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For:

Synthesis of Unsymmetrical 5,6-POCOP'-Type Pincer Complexes of Nickel (II):

Impact of Nickelacycle Size on Structures and Spectroscopic Properties

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Different structures and reactivities have been observed with the unsymmetrical pincertype complex (5,6-POCOP')Ni(II)Br and its various derivatives compared to their analogous symmetrical 5,5-POCOP systems, thus serving to establish the importance of the size and degree of flexibility in the metallacycle rings.

Synthesis of Unsymmetrical 5,6-POCOP'-Type Pincer Complexes of Nickel (II):

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Abstract

This report describes the synthesis and characterization of a family of unsymmetrical pincer complexes of nickel(II) featuring both 5- and 6-membered nickelacycles. The room temperature reaction of NiBr₂(NCCH₃)_x with the bis(phosphinite) ligand 1-(*i*-Pr₂PO),3-(*i*-Pr₂POCH₂)-C₆H₄ (POCHOP') results in direct nickelation at the 2-position of the aromatic ring to give (5,6-POCOP')NiBr (5,6-POCOP' = { $\kappa^{P}, \kappa^{C}, \kappa^{P'}$ -2-(*i*-Pr₂PO),6-(*i*-Pr₂POCH₂)-C₆H₃}). This complex undergoes salt metathesis reactions with M'X to give the corresponding charge neutral derivatives (5,6-POCOP')NiX (X = OSO₂CF₃, OSO₂(4-CH₃-C₆H₄), CH₃, and C≡CCH₃), whereas abstraction of the bromide by AgBPh₄ in acetonitrile gave the cationic derivative [(5,6-POCOP')Ni(NCCH₃)][BPh₄]. The new complexes have been characterized by multinuclear NMR spectroscopy and X-ray diffraction studies. The reactivities of the new complexes (5,6-POCOP')NiX (X = Br, OSO₂CF₃) have been explored briefly to establish the nucleophilicity of the X ligand and the substitutional lability of the phosphinite moiety in the 6-membered cycle.

Keywords: unsymmetrical pincer complex, POCOP, 5,6-POCOP'

Introduction

The term "pincer" was coined in 1989 by van Koten¹ to refer to the then-growing family of terdentate ligands and their complexes introduced in the late 1970's and early 1980's by Shaw,² van Koten³ and Fryzuk.⁴ According to van Koten's original definition, pincer ligands were classified according to the donor atoms of their charge-neutral (E) and monoanionic (X) donor moieties. Thus, the normally *meridional* ligation of metal ions by EXE-type pincer ligands (terdentate, monoanionic) generated the corresponding EXE-type pincer complexes that were, for the most part, robust and thermally stable species displaying a variety of interesting reactivities and physical/material properties.⁵ Over the past two decades, pincer complexes have experienced substantial growth due, primarily, to their versatility in catalysis⁶ and potential applications in functional materials.⁷

Most pincer complexes reported to date are based on a symmetrical ligand architecture featuring two fused, five-membered metallacycles. On the other hand, recent reports have shown a growing interest in the structures and reactivities of nonsymmetrical EXE´-type ligands based on both different donor moieties and differently-sized metallacycles, including : 5,6-NCS;⁸ 5,6-SCN;⁹ 5,6-POCN;¹⁰ 3,6-, 3,7-, and 4,5-PNP´;¹¹ 5,6-PCN;¹² 5,6-POCOP´.^{13,14} These new types of pincer ligands represent a number of potential advantages over their more popular symmetrical analogues. For instance, the presence of differently sized metallacycles allows a modulation of ligand bite angle and binding pocket, thereby altering the lability of a donor moiety and influencing reactivities. Moreover, different donor moieties based on hard-soft and large-small donor

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atoms allow for greater control over electronic and steric tuning of the environment around the metal center.¹⁵

Our laboratory's studies in the area of pincer-Ni chemistry have been focused primarily on the reactivities of symmetrical complexes featuring 5,5-PCP-¹⁶ and 5,5-POCOP-type¹⁷ ligands, but more recently we have initiated new projects aimed at studying the synthesis, structures, and reactivities of unsymmetrical systems. Thus, we have reported Ni complexes featuring 5,5-POCN¹⁸ and 5,6-PimioCOP ligands,¹⁹ and the promising results emerging from these projects have prompted us to explore the reactivities of other closely related ligand systems. We have also been inspired by literature reports on 5,6-POCOP'-Pd complexes^{13a} to examine the structures and reactivities of 5,6-POCOP'-Ni complexes.

This report describes the synthesis, characterization, and preliminary reactivity studies on the unsymmetrical pincer complexes (5,6-POCOP')NiX ($\kappa^P, \kappa^C, \kappa^P-5, 6$ -POCOP' = 2-(*i*-Pr₂PO),6-(*i*-Pr₂POCH₂)-C₆H₃; X = Br, **1**; OSO₂ArCH₃, **2**; OSO₂CF₃, **3**; CCMe, **5**; CH₃, **6**) and [(5,6-POCOP)Ni(NCMe)][Y] (Y = OSO₂CF₃, **4a**; BPh₄, **4b**). All complexes were characterized by NMR spectroscopy and single crystal X-ray diffraction studies in an effort to determine the effect of metallacycle on the spectroscopic properties and structures of the title complexes, as described below.

Results and Discussion

Synthesis of POCHOP' and its nickelation. The previously reported^{13a} synthesis of 1-(*i*-Pr₂PO),3-(*i*-Pr₂POCH₂)-C₆H₄ uses dimethylamino pyridine (DMAP) for phosphination of the precursor diol, 3-hydroxybenzyl alcohol, which was obtained from commercial sources. We have developed a slightly modified synthesis based on in-house prepared

diol and use of NEt₃ in the phosphination step, as illustrated in Scheme 1 and discussed below.



Scheme 1. Synthesis of (5,6-POCOP')NiBr, 1.

Treating the commercially available 3-hydroxybenzaldehyde with excess NaBH₄ in methanol at 0 °C and stirring the sample further at r.t. gave 3-hydroxybenzylalcohol, which was obtained as colorless crystals in 79% yield by recrystallization from ethyl acetate. Reaction of this diol with *i*-Pr₂PCl in the presence of NEt₃ gave the target bis(phosphinite) **a** as an off-white oil in 58% yield. Finally, subsequent treatment of **a** with Br₂Ni(NCMe)_x in toluene and in the presence of NEt₃ gave the target bromo derivative (5,6-POCOP')NiBr, **1**, as a yellow solid in 60 % yield (Scheme 1). Tests established that POCHOP' is readily oxidized in air and must, therefore, be protected from ambient conditions, whereas complex **1** is much easier to handle. For example, solid samples of **1** are indefinitely air-stable, and its r. t. solutions resist air oxidation and hydrolysis for hours. Indeed, this compound can be purified under aerobic conditions by

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extraction into Et_2O , or by column chromatography (silica gel, toluene). Finally, solutions of **1** are thermally stable indefinitely under a nitrogen atmosphere.

