Metathesis reactivity of bis(phosphinite) pincer ligated nickel chloride, isothiocyanate and azide complexes

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Abstract: A series of nickel pincer complexes of the type [4-Z-2,6-(R₂PO)₂C₆H₂]NiX (R = ^tBu, ⁱPr, Ph; Z = H, CO₂Me; X = NCS, N₃) have been synthesized from the reactions of the corresponding nickel chloride complexes [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl and potassium thiocyanate or sodium azide. X-ray structure determinations of these complexes have shown that the thiocyanate ion binds to the nickel center through the nitrogen. A comparable Ni–N bond length (approx. 1.87 Å for the isothiocyanate complexes and 1.91 Å for the azide complexes) and an almost identical Ni–C_{ipso} bond length (approx. 1.89 Å) have been observed for these complexes. Metathesis reactivity of [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl and ligand exchange reactions between the nickel isothiocyanate and nickel azide complexes have been investigated. The metathesis reactions with thiocyanate/azide complexes are faster with a less electron rich and more sterically accessible nickel center. The thermodynamic stability of these nickel complexes has been rationalized using the hard-soft acid-base theory (HSAB theory); a harder ligand prefers a less electron rich nickel center. These

experimental results have been supported by quantum chemical analysis of the coordinating nitrogen atoms in SCN^- and N_3^- .

Keywords: Metathesis reaction, Synthesis, Crystal structure, Nickel, Pincer complex

Introduction

Transition metal complexes bearing a bis(phosphinite) pincer or POCOP-pincer ligand have been extensively studied since the first reports by Jensen [1] and Bedford [2]. This specific class of complexes has been demonstrated as efficient catalysts for a wide range of chemical transformations [3]. The popularity of using these complexes for catalysis has been largely attributed to the high catalyst thermal stability [4], well balanced ligand properties [5] and convenient ligand synthesis [1,2,4a,6]. During the past decade, significant effort has focused on the elucidation of structure-reactivity relationships with the goal of developing more active catalysts [7].

We are particularly interested in *nickel* complexes supported by a POCOP-pincer ligand, and our efforts have led to the development of catalysts for the reduction of aldehydes [8a], ketones [8a], CO_2 [8b-e], cyanomethylation of aldehydes [8f] and C–S cross-coupling reactions [8g]. To gain a deeper understanding of how structural modification could change the performance of these complexes in different catalytic reactions, we have carried out detailed studies about substituent effects on the reactivity of the metal center. In one of our recent studies, we have reported how the substituents on the phosphorus donors influence the Ni–S bond dissociation energies and kinetic stability of nickel arylthiolate complexes [9]. The electrostatic component of the bonding appears to contribute greatly to the strength of the Ni–S bond. To explore the generality of this conclusion, herein we extend the chemistry to nickel POCOP-pincer complexes bearing a *nitrogen*-based ligand. More specifically, we have focused on the metathesis reactivity of $[\text{4-Z-2,6-(R}_2\text{PO)}_2\text{C}_6\text{H}_2]\text{NiX}$ ($\text{Z} = \text{H, CO}_2\text{Me}$; $\text{R} = \text{tBu, } ^i\text{Pr, Ph}$; $\text{X} = \text{Cl, NCS, N}_3$). The introduction of an ester group to the pincer backbone has also allowed us to probe how the remote ligand modification would impact the bond breaking/forming processes.

Results and discussion

Synthesis and structure of nickel pincer complexes

Following previously reported procedures for the synthesis of [2,6-(^tBu₂PO)₂C₆H₃]NiCl (**1aa**) [8a], [2,6-(ⁱPr₂PO)₂C₆H₃]NiCl (**1ab**) [6c] and [2,6-(Ph₂PO)₂C₆H₃]NiCl (**1ac**) [6b], complexes **1ba-c** were synthesized via cyclometalation of the ester-substituted diphosphinite ligand with NiCl₂ (eq 1). Complex **1bb** was reported by Zargarian and co-workers, who developed a one-pot procedure for preparing complexes of this type from resorcinol or its derivatives, R₂PCl and nickel powder [10]. The new complexes **1ba** and **1bc** were characterized by ¹H NMR, ³¹P{¹H} NMR, ¹³C{¹H} NMR and elemental analysis. The structure of **1ba** was also confirmed by X-ray crystallography (see Appendix B. Supplementary data).

Room temperature reactions of nickel chloride complexes **1** with 5 equiv of potassium thiocyanate afforded nickel isothiocyanate complexes **2** in high isolated yields (86-93%) (Scheme 1). Thiocyanate ion is a well-known ambidentate ligand. Depending on the polarizability and the steric environment of the metal, thiocyanate ligand can bind to the metal through either the sulfur or the nitrogen end, resulting in a thiocyanate or isothiocyanate complex. In this study, there was no evidence for sulfur binding; the isothiocyanate complex was isolated as the sole product in all cases, as suggested by X-ray structure analysis of the single crystals as well as the ³¹P{¹H} NMR spectrum in which only one resonance was observed.

Similarly, mixing nickel chloride complexes **1** with 5 equiv of sodium azide in THF/MeOH (1 : 1) for several days yielded nickel azide complexes **3** (Scheme 1).

Complex **3ab** was previously reported by Zargarian *et al.* through the reaction of the corresponding trimethylsiloxide complex with Me_3SiN_3 [7m]. Related nickel azide complexes bearing a $\text{POC}_{\text{sp}^3}\text{OP}$ -pincer ligand [7m] or a PCP-pincer ligand [11] were prepared in a similar fashion using Me_3SiN_3 .

To accelerate the substitution of the chloride ligand in complex **1** by SCN^- and N_3^- , each of the reactions shown in Scheme 1 was conducted under refluxing conditions. However, an extra recrystallization step was needed to ensure the purity of the products, which resulted in lower isolated yields (60-78%) than those for the room temperature reactions.

The nickel isothiocyanate and azide complexes reported here are all air and moisture stable in both solution and solid states. No significant decomposition was observed when a solid sample or a solution (in $\text{CH}_2\text{Cl}_2/n$ -hexane) was exposed to the air for a few weeks.

Scheme 1. Synthesis of POCOP pincer ligated nickel isothiocyanate and azide complexes

The new nickel isothiocyanate and azide complexes were fully characterized by multinuclear NMR, FTIR, X-ray crystallography and elemental analysis. Notable features of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra included the *ipso* carbons appearing as triplets ($^2J_{\text{P-C}} = 20\text{-}25$ Hz) at 123.86-125.37 ppm for **2aa-c** and **3aa-c**, and 131.35-133.25 ppm for **2ba-c** and **3ba-c**. The chemical shift differences for the *ipso* carbons can be attributed to the electronic effects of the *para*-substituents (H vs. CO_2Me). The electron-withdrawing ester group makes the *ipso* carbons more deshielded, leading to a downfield shift of 6-9 ppm. All $^{31}\text{P}\{^1\text{H}\}$ NMR spectra displayed a single

resonance, consistent with a symmetrical structure bearing two equivalent phosphorus atoms. For complexes with the same phosphorus substituents (R groups) and the same ancillary ligand (NCS[−] or N₃[−]), the resonances for the CO₂Me-substituted complexes were located approx. 1 ppm downfield of resonances associated with the unsubstituted complexes (X = H). The phosphorus resonances for the isothiocyanate complexes were found 2-4 ppm downfield from resonances corresponding to the azide complexes with the same ligand.

