1,3-Dinitrone Pincer Complexes of Palladium and Nickel: Synthesis, Structural Characterizations, and Catalysis

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Neutral and cationic Pd(II) and Ni(II) OCO-type pincer complexes have been synthesized from the metalation of 1,3-dinitrones via C−H or C−Br bond activation using Pd(0), Pd(II), and Ni(0) starting materials. In each complex, the two six-membered metallacycles are non-coplanar and atropisomerization proceeds with a low barrier. Palladium dinitrone complexes have been shown as active catalysts for Heck couplings and the related Ni complex for Kumada reactions with turnover numbers up to 950 000.

Introduction

Pincer ligands and their complexes have been well studied since they were reported in the late 1970s,[1] in part owing to the ability of pincer ligands to stabilize metals with both low and high oxidation states. In addition, pincer complexes can display both high robustness and catalytic activity. For instance, transition metals stabilized by pincer ligands are highly active in synthetically important catalytic reactions, such as dehydrogenation,[2] C−C coupling,[3] and hydroamination[4] reactions. Pincer ligands are known to stabilize reactive intermediates in the course of activation of inert bonds, which allows for intermediate isolation and mechanistic studies of complex organometallic reactions.[5] Consequently, there has been an increasing interest in the design and synthesis of various pincer systems.

While different symmetrical DCD (D = a donor atom such as P, N, or S) systems have found wide applications in catalysis and in bond activation,[6] reports on OCO-type pincer systems are rather limited.[7] One of the reasons might be ascribed to the weak donating capacity of neutral O atoms or the reactivity of anionic O atoms such that these systems failed to behave as "spectator" ligands.

We reasoned that a nitrone group might be a good choice in developing new OCO-type pincer ligands in that the dipolar nature of nitrone should render the O atom a stronger donor. In a recent example, Yao and co-workers[8a] reported dimeric palladium complexes derived from the *ortho*-metalation of aryl nitrones, and the chelating aryl-nitrone system was arguably described as carbocyclic carbenes.[8−10,11a] These Pd complexes have shown extremely high catalytic activity in the Heck coupling reactions between aryl bromides and styrenes. In some cases, turnover numbers of such Pd complexes can be even greater than 10^6.

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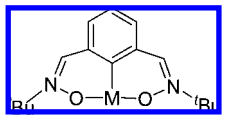
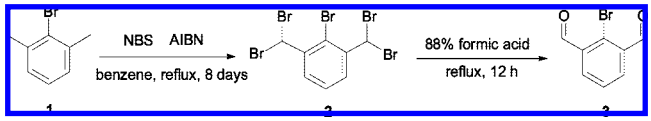
Chart 1. Pincer Dinitrone Complexes



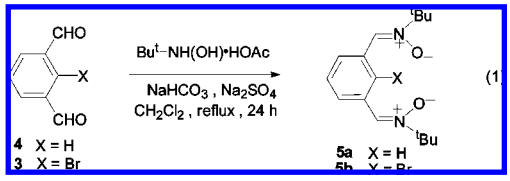
Scheme 1. Synthesis of 1,3-Dinitrone Ligands



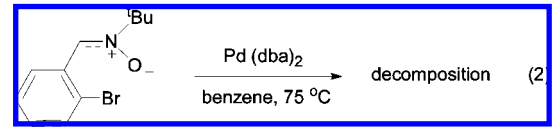
Transition metal complexes stabilized by OCO-type 1,3-dinitrone pincer ligands (Chart 1) should be an interesting target since the pincer entity might offer stability and robustness. It was our hope that the dipolar character of the N−O groups in dinitrone settings could lead to more donating oxygen atoms and give rise to readily isolable transition metal M−O species. We now report the synthesis and structural characterization of palladium and nickel complexes stabilized by OCO dinitrone-based pincer ligands. These complexes are highly active catalysts for Heck and Kumada cross-coupling reactions.

