ORGANOMETALLICS

The Synthesis and Catalytic Activity of New Mixed NHC-Phosphite Nickel(0) Complexes

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Supporting Information

ABSTRACT: Herein we describe the synthesis and isolation of the first low-valent NHC-phosphite nickel complexes of general formula Ni- $(NHC)[P(OAr)_3]_2$. These three-coordinate Ni(0) compounds were fully characterized, including by X-ray crystallography that highlighted their trigonal planar geometry. The representative complex Ni(IMes)[P- $(OPh)_{3}$ was used to show that a phosphite ligand is readily substituted in the presence of an aldehyde or nitrile. These stoichiometric studies then led to an investigation of their catalytic properties in the Suzuki-Miyaura cross-coupling reactions between aryl tosylates and aryl boronic acids, a first for such a NHC-Ni catalyst. Finally, mechanistic investigations led to the isolation of a well-defined oxidative addition product.



INTRODUCTION

Transition-metal-catalyzed cross-coupling reactions are one of the most powerful bond-forming protocols and as such are widely investigated and used in academia and industry.^{1,2} What many of the established catalytic methodologies have in common is the use of palladium as the metal source. Given the elevated price and the relative scarcity of palladium, it does not come as a surprise that intense investigations over the past two decades have been undertaken in order to establish more sustainable, earth-abundant 3d metals as alternative catalysts in these reactions. Among earth-abundant metals, nickel has emerged as a very promising alternative that is also able to offer diverse and novel reactivity in terms of electrophilic coupling reactions that can be used 3^{-10} partners that can be used.³

Contrary to palladium, where the latest generation of catalysts rely on using a single bulky ancillary ligand [L-Pd(0)]with L = bulky phosphine or N-heterocyclic carbene (NHC) ligands, nickel systems normally incorporate two ancillary ligands,^{11,12} in many cases as a combination of ligand classes with differing electronic and steric properties. Another key difference between palladium and nickel is the availability of suitably stable and low-valent precatalysts. Indeed, whereas there are commercially available and robust Pd(0) precursors, much of the early reaction development with Ni(0) relies on using $Ni(COD)_2$, an expensive, highly air-sensitive compound with a limited shelf life.¹³

In the past few years, our group has introduced homoleptic nickel(0) phosphite precatalysts as an easy to handle, stable alternative to using $Ni(COD)_2$. We have shown that these catalysts, in combination with chelating phosphine ligands (BINAP, dppf, Xantphos), provide active catalyst species that can be successfully applied to both $C-S_{1}^{14}$ and $C-N_{1}^{15-18}$

cross-coupling reactions. Other groups have also reported the effectiveness of nickel phosphine-phosphite or nickel phosphite complexes as catalysts.¹⁹⁻²² One limitation that we have noticed though is that these nickel diphosphine-phosphite or homoleptic nickel phosphite systems were sluggish as catalysts when used in some C-C bond forming reactions such as the Suzuki–Miyaura cross-coupling. To address this shortcoming, we surmised that using a monodentate NHC²³ instead of a chelating diphosphine would lead to an appropriately active catalyst system, expecting that the σ -donor character of NHC ligands and the π -acidic phosphites²⁴ would offer unique catalytic properties. Importantly, nickel(0) NHC-phosphite complexes have yet to be isolated or characterized.

Relevant examples of zerovalent tricoordinate NHC nickel complexes include those containing dimethyl fumarate²⁶ and styrene as ligands.²⁷⁻²⁹ Nickel NHC-phosphines have also recently been isolated and characterized containing threecoordinate NHC-phosphine (1:2) Ni(0) systems (Figure 1).³⁰

A catalytic mixture consisting of Ni(COD)₂, IPr (NHC) and P(OPh)₃, applied to reductive alkene/aldehyde coupling reactions, has recently been described in which a nickel NHC-phosphite (1:1) intermediate is proposed as part of the catalytic cycle.³¹ Additionally, nickel-catalyzed hydroarylation of benzothiazoles has very recently been explored with halogenated Ni(II) precursors containing P(OEt), and NHC ligands.³² If nickel(0) NHC-phosphite complexes could be isolated, their further catalytic ability could be fully explored in a range of reactions.

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Figure 1. Examples of zerovalent tricoordinate nickel NHC complexes. $^{26-30}$

Herein, we report the synthesis and characterization of the first isolable, low-valent, mixed nickel NHC-phosphite systems. We also show that these Ni(NHC)[P(OAr)₃]₂ complexes are able to catalyze Suzuki–Miyaura cross-coupling reactions of aryl halides and tosylates where examples of NHC-nickel catalysts are surprisingly rare.^{11,33–35} The precatalyst system can undergo both substitution and oxidative addition steps, elementary reaction steps that give insights into the catalytic mechanism at play.

RESULTS AND DISCUSSION

Syntheses of Nickel Complexes. When the homoleptic, nickel phosphite precursor $Ni[P(OPh)_3]_4$ was treated with 1,3bis (2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SIMes) in toluene under heating (110 °C, 40 min, Scheme 1a), bright red crystals of coordinatively unsaturated Ni-





 $(SIMes)[P(OPh)_3]_2$ (1) were collected in 79% yield. Extended stirring at this temperature led to reduced yield due to decomposition. Through a similar method, a reaction with another commonly used NHC, the unsaturated 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene (IMes) was attempted. In this case the second complex (2) was prepared, in 54% yield. Two related nickel complexes, Ni(SIMes)[P(O-o-tol)_3]_2 (3) and Ni(IMes)[P(O-o-tol)_3]_2 (4) were synthesized using the IMes and SIMes NHC ligands and the sterically bulkier tri(otolyl)phosphite ligand analogue (Scheme 1b). The more reactive unsaturated tris(tri-o-tolyl phosphite) nickel³⁶ was used as the precursor for these reactions, allowing these transformations to be carried out in less time and under slightly reduced temperatures. Through this methodology the red crystalline solids of nickel complex **3** and **4** were isolated in 67% and 57% yields, respectively.³⁰

