

Palladium(II) and Nickel(II) Complexes Bearing N,N,O-Chelate Ligands: Syntheses, Characterization and Catalysis in Heck and Kumada Coupling Reactions

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Two new anionic ligands, namely [2-{OC(Ph)₂CH₂}-6-(3,5-Me₂C₃HN₂)C₅H₃N}][−] (L1[−]) and [2-{OC(Ph)=CH}-6-(3,5-Me₂C₃HN₂)C₅H₃N}][−] (L2[−]), and their palladium and nickel complexes, were synthesized and characterized. 6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-methylpyridine was lithiated with *n*BuLi and the lithiated product treated with benzophenone to give Li(L1) (**2**), whereas treatment of 2-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridin-2-yl]-1-phenylethanone with NaH afforded Na(L2) (**6**). The palladium and nickel complexes [(L1)PdCl] (**3**), [(L1)NiAr] [Ar = *o*-MeC₆H₄ (**4a**), 1-C₁₀H₇ (**4b**)], [(L2)PdCl] (**7**) and [(L2)NiAr] [Ar = *o*-MeC₆H₄ (**8a**), 1-C₁₀H₇

(**8b**)] were obtained by ligand-transfer reactions between Li(L1) or Na(L2) and [PdCl₂(PhCN)₂] or [(Ph₃P)₂Ni(Ar)Cl] (Ar = *o*-MeC₆H₄ and 1-C₁₀H₇, respectively). These complexes are diamagnetic and were characterized by NMR spectroscopy and elemental analyses. The structures of complexes **4b** and **8a** were determined by single-crystal X-ray diffraction techniques. The catalytic activity of the nickel and palladium complexes in the Heck and Kumada cross-coupling reactions were investigated.

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Introduction

Group 10 metal catalyzed C–C coupling has been recognized as one of the most useful methods for C–C bond formation in organic synthesis and has been well developed over the past decades.^[1] The most frequently used cross-coupling reactions include the reactions of alkyl halides or pseudohalides with olefins (Heck reaction) and with nucleophilic organometallic reagents such as Grignard reagents (Kumada reaction), organozinc reagents (Negishi reaction), and organotin (Stille reaction), organoboron (Suzuki reaction), and organosilicon (Hiyama reaction) derivatives.^[1] The Heck reaction, which is mainly catalyzed by palladium complexes, is one of the simplest ways to obtain variously substituted olefins, dienes, and other unsaturated compounds.^[2] Other transition metals can also catalyze this reaction but they normally exhibit lower catalytic activity. The Kumada reaction, which was the first reported cross-coupling (early 1970s),^[3] is still attracting attention over 30 years later. Current investigation focuses mainly on the development of new catalyst systems and extension of this reaction to substrates such as organic chlorides.^[4] Complexes of Ni, Pd, Fe, Co, and other transition metals have been used to catalyze this reaction,^[1,4,5] although nickel and palladium complexes are the most attractive and intensively studied.

The choice of supporting ligands on the central metal atoms is crucial to the catalytic behavior of the complexes. The most often used ligands, which have achieved great success in catalysts for the Heck and Kumada reactions, are tertiary phosphanes. However, phosphane ligands are often expensive, poisonous, air-sensitive, and prone to degrade at elevated temperatures;^[6] therefore the development of phosphane-free ligands is a topic of current interest in this area. A number of phosphane-free ligands have been examined for palladium- and nickel-catalyzed Heck and Kumada couplings, some of which have exhibited excellent behavior.^[7] Herein we report the syntheses and characterization of new N,N,O-chelate ligands and their nickel and palladium complexes as well as the catalytic behavior of these complexes in the Heck and Kumada coupling reactions.

