## **ORGANOMETALLICS**

# Discrete Air-Stable Nickel(II)—Palladium(II) Complexes as Catalysts for Suzuki—Miyaura Reactions

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**Supporting Information** 

**ABSTRACT:** Four novel bidentate phosphine-Pd complexes coordinated by  $NiN_2S_2$  metallodithiolate ligands were synthesized and characterized, including XRD analysis; these redox-active complexes are stable in air, and they survive column chromatography on silica gel. The Ni–Pd bimetallic complexes are demonstrated to be precatalyst for Suzuki–Miyaura cross-coupling reactions. The best of these has an overall yield of over 99% under only 1% catalyst loading. The role of  $NiN_2S_2$  as a stabilizing bidentate ligand that is also oxidizable may account for its efficacy in the support of the catalysis.

#### INTRODUCTION

The acetyl-coA synthase (ACS) enzyme active site offers the intriguing prospect that the tight binding site with contiguous S-N-N-S donors for one of the required pairs of nickels renders a cysteine-glycine-cysteine tripeptide motif into a metallo-cis-dithiolate, NiN<sub>2</sub>S<sub>2</sub>, bidentate metalloligand.<sup>1-3</sup> The second nickel, the catalytic center, is bound by three bridging thiolate sulfurs, two from the NiN2S2 and an additional one to a 4Fe-4S cluster; there is as well in the protein crystal structure an unknown ligand, X.4,5 Mechanistic possibilities for the overall C-C coupling reactions to yield acetyl co-A include  $CH_3^+$  transfer from cobalt in the vitamin  $B_{12}$  cofactor to the active nickel and CO insertion into a Ni-CH<sub>3</sub> bond, with nucleophilic attack on the Ni-C(=O) $-CH_3$  from the thiolate of co-Å reductively releasing the acetyl-coA, thus regenerating the low-valent nickel into the cycle.<sup>1,4,6</sup> Whether the  $NiN_2S_2$ metallodithiolate retains bidentate binding to the active nickel or shifts into a monodentate binding mode is uncertain.<sup>7</sup>

We have pursued the development of  $MN_2S_2$  complexes as a class of ligands in which the *cis*-dithiolate sulfur donors, tamed by transition metal ions such as Ni<sup>2+</sup>, [Fe(NO)]<sup>2+</sup>, or  $[Co(NO)]^{2+}$ , can be viewed as analogues of diphosphines, with similar electronic donor properties.<sup>8,9</sup> They may be used to strategically design bi- and multimetallic complexes. The second lone pair on each sulfur generates a hinge at the bridging dithiolate sulfurs and a butterfly core. This steric feature positions metals just beyond M-M' bonding distances in bimetallic systems but sufficiently close to accommodate bridging ligands. Earlier we suggested that since the natural



(cys-gly-cys)Ni<sup>II</sup> supported CO/CH<sub>3</sub> insertion or coupling reactivity in ACS, we might expect a similar demonstration in palladium chemistry, choosing the copolymerization of ethylene and CO as a prototype.<sup>10</sup> Indeed the  $(NiN_2S_2)Pd(CH_3)Cl$  complex shown in Figure 1 was shown to take up and insert



Figure 1. NiN<sub>2</sub>S<sub>2</sub>-coordinated Pd complex for CO and ethylene insertion reactions.<sup>10</sup> Crystal structure of  $[(NiN_2S_2)Pd(CH_3)(Cl)]$  is overlaid to illustrate the butterfly core.<sup>9</sup>

CO in the Pd–CH<sub>3</sub> bond and also initiate the formation of short chains of  $(-C=O)CH_2CH_2-)_n$  attached to Pd<sup>II</sup>, analogous to the well-known copolymerization process.<sup>10</sup>

With the above results in mind, we have directed attention toward designing Ni–Pd complexes for the purpose of exploring their potential for catalyzing the Suzuki–Miyaura reaction. As one of the most widely applied methods for constructing a C–C bond,<sup>11</sup> extensive studies have focused on palladium and the selection of appropriate ligands for specific reactions. Multimetallic complexes have found application in

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III  $n_1 = 3 n_2 = 2 80\%$ , IV  $n_1 = 3 n_2 = 3 89\%$ 