Selected FTIR data of the isothiocyanate and azide complexes are listed in Table 1. In general, CN stretching or N₃ asymmetric stretching frequency decreases when changing the phosphorus substituents from ^tBu to ⁱPr and from ⁱPr to Ph (e.g., **2aa** > **2ab** > **2ac** for ν_{CN}). The only exception is **3bc** which has a slightly higher ν_{N_3} value than **3bb**. Introducing an electron-withdrawing ester group at the *para* position of the *ipso* carbon results in lower values in ν_{CN} for the ^tBu and ⁱPr-substituted isothiocyanate complexes (**2aa** vs. **2ba**, **2ab** vs. **2bb**), as well as ν_{N_3} for the ⁱPr-substituted azide complexes (**3ab** vs. **3bb**), but has almost no influence on the remaining pairs (**2ac** vs. **2bc**, **3aa** vs. **3ba**, or **3ac** vs. **3bc**).

Table 1

CN stretching or N₃ asymmetric stretching frequencies of [4-Z-2,6-(R₂PO)₂C₆H₂]NiX complexes (cm^{−1})

	Isothiocyanate complexes (X = NCS)			Azide complexes (X = N ₃)		
	R = ^t Bu	R = ⁱ Pr	R = Ph	R = ^t Bu	R = ⁱ Pr	R = Ph
Z = H	2104 (2aa)	2091 (2ab)	2072 (2ac)	2072 (3aa)	2053 (3ab)	2048 (3ac)
Z = CO ₂ Me	2098 (2ba)	2082 (2bb)	2071 (2bc)	2073 (3ba)	2047 (3bb)	2049 (3bc)

The nickel isothiocyanate and azide complexes described in this work crystallized readily and were conveniently studied by X-ray crystallography. As representative examples, structures of **2aa**, **2bb**, **3ac** and **3ba** are shown in Figures 1-4, respectively. The structure of **3ab** has been previously reported by Zargarian and co-workers [7m]. Structures and crystallographic data of the remaining seven complexes (**2ab**, **2ac**, **2ba**, **2bc**, **3aa**, **3bb** and **3bc**) are provided in the Supplementary data (Appendix B). For comparison purposes, Ni–C_{ipso} and Ni–N bond lengths of these complexes are

summarized in Tables 2 and 3, respectively, while the Ni–N–C and Ni–N–N bond angles are listed in Table 4.

As shown in Table 2, the Ni–C_{ipso} bond length is essentially constant for both isothiocyanate and azide complexes (1.88–1.89 Å), and unaffected by the substituents on the phosphorus donors or at the *para* position of the aromatic pincer backbone. Similar results were observed in POCOP-pincer nickel thiolate complexes [9]. The Ni–N bond lengths for the isothiocyanate complexes (1.86–1.87 Å) are slightly shorter than those for the azide complexes (1.90–1.94 Å); however the Ni–N bond lengths for the unsubstituted azide complexes (1.91–1.94 Å) and those adorned by an ester group (1.90–1.92 Å) in the *para* position of the aromatic pincer ligand are unchanged. In the nickel isothiocyanate complexes, the NCS ligand maintains its linear geometry (N–C–S bond angle: 178.7–179.7°, see Appendix B. Supplementary data) and deviates slightly from the C_{ipso}–Ni–N vector in the coordination plane with a Ni–N–C bond angle of 160.5–178.7° (Table 4). In contrast, the N₃ ligand in the nickel azide complexes bends slightly from its original linear geometry (N–N–N bond angle: 175.1–176.2°, see Appendix B. Supplementary data) and deviates significantly from the C_{ipso}–Ni–N vector with a Ni–N–N bond angle of 127.6–139.0°. Similar bending is observed in other metal azide complexes [7m,11,12]. Of all the nickel complexes reported here, **2aa** is the most symmetrical molecule in the solid state (Fig. 5). The linear NCS ligand (N–C–S bond angle: 179.7(2)°) is within the coordination plane and essentially extended from the C_{ipso}–Ni–N vector (Ni–N–C bond angle: 178.7(2)°). The NCS ligand of other isothiocyanate complexes is bent with respect to the C_{ipso}–Ni–N vector, likely influenced by the varying conformations of the R groups bound to phosphorus and/or asymmetry induced by the ester group. Nevertheless, in solution, the rotation of the Ni–N bonds are not restricted as all ³¹P{¹H} NMR spectra display a singlet resonance.

Fig. 1 ORTEP drawing of [2,6-(^tBu₂PO)₂C₆H₃]Ni(NCS) (**2aa**) at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni1–N1 = 1.8643(18), Ni1–C1 = 1.8787(19), Ni1–P1 = 2.1827(6), Ni1–P2 = 2.1927(6), N1–C23 = 1.167(3); C23–S1 = 1.625(2); P1–Ni1–P2 = 164.51(2), P1–Ni1–N1 = 97.51(6), P2–Ni1–N1 = 97.97(6), C1–Ni1–N1 = 179.13(9), C23–N1–Ni1 = 178.7(2), N1–C23–S1 = 179.7(2).

Fig. 2 ORTEP drawing of [4-CO₂Me-2,6-(ⁱPr₂PO)₂C₆H₂]Ni(NCS) (**2bb**) at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni1–N1 = 1.867(3), Ni1–C1 = 1.886(3), Ni1–P1 = 2.1679(10), Ni1–P2 = 2.1680(10), N1–C21 = 1.169(4); C21–S1 = 1.629(3); P1–Ni1–P2 = 163.61(3), P1–Ni1–N1 = 97.82(10), P2–Ni1–N1 = 98.29(10), C1–Ni1–N1 = 178.09(13), C21–N1–Ni1 = 175.4(3), N1–C21–S1 = 179.0(3).

Fig. 3 ORTEP drawing of $[2,6-(\text{Ph}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiN}_3$ (**3ac**) at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni1–N1 = 1.934(2), Ni1–C30 = 1.880(3), Ni1–P1 = 2.1760(9), Ni1–P2 = 2.1587(8), N1–N2 = 1.153(3); N2–N3 = 1.157(4); P1–Ni1–P2 = 162.95(3), P1–Ni1–N1 = 96.92(7), P2–Ni1–N1 = 100.04(7), C30–Ni1–N1 = 177.57(12), N2–N1–Ni1 = 133.7(2), N1–N2–N3 = 175.4(3).

Fig. 4 ORTEP drawing of $[4\text{-CO}_2\text{Me-2,6-}(\text{tBu}_2\text{PO})_2\text{C}_6\text{H}_2]\text{NiN}_3$ (**3ba**) at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni1–N1 = 1.900(6), Ni1–C1 = 1.884(6), Ni1–P1 = 2.1837(15), Ni1–P2 = 2.1884(16), N1–N2 = 1.180(7); N2–N3 = 1.159(7); P1–Ni1–P2 = 163.49(7), P1–Ni1–N1 = 98.16(17), P2–Ni1–N1 = 98.28(17), C1–Ni1–N1 = 169.9(2), N2–N1–Ni1 = 138.3(5), N1–N2–N3 = 175.3(6).

Fig. 5 Side views of **2aa** illustrating the symmetrical geometry

Table 2

Ni–C_{ipso} bond lengths (Å) of nickel isothiocyanate and azide complexes
[4-Z-2,6-(R₂PO)₂C₆H₂]NiX

	Isothiocyanate complexes (X = <u>NCS</u>)			Azide complexes (X = N ₃)		
	R = ⁱ Bu	R = ⁱ Pr	R = Ph	R = ⁱ Bu	R = ⁱ Pr	R = Ph
Z = H	1.8787(19) (2aa)	1.8854(11) (2ab)	1.889(2) (2ac)	1.884(3) (3aa)	1.891(3) (3ab) ^a	1.880(3) (3ac)
Z = CO ₂ Me	1.8765(17) (2ba)	1.886(3) (2bb)	1.8760(18) (2bc)	1.884(6) (3ba)	1.8775(14) (3bb)	1.8866(18) (3bc)

^a Data obtained from the cif file of Ref. 7m.