The role of NEt₃ in the synthesis of **1** deserves some comment. Previous reports²⁰ have shown that the primary role of base in the synthesis of (POCOP)Ni and (POCN)Ni complexes is to merely remove the HX generated during the C-H nickelation step. In other words, the base does *not* facilitate the C-H nickelation step, serving instead to ensure optimal yields by preventing protonation of the unreacted ligand by in-situ generated HX. Thus, most tertiary amines should be equally effective for this purpose. Consistent with this assertion, using DMAP as base instead of NEt₃ gave similar yields of

1.

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Synthesis of new 5,6-POCOP' derivatives. Treatment of 1 with silver tosylate and silver triflate in dry dichloromethane (DCM) gave the corresponding derivatives 2 and 3 (Scheme 2). Given the light-sensitivity of these silver salts, care was taken to minimize exposing the reaction mixtures to ambient light. The cationic acetonitrile adducts 4 were obtained by reacting the tosylate derivative 2 with excess acetonitrile in DCM, or by treating 1 with AgBPh₄ in a 1:1 mixture of DCM and acetonitrile (Scheme 2). The tosylate derivative is stable in ambient atmosphere for days in the solid state and for ca. 24 h in solution, whereas its triflate analogue proved to be less robust, with solid samples decomposing gradually (> 6 h) and solutions over 2-3 h. The cationic adducts were also quite prone to hydrolysis, decomposing over 12 h in the solid and over 5-6 h in wet solvents.



Scheme 2. Synthesis of 5,6-POCOP' complexes 2-6.

The propynyl and methyl derivatives **5** and **6** were synthesized by treating **1** with the corresponding Grignard reagents in mixtures of THF and toluene (Scheme 2). Both reactions led to a color change from yellow to dark brown. The reaction with $(CH_3C=C)MgBr$ required heating at 60 °C for at least 1 h to complete the conversion of the bromo precursor, but even then we obtained no more than a 30% crude yield of the propynyl derivative **5**. In the case of the MeMgBr reaction, the conversion could be pushed to completion at room temperature, but the methyl derivative **6** was obtained with low yields only (< 20%). Using excess MeLi (ca. 10 equiv) at room temperature gave higher yields (ca. 40-45%), but the desired product was always contaminated with sideproducts, even after repeated recrystallizations.²¹ As a result, neither of these hydrocarbyl derivatives could be isolated in analytically pure forms, but small quantities of impurity-free single crystals were obtained for both compounds, allowing analysis by X-ray diffraction studies (vide infra). As described below, the reaction with excess MeLi was investigated briefly in an attempt to shed some light on the side reaction(s) that complicated the synthesis and isolation of pure products.

NMR monitoring the reaction of **1** with excess MeLi showed the emergence of several upfield ¹H signals (0.2 to -1 ppm) and an additional ³¹P peak at -15 ppm. Comparison of the latter signal to the corresponding ³¹P signals for PMe₃ (-60 ppm), PMeEt₂ (-34 ppm), PMe(*i*-Pr)₂ (-10 ppm in C₆D₆), and P(*i*-Pr)₃ (+20 ppm), suggested that the phosphinite moiety in **1** or in the Ni-Me product might be reacting with MeLi to generate P(Me)(*i*-Pr)₂; such a side-reaction would then set into motion the dismantling of the pincer backbone.^{17a}

Spectroscopic characterization. Nickelation of POCHOP' could be confirmed by the absence of the 2-H signal in the ¹H NMR spectrum of **1**, as well as the appearance in its ³¹P{¹H} NMR spectrum of AB doublets at δ 156 and 188 for the two inequivalent and mutually coupled trans P nuclei (²J_{P-P}= 283 Hz). Analogous AB doublets featuring large ²J_{P-P} constants were also observed for the other derivatives (Table 1), as follows: ca. 148 and 189 ppm for the triflate (²J_{P-P}= 285) and tosylate (²J_{P-P}= 302) derivatives; ca. 152 and 194 ppm for the acetonitrile adduct (²J_{P-P}= 260); ca. 160 and 187 ppm for the propynyl derivative (²J_{P-P}= 323), and 160 and 187 ppm for the methyl derivative (²J_{P-P}= 323).

Compound	δ for ArO-P	δ for ArCH ₂ O-P	
	(multicplicity, ${}^{2}J_{pp}$ in Hz)	(multicplicity, ${}^{2}J_{pp}$ in Hz)	
POCHOP	154 (s)	147 (s)	
1	187 (d, 283)	155 (d, 283)	
2	189 (d, 302)	148 (d, 302)	
3	189 (d, 285)	148 (d, 285)	
4b	194 (d, 260)	152 (d, 260)	
5	187 (d, 323)	160 (d, 323)	
6	187 (d, 323)	160 (d, 323)	

Table 1. ³¹P{¹H} NMR chemical shifts of POCHOP' and complexes 1-6

Comparison of the ³¹P signals for the new derivatives **1-6** to the corresponding singlets for the symmetrical POCOP complexes (POCOP)NiBr (ca. 186 ppm), (POCOP)Ni(OTf) (184 ppm), and (POCOP)NiMe (ca. 192 ppm) has allowed us to assign the more downfield of the doublets for **1-6** to the phosphinite moiety in the 5-membered metalacycle. It is interesting to note that coordination to the nickel center results in significant downfield shifts for the ArOP moiety, which changes from ca. 154 ppm in the ligand to 187-194 ppm in the complexes, whereas the ArCH₂OP moiety is much less affected, going from ca. 147 ppm in the ligand to 148-160 ppm in the complexes (Table1).

The ¹H and ¹³C NMR spectra of the new complexes revealed useful information about their symmetry properties in solution. Thus, in all but one case,²² the P-C-CH₃ protons and P-C-CH₃ carbons displayed four (not eight) distinct signals (doublets or singlets), whereas the P-CH protons and P-C carbons displayed two (not four) doublets of Published on 23 June 2015. Downloaded by UNIVERSITY OF OT AGO on 04/07/2015 16:24:48.

doublets (when resolved). These observations imply the maintenance in the coordination plane of a plane of symmetry that renders equivalent the nuclei above and below it. Given the puckered conformation of the 6-membered metalacycle in the solid state (vide infra), the effective planar symmetry inferred from the solution NMR data is likely the result of a rapid "flipping" motion by this ring at ambient temperature.