Results and Discussion

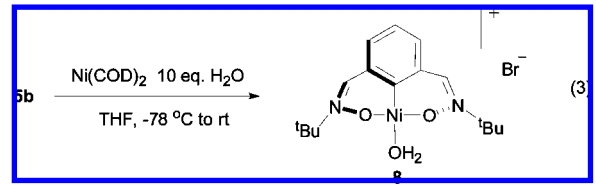
Ligand Synthesis. 2-Bromobenzene-1,3-dicarbaldehyde (**3**), precursor to the 1,3-dinitrone, was synthesized from 2-bromo-*meta*-xylene (**1**) by following a literature report (Scheme 1).[12] Thus two 1,3-dinitrone ligands (**5a**,**b**) were synthesized from the condensation of the corresponding 1,3-dialdehyde and *N*-(*tert*-butyl)hydroxylamine acetate in the presence of a base and a dehydrating reagent (eq 1). [8,13]



Palladium Complexes. We noted that cyclopalladation via C−H bond cleavage has been well-studied.[14,15] Reaction of **5a** and $Pd(OAc)_2$ in acetic acid gave an essentially homogeneous solution, and the crude product was tentatively assigned to Pd(OCO)(OAc). Purification of this crude product met with difficulty, and hence the acetate ligand was exchanged with a chloride when treated with LiCl in acetone. Thus analytically pure complex **6** was obtained after recrystallization. Alternatively, **6** could also be isolated in 61% yield as a result of C−Br bond activation[16] of **5b** when it is treated with $Pd(dba)_2$, followed by bromide to chloride exchange. We also noted that the 1,3-dinitrone functionality is necessary for the desired C−Br bond activation since we failed to isolate any identifiable Pd(II) product for the corresponding mononitrone compound under the same conditions (eq 2), although free dba ligand was obtained after the reaction. The chloride ligand in complex **6** can be readily exchanged with a triflate group when treated with AgOTf, leading to complex **7**.



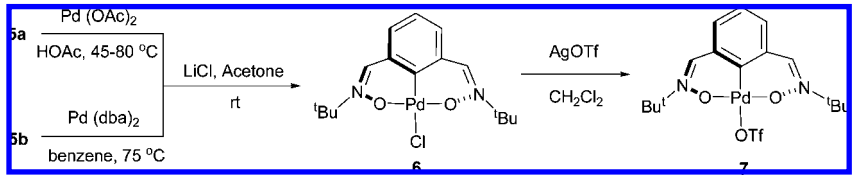
Nickel Complex. Treatment of $Ni(COD)_2$ with **5b** in THF with adventitious or with deliberately added H_2O led to an orange solution, and cationic Ni(II) aquo complex **8** was isolated as a yellow powder in 52% yield as a result of formal oxidative addition of Ni(0) (eq 3).[17,18] Neutral Ni(OCO)Br complex was proposed as the product when this reaction was carried out in dry THF. However, recrystallization using CH_2Cl_2/diethyl ether is necessary for the purification of the crude product, and the adventitiously present water substitutes the bromide ligand to give the final cationic Ni(II) aquo complex. The resonance signal of H_2O was not observable in ^{1}H NMR spectroscopy at room temperature, but was observed at −50 °C as a broad peak (δ 4.57). The molecular structure of complex **8** was further confirmed by X-ray crystallography. The formation of a cationic aquo complex is somewhat surprising, and this may indicate the sterically hindered environment of the (OCO)Ni fragment and that a bromide anion exerts more steric hindrance than H_2O. This explanation is also consistent with the fact that the bromide ligand in the incipient Pd(OCO)Br complex (Scheme 2) can be easily exchanged by a chloride one when treated with LiCl. Complexes **6**−**8** are all stable toward moisture and air, and the stability likely originates from the pincer-type ligation and the steric protection provided by the bulky *tert*-butyl groups that might prevent the C−Pd bond from being cleaved.



All the Pd and Ni pincer complexes have been fully characterized, and they showed symmetrical solution structures on the basis of NMR spectroscopy. For instance, two equivalent ^{t}Bu (δ 1.61) and imine CH (δ 7.93) resonance signals were observed in the ^{1}H NMR spectrum of **6**. In the ^{13}C NMR spectrum of **6**, the Pd-*C* resonates characteristically at δ 144.3. Similar NMR spectroscopic features were observed for complexes **7** and **8**.