Structural Characterization. ¹H NMR spectra of each of the four complexes (1–4) was indicative of their symmetrical nature with all *o*-methyl signals from the *N*-aryl substituents being equivalent. ³¹P NMR showed a singlet between 120 and 122 ppm for each of these complexes, a shift upfield when compared to the starting complexes Ni[P(OPh)₃]₄ and Ni[P(O-*o*-tol)₃]₃ or their free ligands.^{37,38} The ¹³C NMR spectra of each complex (1–4) contained the diagnostic resonance (Table 1) at ~222 ppm (SIMes) or ~198 ppm (IMes) indicative for the carbon (C1) of the NHC ligand bound to nickel, these values being comparable to other nickel(0) NHC complexes.³⁰ The signal was observed as a triplet with a coupling constant of 32 Hz (1 and 2) or 33 Hz (3 and 4) due to ¹³C–³¹P coupling between the carbone carbon to the phosphorus of the phosphite ligands.

The structure of complexes (1-4) was unambiguously confirmed by X-ray crystallographic analysis (Figure 2). Single crystals were grown by slow diffusion of pentane into a concentrated solution in benzene at -28 °C. Each complex was found to adopt a slightly distorted trigonal planar geometry (Table 1) with complexes 1 and 2 and complexes 3 and 4 being isostructurally similar to each other. Variations from the ideal bond angle of 120° can be observed in the interligand angles, particularly in complexes 1 and 2 where one phosphorus ligand takes a more acute angle with respect to the NHC ligand (C1–Ni1–P1 \approx 112°). Interestingly, complexes 3 and 4, containing the bulkier o-tolylphosphite ligand, vary less from the ideal bond angle. Complexes 1 and 2 exhibit a close to perpendicular orientation between the plane of the NHC and the plane set by the phosphite ligands, with a maximum deviation from 90° of $\sim 10^{\circ}$ (P2-Ni1-C1-N5 = 100.47°), while complexes 3 and 4 have a much more skewed orientation with a maximum deviation of approximately 25° $(P1-Ni1-C1-N2 = 64.91^{\circ})$. Most likely due to the steric encumbrance of the phosphite ligands, the Ni-C1 bond length was slightly longer for complexes 3 and 4 at 1.9196 and 1.9256 Å respectively versus 1.9184 Å (1) and 1.9065 Å (2). These bond lengths are consistent with similar Ni-NHC complexes that do not contain a C_p ligand.^{30,35} Furthermore, in these two cases (3 and 4) one of the mesitylene groups in the solid state is skewed out of plane ($\Phi_2 > \Phi_1$, displayed on 3, Table 1) resulting from the steric influences of a single ortho-tolyl group from the phosphite.²⁸ This unsymmetrical change in Φ_2 however, does not affect the $\%V_{bur}$ calculation (Table 1) most likely because the N-substituent is consistent throughout the four complexes.^{39,40} As expected the NHC N2-C3-C4-N5 torsion angle (β) for saturated complexes 2 (10.2°) and 4 (9.4°) was higher than for their unsaturated analogues.²¹

To test thermal stability a degassed solution of nickel complex 1 in benzene- d_6 was stirred at 70 °C under argon which resulted in a slow color change over several hours. When crystals of complexes 1–4 are exposed to air, decolorization begins to occur within minutes. Furthermore, a toluene solution of complex 1 undergoes rapid decolorization, from deep red to orange, also when exposed to air for a 10 min period.

Substitution Chemistry. Substitution reactions of a single phosphine ligand have recently been examined in three-coordinate Ni(0) NHC-phosphine (1:2) systems.³⁰ To understand whether two-coordinate Ni(0) complexes would be accessible with our novel nickel complexes, compound **1**

Complex	$Ni(SIMes)[P(OPh)_3]_2$ 1	$Ni(IMes)[P(OPh)_3]_2 2$	Ni(SIMes)[P(O-o-tol) ₃] ₂ 3	$Ni(IMes)[P(O-o-tol)_3]_2$ 4
Molecular	Me Ne Me		Me Me Me Ni Me Me Ni Me	Me / Me Me N N Me Me Me
structure	(PhO) ₃ P P(OPh) ₃	(PhO) ₃ P P(OPh) ₃	(o-TolO) ₃ P ^P (Oo-Tol) ₃	(o-TolO) ₃ P P(Oo-Tol) ₃
Ni–C1	1.9065 (15) Å	1.9184(18) Å	1.9196 (17) Å	1.9256 (13) Å
Ni–P	Ni1—P2 2.0798 (4) Å	Ni1—P2 2.0793 (5) Å	Ni1—P1 2.0867 (5) Å	Ni1—P1 2.0830 (4) Å
	Ni1—P1 2.0820 (4) Å	Ni1—P1 2.0807 (5) Å	Ni1—P2 2.0914 (5) Å	Ni1—P2 2.0869 (4) Å
	C1—Ni1—P2 124.25 (4)°	C1—Ni1—P2 123.47 (5)°	C1—Ni1—P1 118.57 (5)°	C1—Ni1—P1 117.52 (4)°
Bond Angles	C1—Ni1—P1 112.68 (4)°	C1—Ni1—P1 112.54 (5)°	C1—Ni1—P2 117.84 (5)°	C1—Ni1—P2 118.04 (4)°
	P2—Ni1—P1 122.802 (16)°	P2—Ni1—P1 123.67 (2)°	P1—Ni1—P2 123.40 (2)°	P1—Ni1—P2 124.196 (16)°
N2-C3-C4				
-N5 torsion	−10.16 (18)°	0.0 (2)°	9.39 (18)°	-0.06 (17)°
angle β				
Buried vol- ume ^{40b}	36.0 %V _{Bur}	36.1 %V _{Bur}	36.1 %V _{Bur}	36.2 %V _{Bur}
Tolman				
Electronic	SIMes ²⁴ : 2052.1 cm ⁻¹	IMes ²⁴ : 2050.5 cm ⁻¹	SIMes ²⁴ : 2052.1 cm ⁻¹	IMes ²⁴ : 2050.5 cm ⁻¹
Parameter	$P(OPh)_{3}^{41}: 2085.3 \text{ cm}^{-1}$	$P(OPh)_{3}^{41}$: 2085.3 cm ⁻¹	$P(Oo-tol)_{3}^{41}$: 2084.1 cm ⁻¹ $P(Oo-tol)_{3}^{41}$: 2084.1 cm ⁻¹	
$(\text{TEP})^{a,b}$				
³¹ P NMR				
Ligand	1216 ppm	120.9 ppm	120.9 ppm	120.2 ppm
Chemical			120.9 ppm	12012 FF.11
Shifts				
¹³ C NMR				
Ligand				
Chemical	222.2 ppm	198.4 ppm	222.4 ppm	198.7 ppm
Shifts (δ L)				
C1				

