Exploring the Coordination Chemistry of *N*-Heterocyclic Phosphenium/Phosphido Ligands

Using Nickelocene as a Synthron

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ABSTRACT. Treatment of the *N*-heterocyclic chlorophosphine precursor (PPP)Cl (**1**) with two equivalents of nickelocene (NiCp₂) affords the phosphorus-bridged dimer [(μ-PPP)Ni₂Cp₂]Cl (**2**). In contrast, an equimolar mixture of **1** and NiCp₂ in the presence of PPh₃ generates a different product, (PP(C₅H₅)P)NiCl₂ (**3**), in which a cyclopentadienyl anion has migrated to the *N*-heterocyclic phosphenium center. The phosphorus-bound Cp ring in complex **3** has undergone a [1,5]-hydride shift to afford a vinylic C₅H₅[−] ring, and can be subsequently deprotonated to produce [(PP(C₅H₄)P)NiCl] (**4**).

KEYWORDS: cyclopentadienyl, nickel compounds, *N*-heterocyclic phosphenium cation, pincer ligands

1. Introduction.

Cyclopentadienyl (Cp) ligands are pervasive in organometallic chemistry and, while the η^5 coordination mode is by far the most common, Cp ligands can also adopt η^1 and η^3 binding modes using a combination of both σ and π donation. The coordination of cyclopentadienyl fragments to main group elements has also been studied extensively, revealing a variety of binding modes, rearrangements, and fluxional processes.[1-6] In particular, when R_2P fragments bind to Cp in an η^1 fashion, they can undergo two types of sigmatropic rearrangements (Scheme 1).[2, 7-9] The R_2P -Cp compound can either undergo a [1,5]-hydrogen shift, resulting in a vinylic isomer (**B**), or the R_2P fragment of the allylic isomer (**A**) can migrate about the Cp ring via a so-called "circumambulatory rearrangement" (**A** to **A'**). In the case of $uNHP^{Ar}$ -Cp compounds (NHP = an *N*-heterocyclic phosphonium cation, where "*u*" denotes an unsaturated backbone and "*Ar*" is used to denote *N*-aryl substituents), only the allylic isomer **A** is observed. The accelerated [1,5] migration of the NHP fragment in comparison to its acyclic counterparts has been attributed to the stabilization of the NHP^+ fragment, favoring the ionic resonance form **C** and precluding the formation of the vinylic isomer **B** (Scheme 1).[7]

Scheme 1. Sigmatropic rearrangements observed for R_2P -Cp compounds.

Gudat *et al.* demonstrated that $uNHP^{Mes}$ -Cp (Mes = 2,4,6-trimethylphenyl) can transfer the Cp ring to a transition metal upon addition of $(CO)_5MnBr$ and $FeCl_2$, generating $CpMn(CO)_3$ and Cp_2Fe along with the corresponding halophosphine compounds $uNHP^{Mes}-X$ ($X = Br$ or Cl).^[7] Notably, the reverse reaction in which a Cp^- anion migrates from a transition metal center to a bound NHP^+ phosphonium ligand has not been observed among the numerous reports of cyclopentadienyl-bound transition metal compounds with coordinated NHP^+ ligands.^[10-14]

By incorporating an *N*-heterocyclic phosphonium unit into a diphosphine tridentate ligand framework and subsequently coordinating the ligand to late transition metals (Co, Ni, Pd and Pt), our group has been able to demonstrate the versatility of NHP ligands.[15-18] The NHP fragment of the tridentate NHP-diphosphine ligand has been shown to adopt a terminal phosphido (NHP⁻) binding mode when bound to late transition metals, in addition to adopting bridging phosphido (NHP⁻) and semi-bridging planar phosphonium (NHP⁺) binding modes. Many of the bonding modes and coordination geometries adopted by the NHP fragment in the NHP diphosphine ligand lie in stark contrast to monodentate NHP⁺-containing ligands, suggesting a unique electronic structure imparted by the rigid geometry of the pincer ligand framework. Herein, we report a series of coordination complexes of the NHP-diphosphine pincer ligand derived from nickelocene (NiCp₂), uncovering the first example of Cp⁻ migration from a metal to a bound NHP ligand.