Complexes **6** and **8** were further characterized by X-ray crystallography (Figure 1, Tables 1, 2). Single crystals of **6** and **8**·1/2CH_2Cl_2 suitable for X-ray crystallographic analysis were obtained by layering their CH_2Cl_2 solutions with pentane or diethyl ether at room temperature. Two pseudo-enantiomeric structures with similar corresponding bond lengths and angles were observed as a result of atropisomerization in the asymmetric units of **6** and **8**. Hence only one of them is discussed in

Scheme 2. Synthesis of Pd Complexes 6 and 7



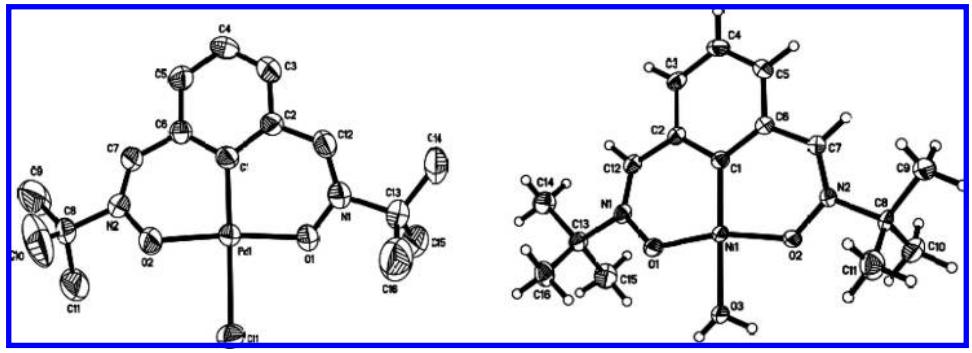


Figure 1. Molecular structures of **6** (left) and the cation of **8** (right) with ellipsoids shown at 50% thermal probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for complexes 6 and 8

	6 (M = Pd)	**8** (M = Ni)
M(1)−C(1)	1.935(5)	1.834(4)
M(1)−O(1)	1.994(4)	1.827(3)
M(1)−O(2)	1.987(4)	1.824(3)
M(1)−Cl(1)	2.434(1)	
M(1)−O(3)		1.963(3)
N(1)−O(1)	1.320(6)	1.331(4)
N(2)−O(2)	1.323(5)	1.322(4)
O(1)−M(1)−C(1)	93.66(19)	97.41(14)
O(2)−M(1)−C(1)	92.74(18)	96.59(14)
C(1)−M(1)−Cl(1)	178.72(15)	
C(1)−M(1)−O(3)		176.74(15)

Table 2. Crystallographic Data for Complexes 6 and 8

	6	**8** •1/2CH_2Cl_2
empirical formula	$C_{16}H_{23}ClN_2O_2Pd$	$C_{16}H_{25}BrN_2NiO_3 \cdot 1/2CH_2Cl_2$
fw	417.21	474.46
temperature (K)	296(2)	173(2)
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	11.5757(4)	15.5218(6)
b (Å)	17.7353(7)	13.2137(5)
c (Å)	18.1998(6)	20.4587(8)
α (deg)	90	90
β (deg)	92.738(2)	94.205(2)
γ (deg)	90	90
V (Å^3)	3732.1(2)	4184.8(3)
Z	8	8
D_{calcd} (g/cm^3)	1.485	1.506
μ (mm^{-1})	1.145	2.980
cryst size (mm^3)	0.20 × 0.15 × 0.10	0.28 × 0.26 × 0.15
total, unique no. of reflns	45 944, 11 264	53 779, 12 729
R(int)	0.0419	0.0375
data, restraints, params	11 264, 75, 409	12 729, 13, 466
R, R_w (all data)	0.0788, 0.1713	0.0747, 0.1324
GOF	1.082	1.093
peak and hole (e Å^{-3})	1.450, −1.148	1.915, −1.787

each case, and selected bond lengths and angles are given in Table 1. For both Pd and Ni complexes, slightly distorted square-planar coordination environments around transition metal centers were observed. Each complex adopts a C_2 symmetrical structure such that the aromatic ring is non-coplanar to the Pd or Ni coordination plane, although the twist is more pronounced for the Pd complex (the torsion angle of O(1)−M−C(1)−C(2) = 18.4° for **6** but 6.2° for **8**). The Pd(1)−C(1) length (1.935(5) Å) in **6** is shorter than that in typical Pd−$C_{carbene}$ complexes (1.990(3)−2.137(5) Å)[19] but comparable to the Pd−$C_{carbene}$ reported by Yao[8a] (1.948(6) Å) and is close to that of Pd−C_{aryl} reported by Canty for cyclometalated Pd(II) aryl complexes.[8b] Similarly, The Ni−C length (1.834(5) Å) in complex **8** is also slightly shorter than those observed in other nickel(II) NHC complexes.[20−23] Although atropisomers were observed in the solid state for complexes **6** and **8**, attempts to freeze this atropisomerization process failed by VT ^{1}H NMR analyses of complexes **6**−**8**, and no decoalescence was observed even at −80 °C (CD_2Cl_2). This indicates that the barrier of atropisomerization is lower than 10 kcal/mol.[24] Atropisomerization is typically a fast process in pincer complexes with six-membered metallacycles.[25] However, this process can be within the NMR time scale ($\Delta H^{\ddagger} \approx 14$ kcal/mol), and the activation barrier can be complicated by ring size and the nature of the pincer donor atoms, as was reported by Crabtree.[26]