Figure 2. Synthesis of Ni-Pd bimetallic complexes I-IV.

catalysis, either as biomimetic complexes of enzyme active sites  $^{12-14}$  or as catalysts in organic reactions.  $^{15,16}$  For the latter, most of the reported multimetallic catalysts are in the form of nanoparticles<sup>16</sup> and metal–organic frameworks.<sup>17–19</sup> There are a few examples of discrete, molecular heterobimetallic complexes such as N-heterocyclic carbene-supported Ir-Pd, Ir-Ir, and Pd-Pd complexes that were found to catalyze tandem dehalogenation/transfer hydrogenation or Suzuki/ transfer hydrogenation reactions.<sup>20</sup> An impressive hydrodefluorination of organic molecules was found to require both Rh and Pd in a discrete heterobimetallic catalyst.<sup>2</sup> Another example uses the iron-modified triaryl phosphine as ligand,  $(\eta^2$ -dppe) $(\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(C $\equiv$ C-Aryl-PPh<sub>2</sub>), coordinated to a Pd(II) complex, which was competent for Stille-type crosscoupling reactions.<sup>22</sup> These few examples, disparate as they are in molecular makeup, have not thus far led to design principles that might define the possible role of two metal centers in proximity.

Building on the success of the NiN<sub>2</sub>S<sub>2</sub>·Pd<sup>II</sup> complex for CO/ olefin copolymerization described above, we have further explored the synthesis and characterization of a group of  $[NiN_2S_2]$ -Pd<sup>II</sup>(diphos) complexes as stable, efficient, wellsoluble catalysts or pro-catalysts for the Suzuki–Miyaura reaction. Mechanism studies establish the requirement for the NiN<sub>2</sub>S<sub>2</sub> metalloligand that we maintain serves as a convenient platform for palladium to enter the catalytic cycle.

#### RESULTS AND DISCUSSION

**Synthesis.** Nickel dithiolates  $(NiN_2S_2)$  built into the sixand seven-membered diazacycles, 2,2'-(piperazine-1,4-diyl)bis-(ethane-1-thiol), Ni(bme-dach\*), and 2,2'-(1,4-diazepane-1,4diyl)bis(ethane-1-thiol), Ni(bme-dach),<sup>23</sup> were chosen to be used in this study. The former was synthesized in the same manner as the latter,<sup>23</sup> and its X-ray crystal structure is provided in the Supporting Information, SI. Palladium(II) was added in the form of Pd(dppe)Cl<sub>2</sub> (dppe = 1,2-bis-diphenylphosphinoethane) or Pd(dppe)Cl<sub>2</sub> (dppp = 1,2-bis-diphenylphosphinoethane) or Pd(dppe)Cl<sub>2</sub> (dppp = 1,2-bis-diphenylphosphinopropane) to the NiN<sub>2</sub>S<sub>2</sub> unit in CH<sub>3</sub>CN solution also containing NH<sub>4</sub>PF<sub>6</sub>. The resulting Ni–Pd bimetallic complexes I–IV were obtained as red solids following solvent removal. Their stability to air and moisture permitted purification by flash chromatography on silica gel; isolated yields are given in Figure 2.

**Solid-State Structures.** Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a concentrated CH<sub>3</sub>CN solution of complexes I–IV. Their molecular structures are shown in Figure 3, and listings of metric data are given in Table 1. Full structure reports are deposited in the Cambridge Crystallographic Data Centre; further refinement parameters and relevant crystal data are in the SI. Complexes I–IV crystallized with Ni<sup>II</sup> and Pd<sup>II</sup> in almost regular square-planar geometries, bridged by thiolate sulfurs. The intersection of the N<sub>2</sub>S<sub>2</sub> best plane with the P<sub>2</sub>S<sub>2</sub> best



**Figure 3.** Solid-state molecular structures presented as a mixture of thermal ellipsoids (50% probability level) and wire frames for the phenyl groups. [Ni(bme-dach\*)Pd(dppe)](PF<sub>6</sub>)<sub>2</sub>, I, [Ni(bme-dach\*)-Pd(dppe)](PF<sub>6</sub>)<sub>2</sub>, II, [Ni(bme-dach)Pd(dppe)](PF<sub>6</sub>)<sub>2</sub>, III, and [Ni-(bme-dach)Pd(dppe)](PF<sub>6</sub>)<sub>2</sub>, III, and [Ni-(bme-dach)Pd(dppe)](PF<sub>6</sub>)<sub>2</sub>, IV. The PF<sub>6</sub><sup>-</sup> counterions, hydrogen atoms, and any cocrystallized solvent molecules are omitted for clarity.