Table 3 Ni–N bond lengths (Å) of nickel isothiocyanate and azide complexes
[4-Z-2,6-(R₂PO)₂C₆H₂]NiX

	Isothiocyanate complexes (X = <u>NCS</u>)			Azide complexes (X = N ₃)		
	R = ⁱ Bu	R = ⁱ Pr	R = Ph	R = ⁱ Bu	R = ⁱ Pr	R = Ph
Z = H	1.8643(18) (2aa)	1.8715(10) (2ab)	1.8739(18) (2ac)	1.914(3) (3aa) ^a	1.935(2) (3ab) ^b	1.934(2) (3ac)
				1.936(14)		
Z = CO ₂ Me	1.8667(16) (2ba)	1.867(3) (2bb)	1.8714(17) (2bc)	1.900(6) (3ba)	1.9174(14) (3bb)	1.9036(16) (3bc)

^a The N-atoms of the N₃ group in complex **3aa** are disordered, both Ni1–N1 and Ni1–N1A bond lengths are listed. ^b Data obtained from the cif file of Ref. 7m.

Table 4

Ni–N–C bond angles (°) of [4-Z-2,6-(R₂PO)₂C₆H₂]Ni(NCS) and Ni–N–N bond angles (°) of [4-Z-2,6-(R₂PO)₂C₆H₂]NiN₃

	Isothiocyanate complexes (X = <u>NCS</u>)			Azide complexes (X = N ₃)		
	R = ⁱ Bu	R = ⁱ Pr	R = Ph	R = ⁱ Bu	R = ⁱ Pr	R = Ph
Z = H	178.7(2) (2aa)	167.13(12) (2ab)	164.11(18) (2ac)	139.0(7) (3aa) ^a	130.2(2) (3ab) ^b	133.7(2) (3ac)
				132.(5)		
Z = CO ₂ Me	170.39(18) (2ba)	175.4(3) (2bb)	160.51(16) (2bc)	138.3(5) (3ba)	127.60(11) (3bb)	133.21(14) (3bc)

^a The N-atoms of the N₃ group in complex **3aa** are disordered, both Ni1–N1–N2 and Ni1–N1A–N2A bond angles are listed. ^b Data obtained from the cif file of Ref. 7m.

Metathesis reaction of [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl

Although the salt metathesis reactions between POCOP-pincer nickel chloride complexes and potassium thiocyanate or sodium azide all ultimately lead to the nickel isothiocyanate or azide complexes quantitatively, it would be useful to understand the reactivity differences of the pincer complexes. In particular, we were interested in knowing how the substituents on the phosphorus donors and the pincer aromatic backbone would influence the rates of the metathesis reactions. Given the fact that NCS⁻ and N₃⁻ both are linear species and in this case coordinate to nickel via nitrogen, we were curious as to whether there is a rate difference upon complexation using the starting chloro complex (refer to Scheme 1). Unfortunately, the poor solubility of potassium thiocyanate and sodium azide in most organic solvents and the relatively fast reaction rates for this type of reactions make it difficult to obtain reliable kinetic data. Using Bu₄NSCN and Bu₄NN₃ would solve the solubility problem; however, with the exception of **1aa** and **1ba**, the salt metathesis reactions are too fast (complete in one min at 0 °C) to tell the difference among the nickel pincer complexes. As an alternative method, the salt metathesis reactions using KSCN and NaN₃ (eq 2) were stopped after a short period of time and the reaction mixtures were analyzed by ³¹P{¹H} NMR spectroscopy. In a typical experiment, a dilute THF solution of [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl (0.1 mmol in 3 mL of THF) was mixed with a saturated THF solution of potassium thiocyanate or sodium azide (0.1 mmol KSCN or NaN₃ mixed with 3 mL of THF) at 0°C. The resulting mixture was stirred at 0°C for 5 min and then quickly quenched by adding 15 mL of water. This procedure resulted in precipitation of nickel pincer complexes while keeping KSCN and NaN₃ in solution. The ratios between [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl and [4-Z-2,6-(R₂PO)₂C₆H₂]NiX (X = NCS, N₃) were determined by ³¹P{¹H} NMR integrations, from which the conversions were calculated [13]. Table 5 summarizes the results for eight different reactions with six of them involving NCS⁻. Because of the poor solubility of KSCN and NaN₃, their concentrations are constant throughout the reactions, and low enough to slow down the reactions so that reactivity difference between the nickel complexes could be observed. It should be noted that all the nickel complexes involved in this

study tolerate water. No pincer species other than the starting nickel chloride complexes and the resulting nickel isothiocyanate or azide complexes was detected by $^{31}\text{P}\{^1\text{H}\}$ NMR. The low concentrations (0.017 M each) of the starting nickel chloride complexes and KSCN or NaN_3 made the salt metathesis reactions slow enough that the conversions could be measured with accuracy within the same period of time (5 min).

Table 5

Conversions of $[4\text{-Z-2,6-(R}_2\text{PO)}_2\text{C}_6\text{H}_2]\text{NiCl}$ to $[4\text{-Z-2,6-(R}_2\text{PO)}_2\text{C}_6\text{H}_2]\text{NiX}$ after 5 min at 0 °C

Entry	Z	R	X	Reactions	Conversion (%)
1	H	^t Bu	<u>NCS</u>	1aa + $\text{NCS}^- \rightarrow \textbf{2aa} + \text{Cl}^-$	10
2	H	ⁱ Pr	<u>NCS</u>	1ab + $\text{NCS}^- \rightarrow \textbf{2ab} + \text{Cl}^-$	76
3	H	Ph	<u>NCS</u>	1ac + $\text{NCS}^- \rightarrow \textbf{2ac} + \text{Cl}^-$	83
4	CO_2Me	^t Bu	<u>NCS</u>	1ba + $\text{NCS}^- \rightarrow \textbf{2ba} + \text{Cl}^-$	18
5	CO_2Me	ⁱ Pr	<u>NCS</u>	1bb + $\text{NCS}^- \rightarrow \textbf{2bb} + \text{Cl}^-$	82
6	CO_2Me	Ph	<u>NCS</u>	1bc + $\text{NCS}^- \rightarrow \textbf{2bc} + \text{Cl}^-$	87
7	H	ⁱ Pr	N_3^-	1ab + $\text{N}_3^- \rightarrow \textbf{3ab} + \text{Cl}^-$	85
8	CO_2Me	ⁱ Pr	N_3^-	1bb + $\text{N}_3^- \rightarrow \textbf{3bb} + \text{Cl}^-$	91

As shown in Table 5, for nickel chloride complexes bearing the same pincer backbone, those with phenyl groups as the phosphorus substituents are the most reactive complexes for the thiocyanate ion (entries 3 and 6), while those with *tert*-butyl groups on the phosphorus atoms are the least reactive ones (entries 1 and 4). Having an electron-withdrawing CO_2Me group at the *para* position of the pincer backbone makes nickel complexes consistently more reactive (entry 1 vs. 4; entry 2 vs. 5; entry 3 vs. 6; entry 7 vs. 8), although the rate difference is small.

The relatively slow reactions for **1aa** and **1ba** are possibly due to sterics. Presumably, the metathesis or substitution reactions are associative or interchange-associative in nature, and the rates depend on how easily SCN^- and N_3^-

can approach the metal center. The bulky *tert*-butyl substituents are expected to be more sluggish. However, electronic effects can also play a role. Among the three different substituents used in this study (^tBu, ⁱPr and Ph), the *tert*-butyl group is the most electron-donating substituent while the phenyl group is the least donating. The nickel center becomes more electron deficient going from **1aa** to **1ab** to **1ac** or **1ba** to **1bb** to **1bc**, thus favoring the association of an incoming ligand. Furthermore, the introduction of an ester group to the *para* position of the pincer backbone accelerates the metathesis reactions, likely due to a more electron deficient metal center. As inferred from the crystal structures, the steric perturbation should be minimal.