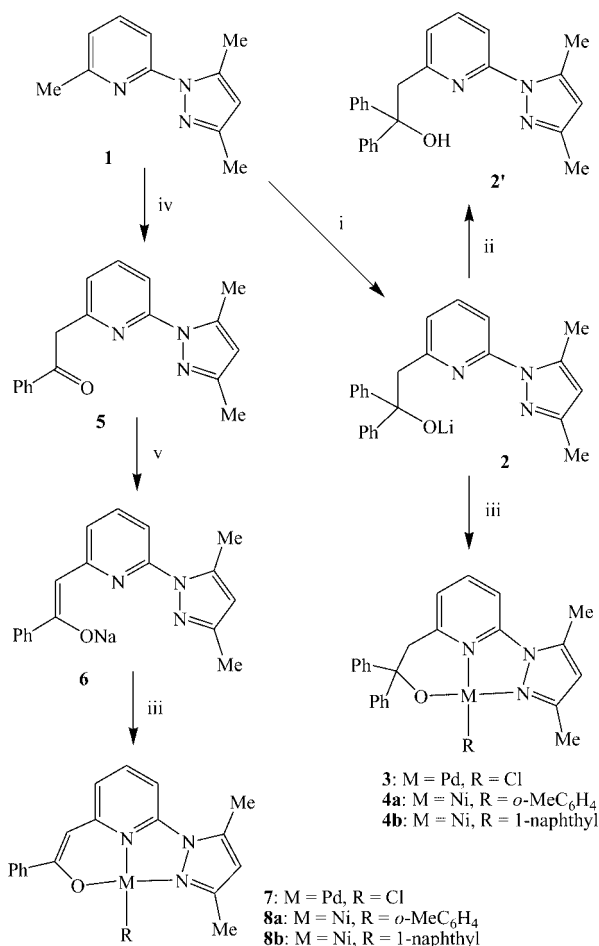
Results and Discussion

Syntheses and Characterization of Compounds 2–8b

The syntheses of the compounds discussed in this paper are shown in Scheme 1. 2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (**1**) was prepared by treatment of 2-hydrazino-6-methylpyridine with pentane-2,4-dione in acetic acid according to our previously reported method.^[8] Compound **1** was readily lithiated by treatment with LDA and the lithiated product treated with benzophenone to afford [Li{2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (**2**) in good yield. Complex **2** proved to be a good ligand-transfer reagent in reactions with [PdCl₂(PhCN)₂] and [(Ph₃P)₂Ni-

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(Ar)Cl] (Ar = *o*-MeC₆H₄, 1-C₁₀H₇), yielding the corresponding complexes **3**, **4a** and **4b**, respectively. Lithiated **1** was treated with PhCN and subsequently dilute H₂SO₄ to afford 2-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridin-2-yl]-1-phenylethanone (**5**). Treatment of **5** with *n*BuLi or LDA gave a mixture of the lithiated product and unreacted **5**. However, the reaction with NaH in thf formed [Na{2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (**6**) cleanly.



Scheme 1. Ligand and complex syntheses. Reagents and conditions: (i) LDA, thf, –60 to –20 °C, 20 min, then Ph₂CO, –80 °C to room temp., 12 h; (ii) 2 M aqueous solution of HCl, room temp., 1 h; (iii) [PdCl₂(PhCN)₂] or [(Ph₃P)₂Ni(Ar)Br] (Ar = *o*-MeC₆H₄ or 1-C₁₀H₇), thf, –80 °C to room temp., 10–30 h; (iv) LDA, thf, –60 to –20 °C, 20 min, then PhCN, –80 to –20 °C, 30 min, room temp., 10 h, then 2 M aqueous H₂SO₄, 0 °C to room temp., 10 h; (v) NaH, thf, refluxing, 12 h.

Treatment of **6** with [PdCl₂(PhCN)₂] afforded the palladium complex [PdCl{2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)-C₅H₃N}] (**7**), while treatment of **6** with [(Ph₃P)₂Ni(Ar)Cl] (Ar = *o*-MeC₆H₄, 1-C₁₀H₇) afforded complexes **8a** and **8b**, respectively. Attempts to synthesize [Ni(X){2-[OC(Ph)=CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] and [Ni(X){2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (X = Cl, Br) by treating **2** and **6**, respectively, with various nickel compounds such as [(dme)NiCl₂], [(R₃P)NiCl₂] (R = Ph, Et), [(Ph₃P)NiBr₂], and NiBr₂ were unsuccessful. Each reaction produced an unidentified white precipitate. The neutral compound **5** is a

pale-yellow solid and was characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. Complexes **2** and **6** are air-sensitive colorless (**2**) or pale-yellow (**6**) crystals. The palladium and nickel complexes are pale-yellow (**3**), brown (**8a**), or red (**4a**, **4b**, **7** and **8b**) crystals and are air-stable in the solid state. The nickel complexes are soluble in CHCl₃, CH₂Cl₂, and thf, but only slightly soluble in toluene. The palladium complexes are soluble in CH₂Cl₂, partly soluble in thf, and almost insoluble in toluene and Et₂O. Each of the complexes was characterized by NMR spectroscopy and elemental analyses and the data were found to be consistent with their respective structures. In addition, the diamagnetism of the four-coordinate palladium and nickel complexes revealed that these complexes have a square-planar geometry at the respective central metal atom, which means that the ligand coordinates to the central metal atom as an N,N,O-tridentate chelate. This was confirmed by single-crystal X-ray diffraction analyses of complexes **4b** and **8a**.