Table 1. Selected Metric Data Bond Length [Å] and Angles [deg] for Complexes I–IV

	I	II	III	IV
N–Ni <sup>a</sup> /Å	1.906(3)	1.902(5)	1.926(4)	1.928(3)
S–Ni <sup>a</sup> /Å	2.143(6)	2.138 (1)	2.156 (7)	2.154 (3)
S-Pd <sup>a</sup> /Å	2.410(8)	2.421 (1)	2.381(6)	2.394(2)
P-Pd <sup>a</sup> /Å	2.267(12)	2.283 (9)	2.282 (2)	2.294 (3)
Ni-Pd/Å	2.883(1)	2.962(3)	3.079 (9)	3.111(1)
N-Ni-N/deg	77.5(1)	77.9(2)	83.50(16)	83.14(1)
S-Ni-S/deg	94.15(4)	94.80(5)	90.74(5)	90.01(4)
S-Pd-S/deg	81.24(3)	81.00(5)	80.26(4)	79.05(3)
P-Pd-P/deg	85.02(3)	90.34(5)	83.50(4)	90.07(3)
S-Pd-P <sup>a</sup> /deg	96.73(3)	93.84(5)	98.03(4)	95.13(3)
N–Ni–S <sup>a</sup> /deg	93.43(8)	93.11(14)	92.12(12)	92.58(9)
Hinge Angle <sup>b</sup> /deg	118.3	128.3	131.3	132.8
Ni–N <sub>2</sub> S <sub>2</sub> disp. <sup>c</sup> / Å	0.164	0.144	0.167	0.178
$Pd-S_2P_2 \text{ disp.}^d/ \text{ Å}$	0.083	0.200	0.098	0.171

"Average value. <sup>b</sup>The angle between the  $N_2S_2$  best plane and  $S_2P_2$  best plane. <sup>c</sup>Displacement of Ni from the  $N_2S_2$  best plane. <sup>d</sup>Displacement of Pd from the  $S_2P_2$  best plane.

plane, defined as the hinge angle in the bimetallic structures, is  $118.27^{\circ}$  for I, increasing by  $10^{\circ}$  for complex II to  $128.3^{\circ}$ ; complexes III and IV have hinge angles of  $131.3^{\circ}$  and  $132.8^{\circ}$ , respectively. This increase is accompanied by an overall increase in the Ni…Pd distance of 0.23 Å.

The S–Ni–S bite angles of the free metallodithiolate ligands, Ni(bme-dach\*), Ni(bme-dach),<sup>23</sup> and Ni(bme-daco) (bme-daco is bis-mercaptoethane diazacyclooctane),<sup>24</sup> are presented in Figure 4 for comparison to the Ni–Pd complexes. Note that



**Figure 4.** Molecular structures of Ni(bme-dach<sup>23</sup>), Ni(bme-dach),<sup>23</sup> and Ni(bme-daco)<sup>24</sup> as thermal ellipsoids (50% probability level). Select metric parameters are shown in the table.

the constriction of the two nitrogen atoms in the mesodiazacycle leads to an increase in the S…S distance due to enlargement of the  $\angle$ S–Ni–S; that is, the  $\angle$ N–Ni–N angle varies inversely as the  $\angle$ S–Ni–S angle with an overall expansion of ca. 12°.<sup>8</sup> In addition, on binding a second metal center, the  $\angle$ S–Ni–S is further constricted by ca. 5–6° in the bimetallic complexes (**I–IV**). Whether there is a role for bite angles in the NiN<sub>2</sub>S<sub>2</sub> metallodithiolates that might govern possible hemilability in the opening of reactive sites on the palladium metal awaits further experimentation.