Heck Coupling. Complexes **6** and **7** were applied as catalysts for Heck reactions. Complex **6** gives a turnover number (TON) of 90 000 in the coupling reaction of iodobenzene and styrene

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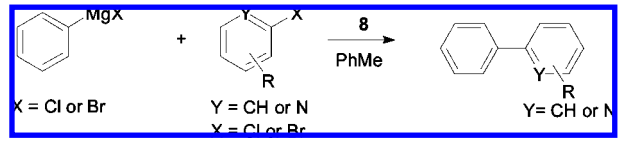
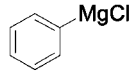
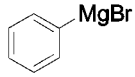
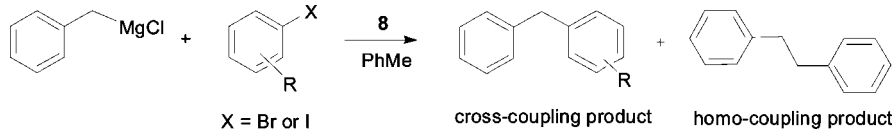
Table 3. Kumada Reactions Catalyzed by Ni Complex 8

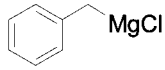


entry[a]	Grignard reagents	Ar-X	8 (mol%)	time (h)	yield (%)[b] (TON)
1		chlorobenzene	1	13	86 (86)
2		bromobenzene	0.01	14	85 (8, 500)[c]
3		bromobenzene	0.001	50	94 (94, 000)
4		bromobenzene	0.0001	50	95 (950, 000)
5		1-bromo-4-butylbenzene	0.5	6	93 (186)
6		1-bromo-4-*tert*-butylbenzene	0.1	48	85 (850)
7		2-bromotoluene	0.5	12	92 (184)
8		2-bromonaphthalene	0.5	12	90 (180)
9		1-bromonaphthalene	0.5	12	97 (194)
10		2-bromopyridine	1	12	74 (71)

[a]Reaction conditions: 1.0 mmol of aromatic halide, 1.05 mmol of Grignard reagent, 5 mL of toluene, 70 °C. [b]Determined by GC analysis using dodecane as an internal standard. [c]Isolated yields based on the average of two parallel runs.

Table 4. Kumada Reactions Catalyzed by Ni Complex 8



entry[a]	Grignard reagents	Ar-X	8 (mol%)	time (h)	yield (%)[b] of cross-coupling product	yield(%)[b] of homo-coupling product
1		bromobenzene	1	12	65 (65)	7.8
2		iodobenzene	1	12	92 (92)	6.0
3		iodobenzene	0.01	16	78 (7, 800)	8.8
4		2-iodotoluene	0.5	20	66 (132)	8.7

[a]Reaction conditions: 1.0 mmol of aromatic halide, 1.05 mmol of Grignard reagent, 5 mL of toluene, 70 °C. [b]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

(see the Supporting Information), and *trans*-stilbene is the only observed product.

Kumada Coupling. Ni pincer complexes have been reported as active catalysts for Kumada coupling reactions.[27] Our studies indicate that complex **8** shows high catalytic activity in the coupling reactions between various aryl halides and Grignard reagents (Table 3). A turnover number up to 950 000 has been achieved in the reaction of benzyl bromide and PhMgCl even though the reaction conditions were not fully optimized (entry 4). The coupling of PhMgCl and the less reactive chlorobenzene was also successful (entry 1). In addition, complex **8** can also catalyze the coupling reactions between aryl halides and benzyl magnesium chloride (Table 4), although aryl iodide substrate is necessary with relatively high catalyst loading for high reaction yield (entry 2, Table 4). In all cases the homocoupling byproduct $PhCH_2CH_2Ph$ was obtained in 6−9% yield.