An ORTEP drawing of complex **4b** is presented in Figure 1 along with selected bond lengths and bond angles. This complex shows a distorted square-planar geometry around the nickel atom. The fact that the N1–Ni1–O1 bond angle [95.73(10)°] is wider than N1–Ni1–N3 [82.54(11)°] is consistent with the corresponding chelate ring size. Similarly, the Ni1–N1–C15 angle [126.3(2)°] is also wider than Ni1–N1–C19 [113.6(2)°]. The Ni1–N3 distance of 1.893(2) Å is shorter than that of Ni1–N1 [1.959(2) Å] and is also much shorter than the distances between the pyrazolyl nitrogen atoms and the nickel atom in [NiCl₂{NCH₂CH₂(N₂C₃HMe₂-3,5)}]·H₂O [2.0334(19) and 2.069(2) Å, respectively],^[9] but similar to the Ni–N dis-

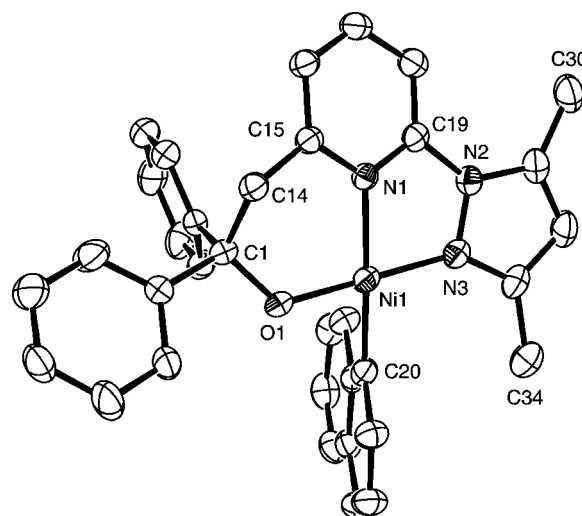


Figure 1. ORTEP drawing of complex **4b** with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ni1–O1 1.840(2), Ni1–N1 1.959(2), Ni1–N3 1.893(3), Ni1–C20 1.900(3), C1–O1 1.397(3), C1–C14 1.553(4), C14–C15 1.486(4), N2–N3 1.395(3), N2–C19 1.406(4), N1–Ni1–O1 95.73(10), N3–Ni1–O1 175.05(10), C20–Ni1–O1 86.30(11), N1–Ni1–N3 82.54(11), N1–Ni1–C20 172.68(12), N3–Ni1–C20 95.98(12), Ni1–N1–C19 113.6(2), Ni1–N3–N2 112.69(18), Ni1–O1–C1 122.03(18), Ni1–N1–C15 126.3(2).

tances in $[\text{Ni}_2\{(\text{NSiMe}_3)_2\text{CPh}\}_2]$ [1.868(5)–1.876(5) Å]^[10] and $[\text{Ni}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\text{C}(\text{H})\text{C}(\text{Ph})\text{O}\}_2]$ [Ni1–N2 = 1.901(3) Å].^[11] The Ni–O and Ni–C distances are within the normal range.

An ORTEP drawing of complex **8a** is presented in Figure 2 along with selected bond lengths and angles. Complex **8a** also shows a distorted square-planar geometry at the nickel atom and its structural skeleton is similar to that of complex **4b**, although with some differences in the bond lengths and angles. For example, the Ni1–N1, Ni1–N3, and Ni1–C19 distances in **8a** are shorter than the corresponding ones in **4b**, while the N1–Ni1–C19 and N3–Ni1–O2 angles in **8a** are wider than the corresponding ones in **4a**. The C6–C7 distance of 1.370(8) Å in **8a** is typical of a C–C double bond. The C5, C6, C7, and O2 atoms are almost coplanar, with a torsion angle of 0.5°.

