

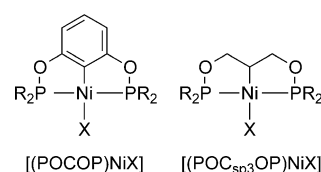
# On the Stability of a $\text{POC}_{\text{sp}^3}\text{OP}$ -Type Pincer Ligand in Nickel(II) Complexes\*\*

Jingjun Hao, Berline Mougang-Soumé, Boris Vabre, and Davit Zargarian\*

**Abstract:** We describe the results of a study on the stabilities of pincer-type nickel complexes relevant to catalytic hydroalkoxylation and hydroamination of olefins, C–C and C–X couplings, and fluorination of alkyl halides. Complexes  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{NiX}]$  are stable for  $X = \text{OSiMe}_3$ ,  $\text{OMes}$  ( $\text{Mes} = 1,3,5\text{-Me}_3\text{C}_6\text{H}_2$ ),  $\text{NPh}_2$ , and  $\text{CC-H}$ , whereas the  $\text{O}(\text{tBu})$  and  $\text{N}(\text{SiMe}_3)_2$  derivatives decompose readily. The phenylacetylide derivative transforms gradually into the zero-valent species  $\text{cis}-[(\kappa^{\text{P}}, \kappa^{\text{C}}, \kappa^{\text{C}}-(\text{iPr}_2\text{POCH}_2\text{CHCH}_2))\text{Ni}(\eta^2, \kappa^{\text{C}}, \kappa^{\text{C}}-(\text{iPr}_2\text{P}(\text{O})\text{C-CPh}))]$ . Likewise, attempts to prepare  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{NiF}]$  gave instead the zwitterionic trinuclear species  $[(\eta^3\text{-allyl})\text{Ni}]_2\{\mu, \kappa^{\text{P}}, \kappa^{\text{O}}-(\text{iPr}_2\text{PO})_4\text{Ni}\}$ . Characterization of these two complexes provides concrete examples of decomposition processes that can dismantle  $\text{POC}_{\text{sp}^3}\text{OP}$ -type pincer ligands by facile C–O bond rupture. These results serve as a cautionary tale for the inherent structural fragility of pincer systems bearing phosphinite donor moieties, and provide guidelines on how to design more robust analogues.

**E**XE-type pincer ligands, where E and X are the elements representing, respectively, the neutral and anionic donor moieties in the ligand framework, are considered to be “privileged” ligand platforms since they provide highly tunable and stable frameworks for supporting and sustaining the action of a metal center in diverse settings.<sup>[1]</sup> Thus, the structurally robust and thermally stable architecture of most EXE-type pincer ligands is thought to be a major contributor to the excellent catalytic reactivities displayed by their complexes at unusually high temperatures.<sup>[2]</sup> On the other hand, there have also been instances where the survival of the pincer framework under forcing conditions has been called into question, and the observed catalytic reactivities have been attributed to decomposed fragments of the pincer-type pre-catalysts used.<sup>[3]</sup> Given the continued use and increasing prominence of pincer complexes in various catalytic reactions, it is of importance from both practical and fundamental perspectives to better understand the decomposition pathways available to pincer complexes.

In this context, there have been sporadic reports describing pincer complexes in which one or more binding moiety undergoes unexpected reactions that introduce major modifications in the pincer framework. A few recent examples include reports on complexes featuring PCP-,<sup>[4]</sup> PNP-,<sup>[5]</sup> and PSiP-type<sup>[6]</sup> pincer ligands, whereas Ni complexes featuring resorcinol-derived POCOP ligands have been shown to be prone to oxidative degradation.<sup>[7]</sup> Indeed, the aliphatic analogues of POCOP ligands,  $\text{POC}_{\text{sp}^3}\text{OP}$  (Scheme 1), are