Table 1. Selected Bond Lengths (Å), Angles (deg), Buried Volume (V_{Bur}), Tolman Electronic Parameter (TEP), ¹³C NMR Ligand Chemical Shifts (δ L), for Complexes 1–4

^aCalculations were based on Ni(NHC)(CO)₃.²⁴ ^bCalculations were based on Ni[P(OAr)₃](CO)₃.⁴¹

was treated with a stoichiometric amount of 3,4,5-trifluorobenzaldehyde in THF at room temperature (Scheme 2). A rapid color change of the red reaction mixture to yellow was observed. The resulting complex 5, formed through ligand displacement of one of the phosphites, retained the original trigonal planar geometry. The X-ray crystal structure of nickel complex 5 (Figure 3) revealed a η^2 -coordination to the aldehyde with elongation of the Ni-C1 bond from 1.918 to 1.927 Å and shortening of the Ni–P bond from 2.079 to 2.058 Å when compared to complex 1. The carbonyl C=O bond was found to be elongated considerably upon coordination to nickel, with a bond length of 1.33 Å compared to the standard length of 1.21 Å for a free C=O bonds (1.205 Å for uncoordinated pentafluorobenzaldehyde),⁴² and that of single C-O bond length (1.43 Å).43 As such, the bond length is consistent with a very similar nickel-aldehyde η^2 -coordination complex.³⁰

The ¹H NMR spectrum of this complex revealed a resonance typically at 2.5 ppm, corresponding to the IMes *o*-methyl, splitting and broadening into two overlapping resonances, indicating the different environments of the methyl groups due to the unsymmetrical nature of this complex. The aldehydic proton resonance was observed as a doublet at 4.21 ppm with a coupling constant of 8.0 Hz consistent with other nickel aldehyde complexes.³⁰ The phosphite resonance in the ³¹P NMR spectra was shifted downfield considerably when compared to the starting Ni(SIMes)[P(OPh)₃]₂ **1** complex, from 121.6 to 141.3 ppm.

Nickel complex 1 also underwent a ligand exchange reaction upon treatment with 2.5 equiv of benzonitrile. Unfortunately, attempts at isolating pure complex proved unsuccessful. However, a detailed NMR reaction monitoring of this mixture provided useful structural information. Immediately following the addition of benzonitrile, a resonance at 149.8 ppm was observed in the ³¹P spectrum, in tandem with a resonance at 128.0 ppm assigned to free triphenylphosphite. These two signals integrated at a 1:1 ratio indicating the loss of a single phosphite, forming a complex likely similar in structure to complex 5. Unfortunately, extensive NMR analysis of the reaction mixture was not conclusive as to whether the benzonitrile is η^1 or η^2 coordinated to the nickel center. Nevertheless, a downfield doublet in the ¹³C spectrum was observed at 159.9 pm suggesting coordination of the nitrile in an η^2 -configuration, with an apparent ${}^{13}C-{}^{31}P$ coupling between the nitrile carbon and phosphite ligand. Such significant downfield shifts ($\Delta = 41$ ppm compared to free benzonitrile) are expected and have been reported in other η^2 bound benzonitrile nickel complexes.⁴⁴ High conversion of $Ni(SIMes)[P(OPh)_3]_2$ 1 to 6 required extended reaction times of approximately 4 days at room temperature. Under more forcing conditions, 70 °C for 1 h, a near complete conversion to the benzonitrile complex 6 could be achieved (for further details please see Supporting Information).

Suzuki-Miyaura Cross-Coupling Using Aryl Halides or Pseudohalides. The Suzuki-Miyaura cross-coupling was chosen to explore the catalytic potential of this family of



Figure 2. ORTEP plot of the molecular structures of Ni(SIMes) $[P(OPh)_3]_2$ (1) CCDC 1958526, Ni(IMes) $[P(OPh)_3]_2$ (2) CCDC 1958527, Ni(SIMes) $[P(O-o-tol)_3]_2$ (3) CCDC 1958528, and Ni(IMes) $[P(O-o-tol)_3]_2$ (4) CCDC 1958529. Ellipsoids are presented at 50% probability. Hydrogen atoms except those attached to C3 and C4 have been omitted for clarity.





precatalysts. The nickel catalyzed Suzuki–Miyaura crosscoupling³ has been reported with a range of nickel catalysts.^{4,33,45–52} The use of nickel monodentate NHCs is rare and often limited in scope when it comes to the Suzuki– Miyaura reaction and sometimes a bis(NHC) nickel complex is used.^{7,34,35,53–55} Protocols using aryl tosylate with NHCnickel catalysts substrates are conspicuously absent from the literature.^{56,57}



Figure 3. ORTEP plot of the molecular structure of Ni(IMes)[P-(OPh)₃](C₆H₂F₃CHO) (5) CCDC 1958530.

