



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]₂NiX (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]₂NiCl 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]₂NiCl 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 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 N₃[−].

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1. 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], CO₂ [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 [4-Z-2,6-(R₂PO)₂C₆H₂]₂NiX (Z = H, CO₂Me; R = ^tBu, ⁱPr, Ph; X = Cl, NCS, N₃). 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.

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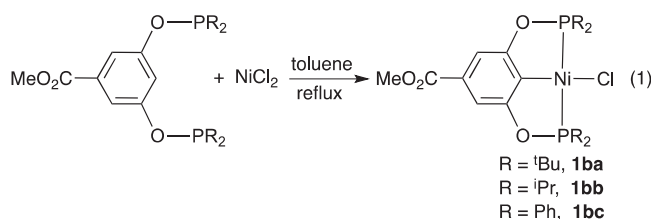
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2. Results and discussion

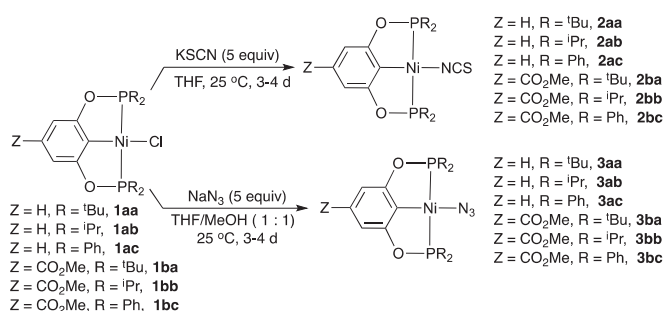
2.1. Synthesis and structure of nickel pincer complexes

Following previously reported procedures for the synthesis of [2,6-(^tBu₂PO)₂C₆H₃]₂NiCl (**1aa**) [8a], [2,6-(ⁱPr₂PO)₂C₆H₃]₂NiCl (**1ab**) [6c] and [2,6-(Ph₂PO)₂C₆H₃]₂NiCl (**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



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

Table 1
CN stretching or N₃ asymmetric stretching frequencies of [4-Z-2,6-(R₂PO)₂C₆H₂]₂NiX 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)

trimethylsiloxide complex with Me₃SiN₃ [7m]. Related nickel azide complexes bearing a POC_{sp}OP-pincer ligand [7m] or a PCP-pincer ligand [11] were prepared in a similar fashion using Me₃SiN₃.

To accelerate the substitution of the chloride ligand in complex **1** by SCN⁻ and N₃⁻, 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 CH₂Cl₂/*n*-hexane) was exposed to air for a few weeks.

The new nickel isothiocyanate and azide complexes were fully characterized by multinuclear NMR, FTIR, X-ray crystallography and elemental analysis. Notable features of the ¹³C{¹H} NMR spectra included the *ipso* carbons appearing as triplets (²J_{p-c} = 20–25 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. CO₂Me). The electron-withdrawing ester group makes the *ipso* carbons more deshielded, leading to a downfield shift of 6–9 ppm. All ³¹P{¹H} 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_{N₃} 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_{N₃} 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**).

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 Figs. 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

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