The protons of the central aromatic moiety in the title complexes were readily identified from their characteristic ¹H resonances, doublets for H3/H5 and pseudo-triplets for H4. The ¹³C{¹H} NMR spectra showed singlets for C4/C5, doublets for C3, doublets of doublets for C2/C6, and the following signals for C1: doublet of doublets in complexes **1** and **6**; weak singlet for complexes **3** and **4b**; doublet for **2**. Interestingly, the Ni-*C*CCH₃ carbon in **5** showed triplets, not doublets of doublets; this is presumably due to an accidental equivalence of the two J_{P-C} values.

Solid state characterization. Single crystals of all but the triflate derivatives were obtained from various recrystallization experiments and subjected to crystallography in order to study their solid state structures. All the structures were successfully refined to a high degree of confidence. Crystal and data collection details for complexes **1**, **2**, **4b**, **5** and **6** are presented in Table 1S, selected structural parameters are listed in Table 2, and ORTEP diagrams are shown in Figure 1.

In all structures, the coordination geometry around the Ni atom is square planar, but some distortions are evident because of the bite angle of the 5,6-POCOP' ligand. For example, the C1-Ni-P1 and P-Ni-P angles are tighter than ideal (ca. 82-84° and 168-170°, respectively), whereas the remaining cis angles are closer to 90° (C1-Ni-P2~ 92-94°; P-Ni-X~ 89-94°) and the C1-Ni-X angles are fairly linear (167-178°).

	1	2	4 b	5†	6
Ni-C(1)	1.920(2)	1.916(2)	1.919(2)	1.936(3)	1.947(2)
Ni-P(1)	2.1443(7)	2.1924(5)	2.1559(5)	2.1267(8)	2.1177(6)
Ni-P(2)	2.1744(7)	2.1684(5)	2.1921(5)	2.1283(8)	2.1355(5)
Ni-X/L	2.3372(4)	1.937(1)	1.881(1)	1.9100(3)	2.065(2)
P(1)-Ni-P(2)	169.26(3)	169.19(2)	169.30(2)	170.26(4)	168.14(3)
P(1)-Ni-X	91.15(2)	94.39(4)	93.71(5)	92.24(9)	92.19(5)
P(2)-Ni-X	92.24(2)	88.55(4)	92.82(5)	91.28(9)	91.89(5)
P(1)-Ni-C(1)	83.39(6)	83.95(5)	81.56(5)	85.39(10)	83.03(6)
P(2)-Ni-C(1)	93.06(6)	92.92(5)	91.86(5)	93.76(10)	92.78(6)
C(1)-Ni-X	174.53(6)	178.26(6)	175.27(7)	176.57(13)	175.22(8)
Twist angle [‡]	21	16	25	9	22
Tetrahedral distortion [*]	0.197	0.280	0.000	0.124	0.213

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 2, and 4b-6.

[†] All the values cited for this complex represent averages of the corresponding values in two independent molecules.

[‡]Twist angle is defined as the angle between the (mean) planes encompassing the benzenic moiety of the 5,6-POCOP' ligand (C(1)-C(6)) and the atoms P(1), C(1), and P(2). See Chart 1 for a schematic representation.

^{*} Distance of Ni from the plane defined by the atoms P(1), C(1), and P(2).



Figure 1. ORTEP diagrams for complexes 1, 2, 4b, 5, and 6. Thermal ellipsoids are set at the 50% probability level for all complexes. The following have been omitted for clarity: calculated H atoms and atom labels for *i*-Pr carbons in all diagrams; the BPh₄ anion in 4b.

Structural distortions similar to those noted above are also observed in all symmetrical (5,5-POCOP)NiX complexes, but there are other structural differences between the latter compounds and those studied here, the most important being the varying degrees of co-planarity of the ligating atoms. Roddick²³ has surveyed this co-planarity feature for a large number of four-coordinate 5,5-pincer complexes, in the process defining the so-called C_2 twist involving the central aryl moiety and the "arms" linking it to the pendant donor atoms. (See Chart 1 for a pictorial definition of the C_2 twist angle θ .)



Chart 1. Schematic representation of "twist angle"

On the basis of this C₂ twist, Roddick has concluded that the twisting is at a minimum for 5,5-POCOP complexes, most of which generate nearly planar P-O-Ar-O-P-M arrays ($\theta \sim 2^{\circ}$), and increasing for the analogous complexes based on the ligands 5,5-PNCNP ($\theta \sim 4^{\circ}$) and 5,5-PCP ($\theta \sim 10^{\circ}$). By comparison to these values, the C₂ twist is generally greater in the title 5,6-POCOP' systems (9-25°, Table 2), which is not surprising given the greater degree of puckering possible in the 6-membered metallacycle. On the other hand, the relatively large variation in the twist angles among our complexes implies that the twisting is energetically "soft" and might not have significant impact on the properties of these complexes; a similar observation has been noted by Roddick for other pincer systems.²³

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Another significant difference in the structures of 5,5-POCOP and 5,6-POCOP' complexes pertains to the generally longer Ni-L distances found in the latter complex. Thus, the following bond distances (all in Å) are longer in the 5,6-POCOP'analogues: Ni-Br (2.3372(4) vs. 2.3231(5); Ni-C(1) in the bromo derivative (1.920(2) vs. 1.885(3)); Ni-CH₃ (2.065(2) vs. 1.996(2)). The Ni-P bond distances are also longer in the 6-membered metalacycles in all compounds except **5**: Δ (Ni-P) ~ 30-70 × (e.s.d.) in **1**, **2**, **4b**, and **6**. On the other hand, the Ni-C1 distances are fairly similar in **1**, **2**, and **4** (ca. 1.92 Å), but much longer in **5** (ca. 1.94 Å) and **6** (1.95 Å); these observations are consistent with the respective trans influences of the various ligands X.

Reactivity tests. An important question about the potential reactivities of pincer complexes touches on the substitutional lability of the donor moieties. This so-called hemilabile character of a pincer system is particularly important in a catalytic setting where strongly donor substrates might displace one or both donor moieties of a pincer ligand, thus disrupting its terdentate binding and, consequently, altering the reactivities of the metal center. In an effort to establish the binding lability of this ligand, we have tested the lability of the two phosphinite moieties in the 5,6-POCOP'complex **1**. Mixtures of **1** with different nucleophiles such as PPh₃, imidazole and 2-methylimidazole, pyrazole, *N*,*N*-dimethylpyridin-4-amine, and nicotinonitrile were heated at 60 °C for 18 h, and ³¹P NMR spectroscopy was used to detect reactivity. The results of these experiments showed that the terdentate binding in **1** is completely stable (Scheme 3).