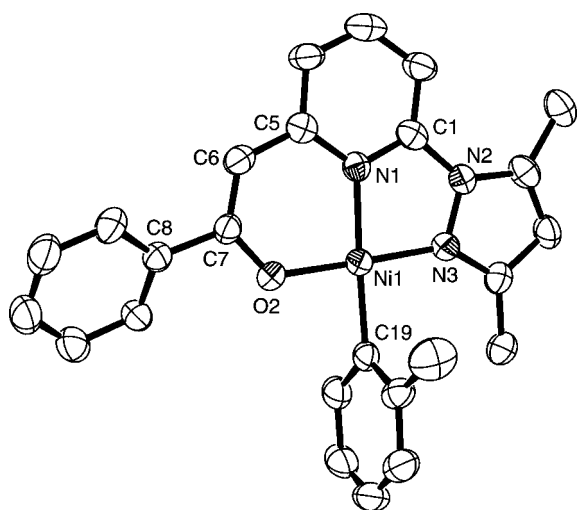


Figure 2. ORTEP drawing of complex **8a** with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ni1–O2 1.840(4), Ni1–N1 1.908(5), Ni1–N3 1.888(5), Ni1–C19 1.886(6), C5–C6 1.423(8), C6–C7 1.370(8), C7–O2 1.300(6), N2–C1 1.410(7), N2–N3 1.408(6), O2–Ni1–C19 85.1(2), O2–Ni1–N3 177.2(2), C19–Ni1–N3 96.0(2), O2–Ni1–N1 95.88(18), C19–Ni1–N1 174.9(2), N1–Ni1–N3 83.2(2).

Catalytic Activity of Complexes **3**, **4**, **7**, and **8** in the Heck and Kumada Reactions

We first examined the catalytic activity of complexes **3**, **4**, **7**, and **8** in the Heck reaction. The palladium complexes **3** and **7** catalyze the coupling of aryl iodides and bromides with butyl acrylate in the presence of a base, whereas under similar reaction conditions the nickel complexes only catalyze the reactions of aryl iodides with butyl acrylate. Complex **3** exhibits a higher catalytic activity than complex **7** in most cases, especially for substrates *p*-MeC(O)C₆H₄Br and *p*-MeOC₆H₄Br. For example, 0.1 mol-% of **3** catalyzes the coupling of *p*-MeOC₆H₄Br with butyl acrylate at 120 °C in NMP in the presence of K₂CO₃ to give the coupling product *trans*-*p*-MeOC₆H₄CH=CHCOOnBu in 86% yield (Table 1, Entry 7), while the reaction of the same substrates

catalyzed by 0.1 mol-% of **7** under the same conditions afforded the coupling product in only 15% yield (Table 1, Entry 22). The iodides were found to be more reactive than the bromides, and aryl chlorides were completely inert. The electronic effects of the substituents on the aryl ring of the halides obviously affect the coupling reactions catalyzed by **7** as both electron-withdrawing and electron-donating groups lead to a large decrease of the reactivity of the aryl bromides (Table 1, Entries 15, 18, 22, 36, 38, and 40). However, the electronic effects of the substituents on the aryl ring of the halides is much smaller in the reactions catalyzed by **3** than in the same reactions catalyzed by **7** (Table 1, Entries 2, 4, 7, 29, 31, and 33). The type of base used also affects the reaction. Thus, K₂CO₃ gave excellent results in the catalyst systems tested, while Et₃N led to relatively poor results in most cases.

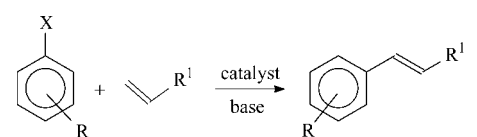
Complexes **4a**, **4b**, **8a**, and **8b** showed similar catalytic activity, with 0.5 mol-% of catalyst being sufficient to drive the reaction between PhI and butyl acrylate to completion with a quantitative yield of coupling product.