The  $\angle$ S–Pd–S angles vary very slightly across the four complexes (79.05–81.24°). The  $\angle$ P–Pd–P differs by 5° according to the two- or three-carbon linker in dppe (ca. 84° or 85°) or dppp (ca. 90°); see Table 1. The six-membered metallocycles such as NiN<sub>2</sub>C<sub>3</sub> in III and IV and PdP<sub>2</sub>C<sub>3</sub> in II and IV Ni(bme-dach\*)/(bme-dach) and Pd(dppp)/(dppe) components are found in chair conformations.

**Comparison of** <sup>31</sup>P{<sup>1</sup>H} NMR Chemical Shifts. All complexes were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (see the SI). The <sup>31</sup>P{<sup>1</sup>H} NMR shifts, summarized in Table 2, show the dppe-containing complexes,

Table 2. <sup>31</sup>P{<sup>1</sup>H} NMR Chemical Shift Data in Dioxane for Complexes I–IV, the Free Diphosphine Ligands, and Pd-Diphosphine Analogues

complex	$^{31}P{^{1}H} shift^{a}$	reference complex	$^{31}P{^{1}H} $ shift <sup>a</sup>
Ι	68.03	dppe/dppp	-11.84/-16.02
II	4.28	Pd(dppe)Cl <sub>2</sub>	68.36
III	65.03	Pd(dppp)Cl <sub>2</sub>	13.72
IV	3.67	$[Pd(dppp)_2]^{2+}$	11.89
a ,			

 ${}^{a}H_{3}PO_{4}$  (0 ppm) was used as reference for the  ${}^{31}P$  NMR shift; values are given in ppm units.

including Pd(dppe)Cl<sub>2</sub>, to be in the 65–68 ppm range. In contrast, the <sup>31</sup>P chemical shifts for complexes II and IV containing the dppp unit are much smaller, around 4 ppm; consistently, their precursor Pd(dppp)Cl<sub>2</sub> showed a <sup>31</sup>P{<sup>1</sup>H} resonance at 13.72 ppm. Resonances for the free diphosphine ligands, dppe and dppp, are at –11.84 and –16.02 ppm, respectively. Resonances from other nuclei are consistent with their chemical environment represented by the solid-state structures.

#### ELECTROCHEMISTRY

**Cyclic Voltammetry.** Cyclic voltammograms (CVs) of complexes I–IV were recorded at 22  $^{\circ}$ C under Ar in CH<sub>3</sub>CN using a glassy carbon working electrode with 0.1 M

 $[{}^{t}Bu_{4}N][PF_{6}]$  as the supporting electrolyte. All potentials are referenced to added  $Fc^{0/+}$  at  $E_{1/2} = 0.0$  V. Figure 5 shows the



Figure 5. Cyclic voltammetry study of 2 mM complexes of I (blue), II (red), III (green), and IV (purple) as  $PF_6^-$  salts under argon in CH<sub>3</sub>CN solutions containing 0.1 M [<sup>t</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] as supporting electrolyte at 200 mV/s.

full scans of all complexes. The CVs were initiated as noted and scanned in the negative direction at a 200 mV/s scan rate; scan reversal was at the solvent window. The results are summarized in Table 3. The four complexes showed similar redox patterns,

### Table 3. Cathodic Potentials for Reductions $(E_{pc})$ of Complexes I–IV<sup>*a*</sup>

entry	complex	$E_{\rm pc}({\rm Pd}^{\rm II}/{\rm I})$	$E_{\rm pc}({\rm Pd}^{{\rm I}/0})$	$E_{\rm pc}({\rm Ni}^{{\rm II/I}})$
1	I	-1.25 V	-1.59 V	-2.38 V
2	II	-1.27 V	-1.61 V	-2.38 V
3	III	-1.28 V	-1.61 V	-2.48 V
4	IV	-1.29 V	-1.59 V	-2.49 V

<sup>*a*</sup>All potentials were referenced to  $Fc^{0/+}$  in CH<sub>3</sub>CN solutions in 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> electrolyte using a glassy carbon working electrode.

with two irreversible reduction events separated by ca. 300 mV with nearly the same  $E_{\rm pc}$  values for each complex. Likewise there is a more negative quasi-reversible redox event at ca. -2.4 V for each.