Scheme 3. Tests of the hemilabile character of complex 1.

Next, we tested the substitutional lability of the X ligand, using the triflate derivative $\mathbf{3}$ as a model complex. Reaction of this species with various ligands led to facile displacement of triflate to form the corresponding cationic species, as confirmed by ³¹P NMR spectroscopy (Scheme 4). The impact of the ligand substitution on the chemical shifts of the phosphinite moieties varied considerably from one case to another. For instance, coordination of morpholine caused significant upfield shifts for both the phosphinite moiety of the 5-membered metallacycles (by 11 ppm) and that of the 6membered metalacycle (by 5 ppm), as well as a much larger coupling constant (${}^{2}J_{P-P} =$ 343 Hz). By comparison, pyridine caused a 5 ppm shift upfield for both phosphinite moieties (${}^{2}J_{P-P} = 271$ Hz). Interestingly, the product obtained from the reaction of 2-N,Ndimethylaminopyridine caused a dramatic color change from yellow to deep red and 13 ppm upfield shifts for both phosphinite moieties, in addition to a weaker P-P coupling; we infer from these observations that a penta-coordinated species forms by the coordination of both nitrogen moieties to the Ni(II) center.²⁴ Finally, stirring a solution of **3** in an atmosphere of CO led to a gradual bleaching of the initial solution. To our surprise, the ³¹P NMR spectrum of the very pale yellow final mixture showed no signals,

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not even those of the ligand. Exposing this sample to ambient air and re-examining its ³¹P NMR spectrum showed two singlets at 62 and 50 ppm, a region characteristic of phosphine oxides. We speculate that coordination of CO to the Ni center generates a stereochemically labile penta-coordinated species featuring one or two CO ligands.²⁴



Scheme 4. Substitution of triflate (OTf) in 3 by various ligands.

Another reactivity that was tested briefly was oxidation of the Ni(II) center. Previous studies have shown that trivalent species are accessible by oxidation of certain Ni(II) pincer complexes, including (POC_{sp3}OP)NiX (POC_{sp3}OP= (R₂POCH₂)₂CH).^{17f, 17g} Symmetrical (POCOP)NiX complexes based on an aromatic backbone do not seem to stabilize trivalent species; nevertheless, we conducted some tests to establish whether the unsymmetrical (5,6-POCOP')NiX derivatives might show different reactivities. Reacting **1** with NBS at room temperature converted the initial orange solution into dark green, a color change we observe frequently when trivalent species are generated from (pincer)Ni(II)Br. The green color of the reaction mixture is persistent at low temperatures, indicating that the putative trivalent species is more stable than the corresponding species generated from (5,5-POCOP)NiBr. Unfortunately, we have not succeeded in isolating a tractable product yet.

Finally, we have briefly investigated the stoichiometric reactions of complexes 2 and 3 to establish the nucleophilic character of the Ni-X moiety (toward aliphatic halides)²⁵ or its basicity (toward alcohols). In all cases, the reactions were conducted at 90 °C for 4 h and their progress was monitored by ³¹P NMR spectroscopy (Table 3); the contents of the final reaction mixture were analyzed by GC/MS. Complex 2 proved generally less reactive toward the substrates tested: no reaction was detected with alcohols, and only partial conversion of 2 to the bromo precursor 1 was noted with 2bromopropane (22%) and 4-bromobutene (5%). On the other hand, complex 3 reacted with all the haloalkanes tested, giving varying degrees of conversion to the corresponding halo derivatives (Table 3). The tests with alcohols showed that complex 3 is inert toward ethanol, trifluoroethanol, and 1-nonanol, but reacted with hexafluoroprapan-2-ol (~24% conversion); the latter reaction gave a new product displaying a pair of ³¹P doublets at ca. 3 ppm downfield of the original signals for 3 (192/151 ppm; $J_{PP} = 258$ Hz). We speculate that this new species is the corresponding alkoxide derivative, but we have not succeeded in isolating pure samples of this compound.

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Table 3. Reactivities of complexes 2 and 3 with R-Y and H-Y

(5,6-POCOP')Ni-X
$$\xrightarrow{R-Y \text{ or } H-Y}$$
 (5,6-POCOP')Ni-Y + $R-X \text{ or } H-X$

		% conversion*		
		2	3	
	CI	0	27	
	Br	22	100	
R-Y	Br	5	54	
	Br	0	20	
H-Y		0	24	

* Conversion is based on integration of ³¹P NMR signals for the Ni-X and Ni-Y derivatives.

Conclusion

The present study has established a viable synthetic route to a new series of Ni(II) species based on an unsymmetrical 5,6-POCOP'-type pincer ligand $1-(i-Pr_2PO),3-(i-Pr_2POCH_2)-C_6H_4$. The ambient temperature nickelation at the C2 position of this ligand has demonstrated that the facile C-H nickelation step characteristic of the symmetrical 5,5-POCOP ligands is preserved in their unsymmetrical counterpart. Indeed, the presence of inequivalent, mutually *trans* phosphinite moieties in the title compounds renders their ³¹P NMR spectra very informative and provides a convenient diagnostic tool for monitoring reactions and assessing the impact of X/L ligands on the two donor moieties.

These practical aspects should facilitate the synthesis of (5,6-POCOP')NiX and [(5,6-POCOP')NiL]⁺ and pave the way for systematic explorations of their reactivities.

The solid state structures presented in this report have allowed us to measure the extent to which the 6-membered metallacycle disrupts the co-planarity of the ligating atoms observed in the symmetrical (5,5-POCOP)Ni systems ("twist angles" = $9-25^{\circ}$). Another impact of the differently-sized metallacycles is reflected in the generally longer Ni-P distance in the 6-membered metallacycles. On the other hand, these structural features do not appear to have significant consequences for the relative lability of the phosphinite moieties in 5,6-POCOP' vs. 5,5-POCOP compounds, at least not on the basis of the preliminary reactivity probes presented here. Future investigations will seek to confirm these findings and also identify potentially promising reactivities for further developments.