**Scheme 1.** POCOP- and  $\text{POC}_{\text{sp}^3}\text{OP}$ -type complexes of nickel.

particularly vulnerable to complex side reactions leading to decomposition. For instance, whereas  $[(\text{POCOP})\text{NiR}]$  complexes ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ) are isolable and stable, their  $\text{POC}_{\text{sp}^3}\text{OP}$  analogues undergo decomposition processes that remain obscure owing to difficulties in identifying the decomposition products.<sup>[8]</sup>

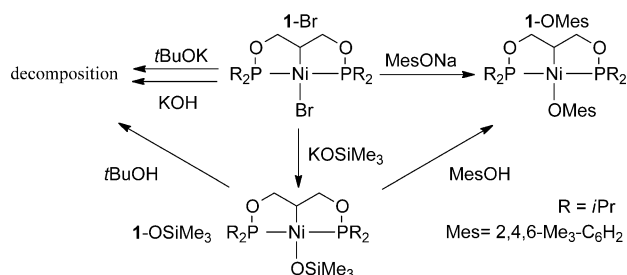
During the course of our studies aimed at developing catalytic transformations promoted by pincer nickel complexes,<sup>[9]</sup> we were prompted by the above findings to examine the stabilities of various ligand frameworks and search for clues on the nature of decomposition processes undermining their integrity. Reported herein are results that establish the relative thermal stabilities of  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{NiX}]$  complexes ( $X = \text{OR}$ ,  $\text{NR}_2$ ,  $\text{F}$ ,  $\text{CCR}$ ) and identify two unprecedented decomposition products arising from the attempted preparation of the fluoro and phenylacetylide derivatives.

Treatment of  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{NiBr}]$ <sup>[9a]</sup> with excess  $\text{KOSiMe}_3$  or  $\text{NaOMes}$  ( $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) in dioxane or THF gave the corresponding derivatives **1-OSiMe<sub>3</sub>** and **1-OMes** in nearly quantitative yields (Scheme 2). In contrast to the clean formation of these derivatives, the analogous reaction with  $\text{tBuOK}$ , under the same conditions, led instead to complete decomposition. Based on the assumption that this decomposition is due to the tendency of the “harder”  $\text{tBuO}^-$  anion to attack the phosphinite moiety instead of the “softer” Ni center, we attempted to prepare the target  $[\text{Ni-O}(\text{tBu})]$  derivative indirectly, by treating **1-OSiMe<sub>3</sub>** with  $\text{tBuOH}$ . Unfortunately, this approach also led to decomposition of the starting material, whereas **1-OMes** was accessible by protonolysis with  $\text{MesOH}$  (Scheme 2). We conclude that the  $[\text{Ni-O}(\text{tBu})]$  derivative forms initially but decomposes sub-

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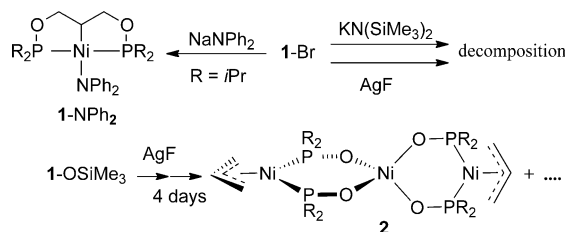
Supporting information for this article (details on experimental procedures as well as spectral and analytical data used to establish the identities and purities of the products) is available on the WWW under <http://dx.doi.org/10.1002/ange.201310386>.