Isothiocyanate/azide exchange reactions

In our previous study [9], nickel thiolate complexes were shown to undergo thiolate exchange between two different pincer units. Interestingly, similar ligand exchange between two different pincer ligated nickel centers was observed in the present study (eq 3). The reactions were clean with no other detectable species by ³¹P{¹H} NMR except the four pincer complexes involved in each equilibrium. The equilibria were typically reached at room temperature in 2-3 d from either direction, or by mixing a random ratio of the four complexes. The equilibrium constants were conveniently measured by ³¹P{¹H} NMR spectroscopy [13] as the complexes usually showed well-separated ³¹P resonances. Table 6 summarizes the equilibrium constants, which were averaged from three individual experiments.

Table 6

Equilibrium constant for the isothiocyanate/azide exchange reactions (T = 298 K)

Entry	Z	Z'	R	R'	Reactions	K_{eq}
1	H	CO ₂ Me	^t Bu	^t Bu	3aa + 2ba $\rightleftharpoons$ 2aa + 3ba	1.33 $\pm$ 0.08
2	H	CO ₂ Me	ⁱ Pr	ⁱ Pr	3ab + 2bb $\rightleftharpoons$ 2ab + 3bb	1.45 $\pm$ 0.02
3	H	CO ₂ Me	Ph	Ph	3ac + 2bc $\rightleftharpoons$ 2ac + 3bc	1.35 $\pm$ 0.02
4	H	H	^t Bu	ⁱ Pr	3aa + 2ab $\rightleftharpoons$ 2aa + 3ab	3.53 $\pm$ 0.08
5	H	H	ⁱ Pr	Ph	3ab + 2ac $\rightleftharpoons$ 2ab + 3ac	2.48 $\pm$ 0.04
6	H	H	^t Bu	Ph	3aa + 2ac $\rightleftharpoons$ 2aa + 3ac	8.4 $\pm$ 0.7
7	CO ₂ Me	CO ₂ Me	^t Bu	ⁱ Pr	3ba + 2bb $\rightleftharpoons$ 2ba + 3bb	3.75 $\pm$ 0.09
8	CO ₂ Me	CO ₂ Me	ⁱ Pr	Ph	3bb + 2bc $\rightleftharpoons$ 2bb + 3bc	2.5 $\pm$ 0.2
9	CO ₂ Me	CO ₂ Me	^t Bu	Ph	3ba + 2bc $\rightleftharpoons$ 2ba + 3bc	10.1 $\pm$ 0.9

The first three equilibria (entries 1-3) involve the exchange of isothiocyanate and azide ligands between an ester-substituted nickel pincer unit and an unsubstituted one. The equilibrium constants are all greater than one, suggesting the azide ligand prefers the more electron-deficient nickel center. As previously mentioned, the electron “richness” of the nickel center follows a decreasing order of $\{[2,6-(^t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{Ni}\}^+ > \{[2,6-(^i\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3]\text{Ni}\}^+ > \{[2,6-(\text{Ph}_2\text{PO})_2\text{C}_6\text{H}_3]\text{Ni}\}^+$. Therefore, altering the phosphorus substituents while keeping the same pincer backbone would establish an equilibrium in which the azide ligand binds preferentially to $\{[2,6-(\text{Ph}_2\text{PO})_2\text{C}_6\text{H}_3]\text{Ni}\}^+$ (entries 5 and 6) followed by $\{[2,6-(^i\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3]\text{Ni}\}^+$ (entry 4). Similar results were obtained when the ester-substituted POCOP-pincer ligands were employed (entries 7-9).

Quantum chemical analysis of the isothiocyanate and azide ions

To gain a better understanding of the aforementioned metathesis and ligand exchange reactions, a quantum chemical analysis of isothiocyanate and azide ions was carried out focusing on the properties of the coordinating nitrogen atoms. The ground-state geometries were optimized by the second-order Møller-Plesset perturbation (MP2) method using the 6-311++G (d, p) basis set, and the charges were obtained from the NPA population analysis. The condensed values of local reactivity descriptors of the coordinating nitrogen atoms in SCN^- and N_3^- are listed in Table 7.

Table 7

Condensed values of local reactivity descriptors of the coordinating nitrogen atoms in SCN^- and N_3^-

	f_k^+	s^+	f_k^-	s^-	f_k^2	S/eV^{-1}	s_k^2/meV^{-1}
SCN^-	0.1691	0.0183	0.2616	0.0283	-0.0925	0.1081	-1.0809
N_3^-	0.4514	0.0417	0.5147	0.0475	-0.0633	0.0923	-0.5393

f_k^+ and f_k^- : condensed Fukui function; s^+ and s^- : local softness; f_k^2 : dual descriptor; S : global softness; s_k^2 : local hypersoftness

The calculations indicate that with a larger condensed Fukui function f_k^- value and a larger local softness s^- value, the coordinating nitrogen atom in N_3^- is more nucleophilic than that of SCN^- [14]. However, the SCN^- nitrogen has a larger global softness value S and a more negative local hypersoftness s_k^2 value. This implies that the nitrogen end of SCN^- is a softer base than the terminal nitrogen of N_3^- .

Substituent effect on the electrophilicity of the nickel center of this type of complexes has been studied by Zargarian and co-workers using cyclic voltammetry [7f,h]. It was found that the oxidation potentials of this type of complexes are affected by both P- and ring-substituents. For complexes with the same aromatic pincer backbone, oxidation of the nickel center becomes more difficult when the P-substituent changes from ^tBu to ^iPr , or from ^iPr to Ph. Oxidation is also more difficult for complexes containing an electron-withdrawing substituent at the *para*-position.

According to the hard-soft acid-base theory (HSAB theory), the acid/base interaction between two hard or two soft species are stronger and generally form a more stable complex than the interaction between one hard and one soft species. The calculations are consistent with the equilibrium constant measurements described in Table 6; the azide ligand, which is a harder base, prefers a less electron rich nickel center (i.e., a harder acid) whereas the isothiocyanate ligand, which is a softer base, prefers a more electron rich nickel center (i.e., a softer acid).

Conclusions

A dozen new nickel isothiocyanate and azide complexes have been synthesized from bis(phosphinite) pincer ligated nickel chloride complexes and KSCN/ NaN_3 . In order to better understand how substituents influence the kinetic and thermodynamic behavior of these complexes, complexes were synthesized with varying substituents on the phosphorus donor atoms and pincer aromatic backbone. X-ray crystallographic studies show little change the Ni–N and Ni–C_{ipso} bond lengths of the resulting nickel pincer isothiocyanate and azide complexes by the P-substituents or aromatic pincer ring modification. However, substituent effects have been observed on the rates of the Ni–N bond formation during the metathesis reactions of the nickel chloride complexes with KSCN/ NaN_3 , and on the strength of the Ni–N bonds that influence the exchange of isothiocyanate and azide ligands on two different nickel pincer units. The metathesis reaction is faster with a less electron rich nickel center. Calculations have shown that the terminal nitrogen of N_3^- is harder than the nitrogen end of SCN^- , thus explaining why the azide ligand prefers a less electron rich nickel center while the isothiocyanate ligand prefers a more electron rich nickel center.

