\text{NiBr}_2$  (ca. 0.06),<sup>31j</sup> and  $(\text{PC}_{\text{sp}^3}\text{P})\text{NiBr}_2$  (ca. 0.028).<sup>3k</sup>

Inspection of the structural parameters in 7 (Table 2) reveals a number of features and deformations commonly found in pentacoordinated complexes of trivalent nickel.<sup>3i–k,14a,c</sup> For instance, the phosphinito moiety is slightly outside of the plane defined by the atoms C, Ni, and N and the aromatic ring (0.41 Å); a pyramidal distortion is also evident from (a) the out-of-plane displacement (by ca. 0.32 Å) of the Ni atom in 7 from the basal plane defined by the atoms P1, C1, N1, and Br1 and (b) the C(1)–Ni–Br(1) angle that is much smaller in 7 than 6 (159° vs 174°). The axial Ni–Br bond is also much longer than its equatorial counterpart: 2.45 vs 2.36 Å; the latter observation



**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Complexes 6, 7, and 9

parameter	6	7	9	( <i>i</i> -Pr-POCNI <sub>imine</sub> <sup>−</sup> Ph)NiBr <sub>2</sub>
Ni–C(1)	1.851(3)	1.902(4)	1.849(2)	1.896(2)
Ni–P(1)	2.1067(8)	2.198(1)	2.1216(9)	2.1919(5)
Ni–N1	2.003(2)	2.012(4)	1.982(2)	2.004(2)
Ni–X(1)	2.3331(5)	2.3570(9)	1.879(2)	2.3597(4)
Ni–X(2)		2.4467(9)		2.4191(3)
N–C <sub>imine</sub>	1.298(3)	1.288(6)	1.292(3)	1.285(3)
C(1)–Ni–P(1)	80.98(9)	78.8(1)	80.41(7)	78.43(6)
C(1)–Ni–N(1)	82.6(1)	81.8(2)	82.84(9)	82.52(7)
C(1)–Ni–X(1)	173.75(9)	159.1(1)	172.7(1)	155.43(5)
C(1)–Ni–Br(2)		97.3(1)		95.92(5)
N(1)–Ni–P(1)	163.58(6)	157.7(1)	163.21(6)	158.25(5)
N(1)–Ni–X(1)	103.55(6)	100.0(1)	98.77(9)	100.17(4)
N(1)–Ni–X(2)		94.8(1)		93.14(4)
P(1)–Ni–X(1)	92.85(2)	94.39(4)	97.99(7)	92.99(2)
P(1)–Ni–X(2)		98.42(4)		99.13(2)
X(1)–Ni–X(2)		103.3(3)		108

can be attributed to the partially filled  $d_z^2$  orbital and steric repulsions between the P-substituents and the lone pairs of the axial bromine atom. As expected, most Ni–ligand bond distances are somewhat longer in 7 vs 6 due to the greater coordination number of the Ni center in 7.

Complex 8 (Figure 5, Table 3) is a trinickel species featuring distorted octahedral units and a central Ni atom that is located on a center of reflection (space group =  $R\bar{3}$ ). The cis and trans angles range from 84° to 95° and 170° to 180°. Perhaps the

most striking feature of this structure is the tetradentate ligand formed from an unexpected “fusing” of three succinimide moieties. The orthoamide-like character of this ligand is defined by the quaternary carbon C1 that has presumably formed via a condensation reaction between a succinimide fragment and two succinimide NH moieties. This in situ generated ligand binds the peripheral Ni atoms in a tripodal  $\kappa^{\text{O}}, \kappa^{\text{N}}, \kappa^{\text{O}}$  fashion, while one carbonyl moiety of a tethered succinimide group serves as a bridge to the central Ni atom. Two bridging chlorides and the carbonyl moiety of an independent succinimide ligand complete the octahedral coordination sphere of the peripheral Ni(II) centers. The bite angle of the bridging succinimide moiety causes the central and peripheral coordination planes to be tilted with respect to each other; the hinge angle defined by the planes Cl1–Ni1–Cl2 and Cl1–Ni2–Cl2 is about 37°.

The Ni(II)–Ni(II) distance of 3.24 Å found in 8 is significantly longer than the sum of two Ni(II) covalent radii (2.5 Å), yet much shorter than in analogous multinuclear compounds featuring a Ni(II)( $\mu$ -Cl)<sub>2</sub>Ni(II) fragment;<sup>32</sup> this is likely due to the constraints of the tetradentate ligand. The shortest Ni–O distance (ca. 2.06 Å) is formed between the central Ni atom and the oxygen of the bridging carbonyl moiety, within the 5-membered chelating ring. Longer and significantly unequal Ni–O distances are found in the two 6-membered chelate rings formed by the tripodal ligand and the peripheral Ni atoms, Ni1–O1–2.06 Å and Ni1–O2–2.12 Å, whereas the monodentate succinimide O atom is at an intermediate distance from the peripheral Ni center (2.08 Å).

Complex 9 (Figure 4c) is isostructural to complexes 2–4 and 6. Comparison of the structural parameters for complexes 6 and 9 (Table 2) reveals that the Ni–C distances are very similar, implying similar trans influences for Br and NCS. On the other hand, replacing Br by NCS results in a slightly longer Ni–P distance, a slightly shorter Ni–N distance, greater C–Ni–X and P–Ni–X angles, and a smaller N–Ni–X angle; all of these observations can be attributed to the shorter Ni–NCS distance in 9 relative to the Ni–Br distance in 6 (ca. 1.88 vs 2.33 Å).<sup>33</sup>

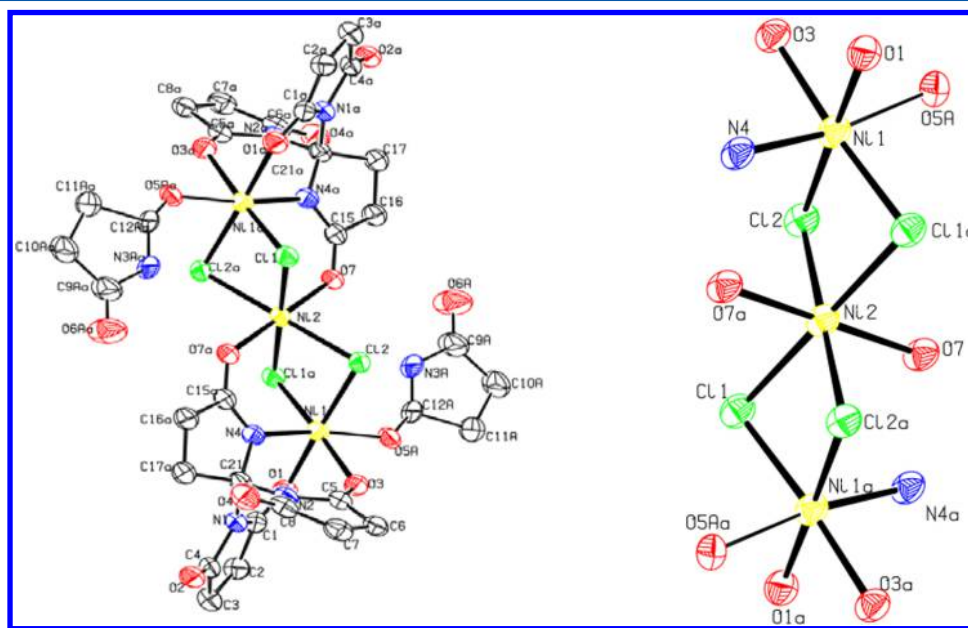




Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 8

distances		angles			
Ni(1)–Ni(2)	3.237(1)	Cl(1)–Ni(2)–O(7)	85.4(1)	Cl(2)–Ni(1)–O(5A)	94.3(5)
Ni(1)–O(1)	2.055(3)	Cl(2A)–Ni(2)–O(7A)	91.0(1)	Cl(2)–Ni(1)–N(4)	94.5(1)
Ni(1)–O(3)	2.116(4)	Cl(2)–Ni(2)–Cl(1)	87.98(4)	O(1)–Ni(1)–O(3)	84.3(1)
Ni(1)–O(5A)	2.09(2)	Cl(1A)–Ni(1)–Cl(2)	90.27(5)	O(1)–Ni(1)–O(5A)	83.8(5)
Ni(1)–N(4)	1.983(4)	Cl(1A)–Ni(1)–O(1)	90.5(1)	O(1)–Ni(1)–N(4)	87.4(2)
Ni(1)–Cl(1A)	2.359(1)	Cl(1A)–Ni(1)–O(3)	174.7(1)	O(3)–Ni(1)–O(5A)	87.3(5)
Ni(1)–Cl(2)	2.386(1)	Cl(1A)–Ni(1)–O(5A)	90.8(5)	O(3)–Ni(1)–N(4)	86.9(1)
Ni(1)–Cl(2A)	2.427(1)	Cl(1A)–Ni(1)–N(4)	94.3(1)	O(5A)–Ni(1)–N(4)	170.9(8)
Ni(2)–Cl(1)	2.416(1)	Cl(2)–Ni(1)–O(1)	177.9(1)	Ni(1)–Cl(1A)–Ni(2)	85.34(4)
Ni(2)–O(7)	2.042(3)	Cl(2)–Ni(1)–O(3)	94.9(1)	Ni(2)–Cl(2A)–Ni(1)	84.53(4)