The couplings of aryl iodides or bromides with PhCH=CH₂ were also investigated. The nickel complexes were found to be almost inactive to the coupling reactions, although the palladium complexes **3** and **7** exhibited catalytic activity. These reactions showed a similar trend with respect to the reactions between aryl halides and butyl acrylate. Between 0.5 and 2 mol-% of the catalysts was required to drive these reactions to completion, depending on the aryl bromides employed. In addition, each coupling reaction gave only the *trans* product (by ¹H NMR spectroscopy); no *cis* isomer was observed.

de Vries and other researchers have recently reported that most of the palladium catalysts used for the Heck reaction decompose to form soluble palladium(0) colloids or nanoparticles at high temperature (higher than 120 °C), and that this colloidal palladium reacts further with aryl halides to form anionic intermediates.^[12] The reaction temperature is as high as 120 °C in our reaction system, and thus it seems that the palladium complexes might have decomposed during reaction. However, we did observe different catalytic activity between complexes **3** and **7**. For comparison, we also tested the Heck reaction catalyzed by PdCl₂ and PdCl₂ together with neutral ligand **2'** using the same substrates and reaction conditions as those for **3**. The results showed that PdCl₂ alone exhibits very low catalytic activity (Table 1, Entries 42 and 44), while PdCl₂+**2'** shows good catalytic activity (Table 1, Entries 43 and 45), although a little lower than that of **3**. This could be because the ligand stabilizes the colloids and prevents their aggregation, as suggested by de Vries.^[12a] The ligand probably also stabilizes the anionic palladium species formed by reaction of colloidal palladium with aryl bromides.

The catalytic behavior of complexes **3**, **4**, **7**, and **8** in the Kumada cross-coupling reaction was also evaluated. Palladium complexes **3** and **7** were found to catalyze the coupling of both aryl iodides and aryl bromides with *p*-MeC₆H₄MgBr to give the cross-coupling products (Table 2). Complex **7** exhibits a slightly better catalytic ac-

Table 1. Coupling of $RCH=CH_2$ ($R = CO_2nBu$ or Ph) and aryl bromides or iodides catalyzed by complexes **3**, **4**, **7**, and **8**.^[a]