Experimental section

General procedures

Unless otherwise indicated, all the syntheses were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques. Solvents used for the reactions were degassed and dried using standard procedures. The pincer-ligated nickel chloride, isothiocyanate and azide complexes reported in this work, once isolated, can be handled in air without noticeable decomposition. $[2,6-(^t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiCl}$ (**1aa**) [8a], $[2,6-(^i\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiCl}$ (**1ab**) [6c] and $[2,6-(\text{Ph}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiCl}$ (**1ac**) [6b] were prepared as described in the literature.

*Synthesis of [4-CO₂Me-2,6-(^tBu₂PO)₂C₆H₂]⁺NiCl⁻ (**1ba**)*

To a solution of 3,5-dihydroxybenzoic acid methyl ester (1.0 mmol) in 15 mL of THF was slowly added (via a syringe) a suspension of NaH (2.1 mmol) in 5 mL of THF (caution: hydrogen gas evolution). The resulting mixture was heated to reflux for 1 h, followed by the addition (via a syringe) of a solution ^tBu₂P-Cl (2.1 mmol) in 5 mL of THF, and then refluxed for an additional 1 h. The solvent was evaporated under vacuum, and the residue was extracted with 40 mL of pentane. The pentane solution was concentrated under vacuum, first at room temperature and then at 55 °C for 2 h to remove the remaining ^tBu₂P-Cl. The crude 3,5-(^tBu₂PO)₂C₆H₃CO₂Me was obtained as a colorless viscous oil which occasionally solidified upon standing. This crude product was used in the next step without further purification and characterization.

Under a nitrogen atmosphere, the crude 3,5-(^tBu₂PO)₂C₆H₃CO₂Me (1.38 g, 3.0 mmol) was mixed with anhydrous NiCl₂ (389 mg, 3.0 mmol) in toluene (50 mL). The resulting mixture was refluxed under nitrogen for 18 h, cooled to room temperature and filtered to remove the small amount of solid formed. The orange filtrate was concentrated under vacuum to 5 mL, after which 30 mL of Et₂O was added. The desired product formed as a precipitate, which was collected by filtration and washed with Et₂O. Complex **1ba** was isolated as an orange-green powder (725 mg, 44% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.06 (s, ArH, 2H), 3.85 (s, OCH₃, 3H), 1.48 (t, *J*_{P-H} = 6.8 Hz, C(CH₃)₃, 36H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.33 (t, *J*_{P-C} = 9.1 Hz, ArC), 167.15 (s, CO₂CH₃), 133.86 (t, *J*_{P-C} = 20.2 Hz, ArC), 130.47 (s, ArC), 105.98 (t, *J*_{P-C} = 6.1 Hz, ArC), 52.12 (s, CO₂CH₃), 39.58 (t, *J*_{P-C} = 7.1 Hz, C(CH₃)₃), 28.06 (t, *J*_{P-C} = 2.8 Hz, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 188.54 (s). Anal. Calcd for C₂₄H₄₁O₄P₂ClNi: C, 52.44; H, 7.52. Found: C, 52.61; H, 7.58.

*Synthesis of [4-CO₂Me-2,6-(ⁱPr₂PO)₂C₆H₂]⁺NiCl⁻ (**1bb**)*

To a Schlenk flask containing 3,5-dihydroxybenzoic acid methyl ester (840 mg, 5.0 mmol), anhydrous NiCl₂ (972 mg, 7.5 mmol), and 4-dimethylaminopyridine (1.28 g, 10.5 mmol) in THF (30 mL) was added ⁱPr₂P-Cl (1.6 mL, 10.1 mmol) at room

temperature. The mixture was stirred under a nitrogen atmosphere and heated to 80 °C for 18 h. After cooling to room temperature, the volatiles were evaporated, and the resulting solid residue was extracted with *n*-hexane (3 × 20 mL) and filtered. Slow evaporation of the combined solutions at ambient temperature produced **1bb** as yellow-orange crystals (2.05 g, 83% yield). The ¹H NMR data are consistent with the literature values [10].

*Synthesis of [4-CO₂Me-2,6-(Ph₂PO)₂C₆H₂]NiCl (**1bc**)*

To the mixture of 3,5-dihydroxybenzoic acid methyl ester (3.8 g, 23.0 mmol) and Ph₂PCl (8.4 mL, 46.0 mmol) in toluene (40 mL) was added triethylamine (7.0 mL, 50.0 mmol) dropwise. The resulting mixture was heated to reflux for 18 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was extracted with THF (3 × 20 mL) and then filtered through a pad of Celite. After the removal of THF under vacuum, 3,5-(Ph₂PO)₂C₆H₃CO₂Me was isolated as a yellow-orange solid. This crude product was used in the next step without further purification and characterization.

Under a nitrogen atmosphere, the crude 3,5-(Ph₂PO)₂C₆H₃CO₂Me (1.01 g, 1.89 mmol) and NiCl₂ (245 mg, 1.89 mmol) were mixed with toluene (50 mL). The resulting mixture was refluxed for 24 h. After cooling to room temperature, solvent was evaporated under vacuum and the residue was extracted with CH₂Cl₂. Removal of CH₂Cl₂ followed by recrystallization from diethyl ether produced **1bc** as a yellow greenish crystalline solid (865 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.94-8.02 (m, ArH, 8H), 7.44-7.56 (m, ArH, 12H), 7.28 (s, ArH, 2H), 3.87 (s, OCH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 166.94 (t, *J*_{P-C} = 12.1 Hz, ArC), 166.69 (s, CO₂CH₃), 134.85 (t, *J*_{P-C} = 23.2 Hz, ArC), 132.14 (t, *J*_{P-C} = 25.2 Hz, ArC), 132.08 (t, *J*_{P-C} = 6.1 Hz, ArC), 131.91 (t, *J*_{P-C} = 7.1 Hz, ArC), 131.84 (s, ArC), 128.99 (t, *J*_{P-C} = 5.1 Hz, ArC), 107.65 (t, *J*_{P-C} = 7.1 Hz, ArC), 52.32 (s, CO₂CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 141.55 (s). Anal. Calcd for C₃₂H₂₅O₄P₂ClNi: C, 61.04; H, 4.00. Found: C, 61.27; H, 4.18.

Synthesis of [2,6-(^tBu₂PO)₂C₆H₃]Ni(NCS) (**2aa**)

A mixture of [2,6-(^tBu₂PO)₂C₆H₃]NiCl (**1aa**) (492 mg, 1.0 mmol) and KSCN (486 mg, 5.0 mmol) in THF (20 mL) was stirred in a sealed flask at room temperature for 5 d. The volatiles were removed under vacuum and the residue was extracted with toluene and then filtered through a pad of Celite. Removal of toluene under vacuum produced **2aa** as an orange solid (452 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃, δ): 6.94 (t, *J*_{H-H} = 8.0 Hz, ArH, 1H), 6.41 (d, *J*_{H-H} = 8.0 Hz, ArH, 2H), 1.46 (t, *J*_{P-H} = 7.6 Hz, CH₃, 36H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.89 (t, *J*_{P-C} = 9.1 Hz, ArC), 146.87 (s, NCS), 129.31 (s, ArC), 124.70 (t, *J*_{P-C} = 20.0 Hz, ArC), 105.42 (t, *J*_{P-C} = 6.1 Hz, ArC), 39.21 (t, *J*_{P-C} = 7.5 Hz, C(CH₃)₃), 27.88 (t, *J*_{P-C} = 3.0 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 193.94 (s). FTIR (KBr): ν_{CN} = 2104 cm⁻¹. Anal. Calcd for C₂₃H₃₉NO₂P₂SNi: C, 53.72; H, 7.64; N, 2.72. Found: C, 53.53; H, 7.54; N, 2.86.