2. Results and Discussion

Previously, we found that treatment of the chlorophosphine (PPP)Cl precursor **1** with group 10 metal(0) precursors such as Ni(COD)₂, Pd(PPh₃)₄ or Pt(PPh₃)₄ affords neutral four coordinate metal complexes, (PPP)MCl (M = Ni, Pd and Pt), in which the P–Cl bond has been cleaved.[17, 18] In each case, the central phosphorus atom of the heterocycle (P^{NHP}) adopts a pyramidal geometry, indicating the presence of a stereochemically active lone pair. Combined with the distorted square planar geometries about the metal centers, the (PPP)MCl compounds have been assigned as NHP⁻/M^{II} complexes resulting from oxidative addition of the P-Cl bond across the metal center. Since nickelocene (NiCp₂) is often considered to be a masked Ni⁰ source,[19, 20] we posited that NiCp₂ may be a suitable precursor for the synthesis of (PPP)NiCl. However, stoichiometric treatment of **1** with NiCp₂ afforded a mixture of products that did not contain

(PPP)NiCl. When **1** was instead combined with 2.2 equivalents of NiCp₂, a single product was isolated and identified as [(μ-PPP)Ni₂Cp₂]Cl (**2**, Scheme 2). The ³¹P{¹H} NMR spectrum of the deep purple crystals of **2** features a downfield triplet at 250.0 ppm and an upfield doublet at 27.4 ppm with relatively small coupling between the two phosphorus atoms (*J*_{P-P} = 52 Hz), indicating a symmetric structure in which both phosphine sidearms are bound to nickel.

Scheme 2. Synthesis of [(μ-PPP)Ni₂Cp₂]Cl (**2**).

Figure 1: Displacement ellipsoid (50%) representation of **2**. For clarity, the outer sphere chloride anion, all hydrogen atoms, and solvate molecules have been omitted. Relevant interatomic distances (Å): P2–Ni1, 2.1435(8); P2–Ni2, 2.1398(8); Ni1–P1, 2.1322(9); Ni2–P3, 2.1319(8); Ni1–Ni2, 3.5068(6).

The structure of **2** was elucidated by single crystal X-ray diffraction, confirming that the ligand symmetrically bridges two Ni centers with one phosphine sidearm bound to each metal (Figure 1). Each Ni center remains bound to an η⁵-Cp ligand and there is one additional outer sphere chloride counteranion per molecule in the asymmetric unit. A similar symmetrical bridging mode was previously observed in a series of group 10 NHP-bridged complexes

(PPP)₂M₂,[18, 21] but **2** is the first example of a single PPP ligand bridging two metal centers. The distances between the two Ni centers and the central NHP phosphorus atom (P^{NHP}) are nearly identical (2.1435(8) Å and 2.1398(8) Å) and are similar to the Ni-P^{NHP} distances in (PPP)₂Ni₂ (2.1191(8) Å), which was assigned as a Ni^I/Ni^I dimer bridged by two NHP⁻ phosphido ligands.[18] Given the symmetric nature of **2**, we assign this compound as an NHP⁻ phosphido-bridged Ni^{II}/Ni^{II} dimer in which the NHP⁺ phosphonium unit present in the precursor **1** has been reduced by two electrons. Previously, phosphido formation has been accompanied by a metal-based formal oxidation; however, in this case the source of the two electrons is presumably oxidative coupling of the two Cp ligands to form a C₁₀H₁₀ product such as 1,1'-dihydrofulvalene.[22]

Scheme 3. Synthesis of (PP(C₅H₅)P)NiCl₂ (**3**)

The addition of phosphines to NiCp₂ has been shown to promote the extrusion of Cp radicals, resulting in the formation of Ni^ICp(PR₃)₂ or Ni⁰(PR₃)₄ compounds.[19, 23-25] Thus, we added PPh₃ to the stoichiometric reaction of **1** with NiCp₂, resulting in the isolation of a single product identified as (PP(C₅H₅)P)NiCl₂ (**3**, Scheme 3). The ³¹P{¹H} NMR spectrum of **2** displays a triplet at 98.1 ppm corresponding to the P^{NHP} atom and a doublet corresponding to the phosphine sidearms at 1.3 ppm (²J_{P-P} = 105 Hz). The significant upfield shift of the P^{NHP} signal in the ³¹P{¹H} NMR spectrum compared to **2** suggests that a Cp ring has migrated to the P^{NHP} atom, since similar upfield shifts have been reported upon migration of aryl groups to the P^{NHP} atom of a metal-bound (PPP)⁺ ligand.[26] This is also supported by the loss of symmetry at the

Cp ring: Four signals that correspond to the protons on the cyclopentadienyl-derived ring are observed in the ^1H NMR spectrum at 6.27 (1H), 5.63 (1H), 5.56 (1H) and 2.59 (2H) ppm. The 1:1:1:2 integral ratio of these proton signals, as well as the upfield-shifted resonance at 2.59 ppm, are characteristic of an η^1 -bound $\text{P}-\text{C}_5\text{H}_5$ vinylic isomer in which the Cp ring has undergone a [1,5]-hydride shift upon migration to phosphorus.