Experimental Section

General. All manipulations were carried out using standard Schlenk and glove box techniques under a nitrogen atmosphere. All solvents used for experiments were dried to water contents of less than 10 ppm (determined using a Mettler Toledo C20 coulometric Karl Fischer titrator) by passage through activated aluminum oxide columns (MBraun SPS) and degassed prior to use. C_6D_6 was dried over 4 Å molecular sieves and then freeze-thaw degassed. The nickel precursor $Br_2Ni(NCMe)_x$ was prepared according to a reported procedure.²⁶ All used chemicals were purchased from Aldrich and, unless otherwise noted, used without further purification.

The NMR spectra were recorded using the following Bruker spectrometers: AV300, AV400RG and AVII400. ¹H and ¹³C chemical shifts are reported in ppm

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downfield of TMS and referenced against the residual C_6D_6 signals (7.15 ppm for ¹H and 128.02 ppm for ¹³C); ³¹P chemical shifts are reported in ppm and referenced against the signal for 85% H₃PO₄ (external standard, 0 ppm). Coupling constants are reported in Hz. Syntheses.

3-Hydroxybenzyl alcohol. NaBH₄ (3.22 g, 85.0 mmol, 2.1 equiv.) was added portionwise and over 1 h to a 0 °C solution of 3-hydroxybenzaldehyde (5.01 g, 41.0 mmol, 1 equiv) in 15 mL of methanol. The resulting mixture was allowed to warm to room temperature, stirred an additional 3 h, and evaporated. Aqueous HCl solution (3M) was then added to bring the pH of the mixture to ~ 2 , and the mixture extracted with ethyl acetate (4 \times 20 mL), the organic phase was dried over MgSO₄, filtered, and evaporated under vacuum to give an off-white solid. Recrystallization from ethyl acetate gave colorless crystals (3.93 g, 79%). ¹H NMR (300 MHz, C_6D_6) δ 7.00 (t, ³J_{HH} = 8, 1H, $\{Ar\}H^{5}$, 6.70 (d, ${}^{3}J_{HH} = 8$, 1H, $\{Ar\}H^{4}$), 6.56 (s, 1H, $\{Ar\}H^{2}$), 6.49 (dd, $J_{HH} = 8$, 2; 1H, {Ar}H⁶), 4.24 (s, 2H, CH₂), 9.21 (s, 1H, Ph-OH), 5.53 (s, 1H, CH₂-OH). ¹³C{¹H}NMR (76 MHz, C_6D_6): δ 115.62 (s, 1C, {Ar} C^4), 113.52 (s, 1C, {Ar} C^6), 128.84 (s, 1C, $\{Ar\}C^{5}$, 113.30 (s, 1C, $\{Ar\}C^{2}$), 159.70 (s, 1C, $\{Ar\}C^{1}$), 143.86 (s, 1C, $\{Ar\}C^{3}$).

1-(*i*-Pr₂PO),3-(*i*-Pr₂POCH₂)C₆H₄, a. *i*-Pr₂PCl (2.8 mL, 17 mmol, 2 equiv.) was added to a mixture of 3-hydroxybenzyl alcohol (1.05 g, 8.50 mmol, 1 equiv.) and NEt₃ (3.60 mL, 25.5 mmol, 3 equiv.) in 30 mL of benzene, and the resulting white suspension was stirred at room temperature for 1 h. Evaporation under vacuum followed by extraction of the solid residues with hexane $(3 \times 20 \text{ mL})$ and evaporation gave the product as an offwhite, air sensitive oil (1.75 g, 4.90 mmol, 58%). ¹H NMR (400 MHz, C_6D_6) : δ 0.91 (dd, $J_{\text{HP/HH}} = 7, 2; 6H, 2 \times CH_3), 1.00 \text{ (dd, } J_{\text{HP/HH}} = 7, 2; 6H, 2 \times CH_3), 1.10 \text{ (dd, } J_{\text{HP/HH}} = 7, 2;$

6H, 2 × CH₃), 1.14 (dd, $J_{HP/HH} = 7$, 2; 6H, 2 × CH₃), 1.76 (m, 4H, 4 × CH), 4.72 (d, ${}^{3}J_{HP} = 8$, 2H, CH₂), 6.82 (d, ${}^{3}J_{HH} = 6$, 1H,{Ar}H⁵), 6.90 (m, 2H, 2 × {Ar}H^{3,4}), 7.10 (d, ${}^{3}J_{HP} = 2$, 1H,{Ar}H²). ${}^{13}C{}^{1}H$ }NMR (101 MHz, C₆D₆) : δ 17.81 (d, $J_{CP} = 20$, 2C, 2 × CH₃), 17.53 (d, $J_{CP} = 20$, 2C, CH₃), 16.92 (d, $J_{CP} = 20$, 2C, 2 × CH₃), 16.82 (d, $J_{CP} = 20$, 2C, 2xCH₃), 28.13 (dd, $J_{CP} = 24$, 3; 2C, 2 × CH), 28.31 (dd, $J_{CP} = 20$, 3; 2C, 2 × CH), 74.03 (d, $J_{CP} = 21$, 1C, CH₂), 114.66 (d, $J_{CP} = 6$, 1C, {Ar}C⁴), 141.45 (s, 1C,{Ar}C⁶), 129.30 (s, 1C, {Ar}C⁵), 120.52 (d, $J_{CP} = 2$, 1C, {Ar}C²) 159.70 (d, $J_{CP} = 9$, 1C,{Ar}C¹), 141.45 (dd, $J_{CP} = 8$, 1C; {Ar}C³). ${}^{31}P{}^{1}H$ } NMR (162 MHz, C₆D₆) : δ 147 (s, 1P, CH2O-*P*-(i-Pr)₂), 154 (s, 1P, O*P*-(i-Pr)₂).