**Scheme 2.** Synthesis of  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{Ni}(\text{OR})]$ .

sequently because of the destabilizing  $d\pi\text{--}p\pi$  interactions that are more prevalent in this case relative to the siloxide or aryloxide derivatives.<sup>[10]</sup>

Consistent with the above observations, potentially strong  $\pi$ -donor ligands, such as amides bearing aliphatic N-substituents gave unstable derivatives, whereas the diphenylamido derivative **1-NPh<sub>2</sub>** could be prepared and isolated in around 70% yield (Scheme 3). To our surprise, the analogous



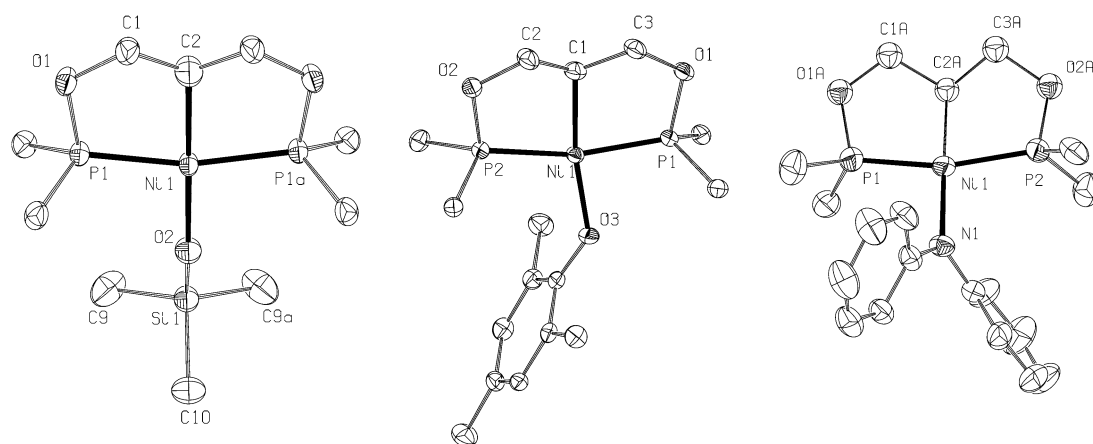
**Scheme 3.** Synthesis of **1-NPh<sub>2</sub>** and attempted syntheses of **1-F** and **1-N(SiMe<sub>3</sub>)<sub>2</sub>**.

hexamethyldisilazide derivative **1-N(SiMe<sub>3</sub>)<sub>2</sub>** also proved to be thermally unstable, leading to intractable yellow solids. Similarly, the fluoride derivative proved inaccessible as the reaction of **1-Br** with AgF led to a colorless solution and an intractable black precipitate. A slow decomposition also resulted from the reaction of **1-OSiMe<sub>3</sub>** with AgF, but in this case an unusual zwitterionic trinuclear complex **2** could be isolated from the reaction mixture (Scheme 3). Thus, stirring

a toluene mixture of **1-OSiMe<sub>3</sub>** and AgF (1.0:1.3) at room temperature and under ambient light caused a slow color change from yellow to green over 4 days; significantly, little or no reactivity was observed in the absence of light. Analysis of the final mixture by <sup>31</sup>P NMR spectroscopy revealed the presence of multiple minor peaks and a major one at  $\delta = 125$  ppm, which is significantly upfield of the region characteristic of  $[(\text{POC}_{\text{sp}^3}\text{OP})\text{NiX}]$  compounds ( $\delta = 200\text{--}170$  ppm). Repeated recrystallization of the mixture from hexane solutions allowed us to isolate single crystals of **2** in approximately 5% yield.

Solid-state samples and solutions of **1-OSiMe<sub>3</sub>**, **1-OMes**, and **1-NPh<sub>2</sub>** decompose in air, but under inert atmosphere they are stable indefinitely as solids and their solutions are thermally stable up to 100°C for more than 5 h. These diamagnetic complexes have been fully characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. Many of their NMR spectroscopic features (e.g., observation of virtual triplets for OCH<sub>2</sub> groups and a singlet <sup>31</sup>P resonance for the equivalent phosphinite moieties) are similar to those of previously studied analogues and consistent with the proposed structures. The OSiCH<sub>3</sub> resonances signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectrum at  $\delta = 0.24$  ppm (<sup>1</sup>H) and  $\delta = 5.46$  ppm (<sup>13</sup>C) fall into the expected range for OSiMe<sub>3</sub> complexes.<sup>[11]</sup>