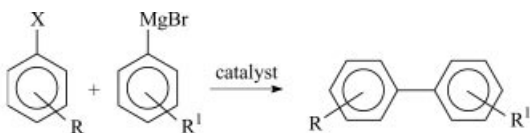


Entry	R	X	R ¹	Catalyst (mol-%)	Solvent	Time [h]	T [°C] ^[b]	Base	Yield [%] ^[c]
1	H	Br	CO ₂ nBu	3 (0.05)	NMP	32	120	K ₂ CO ₃	62
2	H	Br	CO ₂ nBu	3 (0.1)	NMP	32	120	K ₂ CO ₃	98
3	H	Br	CO ₂ nBu	3 (0.5)	DMF	20	120	K ₂ CO ₃	98
4	<i>p</i> -MeCO	Br	CO ₂ nBu	3 (0.1)	NMP	32	120	K ₂ CO ₃	93
5	<i>p</i> -MeCO	Br	CO ₂ nBu	3 (1)	NMP	12	120	NEt ₃	82
6	<i>p</i> -MeCO	Br	CO ₂ nBu	3 (1)	NMP	3	100	K ₂ CO ₃	98
7	<i>p</i> -MeO	Br	CO ₂ nBu	3 (0.1)	NMP	32	120	K ₂ CO ₃	86
8	<i>p</i> -MeO	Br	CO ₂ nBu	3 (1.3)	NMP	3	100	K ₂ CO ₃	98
9	<i>o</i> -Me	Br	CO ₂ nBu	3 (0.1)	NMP	32	120	K ₂ CO ₃	78
10	<i>o</i> -Me	Br	CO ₂ nBu	3 (1)	NMP	12	120	K ₂ CO ₃	97
11	H	I	CO ₂ nBu	4a (0.5)	DMF	12	120	K ₂ CO ₃	99
12	H	I	CO ₂ nBu	4b (0.5)	DMF	12	120	K ₂ CO ₃	99
13	H	I	CO ₂ nBu	7 (0.001)	DMF	10	110	K ₂ CO ₃	99
14	H	Br	CO ₂ nBu	7 (0.05)	NMP	32	120	K ₂ CO ₃	52
15	H	Br	CO ₂ nBu	7 (0.1)	NMP	32	120	K ₂ CO ₃	95
16	H	Br	CO ₂ nBu	7 (0.1)	DMF	24	120	K ₂ CO ₃	78
17	H	Br	CO ₂ nBu	7 (0.2)	DMF	32	120	K ₂ CO ₃	93
18	<i>p</i> -MeCO	Br	CO ₂ nBu	7 (0.1)	NMP	32	120	K ₂ CO ₃	22
19	<i>p</i> -MeCO	Br	CO ₂ nBu	7 (0.2)	NMP	20	120	K ₂ CO ₃	46
20	<i>p</i> -MeCO	Br	CO ₂ nBu	7 (0.2)	DMF	20	120	NEt ₃	62
21	<i>p</i> -MeCO	Br	CO ₂ nBu	7 (0.5)	NMP	12	100	NEt ₃	98
22	<i>p</i> -MeO	Br	CO ₂ nBu	7 (0.1)	NMP	32	120	K ₂ CO ₃	15
23	<i>p</i> -MeO	Br	CO ₂ nBu	7 (1)	NMP	3	100	K ₂ CO ₃	98
24	<i>p</i> -MeO	Br	CO ₂ nBu	7 (1)	NMP	12	120	NEt ₃	75
25	<i>o</i> -Me	Br	CO ₂ nBu	7 (0.1)	NMP	32	120	K ₂ CO ₃	18
26	<i>o</i> -Me	Br	CO ₂ nBu	7 (0.5)	NMP	12	120	K ₂ CO ₃	99
27	H	I	CO ₂ nBu	8a (0.5)	DMF	12	120	K ₂ CO ₃	99
28	H	I	CO ₂ nBu	8b (0.5)	DMF	12	120	K ₂ CO ₃	99
29	H	Br	Ph	3 (0.1)	NMP	32	120	K ₂ CO ₃	89
30	<i>p</i> -Me	Br	Ph	3 (0.8)	NMP	15	120	K ₂ CO ₃	99
31	<i>p</i> -MeCO	Br	Ph	3 (0.1)	NMP	32	120	K ₂ CO ₃	93
32	<i>p</i> -MeCO	Br	Ph	3 (1.5)	NMP	15	120	K ₂ CO ₃	93
33	<i>p</i> -MeO	Br	Ph	3 (0.1)	NMP	32	120	K ₂ CO ₃	88
34	<i>p</i> -MeO	Br	Ph	3 (2)	NMP	24	120	K ₂ CO ₃	94
35	H	I	Ph	4a (2)	NMP	48	120	K ₂ CO ₃	trace
36	H	Br	Ph	7 (0.1)	NMP	32	120	K ₂ CO ₃	94
37	<i>p</i> -Me	Br	Ph	7 (0.5)	NMP	12	120	K ₂ CO ₃	98
38	<i>p</i> -MeCO	Br	Ph	7 (0.1)	NMP	32	120	K ₂ CO ₃	22
39	<i>p</i> -MeCO	Br	Ph	7 (1.5)	NMP	24	120	K ₂ CO ₃	97
40	<i>p</i> -MeO	Br	Ph	7 (0.1)	NMP	32	120	K ₂ CO ₃	16
41	<i>p</i> -MeO	Br	Ph	7 (2)	NMP	24	120	K ₂ CO ₃	97
42	H	Br	CO ₂ nBu	PdCl ₂ (0.1)	NMP	32	120	K ₂ CO ₃	24
43	H	Br	CO ₂ nBu	PdCl ₂ (0.1) + 2' (0.1)	NMP	32	120	K ₂ CO ₃	88
44	H	Br	Ph	PdCl ₂ (0.5)	NMP	32	120	K ₂ CO ₃	64
45	H	Br	Ph	PdCl ₂ (0.5) + 2' (0.5)	NMP	32	120	K ₂ CO ₃	95

[a] Reaction conditions: ArX: 2 mmol; olefin: 3 mmol; solvent: 6 mL; base: 3 mmol. [b] Bath temperature. [c] Yields of isolated products.

tivity than complex **3**. For example, 1 mol-% of **7** gave a 99% yield of the coupling product of PhBr and *p*-MeC₆H₄MgBr, while 1 mol-% of **3** under the same conditions gave only 93% of the coupling product. The nickel complexes also catalyze the coupling of aryl iodides with *p*-MeC₆H₄MgBr efficiently. However, the coupling of aryl bromides gave very low product yields. Complexes **4a**, **4b**, **8a**, and **8b** show very similar catalytic activity in the reac-

tions tested, and 2 mol-% of catalyst was sufficient to drive the reactions to completion. These nickel complexes also proved to be good catalysts for deactivated aryl iodides. For example, 2 mol-% of **4b** or **8b** can catalyze the coupling of *p*-MeOC₆H₄I with *p*-MeC₆H₄MgBr to give the cross-coupling product in excellent yield (Table 2, Entries 10 and 19). We also found that increased steric hindrance of the reaction substrates led to a decrease of the product yields. For