## CONCLUSIONS

The study reported herein has allowed a comparison of spectral and solid state features of  $(\text{POCN}_{\text{imine}})\text{NiX}$  complexes as a function of *P*- and *N*-substituents. Electrochemical measurements indicated that the one-electron oxidation of these complexes is fairly insensitive to the heteroatom substituents, but studies of chemical oxidation showed that divalent precursors featuring the  $\text{OP}(\text{i-Pr})_2$  donor moiety led to trivalent derivatives that are isolable and thermally stable. In contrast, oxidation of their  $\text{OPPh}_2$  counterparts led to decomposition and a mixture of side products, one of which was identified as the zwitterionic complex **5**. Stabilities of trivalent compounds  $(\text{i-Pr-POCN}_{\text{imine}})\text{NiX}_2$  were also found to be sensitive to the nature of oxidation agent, NBS being superior to its chloro analogue, and nature of *X* ligand ( $\text{Br}_2 > \text{Br}(\text{Cl}), \text{Br}(\text{NCS})$ ). Current studies are aimed at probing the electron transfer reactivities of  $(\text{i-Pr-POCN}_{\text{imine-R}})\text{NiBr}_2$  as a function of *N*-substituents *R*.

## EXPERIMENTAL SECTION

**General.** Unless otherwise stated, all manipulations were carried out using standard Schlenk and glovebox techniques under nitrogen atmosphere. All solvents used for experiments were dried to water contents of less than 10 ppm by passage through activated aluminum oxide (MBraun SPS) and deoxygenated by three vacuum–nitrogen purge cycles. Quality of the solvents used for experiments was tested using a Mettler Toledo C20 coulometric Karl Fischer titrator. Compound **a**, 3-((benzylimino)methyl)phenol, was prepared according to a previously reported procedure.<sup>14c</sup> The following were purchased from Aldrich and used without further purification: 3-hydroxybenzaldehyde, benzylamine, aniline, *tert*-butylamine, cyclohexanamine, chlorodiphenylphosphine, chlorodiisopropylphosphine, Ni (metal), *N*-chlorosuccinimide, *N*-bromosuccinimide, bromine, iodine, acetone-*d*<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>, CD<sub>3</sub>OD, and CD<sub>2</sub>Cl<sub>2</sub>. NEt<sub>3</sub> was distilled and kept over 4 Å molecular sieves. Bruker AV 400 and AV 500 spectrometers were used for recording <sup>1</sup>H, <sup>13</sup>C (101 MHz), and <sup>31</sup>P (162 MHz) NMR spectra. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm downfield of TMS and referenced against the residual proton signals for acetone-*d*<sub>6</sub> (2.05 ppm for <sup>1</sup>H and 206.26 ppm for <sup>13</sup>C), CD<sub>3</sub>OD (3.31 ppm for <sup>1</sup>H and 49.00 ppm for <sup>13</sup>C), and CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm for <sup>1</sup>H and 53.84 ppm for <sup>13</sup>C). <sup>31</sup>P NMR chemical shifts are reported in ppm and referenced against the signal for 85% H<sub>3</sub>PO<sub>4</sub> (external standard, 0 ppm). Coupling constants are reported in Hz. The correlation and assignment of <sup>1</sup>H and <sup>13</sup>C NMR resonances were aided by <sup>1</sup>H COSY, HSQC, and HMQC. UV–vis spectra were recorded on Varian Bio 300 equipped with a temperature controlling system using standard sampling cells (1 cm optical path length).

**3-((Phenylimino)methyl)phenol (b).** To a solution of 3-hydroxybenzaldehyde (1.00 g, 8.19 mmol) in 5 mL of ethanol at rt was added a solution of aniline (0.84 g, 9.01 mmol) in 5 mL of ethanol. The resulting mixture was stirred for 3 h while the in situ generated water was being collected in a Dean–Stark trap. The

anticipated Schiff base was obtained as a brown suspension. Removal of the volatiles under vacuum for 1 h gave **b** as a brown powder (1.55 g, 96%). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, 298 K): δ 8.34 (s, 1H,  $-\text{CH}=\text{N}$ ), 7.4–6.9 (m, 9H,  $-\text{H-Ar}$ ), 5.1 (s, 1H,  $-\text{OH}$ , overlapping with MeOD). <sup>13</sup>C {<sup>1</sup>H} NMR (δ CD<sub>3</sub>OD, 400 MHz, 298 K): 163 (s, 1C,  $-\text{CH}=\text{N}$ ), 159.1 (s, 1C, {Ar}C<sup>1</sup>), 152.6 (s, 1C, {Ar}C<sup>8</sup>), 138.4 (s, 1C, {Ar}C<sup>5</sup>), 130.9 (s, 1C, {Ar}C<sup>3</sup>), 130.2 (s, 2C, {Ar}C<sup>10and12</sup>), 127.2 (s, 1C, {Ar}C<sup>11</sup>), 121.9 (s, 2C, {Ar}C<sup>9and13</sup>), 121.9 (s, 1C, {Ar}C<sup>4</sup>), 120 (s, 1C, {Ar}C<sup>4</sup>), 119.3 (s, 1C, {Ar}C<sup>2</sup>), 115.2 (s, 1C, {Ar}C<sup>6</sup>). Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.16; H, 5.62; N, 7.08.

**3-(*tert*-Butyliminomethyl)phenol (c).** To a solution of 3-hydroxybenzaldehyde (1.0 g, 8.29 mmol) in 7 mL of ethanol at rt was added a solution of *tert*-butylamine (0.66 g, 9.04 mmol) in 5 mL of ethanol. The resulting mixture was stirred for 2.5 h while the in situ generated water was being collected in a Dean–Stark trap. The anticipated Schiff base was obtained as a yellow suspension. Removal of the volatiles under vacuum gave **c** as a yellowish powder (1.2 g, 82.5%). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, 298 K): δ 8.26 (s, 1H,  $-\text{CH}=\text{N}$ ), 7.20 (s, 3H, ArH<sup>3,4,5</sup>), 6.88 (s, 1H, ArH<sup>2</sup>), 1.30 (s, 9H, CH<sub>3</sub>–C), 5.05 (s, 1H, OH overlapping with MeOD). <sup>13</sup>C {<sup>1</sup>H} NMR (δ CD<sub>3</sub>OD, 400 MHz, 298 K): 158.8 (s, 1C,  $-\text{C}=\text{OH}$ ), 139.1 (s, 1C, {Ar}C<sup>5</sup>), 130.6 (s, 1C, {Ar}C<sup>3</sup>), 120.9 (s, 1C, {Ar}C<sup>4</sup>), 118.8 (s, 1C, {Ar}C<sup>2</sup>), 115.2 (s, 1C, {Ar}C<sup>6</sup>), 58 (s, 1C, {Ar}C<sup>8</sup>), 30 (s, 3C (CH<sub>3</sub>)<sub>3</sub>); the  $-\text{CH}=\text{N}$  signal was obscured in this spectrum but could be identified at 154.82 ppm from the 2D spectrum (Figure S1 in the Supporting Information). Anal. Calcd for C<sub>11</sub>H<sub>15</sub>NO: C, 74.54; H, 8.53; N, 7.90. Found: C, 73.11; H, 8.48; N, 7.42.

**[3-((Cyclohexylimino)methyl)phenol] (d).** To a solution of 3-hydroxybenzaldehyde (1.0 g, 8.2 mmol) in 10 mL of ethanol at rt was added a solution of cyclohexylamine (0.9 g, 9.02 mmol) in 5 mL of ethanol. The resulting mixture was stirred for 3 h while the in situ generated water was being collected in a Dean–Stark trap. The anticipated Schiff base was obtained as a beige suspension. Removal of the volatiles under vacuum gave **d** as a beige powder (1.1 g, 69%). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, 298 K): δ 8.24 (s, 1H,  $-\text{CH}=\text{N}$ ), 7.24–6.91 (m, 3H, {Ar}H<sup>3,4,6</sup>), 6.89–6.87 (d, 1H, {Ar}H<sup>2</sup>), 5.10 (s, 1H, OH), 3.17 (br m, 1H, CyH<sup>8</sup>), 1.82–1.22 (m, 10H,  $-\text{CyH}^{9,10,11,12,13}$ ). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 400 MHz, 298 K): δ 162.2 (s, 1C,  $\text{N}=\text{CH}-$ ), 159 (s, 1C, ArC<sup>1</sup>), 138.5 (s, 1C, ArC<sup>5</sup>), 130.7 (s, 1C, ArC<sup>3</sup>), 121 (s, 1C, ArC<sup>4</sup>), 119.1 (s, 1C, ArC<sup>2</sup>), 115.4 (s, 1C, ArC<sup>6</sup>), 71.1 (s, 1C, CyC<sup>8</sup>), 35.2 (s, 2C, CyC<sup>ortho</sup>), 26.6 (s, 1C, CyC<sup>para</sup>), 25.8 (s, 1C, CyC<sup>meta</sup>). Anal. Calcd for C<sub>13</sub>H<sub>17</sub>NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.31; H, 9.34; N, 4.74.