(POCOP^{iPr}(5,6))NiBr, 1. A mixture of a (1.75 g, 4.90 mmol, 1equiv.), NEt₃ (0.90 mL, 5.9 mmol, 1.2 equiv.) and (Ni(Br)₂(MeCN)_x (2.6 g, 8.5 mmol, 1.7 equiv.) in toluene (35 mL) was stirred at room temperature for 24 h, filtered through a short silica gel column, and evaporated under vacuum to give the product as air stable yellow crystals (1.45 g, 60 %). ¹H NMR (400 MHz, C₆D₆) : δ 1.09 (dd, $J_{HP/HH} = 13$, 7; 6H, 2 × CH₃), 1.16 (dd, $J_{HP/HH} = 14$, 7; 6H, 2 × CH₃), 1.42 (dd, $J_{HP/HH} = 7$, 2; 6H, 2 × CH₃), 1.46 (dd, $J_{HP/HH} = 7$, 2; 6H, 2 × CH₃), 2.42 (m, 4H, 4 × CH), 4.60 (d, ³ $J_{HP} = 17$, 2H; CH₂), 6.43 (d, ³ $J_{HH} = 6$, 1H,{Ar}H⁵), 6.88 (m, 2H, 2 × {Ar}H^{3.4}). ¹³C{¹H}NMR (101 MHz, C₆D₆) : δ 17.10 (d, $J_{CP} = 15$, 4C, 4 × CH₃), 18.34 (d, $J_{CP} = 4$, 2C, 2 × CH₃), 19.15 (d, $J_{CP} = 5$, 2C, 2 × CH₃), 28.06 (dd, $J_{CP} = 13$, 1C, {Ar}C³), 120.89 (s, 1C,{Ar}C⁵), 127.17 (s, 1C, {Ar}C⁴), 130.64 (dd, $J_{CP} = 19$, 22, 1C, {Ar}C¹Ni) 142.15 (d, $J_{CP} = 12$, 1C,{Ar}C⁶), 170.07 (dd, $J_{CP} = 17$, 2; 1C, {Ar}C²). ³¹P{¹H} NMR (162 MHz, C₆D₆) : δ 155 (d, ² $J_{PP} = 283$, CH2O-

P-(i-Pr)₂), 187 (d, ${}^{2}J_{pp} = 283$, O-P-(i-Pr)₂). Elemental Anal. for C₁₉H₃₃O₂P₂NiBr Calc. (found) % : C, 46.19 (46.50); H, 6.73 (6.96).

(POCOP^{iPr}(5,6))Ni(OTs), 2. A dry Schlenk flask was charged with complex 1 (49 mg, 0.099 mmol, 1 equiv.), silver tosylate (31 mg, 0.11 mmol, 1.1 equiv.), and dry CH₂Cl₂ (4 mL). The mixture was stirred for 30 min at room temperature and then filtered through a pad of Celite. The clear orange yellow solution obtained was slowly evaporated under inert atmosphere to afford complex 2 as a yellow solid (49 mg, 85%). Crystals for X-ray analysis were obtained by recrystallization in CH₂Cl₂. ¹H NMR (400 MHz, C_6D_6) : δ 0.96 $(dd, J_{HP/HH} = 13, 7; 6H, 2 \times CH_3), 1.21 (dd, J_{HP/HH} = 12, 7; 6H, 2 \times CH_3), 1.37 (dd, J_{HP/HH})$ $= 17, 7; 6H, 2 \times CH_3$, 1.74 (dd, $J_{HP/HH} = 19, 7; 6H, 2 \times CH_3$), 1.92 (s, 3H, TsCH₃), 2.02 (m, 2H, 2 × CH), 2.90 (m, 2H, 2 × CH), 4.54 (d, $J_{\rm HP}$ = 17, 2H, CH₂), 6.35 (d, $J_{\rm HH}$ = 7, 1H, Ar} H^3), 6.74 (m, 2H, 2 × {Ar} $H^{4,5}$), 6.84 (d, ${}^{3}J_{HH} = 8$, 2H, 2 × {ArTs} $H^{3,5}$), 7.96 (d, ${}^{3}J_{\text{HH}} = 8, 2\text{H}, 2 \times \{\text{ArTs}\}H^{2,6}\}.{}^{13}\text{C}\{{}^{1}\text{H}\}\text{NMR} (101 \text{ MHz}, \text{C}_{6}\text{D}_{6}) : \delta 16.69 (s, 2\text{C}, 2 \times 10^{-3}\text{ C})$ CH₃), 17.30 (s, 2C, 2 × CH₃), 18.15 (d, $J_{CP} = 6.2C$, 2 × CH₃), 19.83 (d, $J_{CP} = 7.2C$, 2 × *C*H₃), 21.06 (s, 1C, Ts*C*H₃), 27.08 (d, $J_{CP} = 21$, 2C, 2 × *C*H), 29.75 (dd, $J_{CP} = 16$, 3; 1C, $2 \times CH$), 76.99 (s, 1C, CH₂), 111.93 (d, $J_{CP} = 11$, 1C, {Ar} C^3), 121.30 (s, 1C, {Ar} C^5), 126.54 (s, 2C, {TsAr} $C^{3,5}$), 127.46 (s, 1C, {Ar} C^{4}), 128.95 (s, 1C, {TsAr} $C^{2,6}$), 140.42 (s, 1C, {TsAr} C^4), 131.56 (d, $J_{CP} = 21$, 1C, Ni{Ar} C^1), 142.63 (d, $J_{CP} = 12$, 1C, {Ar} C^6), 170.24 (d, $J_{CP} = 15$, 1C, {Ar} C^2). ³¹P{¹H} NMR (162 MHz, C₆D₆) : δ 148 (d, ² $J_{PP} = 302$, 1P, CH₂OP(i-Pr)₂), 189 (d, ${}^{2}J_{PP} = 302$, 1P, OP(i-Pr)₂). Elemental Anal. for $C_{26}H_{40}O_5P_2SNi$ Calc. (found) % : C, 53.35 (53.22); H, 6.89 (7.16).

(POCOP^{iPr}(5,6))Ni(OTf), 3. A dry Schlenk flask covered with aluminum foil was charged with complex 1 (25 mg, 0.051 mmol), silver triflate (74 mg, 0.29 mmol, 5.8