Figure 2: Displacement ellipsoid (50%) representation of **3**. For clarity solvate molecules and all hydrogen atoms except for those bound to the C_5H_5 ring have been omitted. Relevant interatomic distances (Å): P2–Ni1, 2.0856(4); Ni1–P1, 2.1976(4); Ni1–P3, 2.1980(4); Ni1–Cl1, 2.5396(5); Ni1–Cl2, 2.2299(4); P2–C39, 1.779(2); C39–C40, 1.504(3); C40–C41, 1.490(3); C41–C42, 1.342(3); C42–C43, 1.464(2); C43–C39, 1.347(3).

The structure of **3** was confirmed by single crystal X-ray diffraction, revealing a C_5H_5 ring bound η^1 to the P^{NHP} atom and two halides bound to the nickel center (Figure 2). The C_5H_5 ring exhibits shorter C–C bonds between the carbons in the [1, 2] and [3, 4] positions (C39–C43 = 1.347(3) Å and C41–C42 = 1.342(3) Å) compared to those between the carbons in the [2, 3], [4, 5] and [1, 5] positions (C43–C42 = 1.464(2) Å; C41–C40 = 1.490(3) Å; C40–C39 = 1.504(3) Å). Furthermore, upon inspection of the crystal structure, two hydrogen atoms were located at the C5 position of the 5-membered ring (C40) in the electron-density difference map and their

positions were refined. The P^{NHP} -Ni bond distance of 2.0856(4) Å is significantly shorter than in any other structurally characterized (NHP-R)M complex in the literature (range 2.13-2.46 Å, based on a 2016 search of the Cambridge Structural Database). While the comparatively shorter distance can be partially explained by the fact that most of the previously (NHP-R)M complexes involve larger second and third row metals, several first row complexes of this type, including the very similar (PP(Ar)P)CuCl compounds [26], have been reported and also feature longer M-P distances (2.14-2.24 Å) [27-31]. The nickel center has two bound chlorides and adopts a square pyramidal geometry; however, the apical Ni-Cl(1) bond (2.5396(5) Å) is elongated, similar to other reported five coordinate $NiCl_2$ square pyramidal compounds.[32-35]

While the origin of the second halide on the Ni center has not been firmly established, it likely originates from either adventitious CH_2Cl_2 in the reaction mixture or the CH_2Cl_2 used for extraction in the purification procedure. Consistent with this hypothesis, when CH_2Cl_2 was deliberately added to the reaction mixture, compound **3** was generated cleanly. When the reaction was carried out under conditions rigorously free of halogenated solvents, only a very small amount of compound **3** was generated (less than a 10% yield based on ^{31}P NMR integration), confirming that formation of **3** requires a sacrificial halide donor. Although no evidence for intermediates was observed by NMR spectroscopy, we speculate that PPh_3 promotes Cp radical extrusion from $NiCp_2$ to generate a Ni^I intermediate and that such a species would be active towards halogen atom abstraction from adventitious CH_2Cl_2 to return to the Ni^{II} state in $(PP(C_5H_5)P)NiCl_2$ (**3**). In support of the hypothesis that PPh_3 plays a role in displacing the η^5 -Cp ligand bound to Ni, addition of PPh_3 to dimer **2** in CH_2Cl_2 results in formation of **3**. In both cases, PPh_3 remains present in the crude reaction mixture suggesting that it is acting as a catalyst.

The existence of the Cp ring in **3** as the vinylic isomer is in stark contrast to $u\text{NHP}^{\text{Mes}}\text{-Cp}$, which exists exclusively as a highly fluxional allylic isomer in solution.[7] We attribute this difference to metal coordination, which undoubtedly destabilizes the ion pair resonance form **C** (Scheme 1). Gudat and coworkers reported the deprotonation of $u\text{NHP}^{\text{Mes}}\text{-Cp}$ using $n\text{BuLi}$ to afford the monoanionic cyclopentadienide compound $[u\text{NHP}^{\text{Mes}}\text{-C}_5\text{H}_4][\text{Li}(\text{DME})]$,[7] and we were curious to ascertain whether the vinylic species **3** could also be deprotonated and if such deprotonation would affect the binding mode of the tridentate pincer ligand.