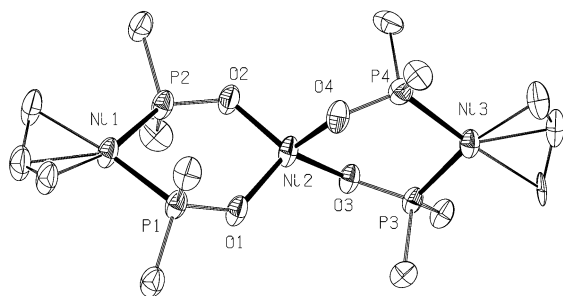
The Ni centers in **1-OSiMe<sub>3</sub>**, **1-OMes**, and **1-NPh<sub>2</sub>** adopt a square-planar geometry in the solid state (Figure 1),<sup>[12]</sup> and most of the structural parameters are comparable to those found in **1-Br**.<sup>[9a]</sup> The Ni–N distance of 1.961(3) Å and the Ni–N–C angles of 120–122° in **1-NPh<sub>2</sub>** are comparable to the corresponding parameters in reported nickel amido complexes,<sup>[13]</sup> whereas the Ni–O bond is longer in **1-OSiMe<sub>3</sub>** (1.873(3) Å) and **1-OMes** (1.895(1) Å) than in two other {Ni–OSiR<sub>3</sub>} complexes (1.820(2)<sup>[14a]</sup> and 1.831(3)<sup>[14b]</sup> Å) and the closely related {(PNP)Ni–OPh} (1.863(2) Å).<sup>[15]</sup> The longer Ni–O bonds in **1-OSiMe<sub>3</sub>** and **1-OMes** are presumably due to the very strong *trans* influence of nickel-bound central carbon atom of the POC<sub>sp</sub><sup>3</sup>OP ligand. The relative sizes of the Ni–O–Si/C angles in **1-OSiMe<sub>3</sub>** and **1-OMes** (151° vs. 136°) are consistent with a greater degree of O→Si electron delocalization that serves presumably to minimize the  $d\pi\text{--}p\pi$  destabi-



**Figure 1.** ORTEP diagrams for **1-OSiMe<sub>3</sub>** (left), **1-OMes** (middle), and **1-NPh<sub>2</sub>** (right). Thermal ellipsoids set at 50% probability.

bilizing interactions anticipated in such square-planar  $d^8$  systems featuring metal-heteroatom linkages.<sup>[10]</sup> The O–Si bond in **1-OSiMe<sub>3</sub>** (1.592(3) Å) is comparable to the corresponding distance found in complexes featuring a M–OSiMe<sub>3</sub> moiety.<sup>[11c,16]</sup> The coordination plane in **1-OMes** (P/Ni/P/C/O) makes an 85° angle with the mesityl ring, and that in **1-NPh<sub>2</sub>** (P/Ni/P/C/N) makes angles of approximately 77–79° with the Ph rings.

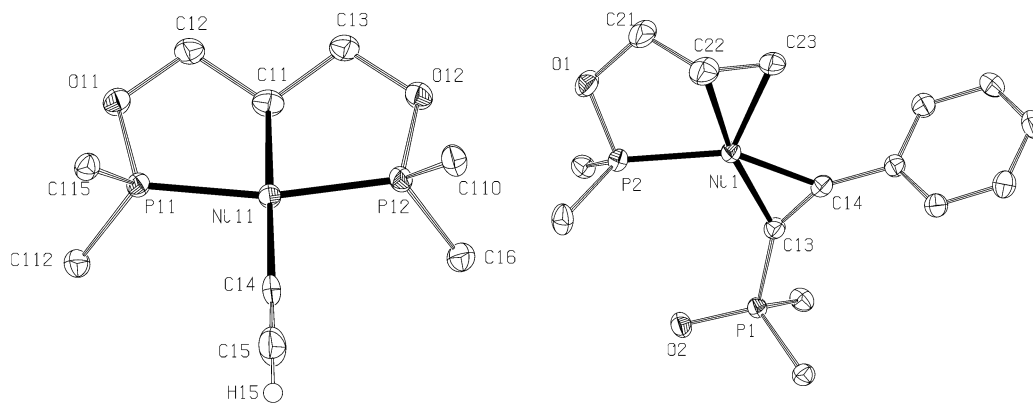
Complex **2** is a zwitterionic trinuclear species featuring two  $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}^{\text{II}}]^+$  fragments (Figure 2),<sup>[12]</sup> each coordinated by two phosphorus atoms of the central unit  $[(i\text{Pr}_2\text{PO})_4\text{Ni}^{\text{II}}]^{2-}$ . The central Ni atom adopts a tetrahedral coordination geometry defined by four oxygen atoms.