equiv.), and CH₂Cl₂ (5 mL), and the resulting brown mixture stirred overnight at room temperature. The final mixture was passed through a column of Celite to remove excess of silver salt, and the resulting clear orange-yellow solution was evaporated slowly under inert atmosphere to give the yellow product as a crystalline solid. (Yield 45 mg, 80%). ¹H NMR (400 MHz, C_6D_6) : δ 0.92 (dd, $J_{HP/HH}$ = 13, 7; 6H, 2×CH₃), 1.05 (dd, $J_{HP/HH}$ = 12, 7; 6H, $2 \times CH_3$), 1.36 (dd, $J_{\text{HP/HH}} = 18$, 7; 6H, $2 \times CH_3$), 1.55 (dd, ${}^{3}J_{\text{HP/HH}} = 19$, 7; 6H, $2 \times CH_3$) CH_3), 2.09 (m, 2H, 2 × CH),), 2.58 (m, 2H, 2 × CH), 4.44 (d, ${}^{3}J_{HP} = 17, 2H, CH_2$), 6.28 (d, ${}^{3}J_{HH} = 7$, 1H, {Ar} H^{5}), 6.61 (d, ${}^{3}J_{HH} = 7$, 1H, 2 × {Ar} H^{3}). 6.70 (dt, ${}^{3}J_{HH} = 7$, 1; 1H, {Ar} H^4). ¹³C{¹H}NMR (101 MHz, C₆D₆) : δ 16.29 (s, 2C, 2 × CH₃), 16.69 (s, 2C, 2 \times CH₃), 17.63 (s, 2C, 2 \times CH₃), 17.69 (s, 2C, 2 \times CH₃), 27.28 (br, 2C, 2 \times CH), 28.47 (br, 2C, 2 × CH), 76.53 (s, 1C, CH₂), 112.00 (d, $J_{CP} = 13$, 1C, {Ar} C^3), 121.39 (s, $1C_{Ar}C^{5}$, 128.80 (s, 1C, {Ar} C^{4}), 136.47 (s, 1C, {Ar} $C^{I}Ni$) 141.51 (d, $J_{CP} = 12$, 1C, {Ar} C^{6}), 169.65 (dd, $J_{CP} = 17, 2$; 1C, {Ar} C^{2}). ³¹P{¹H} NMR (162 MHz, C₆D₆) : δ 189 (d, ${}^{2}J_{pp} = 285$, CH2O-*P*-(i-Pr)₂), 148 (d, ${}^{2}J_{pp} = 285$, O-*P*-(i-Pr)₂). IR (solid state, cm⁻ ¹): $v(C=C^{Ar})= 1420, 1468, 1592, v(SO_3)= 1021, 1235, v(CF_3)= 1100.$

[(POCOP^{iPr}(5,6))Ni(CH₃CN)][BPh₄], 4b. A dry Schlenk flask was charged with complex 1 (25 mg, 0.051 mmol, 1 equiv.), silver tetraphenylborate (25 mg, 0.057 mmol, 1.1 equiv.), and a 1:1 mixture of dry CH₂Cl₂/MeCN (6 mL). The reaction mixture was stirred for 3 h at room temperature, then for 30 min at 60 °C, and finally filtered through a pad of Celite. The resulting clear, light yellow solution was slowly evaporated under inert atmosphere to afford complex 4b as a yellow solid (29 mg, 70%). Crystals for X-ray analysis were obtained by recrystallization from CH₂Cl₂. ¹H NMR (400 MHz, C₆D₆): δ 1.11 (dd, *J*_{HP/HH} = 14, 7; 6H, 2 × CH₃), 1.30 (dd, *J*_{HP/HH} = 14, 7; 6H, 2 × CH₃), 1.38 (dd,

 $J_{\text{HP/HH}} = 7, 6; 6H, 2 \times \text{CH}_3), 1.43 \text{ (t, } J_{\text{HP/HH}} = 7, 6H, 2 \times \text{CH}_3), 1.97 \text{ (m, } 2H, 2 \times \text{CH}), 2.30 \text{ (m, } 2H, 2 \times \text{CH}), 2.57 \text{ (s, } 3H, \text{CH}_3\text{CN}), 4.89 \text{ (d, } {}^3J_{\text{HP}} = 17, 2\text{H}, \text{CH}_2), 6.79 \text{ (d, } {}^3J_{\text{HH}} = 7, 1\text{H}, \text{ {Ar}}H^{3,5}), 6.87 \text{ (d, } {}^3J_{\text{HH}} = 7, 1\text{H}, \text{ {Ar}}H^{3,5}), 7.02 \text{ (t, } J_{\text{HH}} = 7, 1\text{H}, \text{ {Ar}}H^4), 7.12 \text{ (m, } 8H, o-B{Ph}H), 7.30 \text{ (m, } 12\text{H}, m+p-B{Ph}H^{3,5}). {}^{13}\text{C}{}^1\text{H}\text{NMR} \text{ (101 MHz, } C_6\text{D}_6) : \delta 17.54 \text{ (s, } 2\text{C}, 2 \times \text{CH}_3), 18.39 \text{ (s, } 2\text{C}, 2 \times \text{CH}_3), 19.06 \text{ (d, } J_{\text{CP}} = 7, 2\text{C}, 2 \times \text{CH}_3), 20.68 \text{ (d, } J_{\text{CP}} = 8, 2\text{C}, 2 \times \text{CH}_3), 27.93 \text{ (d, } J_{\text{CP}} = 23, 2\text{C}, 2 \times \text{CH}), 30.60 \text{ (dd, } J_{\text{CP}} = 18, 3; 1\text{C}, 2 \times \text{CH}), 77.48 \text{ (s, } 1\text{C}, \text{CH}_2), 112.78 \text{ (d, } J_{\text{CP}} = 10, 1\text{C}, \text{{Ar}}C^3), 122.15 \text{ (s, } 1\text{C}, \text{{Ar}}C^5), 128.31 \text{ (s, } 1\text{C}, \text{{Ar}}C^4), 133.96 \text{ (s, } 1\text{C}, \text{{Ar}}C^1), 143.49 \text{ (d, } J_{\text{CP}} = 14, 1\text{C}, \text{{Ar}}C^5), 124.78 \text{ (s, } 12\text{C}, p+m-B{Ar}C). {}^{31}\text{P}{}^1\text{H} \text{NMR} (162 \text{ MHz}, \text{CD}_3\text{CN}) : \delta 152 \text{ (d, } {}^2J_{\text{PP}} = 260, 1\text{P}, \text{CH}_2\text{OP}(\text{i}-\text{Pr}_2), 194 \text{ (d, } {}^2J_{\text{PP}} = 260, 1\text{P}, \text{OP}(\text{i}-\text{Pr}_2). \text{IR} \text{ (solid state, cm}^{-1}) : v(\text{C}=\text{C}^{\text{Ar}}) = 1430, 1585, v(\text{C}=\text{N}) = 2288. \text{ Elemental Anal. for } \text{C}_{45}\text{BNNiO}_2\text{P}_2 \text{ Calc. (found) }\% : \text{C}, 69.80 (68.99); \text{H}, 7.29 (7.47); \text{N}, 1.81 (1.66).}$