Table 2. Coupling of $R^1C_6H_4MgBr$ and aryl bromides or iodides catalyzed by complexes **3**, **4**, **7**, and **8**.^[a]


Entry	R	R ¹	X	Catalyst (mol-%)	T [°C] ^[b]	Time [h]	Yield [%] ^[c]
1	H	<i>p</i> -Me	I	3 (0.8)	100	12	98
2	H	<i>p</i> -Me	Br	3 (1)	100	6	93
3	<i>o</i> -Me	<i>o</i> -Me	Br	3 (1)	100	24	96
4	<i>o</i> -Me	2,4,6-trimethyl	Br	3 (2)	100	24	74
5	2,4,6-trimethyl	2,4,6-trimethyl	Br	3 (2)	100	24	72
6	H	<i>p</i> -Me	I	4a (2)	100	12	99
7 ^[d]	H	<i>p</i> -Me	I	4a (2)	60	12	81
8	<i>o</i> -Me	<i>o</i> -Me	I	4a (2)	100	20	81
9	H	<i>p</i> -Me	I	4b (2)	100	12	99
10	<i>p</i> -MeO	<i>p</i> -Me	I	4b (2)	100	12	91
11	H	<i>p</i> -Me	I	7 (0.5)	100	12	99
12	H	<i>p</i> -Me	Br	7 (1)	100	6	99
13	<i>o</i> -Me	<i>o</i> -Me	Br	7 (1)	100	24	93
14	<i>o</i> -Me	2,4,6-trimethyl	Br	7 (2)	100	24	46
15	2,4,6-trimethyl	2,4,6-trimethyl	Br	7 (2)	100	24	42
16	H	<i>p</i> -Me	I	8a (2)	100	12	99
17	<i>o</i> -Me	<i>o</i> -Me	I	8a (2)	100	20	80
18	H	<i>p</i> -Me	I	8b (2)	100	12	99
19	<i>p</i> -MeO	<i>p</i> -Me	I	8b (2)	100	12	95

[a] Reactions were carried out in a 1:1 mixture of thf/toluene unless otherwise indicated. [b] Bath temperature. [c] Yields of isolated products. [d] Reaction was carried out in thf.

example, the reactions of 2,4,6-Me₃C₆H₂MgBr with 2,4,6-Me₃C₆H₂Br or *o*-MeC₆H₄Br catalyzed by either **3** or **7** gave relatively low yields of coupling products (Table 2, Entries 4, 5, 14 and 15). The reaction between *o*-MeC₆H₄MgBr and *o*-MeC₆H₄I catalyzed by the nickel catalysts **4a** or **8a** also gave lower yields of coupling product than the reaction between *p*-MeC₆H₄MgBr and C₆H₅I (Table 2, Entries 8 and 17), whereas the reaction of *o*-MeC₆H₄MgBr and *o*-MeC₆H₄Br catalyzed by **3** or **7** seems to be unaffected (Table 2, Entries 3 and 13).

Conclusion

We have synthesized and characterized nickel and palladium complexes of the novel ligands [2-{OC(Ph)₂CH₂}-6-(3,5-Me₂C₃HN₂)C₅H₃N}]⁻ and [2-{OC(Ph)=CH}-6-(3,5-Me₂C₃HN₂)C₅H₃N}]⁻. These complexes have square-planar coordination geometries around the metal centers, as shown by their diamagnetism and single-crystal X-ray diffraction results (for complexes **4b** and **8a**). The palladium complexes exhibit good catalytic activity in the Heck and Kumada reactions. The nickel complexes also catalyze the coupling reaction between aryl iodides and butyl acrylate or *p*-MeC₆H₄MgBr.