**Figure 2.** ORTEP diagram for complex **2**. Thermal ellipsoids set at 50 % probability.

Although the average of O–Ni–O angles is close to the ideal value of 109.5°, there are significant variations in these angles: the ones inside the two 6-membered metallacycles are approximately 98° while the remaining four angles defined by the two spirocyclic rings are approximately 112–119°. The two Ni centers in the terminal  $\{(\text{allyl})\text{NiP}_2\}$  fragments adopt a square-planar geometry defined by  $\eta^3$ -coordination of the allyl ligand and two monodentate phosphinite moieties; accordingly, the sum of angles defining the square plane adds up to approximately 360°. The Ni–P and Ni–O distances are somewhat longer in **2** relative to the pincer complexes **1-OSiMe<sub>3</sub>** and **1-OMes**, whereas the Ni–C distances and C–Ni–C angles are comparable to the corresponding parameters in allyl nickel complexes.<sup>[17]</sup>

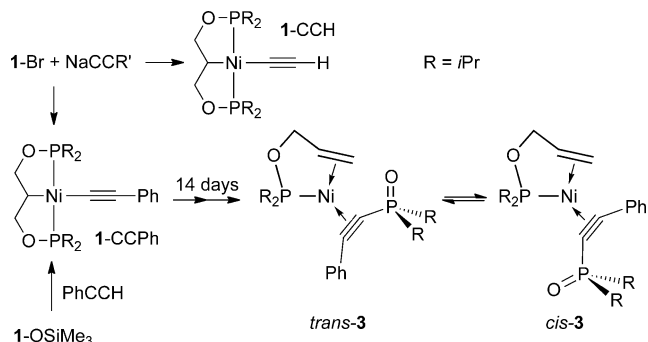
The mechanism for the unusual transformation of **1-OSiMe<sub>3</sub>** to **2** remains elusive, but the finding that ambient light plays a crucial role in initiating the decomposition process implies a radical-initiated reaction sequence. That this decomposition process leads to dismantling of the POC<sub>sp<sup>3</sup></sub>OP ligand framework by C–O bond rupture points



**Figure 3.** ORTEP diagram for complex **1-CCH** (left) and **cis-3** (right). Thermal ellipsoids set at 50 % probability.

out the Achilles' heel of the 1,3-propanediol-based POC<sub>sp<sup>3</sup></sub>OP ligands. The C–O bonds of the resorcinol-based aromatic POCOP ligand are also susceptible to rupture,<sup>[7]</sup> but much less so. For instance, reaction of  $[(\text{POCOP})\text{NiBr}]$  with AgF gives  $[(\text{POCOP})\text{NiF}]$ , which is stable to light and heating.<sup>[18]</sup>

A different but related decomposition of the POC<sub>sp<sup>3</sup></sub>OP ligand was also noted during the synthesis of the alkynyl derivatives, as follows. Reaction of **1-Br** with sodium acetylides at room temperature led to full conversion of the starting material into the anticipated alkynyl derivatives **1-CCH** and **1-CCPh** displaying singlet <sup>31</sup>P resonance signals at approximately  $\delta = 192.7$  ppm and 192.9 ppm, respectively (Scheme 4). Complex **1-CCPh** was also accessible by reaction