The cyclic voltammogram for  $[Pd(dppp)_2]Cl_2$  in dichloromethane solution was recorded (see the SI, Figures S9, S10) for comparison to those of complexes I–IV. Two irreversible redox events at -1.28 and -1.60 V are assigned as  $Pd^{II/I}$  and  $Pd^{I/0}$ reductions, respectively. On the basis of the similarity in pattern and position, the first two reduction events of the Ni–Pd complexes were assigned to the Ni<sup>II</sup>(N<sub>2</sub>S<sub>2</sub>)Pd<sup>II/I</sup>(P<sub>2</sub>) and Ni<sup>II</sup>(N<sub>2</sub>S<sub>2</sub>)Pd<sup>I/0</sup>(P<sub>2</sub>) couples, at ca. -1.27 and ca. -1.60 V, respectively. Electrochemical studies of analogous Ni<sup>II</sup>Ni<sup>II</sup> complexes with similar coordination geometry suggested the likelihood of Ni<sup>II</sup>(N<sub>2</sub>S<sub>2</sub>)Ni<sup>I</sup>(P<sub>2</sub>) and Ni<sup>II</sup>(N<sub>2</sub>S<sub>2</sub>)Ni<sup>0</sup>(P<sub>2</sub>) reduced species.<sup>25</sup> Although phosphine ligands support low oxidation states, the possibility of describing the more reduced species as Ni<sup>I</sup>Ni<sup>I</sup> rather than Ni<sup>II</sup>Ni<sup>0</sup> was raised by others.<sup>26,27</sup>

The quasi-reversible, more negative cathodic event in the CVs of **I**–**IV** displays greater dependency on the nature of the N<sub>2</sub>S<sub>2</sub> and is assigned to the Ni<sup>II/I</sup>(N<sub>2</sub>S<sub>2</sub>)Pd<sup>0</sup>(P<sub>2</sub>) couple. With increasing scan rate, this event becomes more reversible for all complexes; however the less negative events assigned to the palladium reductions are unchanged (see the SI, Figure S14). Overall the  $E_{1/2}$  values of the Ni<sup>II/I</sup>(N<sub>2</sub>S<sub>2</sub>)Pd<sup>0</sup>(P<sub>2</sub>) couple of

Table 4. Reaction Optimization of Suzuki Coupling ReactionCatalyzed by Complexes I–IV

	(CH <sub>2</sub> ) <sub>n1</sub>	S <sup>M</sup> Pd Pd Ph Ph	Ph (CH <sub>2</sub> ) <sub>n2</sub> Ph	2PF <sub>6</sub> I n <sub>1</sub> = 2 n II n <sub>1</sub> = 2 r III n <sub>1</sub> = 3 IV n <sub>1</sub> = 3	$n_2 = 2$ $n_2 = 3$ $n_2 = 2$ $n_2 = 3$
	Ph-I + <b>1a</b>	PhB(OH) <sub>2</sub> <b>2a</b>	Catalyst (1 Base (2 ec Solvent 2 reflux, 15 l	mol %) quiv.) ml 3a	<sup>&gt;</sup> h
entry <sup>a</sup>	cat.	solvent	base	temp (°C)	yield <sup>b</sup> (%)
1	I	dioxane	Na <sub>2</sub> CO <sub>3</sub>	reflux (101)	17
2	Ι	dioxane	K <sub>2</sub> CO <sub>3</sub>	reflux	75
3	Ι	dioxane	$Cs_2CO_3$	reflux	96
4	Ι	dioxane	Et <sub>3</sub> N	reflux	13
5	Ι	dioxane	Pyridine	reflux	0 <sup><i>c</i></sup>
6	II	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	reflux	>99
7	II	toluene	$Cs_2CO_3$	reflux (111)	39
8	II	THF	$Cs_2CO_3$	reflux (66)	85
9	II	CH <sub>3</sub> CN	$Cs_2CO_3$	reflux (82)	26
10	II	dioxane	$Cs_2CO_3$	60	14
11	III	dioxane	$Cs_2CO_3$	reflux (101)	92
12	IV	dioxane	$Cs_2CO_3$	reflux	95
13	-	dioxane	$Cs_2CO_3$	reflux	0 <sup><i>c</i></sup>