Scheme 4.

A reaction of **3** with $\text{K}[\text{N}(\text{SiMe}_3)_2]$ in THF afforded a new diamagnetic compound $[(\text{PP}(\text{C}_5\text{H}_4)\text{P})\text{NiCl}]$ (**4**, Scheme 4). The $^{31}\text{P}\{^1\text{H}\}$ NMR resonances and $J_{\text{P-P}}$ coupling constants of **4** (103.1, 7.8 ppm; $J_{\text{P-P}} = 102$ Hz) are similar to those of **3**, suggesting that the compounds are structurally similar. However, the ^1H NMR spectrum of **4** no longer exhibits the CH_2 signal observed at 2.59 ppm in **3** and only two signals corresponding to the protons on the C_5 ring were observed, each integrating to two protons. The structure of **4** obtained using single crystal X-ray diffraction confirmed the deprotonation of the C_5H_5 ring on the central P^{NHP} atom (Figure 3). The geometry about the Ni center and the $\text{P}^{\text{NHP}}\text{-Ni}$ bond length (2.1077(6) Å) in **4** are essentially

unchanged upon deprotonation. The C₅H₄ ring exhibits shorter C–C bonds in the [2, 3] and [4, 5] positions (1.390(4) Å and 1.380(3) Å) compared to the other C–C bonds in the 5-membered ring (1.42–1.43 Å), consistent with the structural features of [*μ*NHP^{Mes}-C₅H₄][Li(DME)].^[7] The latter compound was described as a phosphine substituted by an appended cyclopentadienyl anion (analogous to resonance form **B** in Scheme 4). However, the anionic fulvalene-type resonance form (**A**) is favored for **4** given the C–C bond metrics and the contraction of the P^{NHP}–C bond in **4** compared to **3** (1.725(2) Å vs 1.779(2) Å).

Figure 3: Displacement ellipsoid (50%) representation of **4**. For clarity, solvate molecules and all hydrogen atoms except those on the C₅H₄ ring have been omitted. Relevant interatomic distances (Å): P17–Ni1, 2.1077(6); Ni1–P3, 2.2095(6); Ni1–P21, 2.1949(6); Ni1–Cl2, 2.1972(6); P17–C40, 1.725(2); C40–C41, 1.426(3); C41–C42, 1.390(4); C42–C43, 1.418(4); C43–C44, 1.380(3); C44–C40, 1.430(3).

3. Conclusions

In summary, nickelocene and an *N*-heterocyclic chlorophosphine precursor with two pendent phosphines were used to synthesize three new nickel coordination compounds. NHP-bridged Ni^{II}Cp dimer **2** was synthesized via direct reaction of (PPP)Cl with NiCp₂.

The addition of PPh_3 to the reaction mixture facilitated the migration of a C_5H_5^- ring to the P^{NHP} atom, forming **3**, in which the phosphorus-bound C_5H_5^- group has undergone a [1,5]-hydride shift to produce the vinylic isomer exclusively. The C_5H_5^- ring in **3** could be deprotonated to afford a nickel-bound $[\text{PP}(\text{C}_5\text{H}_4)\text{P}]^-$ ligand. Migration of the Cp-ring from Ni to the cationic phosphorus center of the NHP ligand is irreversible, with no evidence for preferential metal-Cp coordination even upon deprotonation..

4. Experimental

4.1 General Considerations

All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, pentane, diethyl ether, tetrahydrofuran, and toluene were degassed and dried by sparging with N_2 gas followed by passage through an activated alumina column. All solvents were stored over 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3 Å molecular sieves. The ligand precursor $(\text{PPP})\text{Cl}$ (**1**) was synthesized using literature procedures.[15] All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at ambient temperature on a Varian Inova or 400MR 400 MHz instrument. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts were referenced to residual protonated solvent. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts were referenced to 85% H_3PO_4 . For broad ^1H NMR signals, the full width at half-height (FWHH) is provided. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using

Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

4.2 Synthetic Methods

4.2.1 Synthesis of $[(\mu\text{-PPP})\text{Ni}_2\text{Cp}_2]\text{Cl}$ (2**).** A solution of NiCp_2 (72.0 mg, 0.112 mmol) in benzene (3 mL) was added to a stirring solution of **1** (46.4 mg, 0.246 mmol) in benzene (7 mL). The mixture was stirred overnight at room temperature resulting in a red/brown solution with a dark precipitate. The solids were collected via filtration and washed with diethyl ether (2 x 5 mL), followed by THF (2 x 5 mL). The solids were extracted with CH_2Cl_2 and dried under vacuum resulting in purple solids. The solids were then re-dissolved in CH_2Cl_2 , concentrated, layered with diethyl ether, and stored at -35°C for recrystallization. Yield: 21 mg, 21% yield. X-ray quality crystals were grown via slow diffusion of pentane into a concentrated CH_2Cl_2 solution of **2**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.73 (dd, 2H, $J = 8$ Hz, Ar-*H*), 7.49-7.56 (m, 12H, Ar-*H*), 7.40-7.45 (m, 4H, Ar-*H*), 7.31-7.36 (m, 4H, Ar-*H*), 7.17-7.25 (m, 4H, Ar-*H*), 7.04 (dd, 2H, $J = 8.4$ Hz, Ar-*H*), 4.91 (s, 10H, $\eta^5\text{-Cp}$), 3.17 (d, 2H, $J = 4$ Hz, CH_2), 2.58 (dd, 2H, $J = 13.4, 3.6$ Hz, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.8 MHz, CD_2Cl_2): δ 250.0 (t, 1P, $J = 52$ Hz), 27.4 (d, 2P, $J = 52$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2): δ 148.6 (dd, $J = 8.3$ Hz), 134.0 (d, $J = 13$ Hz), 133.6 (s), 132.5 (d, $J = 49$ Hz), 132.5 (d, $J = 11$ Hz), 132.1 (d, $J = 2.3$ Hz), 131.9 (d, $J = \text{Hz}$), 131.4 (br s), 130.2 (d, $J = 53$ Hz), 129.3 (d, $J = 10$ Hz), 129.2 (d, $J = 11.4$ Hz), 125.1 (d, $J = 7.6$ Hz), 123.9 (m), 122.9 (m), 94.0 (s, Cp), 49.4 (s, CH_2). Anal. Calcd for $\text{C}_{48}\text{H}_{42}\text{N}_2\text{P}_3\text{ClNi}_2$: C, 64.59; H, 4.74; N, 3.14%. Found: C, 64.42; H, 4.92; N, 3.14%. UV-vis ($(\lambda, \text{nm } (\epsilon, \text{cm}^{-1} \text{ M}^{-1}))$): 280 (4.2×10^4), 307 (3.2×10^4), 400 (1.0×10^4), 522 (1.1×10^4).

4.2.2 Synthesis of [PP(C₅H₅)P]NiCl₂ (3). NiCp₂ (13.5 mg, 0.071 mmol) and PPh₃ (19.8 mg, 0.071 mmol) were dissolved in benzene (3 mL) and stirred at room temperature for 5 minutes. This solution was then added to a clear, stirring solution of **1** (46.0 mg, 0.071 mmol) in benzene (1 mL). The reaction mixture began to turn dark red/brown after about 20 min, and was allowed to stir overnight at room temperature. The resulting red precipitate was isolated by filtration, washed with pentane (5 mL) and then extracted into CH₂Cl₂. The volatiles were removed from the resulting solution under vacuum. Yield: 24 mg, 42%. X-ray quality crystals were grown via slow diffusion of THF into a concentrated solution of **3** in CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.74 (m, 4H, Ar-*H*), 7.49-7.56 (m, 4H, Ar-*H*), 7.28-7.38 (m, 4H, Ar-*H*), 7.15-7.25 (m, 12H, Ar-*H*), 6.82-6.88 (m, 2H, Ar-*H*), 6.70 (dd, 2H, *J* = 7 Hz, Ar-*H*), 6.27 (br s, FWHH = 10.5 Hz, 1H, CH C₅H₅), 5.63 (d, 1H, *J* = 8 Hz, C⁵H C₅H₅), 5.56 (br s, FWHH = 11.1 Hz, 1H, CH C₅H₅), 4.36-4.44 (m, 2H, CH₂), 3.95-4.03 (m, 2H, CH₂), 2.59 (s, 2H, C²H₂ C₅H₅). ³¹P{¹H} NMR (161.8 MHz, CDCl₃): δ 98.1 (t, 1P, *J*_{P-P} = 103 Hz), 1.4 (d, 2P, *J*_{P-P} = 103 Hz). ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ 155.1 (m), 147.1 (br s), 141.5 (m), 137.52 (s), 134.3 (br s), 133.8 (br s), 133.6 (s), 132.2 (s), 131.9 (s), 131.8 (s), 130.5 (d, *J* = 15 Hz), 129.5 (s), 128.5 (s), 120.5 (d, *J* = 176 Hz), 48.2 (s, CH₂-backbone), 42.7 (s, CH₂-C₅H₅). Anal. Calcd for C₄₃H₃₇N₂P₃Cl₂Ni: C, 64.21; H, 4.64; N, 3.48%. Found: C, 64.25; H, 4.74; N, 3.48%. UV-vis ((λ, nm (ε, cm⁻¹ M⁻¹)): 260 (6.4x10⁴), 285 (4.8x10⁴), 395 (3.9x10³), 520 (1.6x10³).