Initially, nickel complex 1 (5 mol %) was surveyed with various aryl based substrates bearing an array of leaving groups (Table 2). The simple *p*-methoxyphenylboronic acid as the

 Table 2. Scope of the Leaving Group in the Suzuki–Miyaura

 Cross-Coupling Reaction with *p*-Methoxyphenylboronic

 Acid^a



^{*a*}All reactions were carried out using aryl halide or pseudohalide (0.25 mmol), *p*-methoxyphenylboronic acid (0.375 mmol), **1** (0.0125 mmol), K₃PO₄ (0.75 mmol), THF (1 mL), 70 °C, 18 h. ^{*b*}Isolated yields.

transmetalation partner remained constant in these initial trials. Under relatively mild conditions with Ni precatalyst 1, K_3PO_4 as a base in THF at 70 °C,^{58,59} the aryl chloride and tosylate coupling partners performed exceptionally well (>99%). Unfortunately, other less traditional and more challenging pseudohalides (sulfonamide and *t*-butylcarbonate)⁸ were not compatible under these catalytic conditions. Interestingly, using bromobenzene as the substrate resulted in slightly lower yields of the biaryl product (70%, entry 1) whereas the aryl tosylate performed exceptionally (>99%). For the broader substrate and coupling partner methodological studies aryl tosylates were employed as they are attractive substrates that can be readily prepared from commercially available phenols.

Conducting the reaction at room temperature had a deleterious effect on the reaction outcome (Table 3). However, a reaction carried out using a lower loading of

Table 3. Optimization of Reaction Conditions and Catalyst Screening a

С	Ni(SIMes)[P(OPh) ₃]; 1 (5 mol%) + (HO) ₂ B OMe K ₃ PO ₄ (3 equiv) THF, 70 °C 18 h	OMe
entry	deviation from above	yield (%) ^b
1	none	99
2	25 °C	26
3	2 mol %	70
4	toluene, 2 mol %, 110 °C	89
5	2-MeTHF, 5 mol %	94
6	dioxane, 5 mol %, 110 °C	99
7	dioxane, 2 mol %, 110 °C	60
9	$RB(OH)_2$ (1.1 equiv)	79
10	K ₃ PO ₄ (1.5 equiv)	90
11	$Ni(IMes)[P(OPh)_3]_2$ 2	89
12	$Ni(SIMes)[P(O-o-tol)_3]_2$ 3	99
13	$Ni(IMes)[P(O-o-tol)_3]_2$ 4	88
14	Ni(dppf)[P(OPh) ₃] ₂	44
15	$Ni(BINAP)[P(OPh)_3]_2$	33

"All reactions were conducted on a 0.25 mmol scale using 1.5 equiv of boronic acid coupling partner." ^bIsolated yields.

catalyst (2 mol % of 1) still performed well, especially when the reaction was heated to reflux in toluene (89% yield, entry 4). The reaction also could be conducted in both the green solvent 2-MeTHF⁴⁷ and dioxane with excellent yields. The reactivity of the nickel NHC-phosphite 1 was further examined by lowering the stoichiometry of the coupling partner and the base additive. Gratifyingly, both these modifications resulted in only slightly reduced reaction yields. Nickel NHC-phosphite complexes 2–4 also performed well under the optimum conditions with Ni(SIMes)[P(O-o-tol)]₂ 3 being equally as effective as Ni(SIMes)[P(OPh)₃]₂ 1.

Early reports involving nickel catalyzed Suzuki–Miyaura cross-coupling using Ni(COD)₂ and PCy₃ at room temperature has traditionally focused on substrates containing simple functionalization.⁵² A series of aryl tosylates were therefore synthesized and were used to first examine the catalyst effectiveness (Table 4). Toluene derived substrates performed

Table 4. Suzuki–Miyaura Coupling Reactions of VariousPhenyl Tosylates with Phenylboronic $Acid^a$



 a All reactions were conducted on a 0.25 mmol reaction scale using 1.5 equiv of boronic acid coupling partner. Isolated yields are indicated.

well (leading to biaryls 7a-c) even when the methyl substituent was in the more sterically encumbered *ortho*position. However, when both *ortho*-positions were substituted, a clear drop in yield was observed (7e). The more electron-rich methoxy derived aryl tosylate afforded the biaryl 7d in good yields. Aryl tosylates containing an electron withdrawing substituent also resulted in good to excellent yields of the biaryl products including the carbonyl containing aryl tosylates affording 7h and 7j. Aldehyde 7i was produced in high yields according to analysis of the crude reaction mixture, but unfortunately decomposed during purification on silica gel. The *para*-substituted fluorinated aryl tosylate also coupled efficiently under these conditions (7f). The nitrile-containing aryl tosylate was perfectly amenable to our cross-coupling protocol using both *p*-toluenesulfonyl chloride and chlor-obenzene to afford 7g. Unfortunately, both nitro and quinoline-derived substrates did not result in appreciable formation of the products (7k, 7l).