Alternatively, a mixture of [2,6-(^tBu₂PO)₂C₆H₃]NiCl (**1aa**) (492 mg, 1 mmol) and KSCN (486 mg, 5 mmol) in THF (20 mL) was refluxed under an nitrogen atmosphere for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was extracted with toluene and then filtered through a pad of Celite. Removal of toluene under vacuum followed by recrystallization in CH₂Cl₂/*n*-hexane produced **2aa** as orange crystals (318 mg, 62% yield).

Synthesis of [2,6-(^tPr₂PO)₂C₆H₃]Ni(NCS) (**2ab**)

Complex **2ab** was prepared from **1ab** and KSCN in 93% (room temperature) or 78% (under refluxing) yield by procedures similar to those used for **2aa**. ¹H NMR (400 MHz, CDCl₃, δ): 6.94 (t, *J*_{H-H} = 8.0 Hz, ArH, 1H), 6.39 (d, *J*_{H-H} = 8.0 Hz, ArH, 2H), 2.35-2.41 (m, CH(CH₃)₂, 4H), 1.28-1.42 (m, CH(CH₃)₂, 24H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.06 (t, *J*_{P-C} = 9.8 Hz, ArC), 146.27 (s, NCS), 129.74 (s, ArC), 124.22 (t, *J*_{P-C} = 21.3 Hz, ArC), 105.57 (t, *J*_{P-C} = 6.0 Hz, ArC), 28.17 (t, *J*_{C-P} = 11.3 Hz, CH(CH₃)₂), 17.45 (t, *J*_{C-P} = 3.0 Hz, CH(CH₃)₂), 16.82 (s, CH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 188.57 (s). FTIR (KBr): ν_{CN} = 2091 cm⁻¹. Anal. Calcd for C₁₉H₃₁NO₂P₂SNi: C, 49.81; H, 6.82; N, 3.06. Found: C, 49.85; H, 6.68; N, 3.06.

*Synthesis of [2,6-(Ph₂PO)₂C₆H₃]Ni(NCS) (**2ac**)*

Complex **2ac** was prepared from **1ac** and KSCN in 91% (room temperature) or 75% (under refluxing) yield by procedures similar to those used for **2aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.86-7.89 (m, ArH, 8H), 7.51-7.55 (m, ArH, 12H), 7.11 (t, *J*_{H-H} = 8.0 Hz, ArH, 1H), 6.65 (d, *J*_{H-H} = 8.0 Hz, ArH, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 167.51 (t, *J*_{P-C} = 11.3 Hz, ArC), 145.69 (s, NCS), 132.37 (s, ArC), 131.81 (t, *J*_{P-C} = 24.8 Hz, ArC), 131.55 (t, *J*_{P-C} = 7.5 Hz, ArC), 130.65 (s, ArC), 129.29 (t, *J*_{P-C} = 5.2 Hz, ArC), 125.13 (t, *J*_{P-C} = 23.9 Hz, ArC), 107.01 (t, *J*_{P-C} = 7.0 Hz, ArC). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 144.59 (s). FTIR (KBr): ν_{CN} = 2072 cm⁻¹. Anal. Calcd for C₃₁H₂₃NO₂P₂SNi: C, 62.66; H, 3.90; N, 2.36. Found: C, 62.38; H, 4.12; N, 2.40.

*Synthesis of [4-CO₂Me-2,6-(^tBu₂PO)₂C₆H₂]Ni(NCS) (**2ba**)*

Complex **2ba** was prepared from **1ba** and KSCN in 86% (room temperature) or 65% (under refluxing) yield by procedures similar to those used for **2aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.07 (s, ArH, 2H), 3.85 (s, OCH₃, 3H), 1.45 (t, *J*_{P-H} = 7.2 Hz, C(CH₃)₃, 36H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.53 (t, *J*_{P-C} = 9.1 Hz, ArC), 166.78 (s, CO₂CH₃), 147.65 (s, NCS), 133.16 (t, *J*_{P-C} = 20.2 Hz, ArC), 131.52 (s, ArC), 106.39 (t, *J*_{P-C} = 6.1 Hz, ArC), 52.22 (s, CO₂CH₃), 39.42 (t, *J*_{P-C} = 7.1 Hz, C(CH₃)₃), 27.79 (t, *J*_{P-C} = 3.0 Hz, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 195.18 (s). FTIR (KBr): ν_{CN} = 2098 cm⁻¹. Anal. Calcd for C₂₅H₄₁NO₄P₂SNi: C, 52.47; H, 7.22; N, 2.45. Found: C, 52.37; H, 7.23; N, 2.45.

*Synthesis of [4-CO₂Me-2,6-(ⁱPr₂PO)₂C₆H₂]Ni(NCS) (**2bb**)*

Complex **2bb** was prepared from **1bb** and KSCN in 93% (room temperature) or 78% (under refluxing) yield by procedures similar to those used for **2aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.08 (s, ArH, 2H), 3.85 (s, OCH₃, 3H), 2.39-2.47 (m, CH(CH₃)₂, 4H), 1.30-1.44 (m, CH(CH₃)₂, 24H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 168.80 (t, *J*_{P-C} = 10.1 Hz, ArC), 166.62 (s, CO₂CH₃), 147.11 (s, NCS), 132.58 (t, *J*_{P-C} = 20.2 Hz, ArC), 131.93 (s, ArC), 106.58 (t, *J*_{P-C} = 7.1 Hz, ArC), 52.23 (s, CO₂CH₃),

28.31 (t, $J_{\text{P-C}} = 12.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 17.41 (t, $J_{\text{C-P}} = 3.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 16.80 (s, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ): 189.85 (s). FTIR (KBr): $\nu_{\text{CN}} = 2082\text{ cm}^{-1}$, $\nu_{\text{CO}} = 1721\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{NO}_4\text{P}_2\text{SNi}$: C, 48.86; H, 6.44; N, 2.71. Found: C, 48.88; H, 6.44; N, 2.72.

*Synthesis of [4-CO₂Me-2,6-(Ph₂PO)₂C₆H₂]Ni(NCS) (**2bc**)*

Complex **2bc** was prepared from **1bc** and KSCN in 90% (room temperature) or 65% (under refluxing) yield by procedures similar to those used for **2aa**. ^1H NMR (400 MHz, CDCl_3 , δ): 7.83-7.88 (m, ArH, 8H), 7.51-7.60 (m, ArH, 12H), 7.28 (s, ArH, 2H), 3.87 (s, OCH_3 , 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , δ): 167.17 (t, $J_{\text{P-C}} = 11.1$ Hz, ArC), 166.34 (s, CO_2CH_3), 146.33 (s, NCS), 133.27 (t, $J_{\text{P-C}} = 23.2$ Hz, ArC), 132.69 (s, ArC), 132.58 (s, ArC), 131.51 (t, $J_{\text{P-C}} = 7.1$ Hz, ArC), 131.35 (t, $J_{\text{P-C}} = 25.3$ Hz, ArC), 129.38 (t, $J_{\text{P-C}} = 5.1$ Hz, ArC), 107.89 (t, $J_{\text{P-C}} = 8.1$ Hz, ArC), 52.37 (s, CO_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ): 145.02 (s). FTIR (KBr): $\nu_{\text{CN}} = 2071\text{ cm}^{-1}$, $\nu_{\text{CO}} = 1715\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}_4\text{P}_2\text{SNi}$: C, 60.77; H, 3.86; N, 2.15. Found: C, 60.43; H, 3.94; N, 2.12.