4.2.3 Synthesis of [PP(C₅H₄)P]NiCl (4). Solid K[N(SiMe₃)₂] (2.5 mg, 0.012 mmol) was added to a dark red stirring solution of **2** (10 mg, 0.012 mmol) in THF (4 mL) at room

temperature. The reaction mixture was allowed to stir overnight to ensure a complete reaction. The reaction mixture remained red and a precipitate (KCl) was observed. The volatiles were removed under vacuum and the remaining solids were extracted into CH₂Cl₂ (5 mL) and filtered through Celite. The volatiles were removed under vacuum to give a clean product. Yield: 6 mg, 63%. X-ray quality crystals were grown via slow diffusion of pentane into a concentrated CH₂Cl₂ solution of **4**. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.69-7.74 (m, 4H, Ar-*H*), 7.41-7.49 (m, 8H, Ar-*H*), 7.33-7.39 (m, 10H, Ar-*H*), 7.07-7.09 (m, 2H, Ar-*H*), 6.82-6.86 (m, 2H, Ar-*H*), 6.76-6.81 (m, 2H, Ar-*H*), 6.22-6.25 (m, 2H, Cp), 5.83-5.86 (m, 2H, C₅H₄), 4.14-4.19 (m, 2H, CH₂), 3.49-3.54 (m, 2H, CH₂). ³¹P{¹H} NMR (161.8 MHz, CD₂Cl₂): δ 103.1 (t, 1P, *J*_{P-P} = 102 Hz), 7.8 (d, *J*_{P-P} = 102 Hz). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂): δ 149.1 (m), 136.1 (br, s), 134.8 (m), 134.7 (m), 133.5 (s), 131.3 (s), 131.1 (s), 130.9 (s), 129.1 (t), 128.8 (t), 121.9 (br), 119.2 (br), 115.2 (d, C₅H₄), 113.6 (d, C₅H₄), 46.2 (s, CH₂-backbone). Anal. Calcd for C₄₃H₃₆N₂P₃ClNi: C, 67.26; H, 4.73; N, 3.65%. Found: C, 67.18; H, 4.70; N, 3.75%. UV-vis ((λ, nm (ϕ, cm⁻¹ M⁻¹)): 280 (7.2x10⁴), 390 (4.8x10³).

4.3 X-Ray Crystallography

All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[36] Preliminary cell constants were obtained from three sets of 12 frames. Crystallographic parameters are summarized in Table 1.

Table 1: Crystallographic data collection and refinement details for **2**, **3**, and **4**.

	2•CH₂Cl₂	3•CH₂Cl₂	4•CH₂Cl₂
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chemical formula	C ₄₉ H ₄₄ Cl ₃ N ₂ Ni ₂ P ₃	C ₄₄ H ₃₉ Cl ₄ N ₂ Ni ₁ P ₃	C ₄₄ H ₃₈ Cl ₃ N ₂ Ni ₁ P ₃
fw	977.60	889.25	852.79
T (K)	120	120	120
λ (Å)	0.71073	0.71073	0.71073
a (Å)	9.9420(10)	13.6485(10)	13.2749(7)
b (Å)	13.9190(14)	13.1031(10)	29.2577(17)
c (Å)	17.8739(17)	23.0253(17)	10.2679(6)
α (°)	111.537(5)	90	90
β (°)	95.922(4)	104.956(4)	100.398(3)
γ (°)	95.606(5)	90	90
V (Å ³)	2263.8(4)	3978.3(3)	3922.5(2)
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z, Z'	2, 1	4, 1	4, 1
D _{calc} (g/cm ³)	1.434	1.485	1.444
μ (cm ⁻¹)	11.52	9.13	8.57
R1 (I > 2 σ (I)), wR2 ^a	0.0429, 0.1195	0.0299, 0.0751	0.0462, 0.1151

$$R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

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