<sup>*a*</sup>Reactions were carried out by using aryl halide (0.3 mmol, 1 equiv), phenylboronic acid (0.36 mmol, 1.2 equiv), Ni–Pd complex (0.003 mmol, 1 mol % equiv), and base (0.6 mmol, 2 equiv) in 2 mL of solvent under reflux for 15 h. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Starting material was recycled.

complexes III and IV, (the Ni(bme-dach) derivatives) at -2.48 V are about 100 mV more negative than those of complexes I and II (with Ni(bme-dach\*)), at -2.38 V.

Interestingly the  $E_{1/2}$  values assigned to the nickel in the NiN<sub>2</sub>S<sub>2</sub> binding site of the Ni–Pd complexes are close to that of the Ni<sup>II/1</sup> reduction in the free metalloligands (see the SI, Figure S15).<sup>28</sup> A compilation of Ni<sup>II/1</sup> redox couples in a series of NiN<sub>2</sub>S<sub>2</sub>M' complexes finds that better Lewis acid receivers,

such as W(CO)<sub>4</sub>,<sup>29</sup>  $[(\eta^5-C_5H_5)Fe(CO)]^+$ ,<sup>7</sup>  $[(\eta^5-C_5Me_5)Fe(CO)]^+$ ,<sup>30</sup> or Me<sup>+</sup> (as in the alkylation of the thiolate generating S-bound, Ni<sup>II</sup> thioether complexes),<sup>28</sup> shift the Ni<sup>II/I</sup> reduction to considerably more positive potentials. The absence of such positive shifts at Ni in the cases reported here suggests that the reduced palladium has little effect on the Ni<sup>II/I</sup> reduction. While one might argue that the NiN<sub>2</sub>S<sub>2</sub> metalloligand dissociates from the reduced palladium, there was little evidence of complex degradation in the electrochemical cell; deposition on the electrode surface was minor, as indicated by consistency of multiple scans over the reductive region (see the SI, Figure S12–S14).

**Ni–Pd-Catalyzed Suzuki Coupling Reactions.** Optimizing Conditions. In order to establish the possibility that the NiN<sub>2</sub>S<sub>2</sub> metalloligands might serve as a diphosphine surrogate, we have examined complexes I through IV according to a typical protocol for Suzuki coupling, i.e., establishing optimal conditions for simple phenyl substrates and the scope or tolerance of the reaction to various aryl substituents. In addition the requirement for the NiN<sub>2</sub>S<sub>2</sub> metalloligand was established via several control experiments. In general the reactions were analyzed for product following only one experiment; however entry 6 of Table 4 was performed three times with the same result, while the results of entries 2, 9, and 11 are duplicates.

Scope of Reaction. With the optimized reaction conditions in hand, we extended the reaction to include a range of commercially available aryl halides and phenylboronic acids. As listed in Table 5, phenylboronic acid 2a readily reacted with bromobenzene 1b and gave the corresponding product 3a in excellent yield (entry 2). Reaction with 4-chlorotoluene 1c proceeded slowly; after 4 days, product 3b was isolated in 21% yield with recovery of the starting materials (entry 3). Entry 4 demonstrates the expected selectivity of iodine over fluorine. The reaction slowly proceeded with substrates bearing the OTf group, 1e; after 5 days product 3d was obtained in 34% yield (entry 5). This catalytic system is also compatible with heteroaryl halides such as 2-bromopyridine 1f (entry 6).

Several substituted phenylboronic acids were also tested for the reaction scope. Reaction with *p*-tolylboronic acid **2b** and 4*tert*-butylphenyl boronic acid **2c** proceeds smoothly, giving the corresponding products **3b** and **3f** in excellent yields (entries 7

Table 5. Catalyst II and the Scope of Cross Coupling of Aryl Halides (1a-e) and Arylboronic Acids (2a-e)