Synthesis of (POCOP^{iPr}(5,6))Ni(CCCH₃), 5. A dry Schlenk flask was charged with complex 1 (128 mg, 0.259 mmol, 1 equiv.), MeCCMgBr (1.00 mL of a 0.50 M stock solution in THF, 0.50 mmol, 1.9 equiv.), dry THF (6 mL), and toluene (12 mL). The mixture was stirred at 60 °C until the original orange-yellow colour changed to brown. Evaporation of the resulting mixture and extraction of the residues by hexane, followed by filtration through a short column of Celite gave a yellow solution, which was slowly evaporated under inert atmosphere to afford complex 5 as yellow crystals that appeared to be covered with an oily residue (32 mg, crude yield: 27%). ¹H NMR (400 MHz, C₆D₆): δ 1.21 (m, 12H, 4 × CH₃), 1.40 (dd, $J_{HP/HH} = 16$, 7; 6H, 2 × CH₃), 1.48 (dd, $J_{HP/HH} = 16$, 7;

6H, 2 × CH₃), 1.94 (s, 3H, CCCH₃), 2.56-2.30 (m, 1H), 4.75 (d, ${}^{3}J_{HP}$ = 15, 2H, CH₂), 6.53 (d, J_{HH} = 7, 1H), 6.97 (t, J_{HH} = 7, 1H,), 7.07 (d, J_{HH} = 8, 1H,). 13 C NMR (101 MHz, C₆D₆): δ 4.26 (s, 1C, CC-CH₃), 14.47 (s, 2C, 2 × CH₃), 15.49 (d, J_{CP} = 5, 2C, 2 × CH₃), 16.68 (d, J_{CP} = 5, 2C, 2 × CH₃), 25.68 (dd, J_{CP} = 22, 3, 2C, 2 × CH), 26.67 (dd, J_{CP} = 26, 3, 2C, 2 × CH), 72.59 (s, 1C, CH₂), 86.90 (pseudo triplet, ${}^{2}J_{CP}$ = 40, 1C, CCMe), 108.15 (d, J_{CP} = 13, 1C, {Ar}C³), 117.16 (s, 1C, CCMe), 117.61 (s, 1C, {Ar}C⁵), 124.10 (s, 1C, {Ar}C⁴), 136.21 (t, ${}^{2}J_{CP}$ = 19, 1C, {Ar}C¹), 139.74 (d, J_{CP} = 12, 1C, {Ar}C⁶), 167.71 (dd, J_{CP} = 18, 3, 1C, {Ar}C²). 31 P{ 1 H} NMR (162 MHz, C₆D₆) : δ 160 (d, ${}^{2}J_{PP}$ = 323, 1P, CH₂OP(i-Pr)₂), 187 (d, ${}^{2}J_{PP}$ = 323, 1P, OP(i-Pr)₂).

(POCOP^{iPr}(5,6))Ni(CH₃), 6. A dry Schlenk flask was charged with complex 1 (200 mg, 0.405 mmol), MeLi (92 mg, 4.2 mmol, 10 equiv.), dry THF (6 mL). The mixture was stirred at room temperature until the original orange-yellow color changed to dark brown after 24 h. Evaporation of the resulting mixture and extraction of the residues by hexane, followed by filtration through a column of Celite gave a dark red solution, which was slowly evaporated under inert atmosphere to afford complex 6 as yellow-reddish crystals that appeared to be covered with an oily residue (75 mg, crude yield: 43%). ¹H NMR (400 MHz, C₆D₆): δ -0.38 (t, ³*J*_{HP} = 10, 3H, NiCH₃), 1.11 (dd, ³*J*_{HP/HH} = 13, 7; 6H, 2 × CH₃), 1.16 (dd, ³*J*_{HP/HH} = 13, 7; 6H, 2 × CH₃), 1.20 (dd, ³*J*_{HP/HH} = 19, 7; 6H, 2 × CH₃), 1.25 (dd, ³*J*_{HP/HH} = 19, 7; 6H, 2 × CH₃), 2.15 (brm, 4H, 4 × CH),), 4.76 (d, ³*J*_{HP} = 16, 2H, CH₂), 6.59 (d, ³*J*_{HH} = 8, 1H, {Ar}*H*³), 7.13 (d, ³*J*_{HH} = 8, 1H, {Ar}*H*⁵). 7.00 (dt, ³*J*_{HH} = 7, 2; 1H, {Ar}*H*⁴). ¹³C{¹H}NMR (101 MHz, C₆D₆) : δ -16.70 (t, ²*J*_{CP} = 23, 1C, Ni-CH₃), 16.87 (s, 2C, 2 × CH₃), 17.01 (s, 2C, 2 × CH₃), 17.78 (d, *J*_{CP} = 6, 2C, 2 × CH₃), 18.83 (d, *J*_{CP} = 6, 2C, 2 × CH₃), 27.44 (dd, *J*_{CP} = 12, 3; 2C, 2 × CH), 27.65 (dd, *J*_{CP} = 2

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12, 3; 2C, 2 × *C*H), 75.12 (s, 1C, *C*H₂), 110.47 (d, $J_{CP} = 13$, 1C, {Ar}*C*³), 119.56 (s, 1C, {Ar}*C*⁵), 125.74 (s, 1C, {Ar}*C*⁴), 142.40 (pseudo-triplet, ${}^{2}J_{CP} = 20.4$, 1C, {Ar}*C*¹Ni), 143.05 (d, $J_{CP} = 10$, 1C, {Ar}*C*⁶), 169.20 (dd, $J_{CP} = 18$, 6; 1C, {Ar}*C*²). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, C₆D₆) : δ 187 (d, ${}^{2}J_{pp} = 323$, CH2O-*P*-(i-Pr)₂), 160 (d, ${}^{2}J_{pp} = 323$, O-*P*-(i-Pr)₂). **Crystal Structure Determinations.** Single crystals of complexes **1**, **5** and **6** were grown by slow evaporation of hexane from their respective saturated solutions. The cationic complex **4b** was crystallized from a 9:1 mixture of dichloromethane and acetonitrile. Crystals of complex **2** were obtained by slow evaporation of dichloromethane. The crystallographic data for complexes **1**, **2** and **4b**-**6** were collected on a Bruker Microstar generator (micro source) equipped with a Helios optics, a Kappa Nonius goniometer and a Platinum135 detector.

Cell refinement and data reduction were done using SAINT.²⁷ An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.²⁸ The space group was confirmed by XPREP routine²⁹ in the SHELXTL program.³⁰ The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.³¹ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.

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Supporting Information. Tables of ¹H, ¹³C, ³¹P{¹H}NMRs, details of data collection for the X-ray analyses of complexes **1**, **2**, **4b**, **5**, and **6**, and solid state bond distances and angles. All crystallographic data have been deposited at The Cambridge Crystallographic Data Centre (CCDC) and can be retrieved with the reference numbers 1052508 (**1**), 1052509 (**2**), 1052511 (**4b**), 1052510 (**5**) and 1052512 (**6**). These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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