*Synthesis of [2,6-(^tBu₂PO)₂C₆H₃]NiN₃ (**3aa**)*

A mixture of $[2,6-(^t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiCl}$ (**1aa**) (492 mg, 1 mmol), NaN_3 (325 mg, 5 mmol), THF (10 mL) and MeOH (10 mL) was stirred in a sealed flask at room temperature for 5 d. The volatiles were removed under vacuum and the residue was extracted with toluene and then filtered through a pad of Celite. Removal of toluene under vacuum produced **3aa** as an orange solid (451 mg, 91% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 6.92 (t, $J_{\text{H-H}} = 8.0$ Hz, ArH, 1H), 6.38 (d, $J_{\text{H-H}} = 8.0$ Hz, ArH, 2H), 1.46 (t, $J_{\text{P-H}} = 8.0$ Hz, CH_3 , 36H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , δ): 169.79 (t, $J_{\text{P-C}} = 9.6$ Hz, ArC), 128.77 (s, ArC), 123.86 (t, $J_{\text{P-C}} = 20.2$ Hz, ArC), 105.24 (t, $J_{\text{P-C}} = 5.9$ Hz, ArC), 38.94 (t, $J_{\text{P-C}} = 7.2$ Hz, $\text{C}(\text{CH}_3)_3$), 27.83 (t, $J_{\text{P-C}} = 3.0$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ): 189.85. FTIR (KBr): $\nu_{\text{N}_3} = 2072\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{N}_3\text{O}_2\text{P}_2\text{Ni}$: C, 53.04; H, 7.89; N, 8.43. Found: C, 53.17; H, 7.93. N, 8.39.

Alternatively, a mixture of $[2,6-(^t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{NiCl}$ (**1aa**) (492 mg, 1 mmol),

NaN₃ (325 mg, 5 mmol), THF (10 mL) and methanol (10 mL) was refluxed under a nitrogen atmosphere for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was extracted with toluene and then filtered through a pad of Celite. Removal of toluene under vacuum followed by recrystallization in CH₂Cl₂/*n*-hexane produced **3aa** as orange crystals (348 mg, 70% yield).

*Synthesis of [2,6-(ⁱPr₂PO)₂C₆H₃]NiN₃ (**3ab**)*

Complex **3ab** was prepared from **1ab** and NaN₃ in 89% (room temperature) or 78% (under refluxing) yield by procedures similar to those used for **3aa**. ¹H NMR (400 MHz, CDCl₃, δ): 6.94 (t, *J*_{H-H} = 8.0 Hz, ArH, 1H), 6.39 (d, *J*_{H-H} = 8.0 Hz, ArH, 2H), 2.36-2.43 (m, CH(CH₃)₂, 4H), 1.31-1.45 (m, CH(CH₃)₂, 24H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 168.85 (t, *J*_{P-C} = 10.1 Hz, ArC), 129.11 (s, ArC), 124.44 (t, *J*_{P-C} = 20.2 Hz, ArC), 105.42 (t, *J*_{P-C} = 6.1 Hz, ArC), 27.96 (t, *J*_{C-P} = 10.1 Hz, CH(CH₃)₂), 17.33 (t, *J*_{C-P} = 4.0 Hz, CH(CH₃)₂), 16.82 (s, CH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 185.17 (s). FTIR (KBr): ν_{N3} = 2053 cm⁻¹. Anal. Calcd for C₁₈H₃₁N₃O₂P₂Ni: C, 48.90; H, 7.07; N, 9.50. Found: C, 48.73; H, 7.05; N, 9.40.

*Synthesis of [2,6-(Ph₂PO)₂C₆H₃]NiN₃ (**3ac**)*

Complex **3ac** was prepared from **1ac** and NaN₃ in 88% (room temperature) or 60% (under refluxing) yield by procedures similar to those used for **3aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.88-7.92 (m, ArH, 8H), 7.49-7.57 (m, ArH, 12H), 7.07 (t, *J*_{H-H} = 8.0 Hz, ArH, 1H), 6.60 (d, *J*_{H-H} = 8.0 Hz, ArH, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 167.26 (t, *J*_{P-C} = 11.4 Hz, ArC), 132.23 (s, ArC), 132.13 (t, *J*_{P-C} = 23.8 Hz, ArC), 131.76 (t, *J*_{P-C} = 8.0 Hz, ArC), 130.00 (s, ArC), 129.16 (t, *J*_{P-C} = 5.6 Hz, ArC), 125.37 (t, *J*_{P-C} = 24.4 Hz, ArC), 106.81 (t, *J*_{P-C} = 7.2 Hz, ArC). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 142.47 (s). FTIR (KBr): ν_{N3} = 2048 cm⁻¹. Anal. Calcd for C₃₀H₂₃N₃O₂P₂Ni: C, 62.32; H, 4.01; N, 7.27. Found: C, 62.56; H, 3.98; N, 7.46.

*Synthesis of [4-CO₂Me-2,6-(^tBu₂PO)₂C₆H₂]NiN₃ (**3ba**)*

Complex **3ba** was prepared from **1ba** and NaN₃ in 90% (room temperature) or 60% (under refluxing) yield by procedures similar to those used for **3aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.05 (s, ArH, 2H), 3.85 (s, OCH₃, 3H), 1.46 (t, *J*_{P-H} = 7.2 Hz, C(CH₃)₃, 36H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.46 (t, *J*_{P-C} = 10.1 Hz, ArC), 166.97 (s, CO₂CH₃), 132.85 (t, *J*_{P-C} = 20.2 Hz, ArC), 131.03 (s, ArC), 106.23 (t, *J*_{P-C} = 5.9 Hz, ArC), 52.18 (s, CO₂CH₃), 39.20 (t, *J*_{P-C} = 7.1 Hz, C(CH₃)₃), 27.76 (t, *J*_{P-C} = 3.0 Hz, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 191.13 (s). FTIR (KBr): ν_{N3} = 2073 cm⁻¹, ν_{CO} = 1719 cm⁻¹. Anal. Calcd for C₂₄H₄₁N₃O₄P₂Ni: C, 51.82; H, 7.43; N, 7.55. Found: C, 51.98; H, 7.53; N, 7.46.

*Synthesis of [4-CO₂Me-2,6-(ⁱPr₂PO)₂C₆H₂]NiN₃ (**3bb**)*

Complex **3bb** was prepared from **1bb** and NaN₃ in 92% (room temperature) or 60% (under refluxing) yield by procedures similar to those used for **3aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.06 (s, ArH, 2H), 3.85 (s, OCH₃, 3H), 2.38-2.45 (m, CH(CH₃)₂, 4H), 1.30-1.45 (m, CH(CH₃)₂, 24H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 168.52 (t, *J*_{P-C} = 10.1 Hz, ArC), 166.84 (s, CO₂CH₃), 133.25 (t, *J*_{P-C} = 21.2 Hz, ArC), 131.28 (s, ArC), 106.40 (t, *J*_{P-C} = 6.1 Hz, ArC), 52.18 (s, CO₂CH₃), 28.04 (t, *J*_{P-C} = 11.1 Hz, CH(CH₃)₂), 17.25 (t, *J*_{C-P} = 3.0 Hz, CH(CH₃)₂), 16.75 (s, CH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 186.56 (s). FTIR (KBr): ν_{N3} = 2047 cm⁻¹, ν_{CO} = 1715 cm⁻¹. Anal. Calcd for C₂₀H₃₃N₃O₄P₂Ni: C, 48.03; H, 6.65; N, 8.40. Found: C, 48.04; H, 6.67; N, 8.35.