Conclusion

In conclusion, we have synthesized two 1,3-aryldinitrone ligands and achieved the subsequent metalations of these ligands

via C−H or C−Br bond activation, and palladium and nickel OCO pincer complexes have been isolated as stable products. In the case of the Ni pincer complex, a cationic $[Ni(OCO)(H_2O)]^+$ complex was obtained. Both Pd and Ni complexes were crystallographically characterized. These OCO pincer complexes have twisted C_2 symmetrical structures with a non-coplanar orientation of aromatic ring and the metal coordination plane. These complexes give high catalytic activity for Heck reactions and Kumada reactions. Palladium complexes **6** and **7** have lower catalytic activity for Heck coupling than those cyclometalated dimeric Pd mononitrone complexes that contain labile μ-acetate ligands.[8a] This comparison suggests that although the introduction of a pincer group might increase the thermostability of the catalyst system, the catalytic activity might be sacrificed. To the best of our knowledge, complexes **6**−**8** are the first examples of dinitrone pincer complexes of palladium and nickel.

Experimental Section

General Considerations. Unless otherwise mentioned, all manipulations were carried out using standard Schlenk techniques, and all solvents and chemicals were used as received without any further purification. 2-Bromo-*meta*-xylene (**1**) and benzene-1,3-dicarbaldehyde (**4**) were obtained from commercial sources. NMR spectra were obtained on a Bruker DPX300, AMX400, or 500 spectrometer. Elemental analyses were carried out in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in the ESI mode on a Finnigan MAT95XP GC/HRMS system. GC analyses were carried out with 6890N network GC system from Agilent Technologies, equipped with a Cyclo Sil-B column.

Synthesis of 1,3-Bis(dibromomethyl)-2-bromobenzene (2). To a solution of 2-bromo-*meta*-xylene (6.65 mL, 50 mmol) in benzene (500 mL) were added NBS (71.2 g, 400 mmol) and AIBN (50 g). The mixture was heated under reflux and irradiated with an UV lamp. The reaction was monitored by TLC. After 48 h, additional NBS (35.6 g, 200 mmol) and AIBN (25 g) were added. The reaction was almost complete after 8 days. The reaction mixture was allowed to stand overnight and then filtered to remove succinimide and the NBS in excess. The residue was washed with benzene (3 × 50 mL) followed by 10% aqueous sodium hydrogen sulfite (250 mL). The organic layer was separated and dried with Na_2SO_4. Solvent removal and column chromatography gave **2** in 88% yield (22.0 g, 44.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.8 Hz, 2H, Ar−H), 7.53 (t, J = 7.9 Hz, 1H, Ar−H), 7.13 (s, 2H, $CHBr_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 141.0 (Ar−C), 132.7 (Ar−C), 130.0 (Ar−C), 117.4 (Ar−C), 41.6 ($CHBr_2$). Anal. Calcd for $C_8H_9Br_5$ (500.6): C, 19.19; H, 1.01. Found: C, 19.10; H, 1.13.

Synthesis of 2-Bromobenzene-1,3-dialdehyde (3). A mixture of **2** (2.02 g, 4 mmol) and 88% formic acid (40 mL) was stirred and refluxed for 12 h. The mixture was cooled to room temperature, followed by removal of the solvent. The residue was poured into water (80 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The organic phases were combined and dried with Na_2SO_4. Analytically pure **2** was obtained from the removal of the solvent and purification by column chromatography on silica gel. Yield: 90% (775.5 mg, 3.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 2H, CHO), 8.15 (d, J = 7.6 Hz, 2H, Ar−H), 7.57 (t, J = 7.5 Hz, 1H, Ar−H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.7 (CHO), 135.3 (Ar−C), 134.5 (Ar−C), 130.9 (Ar−C), 128.3 (Ar−C). Anal. Calcd for $C_8H_5BrO_2$ (213.0): C, 45.10; H, 2.37. Found: C, 45.25; H, 2.31.

General Method for the Synthesis of Compounds 5a,b. A 50 mL round-bottom flask was charged with *N-tert*-butylhydroxylamine acetate (298.4 g, 2.0 mmol), **4** (134.1 mg, 1.0 mmol), $NaHCO_3$ (252.0 mg, 3.0 mmol), anhydrous Na_2SO_4 (426.0 g, 3.0 mmol), and dry CH_2Cl_2 (10 mL). The reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the solvent was removed under vacuum. **5a** was obtained after column chromatography (silica gel, hexane/ethyl acetate, 6:1 to 1:2 v/v). Analogously, **5b** was synthesized using **3** as a stating material.