**3-((Diphenylphosphino)oxy)benzylidene)-1-phenylmethanamine (e).** To a solution of ClPPh<sub>2</sub> (2.45 mL, 11.12 mmol) in THF (10 mL) was added a solution of **a** (1.56 g, 7.41 mmol) and NEt<sub>3</sub> (1.34 mL, 9.63 mmol) in THF (10 mL). The resulting mixture was stirred for 3 h. Evaporation of the solvent and extraction of the residue with toluene (4 × 10 mL) followed by filtration of the combined extracts and evaporation gave the desired product **e** as a yellowish oil (2.40 g, 82%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 298 K): δ 8.26 (br s, 1H,  $\text{CH}=\text{N}$ ), 7.5–7.4 (m, 6H, {Ph<sub>2</sub>P}H<sup>ortho</sup> and {Ph<sub>2</sub>P}H<sup>para</sup>), 7.37–7.30 (m, 8H, {Ph<sub>2</sub>P}H<sup>meta</sup>, {Bn}H<sup>ortho</sup> and {Bn}H<sup>meta</sup>), 7.28 (m, 1H, {Bn}H<sup>para</sup>),

7.24–7.18 (m, 2H, {Ar}H<sup>meta</sup>), 7.14–7.12 (m, 1H, {Ar}H<sup>para</sup>), 4.74 (br s, 2H, {Bn}CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 125 MHz, 298 K): 65 (s, 1C, {Bn}CH<sub>2</sub>), 118.54–114.46 (d, *J* = 10, 1C, {Ar}C<sup>3</sup>), 121.25–121.15 (d, *J* = 12, 1C, {Ar}C<sup>5</sup>), 122.8 (br s, 1C, {Ar}C<sup>4</sup>), 127 (s, 1C, {Bn}C<sup>para</sup>), 128 (br s, 2C, {Bn}C<sup>ortho</sup>), 128.7 (s, 2C, {Bn}C<sup>meta</sup>), 128.6 (br s, 4C, *m*-C in PPh<sub>2</sub>), 130 (s, 2C, *p*-C in PPh<sub>2</sub>), 130.8–130.6 (d, *J*<sub>CP</sub> = 22 Hz, 4C, *o*-C in PPh<sub>2</sub>), 132–131.8 (d, *J*<sub>CP</sub> = 24 Hz, 2C, *i*-C in PPh<sub>2</sub>), 138 (s, 1C, {Bn}C<sup>ipso</sup>), 139.3 (s, 1C, {Ar}C<sup>6</sup>), 140.98–140.75 (d, <sup>2</sup>*J* = 17 Hz, 1C, {Ar}C<sup>1</sup>), 157.82–157.73 (d, <sup>2</sup>*J* = 10 Hz, 1C, {Ar}C<sup>2</sup>), 161.6 (br s, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 202 MHz, 298 K): δ 111 (s, 1P). MS (ESI-HRMS, hexane) (*m/z*): [M + H]<sup>+</sup> (C<sub>26</sub>H<sub>23</sub>NOP) calcd 396.15118; found 396.15065; diff 1.33 ppm.

**3-((Diphenylphosphino)oxy)benzylidene)aniline (f).** To a solution of ClPPh<sub>2</sub> (2.13 mL, 9.64 mmol) in THF (5 mL) was added a solution of **b** (1.46 g, 7.42 mmol) and NEt<sub>3</sub> (1.55 mL, 11.12 mmol) in THF (15 mL). The resulting mixture was stirred for 2 h. Evaporation of the solvent and extraction of the residue with toluene (4 × 10 mL) followed by filtration of the combined extracts and evaporation gave the desired product **f** as a brown oil, (2.32 g, 82%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 298 K): δ 8.4 (br s, 1H, CH=N), 7.7–7.26 (m, 13H, {Ph<sub>2</sub>P}H<sup>ortho</sup>, {PhN}H<sup>para</sup>, {Ph<sub>2</sub>P}H<sup>para</sup>, {Ph<sub>2</sub>P}H<sup>meta</sup>, {PhN}H<sup>ortho</sup>), 7.25–7.21 (m, 2H, {PhN}H<sup>meta</sup>), 7.20–7.17 (m, 3H, {Ar}H<sup>meta</sup> and {Ar}H<sup>para</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 125 MHz, 298 K): 118.84–118.76 (d, <sup>3</sup>*J*<sub>CP</sub> = 11 Hz, 1C, {Ar}C<sup>5</sup>), 126 (s, 1C, {Ar}C<sup>3</sup>), 128 (br s, 2C, {Ar}C<sup>para</sup> and {PhN}C<sup>para</sup>), 129 (br s, 2C, {PhN}C<sup>ortho</sup>), 130 (s, 2C, {PhN}C<sup>meta</sup>), 130.8–130.6 (d, *J*<sub>CP</sub> = 23 Hz, 4C, *o*-C in PPh<sub>2</sub>), 132.8–131.4 (m, 6C, *m*-C in PPh<sub>2</sub> and *p*-C in PPh<sub>2</sub>), 135.6–135.4 (m, 1C, {Ar}C<sup>2</sup>), 138 (s, 1C, {PhN}C<sup>ipso</sup>), 140.81–140.67 (d, *J*<sub>CP</sub> = 18 Hz, 2C, *i*-C in PPh<sub>2</sub>), 152 (s, 1C, {Ar}C<sup>1</sup>), 157.95–157.87 (d, <sup>2</sup>*J* = 10 Hz, 1C, {Ar}C<sup>6</sup>), 160 (br s, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 202 MHz, 298 K): δ 112 (s, 1P). MS (ESI-HRMS, hexane) (*m/z*): [M + H]<sup>+</sup> (C<sub>25</sub>H<sub>21</sub>NOP) calcd 382.13553; found 382.13516; diff 0.96 ppm.

**3-((Diphenylphosphino)oxy)benzylidene)-tert-butyl (g).** To a solution of **c** (0.9 g, 5.09 mmol) and NEt<sub>3</sub> (1.06 mL, 7.63 mmol) in THF (15 mL) was added ClPPh<sub>2</sub> (1.13 mL, 6.1 mmol). The resulting mixture was stirred at 60 °C for 3 h and evaporated under pressure to give an oily heterogeneous mixture. The desired product was extracted from the salt with toluene (5 × 10 mL). Evaporation of the combined extracts furnished **g** as a yellowish oil (*m* = 1.72 g, 94%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz, 298 K): δ 112 (s, 1P).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 298 K): δ 8.01 (br s, 1H, CH=N), 7.81–7.5 (m, 8H, {Ph<sub>2</sub>P}H<sup>ortho</sup> and {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.4–7.3 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.17–7.12 (m, 2H, {Ar}H<sup>meta</sup>), 7.03 (m, 1H, {Ar}H<sup>para</sup>), 1.16 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>-C=N). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 125 MHz, 298 K): 29.8 (s, 3C, (CH<sub>3</sub>)<sub>3</sub>-C=N), 57 (s, 1C, (CH<sub>3</sub>)<sub>3</sub>-C=N), 118 and 120 (m, 2C, {Ar}C<sup>meta</sup>), 122 (br s, 1C, {Ar}C<sup>2</sup>), 128.66–128.60 (d, *J*<sub>CP</sub> = 7 Hz, 4C, *m*-C in PPh<sub>2</sub>), 129.9–129.7 (m, 2C, *p*-C in PPh<sub>2</sub>), 130.7–130.6 (d, <sup>3</sup>*J*<sub>CP</sub> = 23 Hz, 4C, *o*-C in PPh<sub>2</sub>), 132–131.9 (d, *J*<sub>CP</sub> = 10.5 Hz, 2C, *i*-C in PPh<sub>2</sub>), 139 (s, 1C, {Ar}C<sup>para</sup>), 141–140.8 (d, <sup>2</sup>*J*<sub>CP</sub> = 18 Hz, 1C, {Ar}C<sup>1</sup>), 157.73–157.65 (d, <sup>2</sup>*J* = 10 Hz, 1C, {Ar}C<sup>6</sup>), 154.8 (s, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 202 MHz, 298 K): δ 110 (s, 1P). MS (ESI-HRMS, hexane) (*m/z*): [M + H]<sup>+</sup> (C<sub>23</sub>H<sub>23</sub>NOP) calcd 362.16683; found 362.16689; diff -0.17 ppm.