Next, we investigated the reaction outcome when using a diverse array of aryl boronic acid nucleophiles (Table 5).





^{*a*}All reactions were conducted on a 0.25 mmol reaction scale using 1.5 equiv of boronic acid coupling partner. Isolated yields are indicated.

Reactions involving electron-rich and poor *para*-substituted boronic acids afforded the corresponding biaryl products (7b, 7d, 7j, and 8a) in good to excellent yields (Table 5). Importantly, thiophenyl and furanyl boronic acids (8b, 8c, and 8d) readily underwent coupling under our conditions resulting in moderate to excellent yields. Unfortunately, pyridine and 4-cyanophenylboronic acid only resulted in trace amount of the desired biaryl product. The larger naphthalene coupling partner was successful, providing the corresponding 1-phenylnaphthalene (8g) in 80% yield.

Kinetics. Catalyst kinetics were explored by monitoring the reaction between 4-fluorophenyltosylate and phenylboronic acid via ¹⁹F NMR (Figure 4). Monitoring of the ¹⁹F nuclei of product 7f at -116.4 ppm and comparing to 4-fluorophenyltosylate at -115.7 ppm provided a precise reaction curve. The plot showing the conversion over time (Figure 4, top) indicates that each of these complexes have a small induction period. This induction period is likely the time needed for the precatalyst to lose one of its phosphite ligands and form the presumed catalytically active species Ni(NHC)(phosphite). Not surprisingly then, complexes 3 and 4, that contain the sterically more encumbered *o*-tolylphosphite had the fastest initial reaction rate with k_{obs} of 28.2 (×10⁻²) min⁻¹ and 15.7 (×10⁻²) min⁻¹, respectively.⁴⁸ Complexes 1 and 2 containing triphenylphosphite were found to be slower with k_{obs} of 8.9



Figure 4. Determination of k_{obs} and reaction conversion of 4-fluorophenyl tosylate to 4-fluorobiphenyl. Top: Reaction conversion over time for complexes 1–4. Bottom: In of starting material concentration at time t_0 over starting material concentration at t_x for complex 1–4.

 $(\times 10^{-2})$ min⁻¹ and 3.4 $(\times 10^{-2})$ min⁻¹, respectively. TOF₅₀ values for complexes **1**, **2**, **3** and **4** were calculated to be 50.4, 46.8, 133.2, and 255.6 h⁻¹ respectively. Ni(SIMes)[P(OPh)₃]₂ **1** was found to give the highest reaction conversion (90%), while the other three complexes achieved conversions between 60 and 75%. These differences in conversion are likely due to catalyst decomposition, and nickel complexes featuring the saturated SIMes ligand (1, 3) seem clearly less prone to decomposition than their IMes counterparts (2, 4), at the same time showing slower initial reaction rates.

The addition of 5 mol % of $P(OPh)_3$ was also investigated in the case of Ni(SIMes)[$P(OPh)_3$]₂ 1 (5 mol %). It was found that excess phosphite ligand greatly reduced reaction rates, indicating that phosphite dissociation is an integral step in the catalytic cycle and that reassociation of this ligand is in competition with oxidative addition (see Supporting Information).

Mechanistic Considerations. NMR studies were conducted to better understand the catalytic cycle of this reaction and elucidate the structure of the complex formed upon oxidative addition. It was found that no new product was formed from a reaction of nickel complex 1 in C_6D_6 with chlorobenzene or phenyl tosylate at room temperature, even after extended reaction times. Previous work investigating the oxidative addition into a Ni(R-BINAP)(COD) catalyst, conducted by Hartwig, et al. suggested that a benzonitrile substituted substrate is able to provide the oxidative addition complex when other substrates failed, via the formation of an η^2 -bound intermediate.⁶⁰ Pleasingly, stirring 4-chlorobenzonitrile with Ni(SIMes) $[P(OPh)_3]_2$ 1 provided a new resonance at approximately 150.4 ppm in the ³¹P NMR and a minor signal at 95.1 ppm after 2 h at room temperature. Given our results on substitution reactions with benzonitrile (Scheme 3),

Scheme 3. Ligand Dissociation and Reaction of Nickel Complex 1 with Benzonitrile



it was deduced that the signal at 150.4 ppm was likely the nitrile coordinated η^2 -complex, suggesting that the signal at 95.1 ppm would possibly correspond to the oxidative addition product **9**. Heating this solution at 70 °C in benzene indeed proved to yield near complete conversion of nickel complex **1** to the aforementioned complex **9** (³¹P NMR at 95.1 ppm) within 1 h (Scheme 4).

Scheme 4. Oxidative Addition of 4-Chlorobenzonitrile with Complex 1



Although we were not able to isolate complex 9 in pure form, NMR analysis (¹H, ¹³C and ³¹P, see the Supporting Information for details) suggested its formation, with coordination of both the aryl and halide ligands via oxidative addition of the substrate, rather than simple ligand exchange and η^2 -bonding of the nitrile as in complex 6. Notably, the ¹H NMR resonances corresponding to the NHC backbone split into two separate triplets, indicating the unsymmetrical nature of the new complex. The o-methyl signals of the N-aryl substituents were also now inequivalent, splitting into three separate singlets. The ³¹P NMR signal is considerably shifted upfield to 95.1 ppm. The triplet that was assigned to the carbonic carbon in the ¹³C NMR spectra in the starting complex 1 (222.2 ppm) was now observed as a doublet at 206.3 ppm with a large coupling constant (151.8 Hz), suggesting a trans arrangement of NHC and phosphite ligand. A doublet at \sim 160 ppm with a smaller coupling constant (45.6 Hz) was assigned to the ipso-carbon of aryl ligand, suggesting it is *cis* to the phosphite.