**Scheme 4.** Syntheses of **1-CCH**, **1-CCPh**, and **3**.

of **1-OSiMe<sub>3</sub>** with PhCCH. The new alkynyl complexes were isolated in nearly quantitative yields as yellow microcrystals (**1-CCH**) or an oily yellow solid (**1-CCPh**), and characterized by NMR spectroscopy. Both compounds showed the expected aliphatic <sup>1</sup>H NMR resonance signals for the POC<sub>sp<sup>3</sup></sub>OP ligand, in addition to the signals for C<sub>sp</sub>–H ( $\delta = 2.78$  ppm) and three aromatic peaks due to Ni–CC–C<sub>6</sub>H<sub>5</sub>. Triplet resonances observed at  $\delta = 104$  ppm and 112 ppm ( $^2J_{\text{P-C}} = 28\text{--}29$  Hz) in the <sup>13</sup>C NMR spectra of **1-CCH** and **1-CCPh**, respectively, were assigned to the Ni–C<sub>sp</sub> nuclei by comparison to the corresponding spectrum of the reported alkynyl complex  $[(\text{PCP})\text{Ni}(\text{CCPh})]$ .<sup>[9d]</sup>

Single crystals suitable for X-ray analysis were obtained for **1-CCH**, allowing us to examine its solid-state structure (Figure 3).<sup>[12]</sup> The main structural parameters of **1-CCH** are

similar to those observed for the derivatives reported previously and discussed above, and the  $C_{sp}-C_{sp}$  bond is comparable to a reported Ni–CCH complex.<sup>[19]</sup> The Ni– $C_{sp}$  distance (1.913(2) Å) is intermediate between the corresponding distances found in [(POCOP<sup>Ph</sup>)Ni(CCPh)]<sup>[9]</sup> (1.878(2) Å) and [(PCP)Ni(CCPh)]<sup>[9d]</sup> (1.944(2) Å). Observation of comparable Ni– $C_{bridgehead}$  distances in **1**–CCH and the **1**–X derivatives discussed above (1.97–1.98 Å) implies comparable *trans* influences for the acetylide, siloxide and aryloxy, and  $NPh_2$  ligands.

All attempts at growing single crystals of **1**–CCPh were circumvented by a gradual decomposition process as revealed by <sup>31</sup>P NMR spectroscopic monitoring of solutions set aside for crystallization. Thus, the singlet resonance signal attributed to this compound was gradually replaced by two sets of doublets of doublets, one centered at approximately  $\delta = 43$  and 201 ppm ( $J = 34$  Hz) and the other at approximately  $\delta = 45$  and 193 ppm ( $J = 9$  Hz). That these sets of signals represent interconverting isomers as opposed to unrelated, different species was inferred from the observation that the ratios of the two sets of signals varied with the nature of the solvent, as follows:  $CD_2Cl_2$  and  $C_6D_6/C_7D_8$  samples showed a 1:2 and 2.5:1 ratio, respectively, whereas a sample made from equal volumes of  $CD_2Cl_2$  and  $C_6D_6$  gave a 1:1 ratio of the two doublets of doublets. The thermal stability of the isomeric products was also solvent-dependent: solutions in hexane, benzene, or toluene proved to be fairly stable over extended periods at ambient temperature or over hours at higher temperatures, whereas solutions of chlorinated solvents decomposed over several hours at ambient temperature. Curiously, however, variable temperature (VT) NMR experiments performed on a  $C_7D_8$  sample over the range of –70 to 90 °C showed no intensity variation for the observed resonances. These two isomers were also analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Supporting Information).