**3-((Diphenylphosphino)oxy)benzylidene)cyclohexylamine (h).** To a solution of **d** (0.9 g, 4.33 mmol) and NEt<sub>3</sub> (1.06 mL, 7.63 mmol) in THF (15 mL) was added ClPPh<sub>2</sub> (0.96 mL, 5.2 mmol). The resulting mixture was stirred at 60 °C for 4 h and evaporated under pressure to give an oily heterogeneous mixture. The desired product was extracted from the salt with toluene (4 × 10 mL). Evaporation of the combined extracts furnished **h** as brown gel (*m* = 1.38 g, 82%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 298 K): δ 8.13 (br s, 1H, CH=N), 7.49–7.46 (m, 4H, {Ph<sub>2</sub>P}H<sup>ortho</sup>), 7.41–7.39 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.37–7.32 (m, 4H, {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.17 and 7.1 (m, 3H, {Ar}H<sup>meta</sup> and {Ar}H<sup>para</sup>), 7.05 and 7.03 (m, 1H, {Ar}H<sup>2</sup>), 1.7, 1.57, and 1.44 (m, 11H, {Cy}H). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 125 MHz, 298 K): 24.9 (s, 2C, {Cy}C<sup>meta</sup>), 25.8 (s, 1C, {Cy}C<sup>para</sup>), 34.4 (s, 2C, {Cy}C<sup>ortho</sup>), 70 (s, 1C, {Cy}C<sup>ipso</sup>), 118.43–118.36 (d, *J*<sub>CP</sub> = 10 Hz, 1C, {Ar}C<sup>5</sup>), 120.66–120.56 (d, *J*<sub>CP</sub> = 12 Hz, 1C, {Ar}C<sup>2</sup>), 122.5 (s, 2C, *p*-C in PPh<sub>2</sub>), 124.3 (s, 1C, 1C, {Ar}C<sup>3</sup>), 128.66–128.60 (d, *J*<sub>CP</sub> = 7 Hz, 4C,

*m*-C in PPh<sub>2</sub>), 130.74–130.57 (d, <sup>3</sup>*J*<sub>CP</sub> = 22.3 Hz, 4C, *o*-C in PPh<sub>2</sub>), 135.56–135.34 (dd, *J*<sub>CP</sub> = 19.25 Hz, 2C, *i*-C in PPh<sub>2</sub>), 138.45 (s, 1C, {Ar}C<sup>para</sup>), 140.95–140.82 (d, <sup>2</sup>*J*<sub>CP</sub> = 17.5 Hz, 1C, {Ar}C<sup>1</sup>), 157.73–157.65 (m, 1C, {Ar}C<sup>6</sup>), 158.2 (br s, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 202 MHz, 298 K): δ 110 (s, 1P). MS (ESI-HRMS, hexane) (*m/z*): [M + H]<sup>+</sup> (C<sub>25</sub>H<sub>27</sub>NOP) calcd 388.18248; found 388.18228; diff 0.51 ppm.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(Ph<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=NBNi)NiBr (1).** A solution of **e** (0.30 g, 0.76 mmol) in 2 mL of toluene was slowly added to the stirring suspension of NiBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>x</sub> (0.34 g, 1.14 mmol) and NEt<sub>3</sub> (0.16 mL, 1.14 mmol) in toluene (5 mL) at rt. The resulting dark brown mixture was then heated for 2 h at 110 °C. Removal of the solvent and purification of the solid residues by column chromatography on SiO<sub>2</sub> (eluents: 50:50 CH<sub>2</sub>Cl<sub>2</sub>:hexane) furnished **1** as an orange solid (0.36 g, 88%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz, 298 K): δ 8.25–8.24 (d of ps-t, <sup>4</sup>*J*<sub>HP</sub> = 3.8 Hz, 1H, CH=N), 7.97–7.93 (m, 4H, {Ph<sub>2</sub>P}H<sup>ortho</sup>), 7.64–7.60 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.56–7.52 (m, 4H, {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.46–7.44 (m, 2H, {Bn}H<sup>ortho</sup>), 7.39–7.36 (m, 2H, {Bn}H<sup>meta</sup>), 7.32–7.29 (m, 1H, {Bn}H<sup>para</sup>), 7.12–7.06 (m, 2H, {Ar}H<sup>meta</sup>), 6.84–6.82 (dd, *J*<sub>HH</sub> = 1.4 Hz, 1H, {Ar}H<sup>para</sup>), 4.94 (br s, 2H, {Bn}CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, (CD<sub>3</sub>)<sub>2</sub>CO, 125 MHz, 298 K): 60 (s, 1C, {Bn}CH<sub>2</sub>), 114.89–114.77 (d, *J* = 14, 1C, {Ar}C<sup>3</sup>), 122.8 (br s, 1C, {Ar}C<sup>5</sup>), 128.3 (br s, 2C, {Ar}C<sup>4</sup> and {Bn}C<sup>para</sup>), 128.4 (br s, 2C, {Bn}C<sup>ortho</sup>), 130 (s, 2C, {Bn}C<sup>meta</sup>), 129.68–129.48 (t, <sup>3</sup>*J*<sub>CP</sub> = 13 Hz, 4C, *m*-C in PPh<sub>2</sub>), 133.07–132.76 (m, 6C, *o*-C in PPh<sub>2</sub> and *p*-C in PPh<sub>2</sub>), 133.64–133.33 (d, *J*<sub>CP</sub> = 39 Hz, 2C, *i*-C in PPh<sub>2</sub>), 139.11 (s, 1C, {Bn}C<sup>ipso</sup>), 149.2 (s, 1C, {Ar}C<sup>6</sup>), 153.54–153.24 (d, <sup>2</sup>*J* = 37 Hz, 1C, {Ar}C<sup>1</sup>), 164.39–164.28 (d, <sup>2</sup>*J* = 13 Hz, 1C, {Ar}C<sup>2</sup>), 175.7 (br s, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 202 MHz, 298 K): δ 150 (s, 1P). Anal. Calcd for [C<sub>26</sub>H<sub>21</sub>NBrNiOP]: C, 58.59; H, 3.97; N, 2.63. Found: C, 59.55; H, 3.98; N, 2.52.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(Ph<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=NPh)NiBr (2).** A solution of **f** (2.32 g, 6.08 mmol) in 5 mL of toluene was slowly added to the stirring suspension of NiBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>x</sub> (2.74 g, 9.12 mmol) and NEt<sub>3</sub> (1.27 mL, 9.12 mmol) in toluene (5 mL) at rt. The resulting dark brown mixture was then heated for 3 h at 110 °C. Removal of the solvent and purification of the solid residues by column chromatography on SiO<sub>2</sub> (eluents: 30:70 CH<sub>2</sub>Cl<sub>2</sub>:hexane) furnished complex **2** as a brick-red powder (2.40 g, 76%). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 500 MHz, 298 K): δ 8.48–8.47 (d, <sup>4</sup>*J*<sub>HP</sub> = 4 Hz, 1H, CH=N), 8.09–8.05 (m, 4H, {Ph<sub>2</sub>P}H<sup>ortho</sup>), 7.92–7.89 (m, 1H, {PhN}H<sup>para</sup>), 7.66–7.62 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.58–7.55 (m, 4H, {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.51–7.37 (m, 2H, {PhN}H<sup>ortho</sup>), 7.30–7.27 (m, 2H, {PhN}H<sup>meta</sup>), 7.20–7.10 (m, 2H, {Ar}H<sup>meta</sup>), 6.96–6.94 (dd, <sup>4</sup>*J*<sub>HP</sub> = 7.5 Hz, 1H, {Ar}H<sup>para</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, (CD<sub>3</sub>)<sub>2</sub>CO, 125 MHz, 298 K): 115.42–115.31 (d, <sup>3</sup>*J*<sub>CP</sub> = 14 Hz, 1C, {Ar}C<sup>5</sup>), 121.9 (s, 1C, {Ar}C<sup>3</sup>), 124 (br s, 2C, {Ar}C<sup>para</sup> and {PhN}C<sup>para</sup>), 125.1 (br s, 2C, {PhN}C<sup>ortho</sup>), 130 (s, 2C, {PhN}C<sup>meta</sup>), 128.49–127.91 (d, *J*<sub>CP</sub> = 72 Hz, 4C, *o*-C in PPh<sub>2</sub>), 129.8–129.5 (m, 6C, *m*-C in PPh<sub>2</sub> and *p*-C in PPh<sub>2</sub>), 133.11–133.09 (d, <sup>3</sup>*J*<sub>CP</sub> = 2 Hz, 1C, {Ar}C<sup>2</sup>), 133.32–133.28 (d, <sup>3</sup>*J*<sub>CP</sub> = 12 Hz, 1C, {PhN}C<sup>ipso</sup>), 149.86–149.29 (d, *J*<sub>CP</sub> = 72 Hz, 2C, *i*-C in PPh<sub>2</sub>), 154.44–154.13 (d, <sup>2</sup>*J*<sub>CP</sub> = 38 Hz, 1C, {Ar}C<sup>1</sup>), 164.6–164.49 (d, <sup>2</sup>*J* = 13 Hz, 1C, {Ar}C<sup>6</sup>), 175.7 (br d, *J*<sub>CP</sub> = 3 Hz, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 202 MHz, 298 K): δ 149 (s, 1P). Anal. Calcd for [C<sub>25</sub>H<sub>19</sub>BrNNiOP]: C, 57.86; H, 3.69; N, 2.70. Found: C, 59.55; H, 4.03; N, 2.45.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(Ph<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=N<sup>t</sup>Bu)NiBr (3).** A solution of **g** (1.72 g, 4.77 mmol) in 5 mL of toluene was slowly added to the stirring suspension of NiBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>x</sub> (1.37 g, 6.20 mmol) and NEt<sub>3</sub> (1 mL, 7.16 mmol) in toluene (5 mL) at rt. The resulting red mixture was then heated for 3 h at 110 °C. Removal of the solvent and purification of the solid residues by column chromatography on SiO<sub>2</sub> (eluents: 30:70 CH<sub>2</sub>Cl<sub>2</sub>:hexane) furnished **3** as an orange powder (1.71 g, 71.84%). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 500 MHz, 298 K): δ 8.34–8.33 (d, <sup>4</sup>*J*<sub>HP</sub> = 4 Hz, 1H, CH=N), 8.06–8.02 (m, 4H, {Ph<sub>2</sub>P}H<sup>ortho</sup>), 7.65–7.62 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.58–7.54 (m, 4H, {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.10 and 6.78 (m, 3H, {Ar}H<sup>meta</sup> and {Ar}H<sup>para</sup>), 1.56 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>-C=N). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, (CD<sub>3</sub>)<sub>2</sub>CO, 125 MHz, 298 K): 30 (s, 3C, (CH<sub>3</sub>)<sub>3</sub>-C=N), 63 (s, 1C, (CH<sub>3</sub>)<sub>3</sub>-C=N), 114 and 123 (m, 2C, {Ar}C<sup>meta</sup>), 129.5–129.4 (d, *J*<sub>CP</sub> = 17 Hz, 1C, 1C, {Ar}C<sup>2</sup>), 133 (d, *J*<sub>CP</sub>