To unequivocally assign the structure of complex 9, X-ray quality crystals were obtained via slow diffusion with pentane into a solution of DCM (Figure 5). As expected, complex 9



Figure 5. ORTEP plot of the molecular structure of complex $Ni(SIMes)[P(OPh)_3](C_6H_4CN)Cl$ (9) CCDC 1958531. Ellipsoids are presented at 50% probability. Hydrogen atoms except those attached to C3 and C4 have been omitted for clarity.

was found to have a square planar geometry with the aryl ligand *trans* to the halide ligand, consistent with the NMR analysis. Complexes similar to **9**, formed via oxidative addition of an aryl halide into a Ni(0) or transmetalation of a Grignard reagent into Ni(II), have found increasing use as air-stable Ni(II) precatalysts.^{60–64} The Ni–Cl bond length of 2.2115 Å is consistent with Ni–Cl distances observed in other Ni(II) *trans*-complexes. The nickel carbene bond distance of 1.934 Å was also found to be similar to another Ni(II) complexes consisting of an IPr ligand and a branched phosphite.⁷ The Ni–P bond length was longer when compared to complex **1**. The bond angles between the ligands only deviated by 5° from the ideal square planar angles. The saturated NHC backbone became flat with a minimal 1.1° torsion angle (N2–C3–C4–N5).

CONCLUSION

In conclusion, we have reported the preparation and full characterization of a novel family of three-coordinate Ni- $(NHC) [P(OAr_3)]_2$ complexes. All four complexes were found to exhibit a trigonal planar geometry. Ni(SIMes) $[P(OPh)_3]_2$ 1 was found to readily undergo substitution of a phosphite ligand in the presence of 3,4,5-trifluorobenzaldehyde or benzonitrile, giving the corresponding η^2 -coordinated compounds 5 and 6. The catalytic ability of this family of nickel NHC-phosphite complexes was tested using the Suzuki-Miyaura crosscoupling reaction. It was found that each of the complexes was able to effectively catalyze the reaction of aryl tosylates (and chlorides), with complexes Ni(SIMes) $[P(OPh)_3]_2$ 1 and $Ni(SIMes)[P(O-o-tol)_3]_2$ 3 being the most effective. A library of aryl tosylates and phenylboronic acids were successfully coupled using nickel complex 1. The kinetics of each of these complexes was tested via NMR techniques, and the mechanism was investigated by analyzing important reaction intermediates. From this study, the product of oxidative addition of 4chlorobenzonitrile, Ni(SIMes) $[P(OPh)_3](C_6H_4CN)Cl$ (9), was also isolated and characterized. Currently we are investigating further ligand modifications of this family of mixed nickel NHC phosphite complexes. Additional studies are being conducted on the reactivity of Ni(II) complex 9.

EXPERIMENTAL SECTION

General Information. All reactions were performed with standard Schlenk (nitrogen) or glovebox (Innovative Technology, argon) techniques unless otherwise specified. THF, diethyl ether, pentane, toluene, DCM, and hexane were purged with argon and passed through active alumina columns (Innovative Technology, Inert) and stored over activated molecular sieves in argon filled glove boxes. All other reagents were used as received unless otherwise noted. Deuterated solvents for NMR analysis were degassed with nitrogen and stored in the glovebox over activated molecular sieves. The N-heterocyclic carbenes IMes and SIMes were prepared from the corresponding NHC·HBF₄ salts following literature procedures.⁶⁵ Ni[P(OPh)₃]₄ and Ni[P(O-*o*-tol)₃]₃ were prepared according reported procedures.³⁸

NMR spectra were recorded with Bruker Avance IIIHD600 or Bruker Avance IIIHD500 instruments. Chemical shifts are displayed in ppm. ¹H and ¹³C NMR were referenced to the residual protiated solvent, ³¹P NMR were referenced to external H₃PO₄ standard. Multiplicities are abbreviated as the following: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (b). High resolution accurate mass data mass spectra were recorded on a Waters LCT Premier XE instrument. Elemental analysis was performed at London Metropolitan University (UK) by Dr. Stephen Boyer. Flash column chromatography was performed on silica gel (Davisil, particle size 40–63 µm, Merck) and eluted with petroleum ether/ethyl acetate. Preparative thin layer chromatography (PTLC) was performed with in-house prepared plates (20 × 20 × 0.1 cm) using silica gel 60 PF254 containing gypsum (Merck).

 $Ni(SIMes)[P(OPh)_3]_2$ (1). In a glovebox, nickel tetrakis-(triphenylphosphite) (429 mg, 0.33 mmol) and SIMes (204 mg, 0.66 mmol) were placed into a Schlenk flask. Toluene (20 mL) was added and the vessel sealed and removed from the glovebox and heated at 110 °C for 40 min. The mixture was then cooled to room temperature, and the solvent was completely removed under a high vacuum (cold trap). The flask was then returned to the glovebox and the red oil was dissolved in THF (ca. 2 mL), filtered through a short plug of Celite, and the residue was further washed with THF (2×2 mL). The solution was concentrated in a minimal volume of THF (ca. 1.5 mL) and layered with pentane (10 mL) and allowed to crystallize at -28 °C. A mixture of white powder and red crystals was obtained, the supernatant solution was decanted, and 3 mL of pentane was added and swirled to suspend the white precipitate that was then decanted. This process was repeated until the white precipitate was removed. Complex 1 was obtained as bright red crystals (256 mg, 0.3 mmol, 79%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of 1 in benzene at -28 °C. ¹H NMR (600 MHz, C₆D₆) δ 6.95–6.90 (m, 12H), 6.87 (d, J = 7.5 Hz, 12H), 6.80 (t, J = 7.2 Hz, 6H), 6.76 (s, 4H), 3.33 (s, 40)4H), 2.50 (s, 12H), 2.17 (s, 6H) ppm. ¹³C NMR (151 MHz, C_6D_6) δ 222.2 (t, $J_{CP} = 32.0 \text{ Hz}$), 152.3, 137.0, 136.4, 136.0, 128.9, 128.1, 127.4, 121.6, 120.3, 49.9, 20.2, 17.2 ppm. ³¹P NMR (243 MHz, C₆D₆) δ 121.6 ppm. Anal. Calcd for C₅₇H₅₆N₂O₆P₂Ni: C, 69.45; H, 5.73; N, 2.84. Found: C, 69.30; H, 5.79; N, 2.77.