Compound 5a. Yield: 74% (205.1 mg, 0.74 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (s, 1H, Ar−H), 8.40 (dd, J = 1.3 Hz, 7.9 Hz, 2H, Ar−H), 7.62 (s, 2H, CH═N), 7.48 (t, J = 7.9 Hz, 1H, Ar−H), 1.61(s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 131.1 (Ar−C), 130.2 (Ar−C), 129.9 (CH═N), 129.5 (Ar−C), 128.7 (Ar−C), 71.0 ($C(CH_3)_3$), 28.3 (CH_3). HRMS (ESI^+): 277.1907, calcd for $[C_{16}H_{25}N_2O_2]$ 277.1916. Anal. Calcd for $C_{16}H_{24}N_2O_2$ (276.4): C, 69.53; H, 8.75; N, 10.14. Found: C, 69.43; H, 8.59; N, 10.05.

Compound 5b. Yield: 73% (259.2 mg, 0.73 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (d, J = 8.0 Hz, 2H, Ar−H), 8.12 (s, 2H, CH═N), 7.45 (t, J = 8.0 Hz, 1H, Ar−H), 1.64 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 130.6 (Ar−C), 130.5 (Ar−C), 128.8 (CH═N), 127.4 (Ar−C), 125.1 (Ar−C), 72.2 ($C(CH_3)_3$), 28.3 (CH_3). HRMS (ESI^+): 355.1017, calcd for $[C_{16}H_{24}N_2O_2Br]$ 355.1021. Anal. Calcd for $C_{16}H_{23}N_2O_2Br$ (355.3): C, 54.09; H, 6.53; N, 7.89. Found: C, 53.93; H, 6.61; N, 7.68.

Synthesis of Palladium Complex 6. Method A (via C−H activation of **5a**). Under N_2 atmosphere, a 25 mL Schlenk tube was charged with **5a** (138.6 mg, 0.5 mmol), $Pd(OAc)_2$ (112.3 mg, 0.5 mmol), and HOAc (6 mL). The mixture was stirred and heated at 45 °C for 1 h, 60 °C for 1 h, and 80 °C for 4 h. The solvent was then removed under vacuum. To this residue were added LiCl (212.0 mg, 5.0 mmol) and acetone (6 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed, and the crude product was purified by passing through a short column (Al_2O_3, CH_2Cl_2/acetone, 5:1). **6** was obtained as a yellow solid. Yield: 62% (129 mg, 0.31 mmol).

Method B (via C−Br activation of **5b**). Under N_2 atmosphere, a 50 mL Schlenk tube was charged with **5b** (177.6 mg, 0.5 mmol), $Pd(dba)_2$ (287.5 mg, 0.5 mmol), and dry benzene (18 mL), and the mixture was stirred and heated to 75 °C for 24 h. The solvent was then removed under vacuum. To this residue were added LiCl (212.0 mg, 5.0 mmol) and acetone (6 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed, and the crude product was passed through a short column (Al_2O_3, CH_2Cl_2/acetone, 5:1) to give **6** as a yellow solid. Yield: 61% (129 mg, 0.31 mmol). Single crystals of **6** suitable for X-ray crystallographic analysis were obtained by layering a CH_2Cl_2 solution of **6** with pentane. ^{1}H NMR (500 MHz, CD_2CL_2): δ 7.93(s, 2H, CH═N), 7.33 (d, J = 7.3 Hz, 2H, Ar−H), 7.26−7.29 (m, 1H, Ar−H), 1.61 (s, 18H,CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 144.3 (Ar−C), 138.5 (CH═N), 131.9 (Ar−C), 127.1 (Ar−C), 71.2 ($C(CH_3)_3$). Anal. Calcd for $C_{16}H_{23}ClN_2o_2Pd$ (417.2): C, 46.06; H, 5.56; N, 6.71. Found: C, 45.93; H, 5.71; N, 6.58.