= 3.5 Hz, 4C, *m*-C in PPh<sub>2</sub>) 128.3 (s, 2C, *p*-C in PPh<sub>2</sub>), 133.66–133.56 (d, <sup>3</sup>J<sub>CP</sub> = 18.5 Hz, 4C, *o*-C in PPh<sub>2</sub>), 133.3–132.9 (d, J<sub>CP</sub> = 84 Hz 2C, *i*-C in PPh<sub>2</sub>), 149.8 (s, 1C, {Ar}C<sup>para</sup>), 151.1–150.8 (d, <sup>2</sup>J<sub>CP</sub> = 65.5 Hz, 1C, {Ar}C<sup>1</sup>), 164.33–164.22 (d, <sup>2</sup>J = 22 Hz, 1C, {Ar}C<sup>6</sup>), 169.37–169.35 (br d, J<sub>CP</sub> = 4.5 Hz, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 202 MHz, 298 K): δ 141 (s, 1P). Anal. Calcd for [C<sub>23</sub>H<sub>23</sub>BrNNiOP]: C, 55.36; H, 4.65; N, 2.81. Found: C, 56.4; H, 4.64; N, 2.49.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(Ph<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=Ncy)]NiBr (4).** A solution of **h** (1.38 g, 3.55 mmol) in solution in 7 mL of toluene was slowly added to the stirring suspension of NiBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>x</sub> (1.39 g, 4.62 mmol) and NEt<sub>3</sub> (0.7 mL, 5.33 mmol) in toluene (5 mL) at rt. The resulting red mixture was then heated for 3.5 h at 110 °C. Removal of the solvent and purification of the solid residues by column chromatography on SiO<sub>2</sub> (eluents: 70:30 CH<sub>2</sub>Cl<sub>2</sub>:hexane) furnished **4** as an orange powder (1.73 g, 93%). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 500 MHz, 298 K): δ 8.34–8.33 (d, <sup>4</sup>J<sub>HP</sub> = 5 Hz, 1H, CH=N), 8.07–8.02 (m, 4H, {Ph<sub>2</sub>P}H<sup>ortho</sup>), 7.64–7.61 (m, 2H, {Ph<sub>2</sub>P}H<sup>para</sup>), 7.58–7.55 (m, 4H, {Ph<sub>2</sub>P}H<sup>meta</sup>), 7.10 and 6.82 (m, 3H, {Ar}H<sup>meta</sup> and {Ar}H<sup>para</sup>), 2.13, 1.81, 1.68, 1.38, and 0.87 (m, 11H, {Cy}H). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, (CD<sub>3</sub>)<sub>2</sub>CO, 125 MHz, 298 K): 26.36 (s, 2C, {Cy}C<sup>meta</sup>), 26.42 (s, 1C, {Cy}C<sup>para</sup>), 34.1 (s, 2C, {Cy}C<sup>ortho</sup>), 63.54 (s, 1C, {Cy}C<sup>ipso</sup>), 114.4 (d, J<sub>CP</sub> = 14 Hz, 1C, {Ar}C<sup>5</sup>), 122.5 (d, J<sub>CP</sub> = 1.7 Hz, 1C, {Ar}C<sup>3</sup>), 128.2 (s, 2C, *p*-C in PPh<sub>2</sub>), 129.7–129.62 (d, J<sub>CP</sub> = 11 Hz, 1C, 1C, {Ar}C<sup>2</sup>), 133 (d, J<sub>CP</sub> = 2.2 Hz, 4C, *m*-C in PPh<sub>2</sub>) 133.23–133.13 (d, <sup>3</sup>J<sub>CP</sub> = 12.3 Hz, 4C, *o*-C in PPh<sub>2</sub>), 133.7–132.7 (d, J<sub>CP</sub> = 106 Hz 2C, *i*-C in PPh<sub>2</sub>), 150.15 (s, 1C, {Ar}C<sup>para</sup>), 152.7–152.4 (d, <sup>2</sup>J<sub>CP</sub> = 38.5 Hz, 1C, {Ar}C<sup>1</sup>), 164.44–164.33 (d, <sup>2</sup>J = 13 Hz, 1C, {Ar}C<sup>6</sup>), 171.07–171.04 (br d, J<sub>CP</sub> = 3 Hz, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 202 MHz, 298 K): δ 148.5 (s, 1P). Anal. Calcd for [C<sub>25</sub>H<sub>25</sub>BrNNiOP]: C, 57.19; H, 4.80; N, 2.67. Found: C, 57.53; H, 4.89; N, 2.59.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(<sup>i</sup>Pr<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=NPh)]NiBr (6).** To a solution of chlorodiisopropylphosphine (0.90 mL, 5.64 mmol) in THF (5 mL) was added a solution of **b** (1.01 g, 5.13 mmol) and NEt<sub>3</sub> (1.72 mL, 7.70 mmol) in THF (10 mL). The resulting mixture was stirred at 60 °C for 2 h followed by the evaporation of the volatiles, and to this residue was added slowly a suspension of NiBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>x</sub> (2.01 g, 6.67 mmol) and NEt<sub>3</sub> (1.72 mL, 7.70 mmol) in toluene (10 mL). The resulting dark red mixture was then heated for an additional 2 h at 110 °C. Removal of the solvent and purification of the solid residues by column chromatography on SiO<sub>2</sub> (eluents: 20:80 CH<sub>2</sub>Cl<sub>2</sub>:hexane) furnished **5** as a red powder (1.73 g, 75%). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 500 MHz, 298 K): δ 1.38 (dd, <sup>3</sup>J<sub>HH</sub> = 7, <sup>3</sup>J<sub>HP</sub> = 15, 6H, 2 × CHCH<sub>3</sub>), 1.49 (dd, <sup>3</sup>J<sub>HH</sub> = 7, <sup>3</sup>J<sub>HP</sub> = 18, 6H, 2 × CHCH<sub>3</sub>), 2.52–2.45 (m, 2H, 2 × CHCH<sub>3</sub>), 6.79 (d, <sup>4</sup>J<sub>HH</sub> = 8, 1H, {Ar}H<sup>5</sup>), 7.10 (t, <sup>5</sup>J<sub>HH</sub> = 7.4, 1H, {Ar}H<sup>4</sup>), 7.20 (d, <sup>5</sup>J<sub>HH</sub> = 8, 1H, {Ar}H<sup>3</sup>), 7.30–7.27 (m, 1H, {Ph}H<sup>para</sup>), 7.38–7.37 (m, 4H, 2 × {Ph}H<sup>ortho</sup>), and 2 × {Ph}H<sup>meta</sup>), 8.43 (d, <sup>4</sup>J<sub>HP</sub> = 4, 1H, CH=N). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, (CD<sub>3</sub>)<sub>2</sub>CO, 125 MHz, 298 K): 17.18 (d, <sup>2</sup>J<sub>CP</sub> = 1.5, 2C, CHCH<sub>3</sub>), 18.56 (d, <sup>2</sup>J<sub>CP</sub> = 3.6, 2C, CHCH<sub>3</sub>), 29.53 (d, <sup>1</sup>J<sub>CP</sub> = 24, 2C, CHCH<sub>3</sub>), 114.39 (d, <sup>3</sup>J<sub>CP</sub> = 12.41, 1C, {Ar}C<sup>5</sup>), 123.34 (br s, {Ar}C<sup>3</sup>), 125 (s, 1C, {Ar}C<sup>4</sup> and {Ph}C<sup>para</sup>), 127.8 (s, 2C, 2 × {Ph}C<sup>ortho</sup>), 129 (s, 2C, 2 × {Bn}C<sup>meta</sup>), 149.14 (s, 1C, {Ph}C<sup>ipso</sup>), 149.81 (s, 1C, {Ar}C<sup>2</sup>), 153.73 (d, <sup>2</sup>J<sub>CP</sub> = 35.3, 1C, {Ar}C<sup>1</sup>), 166.27 (d, <sup>2</sup>J<sub>CP</sub> = 10, 1C, {Ar}C<sup>6</sup>), 174.40 (d, <sup>3</sup>J<sub>CP</sub> = 2.5, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 202 MHz, 298 K): δ 200 (s, 1P). Anal. Calcd for [C<sub>19</sub>H<sub>23</sub>BrNNiOP]: C, 50.60; H, 5.14; N, 3.11. Found: C, 50.58; H, 5.10; N, 3.04.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(<sup>i</sup>Pr<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=NPh)]NiBr<sub>2</sub> (7).** *Method A.* To a solution of **6** (101 mg, 0.22 mmol) in 5 mL of dry and degassed DCM at –78 °C was added a DCM solution of Br<sub>2</sub> (3 mL, 0.22 mmol). The resulting mixture was allowed to stir to room temperature for 5 min before removal of the solvent in vacuum. The dark brown-black powder was then washed with cold hexane (3 × 5 mL) and dried under vacuum to yield the desired product as black solid (0.096 mg, 84%).