 $Ni(IMes)[P(OPh)_3]_2$ (2). In a glovebox, nickel tetrakis-(triphenylphosphite) (244 mg, 0.19 mmol) and IMes (115 mg, 0.38 mmol) were placed into a Schlenk flask. Toluene (15 mL) was added and the vessel sealed and removed from the glovebox and heated at 120 °C for 50 min. The mixture was then cooled to room temperature and the solvent was completely removed under a high vacuum (cold trap). The flask was then returned to the glovebox, and the red oil was dissolved in THF (ca. 2 mL) and filtered through a short plug of Celite; the residue was further washed with THF (2 × 2 mL). The solution was concentrated to a minimal volume of THF (ca. 1.5 mL) and layered with pentane (10 mL) and allowed to recrystallize at -28 °C. A mixture of white powder and red crystals are obtained, the supernatant solution was decanted, and 3 mL of pentane was added and swirled to suspend the white precipitate and then decanted. This process was repeated until the white precipitate was removed. Complex **2** was obtained as bright red crystals (100 mg, 0.1 mmol, 54%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of **2** in benzene at -28 °C. ¹H NMR (600 MHz, C₆D₆) δ 6.97–6.88 (m, 24H), 6.85–6.77 (m, 6H), 6.73 (s, 4H), 6.33 (s, 2H), 2.30 (s, 12H), 2.15 (s, 6H) ppm. ¹³C NMR (151 MHz, C₆D₆) δ 198.4 (t, *J*_{CP} = 32.0 Hz), 153.0, 137.6, 137.3, 136.1, 129.2, 128.7, 128.0, 122.2, 121.3, 120.9, 20.9, 17.8 ppm. ³¹P NMR (243 MHz, C₆D₆) δ 120.9 ppm. Anal. Calcd for C₅₇H₅₄A₂O₆P₂Ni: C, 69.60; H, 5.53; N, 2.85. Found: C, 69.42; H, 5.42; N, 2.79.

Ni(SIMes)[P(O-o-tol)₃]₂ (3). In a glovebox, nickel tris(tri-otolylphosphite) (200 mg, 0.18 mmol) and SIMes (110 mg, 0.36 mmol) were placed into a Schlenk flask. Toluene (15 mL) was added and the vessel sealed and removed from the glovebox and heated at 100 °C for 15 min. The mixture was cooled to room temperature and the solvent was completely removed under a high vacuum (cold trap). The flask was then returned to the glovebox, and the red oil was dissolved in THF (ca. 2 mL) and filtered through a short plug of Celite; the residue was further washed with THF ($2 \times 2 \text{ mL}$). The solution was concentrated to a minimal volume of THF (ca. 1.5 mL) and layered with pentane (10 mL) and allowed to recrystallize at -28°C. Complex 3 was obtained as bright red crystals (130 mg, 0.12 mmol, 67%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of 3 in benzene at -28 °C. ¹H NMR (600 MHz, C₆D₆) δ 7.13 (d, J = 7.6 Hz, 6H), 6.90-6.84 (m, 6H), 6.78 (d, J = 0.4 Hz, 4H), 6.74 (td, J = 7.3, 1.5 Hz, 6H), 6.72-6.68 (m, 6H), 3.33 (s, 4H), 2.53 (s, 12H), 2.17 (s, 6H), 1.96 (s, 18H) ppm. ¹³C NMR (126 MHz, C_6D_6) δ 222.4 (t, J_{CP} = 32.9 Hz), 151.5, 137.9, 136.9, 136.8, 130.3, 129.6, 128.8, 128.0, 126.1, 122.0, 120.1, 50.7, 20.9, 18.3, 16.7 ppm. ³¹P NMR (243 MHz, C₆D₆) δ 120.9 ppm. Anal. Calcd for C₆₃H₆₈N₂O₆P₂Ni: C, 70.73; H, 6.41; N, 2.62. Found: C, 70.84; H, 6.33; N, 2.65.

Ni(IMes)[P(O-o-tol)₃]₂ (4). In a glovebox, nickel tris(tri-otolylphosphite) (200 mg, 0.18 mmol) and IMes (109 mg, 0.36 mmol) were placed into a Schlenk flask. Toluene (15 mL) was added and the vessel sealed and removed from the glovebox and heated at 100 °C for 30 min. The mixture was cooled to room temperature and the solvent was completely removed under a high vacuum (cold trap). The flask was then returned to the glovebox, and the red oil was dissolved in THF (ca. 2 mL) and filtered through a short plug of Celite; the residue was further washed with THF (2×2 mL). The solution was concentrated to a minimal volume of THF (ca. 1.5 mL) and layered with pentane (10 mL) and allowed to recrystallize at -28°C. Complex 4 was obtained as bright red crystals (109 mg, 0.10 mmol, 57%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of 4 in benzene at -28 °C. ¹H NMR (600 MHz, C₆D₆) δ 7.27-7.19 (m, 6H), 6.91-6.84 (m, 6H), 6.78-6.67 (m, 16H), 6.33 (s, 2H), 2.33 (s, 12H), 2.15 (s, 6H), 1.94 (s, 18H). ¹³C NMR (151 MHz, C_6D_6) δ 198.7 (t, J_{CP} = 33.2 Hz), 151.9, 138.1, 137.9, 136.4, 130.7, 129.6, 129.2, 128.4, 126.5, 122.3, 121.9, 120.4, 21.2, 18.6, 17.0 ppm. ³¹P NMR (243 MHz, C₆D₆) δ 120.2 ppm. Anal. Calcd for C₆₃H₆₆N₂O₆P₂Ni: C, 70.86; H, 6.23; N, 2.62. Found: C, 70.69; H, 6.46; N, 2.62.