Synthesis of Palladium Complex 7. A mixture of **6** (83.4 mg, 0.2 mmol) and silver trifluoromethanesulfonate (51.4 mg, 0.2 mmol) in dry CH_2Cl_2 (5 mL) was stirred under argon at room temperature for 2 h in the dark. The mixture was then filtered to remove the insolubles. Solvent removal afforded **7** as a yellow powder. Yield: 61% (64.8 mg, 0.12 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.96 (s, 2H, CH═N), 7.39 (s, 3H, Ar−H), 1.66 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 141.0 (Ar−C), 138.8 (CH═N), 132.2 (Ar−C), 126.9 (Ar−C), 125.6 (Ar−C), 120.4 (q, $^1J_{F-C}$ = 317.7 MHz, CF_3), 71.8 ($C(CH_3)_3$), 27.9 (CH_3). ^{19}F NMR (212 MHz, CD_2Cl_2): δ −78.5. Anal. Calcd for $C_{17}H_{23}F_3N_2O_5PdS$ (530.9): C, 38.46; H, 4.37; N, 5.28. Found: C, 38.95; H, 4.01; N, 5.12.

(27) (a) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399. (b) Wang, Z.-X.; Wang, L. *Chem. Commun.* **2007**, 2423. (c) Sun, K.; Wang, L.; Wang, Z.-X. *Organometallics* **2008**, *27*, 5649. (d) Csok, Z.; Vechorkin, O.; Harkins, S. B.; Scopelliti, R.; Hu, X. *J. Am. Chem. Soc.* **2008**, *130*, 8156.

Synthesis of Nickel Complex 8. An oven-dried Schlenk tube was charged with $Ni(COD)_2$ (137.5 mg, 0.5 mmol) and THF (5 mL). A solution of **5b** (177.6 mg, 0.5 mmol) in THF (1.5 mL) was added dropwise to the mixture at −78 °C, followed by the addition of 10 equiv of H_2O. The reaction mixture was then allowed to warm slowly to room temperature and was stirred for 12 h. The color of reaction mixture changed from gray to orange with the formation of an orange precipitate. All the volatiles were removed under reduced pressure. The residue was washed with diethyl ether to give complex **8** as an air-stable orange solid. Yield: 52% (112.3 mg, 0.26 mmol). Single crystals suitable for X-ray crystallographic analysis were obtained by the diffusion of diethyl ether into a solution of **8** in CH_2Cl_2 at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2, 223K): δ 7.86 (s, 2H, CH═N), 7.30−7.35 (m, 1H, Ar−H), 7.20 (d, J = 7.0 Hz, 2H, Ar−H), 4.57 (br, 2H, H_2O), 1.52 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 140.5 (Ar−C), 139.8 (CH═N), 132.7 (Ar−C), 130.2 (Ar−C), 125.7 (Ar−C), 69.9 ($C(CH_3)_3$), 27.7 (CH_3). Anal. Calcd for $C_{16.5}H_{26}BrClN_2NiO_3$: C, 41.77; H, 5.52; N, 5.90. Found: C, 41.98; H, 5.71; N, 6.25.

The Heck Reactions (Table S1, Supporting Information). General Procedure. An oven-dried Schlenk tube was charged with aryl halide (1.0 mmol), styrene (1.2 mmol), internal standard 1,3,5-trimethoxybenzene (0.3 mol), base (1.5 mmol), and 5 mL of dry solvent under argon. Afterward, a freshly prepared stock solution of **6** or **7** (0.001−1.0 mol %) in an appropriate solvent was added. The reaction mixture was stirred at 140 °C for the desired time. The conversion of reaction was detected by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

The Kumada Reactions Catalyzed by Complex 8 (Table 3 and 4). General Procedure. An oven-dried Schlenk tube was charged with substituted aryl halide or alkyl halide (1 mmol), internal standard (0.25 mmol of 1,3,5-trimethoxybenzene for ^{1}H NMR spectroscopy or 0.5 mmol of dodecane for GC analysis), and 5 mL of dry toluene under argon. Afterward, a solution of nickel catalyst **8** (0.0001−1.0 mol %) in toluene and Grignard reagent (1 mol/L in THF, 1.05 mmol) was added via syringe. The reaction mixture was stirred at 70 °C for the desired time. The conversion of reaction was measured by GC or ^{1}H NMR spectroscopy versus the internal standard. In the case of reaction of bromobenzene with phenyl magnesium chloride, the solvent was removed under vacuum after cooling to room temperature. The residue was dissolved in CH_2Cl_2, filtered through Celite, and then purified by silica gel chromatography (hexane/EtOAc) to give analytically pure products.

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Supporting Information Available: Crystallographic data of complexes **6** and **8** (CIF and PDF) and results of Heck reactions catalyzed by complexes **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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