*Method B.* To a solution of **6** (100 mg, 0.22 mmol) in 5 mL of dry and degassed DCM at rt was added *N*-bromosuccinimide (51 mg, 0.29 mmol), and the resulting mixture was stirred at room temperature for 30 min before removal of the solvent under vacuum. The remaining dark brown-black powder was then washed with cold hexane (3 × 5

mL) and dried under vacuum to yield the desired product as black (0.073 g, 63%).

**The Trinuclear Complex 8.** To a solution of **6** (100 mg, 0.22 mmol) in 5 mL of dry and degassed DCM at rt was added *N*-chlorosuccinimide (38 mg, 0.29 mmol), and the resulting mixture was stirred at rt for 45 min. Removal of the volatiles under vacuum gave a mixture of black and dark-red powder (ca. 82 mg), which was washed with cold hexane (3 × 5 mL) to remove hexane-soluble impurities and recrystallized from DCM (2 mL) to give a black powder containing red crystals suitable for X-ray diffraction analysis. In spite of the fairly different solubilities of these two solids (the black solid is more soluble in THF, DCM, and acetonitrile), we have not succeeded in isolating analytically pure samples of these materials. Both of these solids are NMR-silent.

**κ<sup>P</sup>,κ<sup>C</sup>,κ<sup>N</sup>-[2,6-(<sup>i</sup>Pr<sub>2</sub>PO)(C<sub>6</sub>H<sub>3</sub>)(CH=NPh)]Ni-NCS (9).** A mixture of **6** (52 mg, 0.12 mmol) and KSCN (112 mg, 1.15 mmol) in 5 mL of DCM was stirred overnight (15 h) at room temperature. Addition of 10 mL of hexane to the reaction mixture and filtration over a Celite column furnished **9** as an orange jelly compound (33 mg, 67%). <sup>1</sup>H NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>): 1.35–1.31 (dd, <sup>3</sup>J<sub>HH</sub> = 7, <sup>3</sup>J<sub>HP</sub> = 15, 6H, 2 × CHCH<sub>3</sub>), 1.45–1.41 (dd, <sup>3</sup>J<sub>HH</sub> = 7, <sup>3</sup>J<sub>HP</sub> = 18.5, 6H, 2 × CHCH<sub>3</sub>), 2.36–2.29 (m, 2H, 2 × CHCH<sub>3</sub>), 6.63 (d, <sup>3</sup>J<sub>HH</sub> = 8, 1H, {Ar}H<sup>5</sup>), 6.90 (d, <sup>3</sup>J<sub>HH</sub> = 7, 1H, {Ar}H<sup>3</sup>), 7.0 (t, <sup>3</sup>J<sub>HH</sub> = 8, 1H, {Ar}H<sup>4</sup>), 7.35 (m, 1H, {Ph}H<sup>para</sup>), 7.4 (m, 4H, 2 × {Ph}H<sup>ortho</sup> and {Ph}H<sup>meta</sup>), 7.9 (br s, 1H, CH=N). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>): 16.92 (d, <sup>2</sup>J<sub>CP</sub> = 1, 2C, CHCH<sub>3</sub>), 17.6 (d, <sup>2</sup>J<sub>CP</sub> = 5, 2C, CHCH<sub>3</sub>), 28.75 (d, <sup>1</sup>J = 23, 2C, CHCH<sub>3</sub>), 112.5 (d, J = 13, 1C, {Ar}C<sup>3</sup>), 121.7 (d, <sup>4</sup>J = 2, {Ar}C<sup>5</sup>), 127.62 (s, 1C, {Ar}C<sup>4</sup>), 128.2 (s, 1C, {Ph}C<sup>para</sup>), 129.17 (s, 2C, 2 × {Ph}C<sup>ortho</sup>), 129.27 (s, 2C, 2 × {Ph}C<sup>meta</sup>), 136.85 (s, 1C, {Ph}C<sup>ipso</sup>), 142 (s, 1C, {Ar}C<sup>6</sup>), 149 (s, 1C, NCS), 151 (d, <sup>2</sup>J = 35, 1C, {Ar}C<sup>1</sup>), 165 (d, <sup>2</sup>J = 10, 1C, {Ar}C<sup>2</sup>), 173 (d, <sup>2</sup>J = 3, 1C, CH=N). <sup>31</sup>P{<sup>1</sup>H} NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>): 199 (s, 1P). Most of the samples isolated were oily solids that did not give dry powders even after several hours under reduced pressure. Elemental analysis of one such sample showed it to have significantly lower N and S but higher C and H compositions, consistent with the presence of hydrocarbon impurities. (Anal. Calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>NiOPS: C, 55.98; H, 5.40; N, 6.53; S, 7.47. Found: C, 63.91; H, 8.28; N, 3.90; S, 4.88.) Thus, inclusion of two molecules of hexane into the molecular formula of the complex would generate a better agreement between calculated and experimental compositions, in particular for C and H contents (Anal. Calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>NiOPS·2C<sub>6</sub>H<sub>14</sub>: C, 63.90; H, 8.55; N, 4.66; S, 5.33). The <sup>1</sup>H NMR spectra of the oily solid showed aliphatic resonances attributable to the recrystallization solvent, hexane, whereas X-ray diffraction of a crystalline sample showed no crystallization solvent in the unit cell.

**Attempted Oxidation of Complex 9.** To an orange solution of **9** (25 mg, 0.057 mmol) in 5 mL of dry and degassed DCM was added *N*-bromosuccinimide (13 mg, 0.074 mmol), and the resulting mixture was stirred at rt for 1 h before removal of the solvent under vacuum. The remaining powder was then washed with cold hexane (3 × 5 mL) and dried under vacuum to yield a mixture of dark red and brown powder (19 mg). Unable to separate these solids, the product was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> and kept in the glovebox freezer (–35 °C) for 2 days. We obtained two distinct batches of crystals, red blocks and brown plates, which were subjected to X-ray analysis. The brown crystals proved to be the known compound *N*-thiocyanate succinimide (NTS),<sup>30</sup> whereas the red crystals were confirmed to be complex **6**.