Ni(IMes)[*P*(*OPh*)₃](*C*₆*H*₂*F*₃*CHO*) (**5**). Ni(SIMes)[P(OPh)₃]₂ (1) (20 mg, 20 μmol) was dissolved in THF (0.5 mL) followed by addition of 3,4,5-trifluorobenzaldhyde (2.5 μL, 20 μmol). The solution turned from bright red to yellow within 2 min and the mixture was allowed to stir for a further 10 min. The ensuing mixture was concentrated under reduced pressure to afford a yellow solid, which was dissolved in a small portion of benzene (ca. 0.5 mL), layered with pentane and cooled to -28 °C. Filtration provided title complex **5** (49.6 mg, 0.06 mmol, 72%) as yellow needles. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of **5** in benzene at -28 °C. ¹H NMR (600 MHz, C₆D₆) δ 7.03 (br s, 2H), 6.97 (s, 2H), 6.95–6.90 (m, 6H), 6.83 (t, *J* = 7.4 Hz,

3H), 6.76 (d, J = 8.1 Hz, 6H), 6.24 (t, J = 7.3 Hz, 2H), 4.21 (d, J = 8.0 Hz, 1H), 3.27 (s, 4H), 2.57 (s, 6H), 2.54 (s, 6H), 2.30 (s, 6H) ppm. ¹³C NMR (151 MHz, C_6D_6) δ 222.7 (d, J = 4.6 Hz), 152.2 (d, J = 7.2 Hz), 152.0 (d, J = 5.9 Hz), 150.5 (d, J = 10.2 Hz), 145.8, 138.2, 137.5, 129.8, 129.3, 128.4, 124.1, 121.2 (d, J = 4.9 Hz), 107.2 (d, J = 19.2 Hz), 80.3, 50.9, 21.2, 18.5, 18.4 ppm. ³¹P NMR (243 MHz, C_6D_6) δ 141.3 ppm. Anal. Calcd for $C_{46}H_{44}N_2O_4PF_3Ni: C, 66.13; H, 5.31; N, 3.35. Found: C, 65.90; H, 5.19; N, 3.24.$

 $Ni(SIMes)[P(OPh)_3](C_6H_4CN)CI$ (9). $Ni(SIMes)[P(OPh)_3]_2$ (1) (113.3 mg, 0.12 mmol) in benzene (6 mL) was added 4chlorobenzonitrile (32.4 mg, 0.24 mmol). The resulting solution was heated at 70 °C for 1 h. The solution was concentrated to dryness and the residue recrystallized from DCM/pentane (1/8 v/v) at -28°C. Complex 9 was obtained as pale yellow crystals (51.6 mg, 0.068 mmol, 59%). Single crystals were grown via slow diffusion of pentane into a saturated solution of 9 in DCM at -28 °C. ¹H NMR (600 MHz, C_6D_6) δ 7.08 (d, J = 8.2 Hz, 6H), 6.96–6.93 (m, 3H), 6.92– 6.88 (m, 1H), 6.83-6.78 (m, 1H), 6.76 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.60 (d, J = 7.7 Hz, 1H), 3.08 (t, J = 9.5 Hz, 2H), 2.83 (t, J = 9.6 Hz, 2H), 2.61 (s, 6H), 2.22 (s, 6H), 1.52 (s, 6H). ³¹P NMR (243 MHz, C₆D₆) δ 95.1 ppm. Anal. Calcd for C₄₆H₄₅N₃O₃PClNi: C, 67.96; H, 5.58; N, 5.17. Found: C, 67.93; H, 5.67; N, 4.97. HRMS-EI (m/z) predicted C₄₆H₄₅N₃O₃PNi⁺ [M-Cl]⁺ 776.2552, found 776.2551.

General Procedure for the Suzuki–Miyaura Cross-Coupling of Aryl Tosylates and Boronic Acids. An oven-dried 3 mL reaction vial equipped with a stir bar was charged with aryl tosylate substrate (0.25 mmol), boronic acid (0.375 mmol), K_3PO_4 (0.75 mmol) and a nickel NHC/phosphite catalyst (0.0125 mmol) inside a glovebox. THF (1 mL) was added, the vial was sealed, removed from the glovebox, and heated in an oil bath for 18 h. Following this time the vial was removed from the bath and allowed to cool to room temperature. Water (1 mL) was added, and the resulting mixture was extracted with EtOAc (5 × 1 mL), and the combined organic layers filtered through Celite. Purification by flash chromatography or PTLC afforded the desired biaryl products. See the Supporting Information for individual reactions.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00672.

The preparation of nickel NHC/Phosphite complex derivatives; the procedure for the preparation of aryl tosylates; the procedure for the Suzuki–Miyaura cross-coupling reactions; reaction kinetics, X-ray crystallo-graphic data, and NMR spectra (PDF)

Accession Codes

CCDC 1958526–1958531 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, 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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