*Synthesis of [4-CO₂Me-2,6-(Ph₂PO)₂C₆H₂]NiN₃ (**3bc**)*

Complex **3bc** was prepared from **1bc** and NaN₃ in 91% (room temperature) or 60% (under refluxing) yield by procedures similar to those used for **3aa**. ¹H NMR (400 MHz, CDCl₃, δ): 7.96-8.01 (m, ArH, 8H), 7.46-7.55 (m, ArH, 12H), 7.28 (s, ArH, 2H), 3.87 (s, OCH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 166.93 (t, *J*_{P-C} = 11.1 Hz, ArC), 166.57 (s, CO₂CH₃), 133.96 (t, *J*_{P-C} = 22.2 Hz, ArC), 132.42 (s, ArC), 131.92 (s, ArC), 131.73 (t, *J*_{P-C} = 8.1 Hz, ArC), 131.73 (t, *J*_{P-C} = 24.2 Hz, ArC),

129.24 (t, $J_{\text{P-C}} = 5.1$ Hz, ArC), 107.71 (t, $J_{\text{P-C}} = 7.1$ Hz, ArC), 52.31 (s, CO_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ): 143.09 (s). FTIR (KBr): $\nu_{\text{N}_3} = 2049$ cm^{-1} , $\nu_{\text{CO}} = 1716$ cm^{-1} . Anal. Calcd for $\text{C}_{32}\text{H}_{25}\text{N}_3\text{O}_4\text{P}_2\text{Ni}$: C, 60.41; H, 3.96; N, 6.60. Found: C, 60.57; H, 3.93; N, 6.65.

Comparative study of the reactions of [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl with KSCN or NaN₃

In a 25 mL flask, 0.10 mmol of potassium thiocyanate or sodium azide was mixed with 3 mL of THF. The mixture was stirred at 0°C for 10 min, followed by the addition of a [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl (R = ^tBu, ⁱPr, Ph; Z = H, CO₂Me) solution (0.10 mmol) in 3 mL of THF. The resulting reaction mixture was further stirred at 0°C for 5 min, after which 15 mL of water was quickly added with stirring. The precipitate was collected by filtration, dried and analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR. The ratio between [4-Z-2,6-(R₂PO)₂C₆H₂]NiCl and [4-Z-2,6-(R₂PO)₂C₆H₂]NiNCS or [4-Z-2,6-(R₂PO)₂C₆H₂]NiN₃ was determined based on $^{31}\text{P}\{^1\text{H}\}$ NMR integrations, from which the conversion was calculated.

Equilibrium constant measurement for the isothiocyanate/azide exchange reactions

The exchange reactions were carried out at room temperature (T = 298 K) in sealed NMR tubes using CDCl_3 as the solvent. The reactions were monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Three individual experiments were carried out for any given exchange reaction. As a representative example, for the exchange reaction of **3aa** + **2ba** $\rightleftharpoons$ **2aa** + **3ba**, the three experiments were: (1) 5 mg of **3aa** and 5 mg of **2ba** were mixed with 0.5 mL of CDCl_3 in a NMR tube; (2) 5 mg of **2aa** and 5 mg of **3ba** were mixed with 0.5 mL of CDCl_3 in a NMR tube; (3) 2-3 mg of **3aa**, 2-3 mg of **2ba**, 2-3 mg of **2aa** and 2-3 mg of **3ba** were mixed with 0.5 mL of CDCl_3 in a NMR tube. The NMR tubes were then sealed and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded every 8 h. The equilibrium was considered to be established when the ratios of the NMR integration values were unchanged. Each reported equilibrium constant was the average of the values from the three experiments.

Quantum chemical analysis

A quantum chemical analysis for the coordinating nitrogen atoms of SCN^- and N_3^- was performed. The ground-state geometries were optimized by the second-order Møller-Plesset perturbation (MP2) method using the 6-311++G (d, p) basis set. Condensed values of local reactivity descriptors, described by conceptual density functional theory (CDFT) [15] were calculated according to the literature procedure [16]. The charges were obtained from the NPA population analysis. All calculations were carried out using the Gaussian 09 software package [17].

X-ray structure determinations

Single crystals of the nickel isothiocyanate and azide complexes were obtained from recrystallization in $\text{CH}_2\text{Cl}_2/n$ -hexane. Single crystals of **1ba** were grown from CH_2Cl_2 . Crystal data collection and refinement parameters of **2aa**, **2bb**, **3ac** and **3ba** are summarized in Table 8. The data for the remaining nickel complexes can be found in Supplementary data (Appendix B). Intensity data were collected at 103 K for **2aa**, **2ba**, **2bb**, **2bc**, **3aa**, **3ba**, **3bb** and **3bc**, and 296 K for **2ab** and **3ac** on a Bruker SMART6000 CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$. Intensity data of **2ac** were collected at 150 K for on a Bruker SMART6000 CCD diffractometer using graphite-monochromated $\text{CuK}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$. Intensity data of **1ba** were collected at 150 K on a Bruker PHOTO100 CMOS detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.7749 \text{ \AA}$. The frames were integrated with the Bruker APEX2 software package using a narrow-frame algorithm. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. Two independent molecules of **1bc** crystallize in the lattice. Disorder is

observed for some of the carbon atoms of the ^tBu groups of **1bc** and the nitrogen atoms of the N₃ group of **3aa**; for **1bc** a two-component disorder models is presented for C10B/C and C14B/C, and for **3aa** a two-component model with 85:15 occupancy is given. No solvent of crystallization is present in the lattice for any of the structures.

Table 8

Summary of crystallographic data and structure refinement for representative nickel complexes

	2aa	2bb	3ac	3ba
Empirical formula	C ₂₃ H ₃₉ NNiO ₂ P ₂ S	C ₂₁ H ₃₃ NNiO ₄ P ₂ S	C ₃₀ H ₂₃ N ₃ NiO ₂ P ₂	C ₂₄ H ₄₁ N ₃ NiO ₄ P ₂
Formula weight	514.26	516.19	578.14	556.25
Temp, K	103(2)	103(2)	296(2)	103(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P -1	Pca2 ₁	P2 ₁ 2 ₁ 2 ₁	Pca2 ₁
<i>a</i> , Å	8.3477(10)	22.3789(10)	9.290(2)	25.048(2)
<i>b</i> , Å	12.0771(14)	7.9931(4)	14.067(3)	8.6616(8)
<i>c</i> , Å	13.5837(16)	14.1551(6)	19.763(4)	12.8253(7)
<i>α</i> (°)	102.639(2)	90.00	90.00	90.00
<i>β</i> (°)	93.182(3)	90.00	90.00	90.00
<i>γ</i> (°)	103.943(2)	90.00	90.00	90.00
Volume, Å ³	1288.4(3)	2532.0(2)	2582.8(10)	2782.5(4)
<i>Z</i>	2	4	4	4
<i>d</i> _{calc} , g cm ⁻³	1.326	1.354	1.487	1.328
<i>λ</i> , Å	0.71073	0.71073	0.71073	0.71073
<i>μ</i> , mm ⁻¹	0.977	1.001	0.910	0.845
No. of data collected	49168	23360	23478	23633
No. of unique data	13206	7884	5960	7688
<i>R</i> _{int}	0.1101	0.0686	0.0489	0.1216
Goodness-of-fit on <i>F</i> ²	0.977	0.833	1.059	0.986
<i>R</i> ₁ , w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0597, 0.1219	0.0385, 0.0616	0.0390, 0.0988	0.0627, 0.1100
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.1208, 0.1483	0.0479, 0.0643	0.0432, 0.1051	0.1017, 0.1270

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Appendix A. Supplementary material

CCDC 1404255 (**1ba**), 1404256 (**2ac**), 1034585 (**2ab**), 1034586 (**2bb**), 1034587 (**3ac**), 1404901 (**2ba**), 1404902 (**2bc**), 1404903 (**3aa**), 1404904 (**3ba**), 1404905 (**3bc**), 1404906 (**2aa**) and 1404907 (**3bb**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Summary of crystallographic data and structure refinement results, ORTEP drawings, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters. These data can be found at <http://dx.doi.org/10.1016/j.jorganchem.xxxx.xx.xxx>.

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