## ■ ASSOCIATED CONTENT

### Supporting Information

NMR, IR, and UV–vis spectra; cyclic voltammograms; detailed description of the procedures used for the single X-ray diffraction studies, and tables of crystal data. This material is available free of charge via the Internet at <http://pubs.acs.org>. Complete details of the X-ray analyses for ligand **f** (1002783) and complexes **2** (1001949), **3** (1001950), **4** (1001951), **5** (1001952), **6** (1001953), **7** (1001954), **8** (1002512), and **9** (1001955) have been deposited at The Cambridge Crystallo-

graphic Data Centre. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; 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. *Dalton Trans.* **1976**, 1020. (b) Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L.; Goodfellow, R. J. *J. Chem. Soc., Chem. Commun.* **1979**, 498.
- (2) (a) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *Organometallics* **1984**, *3*, 1003. (c) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169.
- (3) Examples of pincer complexes based on an aliphatic backbone: (a) Jonasson, K. J.; Ahlsten, N.; Wendt, O. F. *Inorg. Chim. Acta* **2011**, *379*, 76. (b) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080. (c) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592. (d) Andrushko, N.; Andrushko, V.; Roose, P.; Moonen, K.; Börner, A. *Chem. Catal. Chem.* **2010**, *2*, 640. (e) Choi, J. H.; Schloerer, N. E.; Berger, J.; Precht, M. H. G. *Dalton Trans.* **2014**, 43, 290. (f) Huang, Z.; Zhou, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 11458. (g) Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *Eur. J. Inorg. Chem.* **2012**, 4898. (h) Li, S. W. X.; Xiong, Z.; Xu, W.; Lu, Y.; Sun, H. *Organometallics* **2013**, *32*, 3227. (i) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978. (j) Pandarus, V.; Zargarian, D. *Organometallics* **2007**, *26*, 4321. (k) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2008**, *27*, 5723. (l) Castonguay, A.; Spasyuk, D. M.; Madern, N.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2009**, *28*, 2135. (m) Hao, J.; Mougang-Soumé, B.; Vabre, B.; Zargarian, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 3218.
- (4) Examples of pincer complexes based on an aromatic backbone: (a) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. (b) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*, 958. (c) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144. (d) Salem, H.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2006**, *25*, 2292. (e) Sykes, A. C.; White, P.; Brookhart, M. *Organometallics* **2006**, *25*, 1664. (f) Benito-Garagorri, D.; Bocokic, V.; Mereiter, K.; Kirchner, K. *Organometallics* **2006**, *25*, 3817. (g) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. (h) Wingard, L. A.; Finnis, M. C.; Norris, M.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2013**, *52*, 515. (i) Yao, W.; Zhang, Y.; Jia, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 1390. (j) Ogawa, H.; Yamashita, M. *Dalton Trans.* **2013**, 42, 625. (k) Zuo, W.; Braunstein, P. *Dalton Trans.* **2012**, 41, 636. (l) Zhang, J.; Gao, W.; Lang, X.; Wu, Q.; Zhang, L.; Mu, Y. *Dalton Trans.* **2012**, 41, 9639.
- (5) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 9531.
- (6) Example of nonsymmetrical pincer systems: (a) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Chem.—Eur. J.* **2004**, *10*, 4673. (b) Gagliardo, M.; Selander, N.; Mehendale, N.; van Koten, G.; Klein-Gebbink, R.; Szabo, K. *Chem.—Eur. J.* **2008**, *14*, 4800. (c) Zhang, J.; Gandelman, M.; Herrman, D.; Leitens, G.; Shimon, L. J.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2006**, 359, 1955. (d) Fischer, J.; Schurmann, M.; Mehring, M.; Zachwieja, U.; Jurkschat, K. *Organometallics* **2006**, *25*, 2886. (e) Debono, N.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2007**, *349*, 2470. (f) Durand, J.; Gladiali, S.; Erre, G.; Zangrando, E.; Milani, B. *Organometallics* **2007**, *26*, 810. (g) Boronat, M.; Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Organometallics* **2010**, *29*, 134.
- (7) For reports on catalytic activities of pincer complexes see: (a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (b) Miyazaki, F.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (c) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (d) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (e) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3569. (f) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (g) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (h) Sebelius, S.; Olsson, V. J.; Szabo, K. J. *J. Am. Chem. Soc.* **2005**, *127*, 10478. (i) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257. (j) Naghipour, A.; Sabounchei, S. J.; Morales-Morales, D.; Canseco-González, D.; Jensen, C. M. *Polyhedron* **2007**, *26*, 1445. (k) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790. (l) Bernskoetter, W. H.; Brookhart, M. *Organometallics* **2008**, *27*, 2036. (m) Zweifel, T.; Naubron, J.-V.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 559.
- (8) Selander, N.; Szabo, K. J. *Chem. Rev.* **2011**, *111*, 2048.
- (9) For reports on material properties of pincer complexes see: (a) Jude, H.; Bauer, J. A. K.; Connick, W. B. *Inorg. Chem.* **2002**, *41*, 2275. (b) Kanbara, T.; Okada, K.; Yamamoto, T.; Ogawa, H.; Inoue, T. *J. Organomet. Chem.* **2004**, 689, 1860. (c) Okamoto, K.; Kanbara, T.; Yamamoto, T.; Wada, A. *Organometallics* **2006**, *25*, 4026. (d) Batema, G. D.; Lutz, M. A. L.; Spek, C. A.; Walree, V.; 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.; van Koten, G. *Organometallics* **2008**, *27*, 1690.
- (10) For reports on photophysical properties of pincer complexes see: (a) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048. (b) Kanbara, T.; Yamamoto, T. *J. Organomet. Chem.* **2003**, 688, 15. (c) Kanbara, T.; Okada, K.; Yamamoto, T.; Ogawa, H.; Inoue, T. *J. Organomet. Chem.* **2004**, 689, 1860. (d) Kuwabara, J.; Kanbara, T. *J. Photopolym. Sci. Technol.* **2008**, *21*, 349. (e) Okamoto, K.; Kanbara, T.; Yamamoto, T.; Wada, A. *Organometallics* **2006**, *25*, 4026. (f) Hu, J.; Xu, H.; Nguyen, M.-H.; Yip, J. H. K. *Inorg. Chem.* **2009**, *48*, 9684. (g) Jude, H.; Krause, J. A. B.; Connick, W. B. *Inorg. Chem.* **2002**, *41*, 2275. (h) Jude, H.; Krause, J. A. B.; Connick, W. B. *Inorg. Chem.* **2004**, *43*, 725. (i) Jude, H.; Krause, J. A. B.; Connick, W. B. *Inorg. Chem.* **2005**, *44*, 1211.
- (11) (a) For a summary of the early contributions to this area of pincer complexes see: van Koten, G. The Monoanionic ECE-Pincer Ligand: A Versatile Privileged Ligand Platform—General Considerations. In *Organometallic Pincer Chemistry*; van Koten, G., Milstein, D., Eds.; Topics in Organometallic Chemistry 40; Springer-Verlag: Berlin Heidelberg, 2013; pp 1–20; doi: 10.1007/978-3-642-31081-2\_1. (b) 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.; Topics in Organometallic Chemistry 40; Springer-Verlag: Berlin Heidelberg, 2013; pp 131–174; doi: 10.1007/978-3-642-31081-2\_5.