Isolation of X-ray quality single crystals from the above reaction mixture allowed us to unambiguously identify one of the above-mentioned isomers, which in turn let us shed some light on the decomposition of **1**–CCPh. Figure 3, right<sup>[12]</sup> shows that the new product, *cis*-**3**, consists of a Ni<sup>0</sup> center ligated by a bidentate phosphinite-alkene and a  $\pi$ -coordinated phosphinoxy alkyne, both originating from the POC<sub>sp3</sub>OP and phenylacetylide ligands. The C22–Ni–C23 and C13–Ni–C14 angles are equivalent (39–40°), the Ni–CC<sub>centroid</sub> distances are very similar (1.902 Å for C=C and 1.801 Å for C≡C), and sum of two P–Ni–C and three C–Ni–C angles is 359.82°, all indicating that the geometry around the nickel atom in complex *cis*-**3** is trigonal planar. The alkyne and alkene fragments can be treated as two- $\pi$ -electron-donor moieties based on the observed bond lengths for C22–C23 (1.374(3) Å) and C13–C14 (1.273(2) Å), which are comparable to metal-coordinated C=C<sup>[20]</sup> and C≡C<sup>[21]</sup> bonds, respectively. Moreover, the angles C13–C14–C15 (ca. 153°) and P1–C13–C14 (ca. 146°) deviate considerably from linearity as in most alkyne complexes.<sup>[20]</sup>

The irreversible conversion of **1**–CCPh into the (presumably) thermodynamically more stable Ni<sup>0</sup> species **3** results from a cascade of bond making and breaking steps reminiscent of Arbuzov rearrangements. Caulton's group has

observed a similar rearrangement when the Lewis acidic fragment [(PNP)Ni]<sup>+</sup> was treated with terminal alkynes.<sup>[5c]</sup> In this case, the P–C bond making step generates a phosphonium group linking the pincer backbone to the newly formed alkyne moiety, whereas in our system the alkyne ligand detaches from the pincer backbone following the C–O bond rupture. The relatively facile “flipping” of the non-chelating phosphinoalkyne ligand in **3** helps explain the fluxional process alluded to above.

The results described in this report establish the stabilities of [(POC<sub>sp3</sub>OP)NiX] as a function of the ligand X. Potentially strong  $\pi$ -donor ligands OR can form stable and isolable derivatives if the R substituent is “tuned” to attenuate the destabilizing  $\pi$ – $d\pi$  interactions with the filled nickel-based orbitals. The analogous NR<sub>2</sub> derivatives are also sensitive to the nature of N-substituents, but the observed instability of the N(SiMe<sub>3</sub>)<sub>2</sub> derivative indicates that factors other than  $\pi$ – $d\pi$  interactions must contribute to the stability of these complexes.<sup>[22]</sup> Similarly, other factors, such as ambient light appear to destabilize the Ni–F derivative. Finally, an even more subtle interplay of factors appears to govern the stability of alkynyl derivatives, the normally more-stable phenylacetylide derivative being less stable than the unsubstituted acetylide.

The ligand decomposition reactions noted above proceed by complex and as yet obscure pathways, but the isolation and characterization of complexes **2** and *cis*-**3** from the reaction mixtures has helped identify the potential structural weaknesses of this family of pincer-type ligands. This information will serve as a cautionary tale alerting us to the possible pitfalls in the use of POC<sub>sp3</sub>OP complexes in various catalytic applications. On the other hand, the seemingly facile C–O bond cleavage reactions generating allylic and phosphate fragments from this ligand framework constitute new reactivities that might be exploited in the context of transforming highly oxygenated feedstocks into value-added petrochemicals. Our future investigations will be directed toward taking advantage of the opportunities afforded to us by the decomposition reactions described herein.

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- [22] A reviewer has suggested that a strong Brønsted base, such as (Me<sub>3</sub>Si)<sub>2</sub>N<sup>−</sup>, can deprotonate the Ni-bound C–H moiety to generate an unstable alkylidene that would decompose subsequently.