		R <sub>1</sub> + + 1a-1f	R <sub>2</sub> B(OH <b>2a-2e</b>	) <sub>2</sub> Cat. II 1 mol% Cs <sub>2</sub> CO <sub>3</sub> 2 equi 1,4-dioxane reflux	$r \sim R_1$	3a-3g		
entry <sup>a</sup>	R <sub>1</sub>	Х		$R_2$		time	product	yield <sup>b</sup> (%)
1	Н	Ι	1a	Н	2a	15 h	3a	>99
2	Н	Br	1b	Н	2a	16 h	3a	94
3	4-Me	Cl	1c	Н	2a	4 d	3b	21 <sup>c</sup>
4	4-F	Ι	1d	Н	2a	19 h	3c	83
5	4-OMe	OTf	1e	Н	2a	5 d	3d	34
6	2-bromopyridine	Br	1f	Н	2a	20 h	3e	81
7	Н	Ι	1a	4-Me	2b	12 h	3b	85
8	Н	Ι	1a	4- <sup>t</sup> Bu	2c	14 h	3f	87
9	Н	Ι	1a	4-Cl	2d	12 h	3g	93
10	Н	Ι	1a	4-OMe	2e	13 h	3d	88 <sup>d</sup>

<sup>*a*</sup>Reactions were carried out by using aryl halide (0.3 mmol, 1 equiv), boronic acid (0.36 mmol, 1.2 equiv), compound II (0.003 mmol, 1% equiv), and Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 2 equiv) in 2 mL of solvent under reflux. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Starting material was recycled. <sup>*d*</sup>92% NMR yield by using *p*-toluidine as an internal reference.

and 8). Boronic acid bearing phenyl-substituted Cl 2d and OMe groups 2e also react well under standard conditions (entries 9 and 10).

Catalyst Control Experiments. To further explore the role of the  $NiN_2S_2$  unit, several control reactions were carried out, as shown in Table 6, for comparison to the standard reaction

## Table 6. Control Reaction of Ni–Pd Complex Catalyzed Suzuki–Miyaura Reaction

$\bigcirc$	+ B(OH) <sub>2</sub> Ca - Cs <sub>2</sub> CO <sub>3</sub> 1,4-dioxane,	nt. 2 equiv. , reflux, 15h	
1a	2a		3a
entry <sup>a</sup>	cat.	loading	yield <sup>b</sup> (%)
1	[Ni(bme-dach*)Pd(dppp)](PF_6)_2	1 mol %	>99
2	Ni(bme-dach*)	1 mol %	0 <sup>c</sup>
3	$[Pd_2(Ni(bme-dach))_4]^{4+}$	1 mol %	0 <sup>c</sup>
4	Pd(dppp)Cl <sub>2</sub>	1 mol %	43
5	[Pd(dppp) <sub>2</sub> ]Cl <sub>2</sub>	1 mol %	94
6	Pd(dppp)Cl <sub>2</sub> /Ni(bme-dach*)	1 mol % (each)	91
7	Pd(dppp)Cl <sub>2</sub> /bme-dach	1 mol % (each)	0 <sup>c</sup>
8	Pd(dppp)Cl <sub>2</sub> /bme-dach	d	0 <sup>c</sup>
-			

<sup>*a*</sup>Reactions were carried out by using iodobenzene (0.3 mmol, 1 equiv), phenylboronic acid (0.36 mmol, 1.2 equiv),  $Cs_2CO_3$  (0.6 mmol, 2 equiv), and catalyst (see entries) in 2 mL of 1,4-dioxane under reflux for 15 h. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Recycle of starting material. <sup>*d*</sup>1% Pd(dppp)Cl<sub>2</sub> and 10% bme-dach ligand (as dithiol) were used.