- (11) (a) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (b) Cámpora, J.; Palma, P.; del Río, D.; Conejo, M. M.; Álvarez, E. *Organometallics* **2004**, *23*, 5655. (c) Castonguay, A.; Charbonneau, F.; Beauchamp, A. L.; Zargarian, D. *Acta Crystallogr.* **2005**, *E61*, m2240. (d) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. (e) Sui-Seng, C.; Castonguay, A.; Chen, Y.; Gareau, D.; Groux, L. F.; Zargarian, D. *Top. Catal.* **2006**, *37*, 81. (f) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Acta Crystallogr.* **2007**, *E63*, m196. (g) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582. (h) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Inorg. Chem.* **2009**, *48*, 3177. (i) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872. (j) Solano-Prado, M. A.; Estudiante-Negrete, F.; Morales-Morales, D. *Polyhedron* **2010**, *29*, 592. (k) Rossin, A.; Peruzzini, M.; Zanobini, F. *Dalton Trans.* **2011**, *40*, 4447. (l) Levina, V. A.; Rossin, A.; Belkova, N. V.; Chierotti, M. R.; Epstein, L. M.; Filippov, O. A.; Gobetto, R.; Gonsalvi, L.; Lledós, A.; Shubina, E. S.; Zanobini, F.; Peruzzini, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 1367. (m) Lefèvre, X.; Durieux, G.; Lesturgez, S.; Zargarian, D. *J. Mol. Catal. A* **2011**, *335*, 1. (n) Lefèvre, X.; Spasyuk, D. M.; Zargarian, D. *J. Organomet. Chem.* **2011**, *864*. (o) Salah, A.; Zargarian, D. *Acta Crystallogr.* **2011**, *E67*, m940. (p) Salah, A.; Zargarian, D. *Acta Crystallogr.* **2011**, *E67*, m437. (q) Salah, A.; Zargarian, D. *Dalton Trans.* **2011**, *40*, 8977. (r) Zhang, J.; Adhikary, A.; King, K. M.; Krause, J. A.; Guan, H. *Dalton Trans.* **2012**, *41*, 7959. (s) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. *Polyhedron* **2012**, *32*, 30. (t) Estudiante-Negrete, F.; Hernández-Ortega, S.; Morales-Morales, D. *Inorg. Chim. Acta* **2012**, *387*, 58. (u) Martínez-Prieto, L. M.; Melero, C.; del Río, D.; Palma, P.; Cámpora, J. *Organometallics* **2012**, *31*, 1425. (v) Vabre, B.; Spasyuk, D. M.; Zargarian, D. *Organometallics* **2012**, *31*, 8561. (w) Vabre, B.; Lindeperg, F.; Zargarian, D. *Green Chem.* **2013**, *15*, 3188. (x) Chierotti, M. R.; Rossin, A.; Gobetto, R.; Peruzzini, M. *Inorg. Chem.* **2013**, *52*, 12616.
- (12) Vabre, B.; Canac, Y.; Duhayon, C.; Chauvin, R.; Zargarian, D. *Chem. Commun.* **2012**, *48*, 10446.
- (13) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D. *Can. J. Chem.* **2005**, *83*, 634.
- (14) (a) Spasyuk, D. M.; Zargarian, D.; van der Est, A. *Organometallics* **2009**, *28*, 6531. (b) Spasyuk, D. M.; Zargarian, D. *Inorg. Chem.* **2010**, *49*, 6203. (c) Spasyuk, D. M.; Gorelsky, S. I.; van der Est, A.; Zargarian, D. *Inorg. Chem.* **2011**, *50*, 2661.
- (15) Sanford, J.; Dent, C.; Masuda, J.; Xia, A. *Polyhedron* **2011**, *30*, 1091.
- (16) Yoon, H.; Wagler, T. R.; O'Connor, K. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4568.
- (17) See the following and references therein: (a) Madhira, V. N.; Ren, P.; Vechorkin, O.; Hu, X.; Vivic, D. A. *Dalton Trans.* **2012**, *41*, 7915–7919. (b) Zhang, C.-P.; Wang, H.; Klein, A.; Biewer, C.; Stirnat, K.; Yamaguchi, Y.; Xu, L.; Gomez-Benitez, V.; Vivic, D. A. *J. Am. Chem. Soc.* **2013**, *135*, 8141–8144. (c) Zheng, B.; Tang, F.; Luo, J.; Schultz, J. W.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2014**, *136*, 6499–6504.
- (18) Trivalent nickel species also play central functions in many bioinorganic and enzymatic reactions, including the C–H activation step involved in the anaerobic oxidation of methane by methanotrophic archaea. The following reports describe this field of study: (a) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297. (b) Lancaster, J. R., Jr. Ed. *Bioinorganic Chemistry of Nickel*; VCH: New York, 1988. (c) Halcrow, M. A.; Christou, G. *Chem. Rev.* **1994**, *94*, 2421. (d) Ermler, U.; Grabarse, W.; Shima, S.; Goubeaud, M.; Thauer, R. K. *Science* **1997**, *278*, 1457. (e) Evans, D. J. *Coord. Chem. Rev.* **2005**, *249*, 1582. (f) Yang, N.; Reiher, M.; Wang, M.; Harmer, J.; Duin, E. C. *J. Am. Chem. Soc.* **2007**, *129*, 11028. (g) Dey, M.; Telser, J.; Kunz, R. C.; Lees, N. S.; Ragsdale, S. W.; Hoffman, B. M. *J. Am. Chem. Soc.* **2007**, *129*, 11030. (h) Ragsdale, S. W. *J. Biol. Chem.* **2009**, *284*, 18571. (i) Scheller, S.; Goenrich, M.; Mayr, S.; Thauer, R. K.; Jaun, B. *Angew. Chem., Int. Ed.* **2010**, *49*, 8112. (j) Scheller, S.; Goenrich, M.; Boecher, R.; Thauer, R. K.; Jaun, B. *Nature* **2010**, *465*, 606.
- (19) Roddick, D. M.; Zargarian, D. *Inorg. Chim. Acta* **2014**, *422*, 251–264, DOI: 10.1016/j.ica.2014.07.065.
- (20) (a) Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379–1380. (b) Grove, D. M.; van Koten, G.; Mul, W. P.; Zoet, R.; van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27*, 2466–2473. (c) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A. H.; Terheijden, J. *Organometallics* **1986**, *5*, 322–326. (d) Kozhanov, K. A.; Bubnov, M. P.; Cherkasov, V. K.; Fukin, G. K.; Vavilina, N. N.; Efremova, L. Y.; Abakumov, G. A. *J. Magn. Reson.* **2009**, *197*, 36–39.
- (21) (a) Collins, T. J.; Nichols, T. R.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, *113*, 4708. (b) Lee, C. M.; Chen, C. H.; Liao, F. X.; Hu, C. H.; Lee, G. H. *J. Am. Chem. Soc.* **2010**, *132*, 9256. (c) Lipschutz, M. I.; Yang, X.; Chatterjee, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2013**, *135*, 15298.
- (22) Many more trivalent Ni complexes are known that do not possess a Ni–C bond. For a selection of these complexes see: (a) Zeigerson, E.; Bar, I.; Bernstein, J.; Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 73. (b) McAuley, A.; Norman, P. R.; Olubyide, O. *J. Chem. Soc., Dalton Trans.* **1984**, 1501. (c) Wiegardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650. (d) Calligaris, M.; Carugo, O.; Crippa, G.; Santis, G. D.; Casa, M. D.; Fabbri, L.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1990**, *29*, 2964. (e) McAuley, A.; Subramanian, S. *Inorg. Chem.* **1991**, *30*, 371. (f) McAuley, A.; Palmer, T.; Whitcombe, T. W. *Can. J. Chem.* **1993**, *71*, 1792.
- (23) Motoyama, Y.; Shimozone, K.; Nishiyama, H. *Inorg. Chim. Acta* **2006**, *359*, 1725.
- (24) We suppose that the nickelation of POCN ligands proceeds similarly to those of POC(H)OP ligands, which are thought to involve an electrophilic substitution type mechanism. For a discussion of this issue see the following report: Vabre, B.; Lambert, M. L.; Petit, A.; Ess, D. H.; Zargarian, D. *Organometallics* **2012**, *31*, 6041.
- (25) See, for instance, the reported structures of the simple salt [*t*-Bu<sub>3</sub>PH][*t*-Bu<sub>3</sub>PNiBr<sub>3</sub>] displaying fairly uniform structural parameters Ni–Br ~ 2.37(2)–2.39(1) Å and Br–Ni–Br ~ 109–110°<sup>25a</sup> and the zwitterionic compound {MesImCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}NiBr<sub>3</sub> (MesIm = *N*-mesityl imidazolium) displaying different parameters Ni–Br ~ 2.31–2.37 Å and Br–Ni–Br ~ 107–123°<sup>25b</sup>: (a) Alyea, E. C.; Costin, A.; Ferguson, G.; Fey, G. T.; Goel, R. G.; Restivo, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1294. (b) Wolf, J.; Labande, A.; Daran, J.-C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 433.
- (26) Kozhanov, K. A.; Bubnov, M. P. *Dokl. Akad. Nauk* **2006**, *407*, 49.
- (27) The resulting low-resolution structure appeared to be similar to that of **5** except for the different unit cell and also the presence of a new atom at the *para* position of the *N*-Ph. Tests indicated that this position might be disordered and occupied by 12% Br and 88% H.
- (28) The authors wish to thank an anonymous reviewer who has brought to our attention a similar case of unintended aromatic C–H halogenation during the attempted oxidation of the complexes [(*tpy*)LRu(II)]<sup>+</sup> (L = NCN or 2,6-bis(2-pyridyl)phenyl). Given the similarities between these systems and complex **6**, the reviewer is probably correct in stating that a similar mechanism must be occurring in both cases, but further studies are required to confirm this hypothesis: Wadman, S. H.; Havenith, R. W. A.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *J. Am. Chem. Soc.* **2010**, *132*, 1914–1924.
- (29) Previous attempts at preparation of (PC<sub>sp3</sub>P)Ni(Br)Cl had given material that was difficult to characterize with confidence due to disorder in the positions of the halides. We reasoned, therefore, that a triatomic ligand bearing atoms much lighter than Br should be less prone to crystallographic disorder.
- (30) Ashby, M. T.; Annetha, H. *J. Am. Chem. Soc.* **2004**, *126*, 10216.
- (31) The  $\tau$  parameter is calculated according to the relationship  $\tau = (\beta - \alpha)/60$ , wherein  $\beta$  and  $\alpha$  refer to the largest basal angles in the complex ( $\beta > \alpha$ ); values approaching zero imply small degrees of deviation from an ideal square-pyramidal geometry, whereas values approaching 1 signal significant distortions toward a trigonal

bipyramidal geometry: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(32) For instance, compare to a Ni...Ni distances of 3.6–3.7 Å<sup>32a</sup> and 3.5–3.8 Å.<sup>32b</sup> (a) Xue, F.; Zhao, J.; Hor, T. S. A. *Dalton Trans.* **2013**, 42, 5150. (b) Luo, F.; Zheng, J.-M.; Kurmoo, M. *Inorg. Chem.* **2007**, 46, 8448.

(33) It is interesting to note that the Ni–NCS distance in **8** is much shorter than the analogous distance in (NCN)<sup>Me</sup> (ca. 1.96 Å). See ref 20c.