conditions (entry 1). The use of 1 mol % Ni(bme-dach\*) as a potential catalyst in the reaction did not give any biaryl compound 3a (entry 2). It is known that the  $NiN_2S_2$  complexes combine with Pd<sup>2+</sup> to form thermodynamically stable hexametallic  $[Pd_2(NiN_2S_2)_4]^{4+}$  complexes of a paddle-wheeltype structure.<sup>31</sup> This complex was independently prepared as its chloride salt with Ni(bme-dach) "paddles".<sup>31</sup> This aggregate was found to be inactive as a catalyst under the conditions employed. Thus, we conclude that the NiN<sub>2</sub>S<sub>2</sub> unit is catalytically inactive in this reaction and becomes an active bimetallic Ni-Pd catalyst only in the presence of a palladiumdiphosphine. On using 1 mol %  $Pd(dppp)Cl_2$  as catalyst in the absence of nickel, a 43% yield of the 3a product was obtained; the use of  $[Pd(dppp)_2]Cl_2$  gave 3a in 94% yield. This result suggests that the diphosphine ligand is required for the catalysis by palladium, and we assume that an excess of the diphosphine reduces Pd(II) to Pd(0).<sup>32,33</sup> When a combination of 1 mol % Pd(dppp)Cl<sub>2</sub> and 1 mol % Ni(bme-dach\*) was used as catalyst, 3a was isolated in 91% yield. A possible explanation is that the NiN<sub>2</sub>S<sub>2</sub> unit might serve as a reducing agent, affording the [Pd(0)(dppp)] species as the "real" catalyst. This hypothesis was somewhat supported by a MS analysis obtained on a sample derived from a crude reaction mixture using 20% of II as catalyst. While the formation of disulfide is possible, a prominent signal of mass 32 greater than that for Ni(bmedach\*) was observed and may be interpreted as a  $\text{NiN}_2\text{S}_2{\cdot}\text{O}_2$ product (a bis-sulfoxide or sulfenate).<sup>28</sup> Control reactions were also carried out employing a combination of  $Pd(dppp)Cl_2$  with 1 mol % and 10 mol % of the free bme-dach ligand; neither reaction gives the product 3a. This result suggests that the free bme-dach ligand does not reduce the Pd(II); however it might competitively bind to the Pd(II) center and deactivate the catalyst.

The mechanism for this reaction is assumed to be typical in that the  $NiN_2S_2$  is a surrogate for bidentate diphosphines, Figure 6. We hypothesize that the needed Pd(0) species is



Figure 6. Presumed mechanism of discrete air-stable nickel-palladium(II) complexes catalyzed Suzuki-Miyaura reactions.

generated on oxidation of the NiN<sub>2</sub>S<sub>2</sub> unit; the release of thioloxidized NiN<sub>2</sub>S<sub>2</sub> could be mediated by a trace amount of water. Such an *in situ* generated Pd(0)(dppp) is expected to proceed with the oxidative addition of iodobenzene. In fact, the expected intermediate, [PhPdI(dppp)], was indicated as a pair of douplets (d, 11.2 ppm, J = 52.3 Hz) and (d, -9.3 ppm, J = 52.3 Hz) in the time-resolved <sup>31</sup>P NMR spectra recorded on crude reaction mixtures in dioxane, using 20% catalyst II (see the SI, Figure S7). For comparison the literature reported values in  $d_6$ -acetone are (d, 11.94 ppm, J = 53.6 Hz) and (d, -9.05 ppm, J = 53.6 Hz).<sup>34</sup> In accordance with the accepted Suzuki–Miyaura reaction mechanism, transmetalation and reductive elimination lead to the biaryl product and regeneration of the Pd(0) species, thus completing the catalytic cycle. There is no expectation, nor is there evidence, of the reformation of the Ni–Pd precatalyst.

In summary, we have developed a series of  $NiN_2S_2$ metalloligand-coordinated Pd(II) complexes; their structures were characterized by NMR spectroscopy and X-ray diffraction analysis. Analogous to the well-known (dppp)<sub>2</sub>Pd<sup>2+</sup>, the Ni–Pd complexes are precatalysts for Suzuki cross-coupling reactions with benefits in terms of solubility, stability, and ease of preparation. The reaction scope and the requirement of the  $NiN_2S_2$  metallodithiolates have been established; preliminary results show that sulfoxygenation might account for the needed reduction of Pd(II) to Pd(0). As the possibilities for modifying the  $MN_2S_2$  metallodithiolate ligands, both at M and in the organic framework, are extensive,<sup>8</sup> our study provides a foundation for further exploration of this new class of ligands in catalyst design and mechanism study.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00176.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra for all complexes and other details of syntheses and extensive electrochemical studies (PDF)

Crystallographic data for complexes I–IV and Ni(bme-dach\*) (CIF)

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#### Notes

The authors declare no competing financial interest.

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