Experimental Section

General Procedure: All experiments were performed under nitrogen using standard Schlenk and vacuum-line techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium/benzophe-

none (thf, Et₂O and *n*-hexane), or CaH₂ (CH₂Cl₂) and degassed prior to use; dmf and dmp were dried with activated molecular sieves, distilled under nitrogen, and degassed prior to use. CDCl₃, C₅D₅N, and C₆D₆ (Acros Organics) were degassed and stored over either activated molecular sieves (CDCl₃ and C₅D₅N) or Na/K alloy (C₆D₆). 2-Hydrazino-6-methylpyridine,^[13] [(Ph₃P)₂Ni(Ar)-Br],^[14] and [PdCl₂(PhCN)₂]^[15] were prepared according to literature methods. Diisopropylamine was dried with NaOH, distilled under nitrogen, and degassed prior to use. The aryl bromides used for preparation of Grignard reagents, including *p*-MeC₆H₄Br, *o*-MeC₆H₄Br, and α -bromonaphthalene, were distilled and degassed prior to use. All other chemicals were obtained commercially and used as received. NMR spectra were recorded with a Bruker av300 spectrometer at ambient temperature. ¹H and ¹³C NMR chemical shifts are referenced to TMS or internal solvent resonances. Elemental analyses were performed by the Analytical Center of the University of Science and Technology of China.

Preparations

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (1):^[8] Pentane-2,4-dione (0.48 g, 48 mmol) was added dropwise to a stirred solution of 2-hydrazino-6-methylpyridine (0.50 g, 40.6 mmol) in acetic acid (10 mL) at room temperature and the resultant mixture refluxed for 12 h. The acetic acid was then removed under reduced pressure and the residue dissolved in CH₂Cl₂ (20 mL). This CH₂Cl₂ solution was washed twice with 10% Na₂CO₃ solution and then dried with Na₂SO₄. The Na₂SO₄ was removed by filtration and the solvent removed from the filtrate by rotary evaporation. The residue was distilled under reduced pressure to give a colorless oil (0.71 g, 93%), b.p. 78–80 °C/0.1 Torr. ¹H NMR (CDCl₃): δ = 2.24 (s, 3 H, Me), 2.46 (s, 3 H, Me), 2.55 (s, 3 H, Me), 5.90 (s, 1 H, pyrazolyl), 6.93 (dd, *J* = 0.9, 7.4 Hz, 1 H, Py), 7.52–7.61 (m, 2 H, Py) ppm.

[Li{2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (2): A solution of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (0.48 g, 2.57 mmol) in thf (10 mL) was cooled to about –60 °C and a solution of LDA in Et₂O [prepared from diisopropylamine (0.29 g, 2.8 mmol) and *n*BuLi (1.2 mL of a 2.5 M solution in hexane, 3 mmol) in Et₂O] was added with stirring. After stirring at –20 °C for 20 min, the mixture was added dropwise to a solution of benzophenone (0.50 g, 2.75 mmol) in thf (5 mL) at about –80 °C. The resultant mixture was warmed to room temperature and stirred for 12 h. The solvent was then removed under vacuum and the residue dissolved in toluene (10 mL). The solution was filtered and the filtrate was concentrated to about 2 mL. Diethyl ether (2 mL) was added to the solution to give compound **2** (0.54 g, 56%) as colorless crystals, m.p. 227–228 °C. ¹H NMR (C₆D₆): δ = 1.79 (s, 3 H, Me), 2.20 (s, 3 H, Me), 3.86 (s, 2 H, CH₂), 5.41 (s, 1 H, pyrazolyl), 6.12 (d, *J* = 8.1 Hz, 1 H, Py), 6.23 (d, *J* = 7.5 Hz, 1 H, Py), 6.68 (t, *J* = 7.8 Hz, 1 H, Py), 6.84–6.87 (m, 2 H, Ph), 6.98 (br., 4 H, Ph), 7.65 (d, *J* = 7.2 Hz, 4 H, Ph) ppm. ¹³C NMR (C₆D₆): δ = 13.03, 14.01, 53.27, 81.62, 109.45, 122.48, 124.31, 126.84, 137.06, 138.04, 148.64, 151.04, 162.25 ppm. C₂₄H₂₂LiN₃O (375.39): calcd. C 76.79, H 5.91, N 11.19; found C 76.90, H 5.90, N 11.11.

2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N (2'): Hydrochloric acid (2 M, 20 mL) was added to a solution of **2** [prepared from **1** (0.72 g, 3.85 mmol), LDA, and Ph₂CO according to the above procedure] in thf (15 mL). The mixture was stirred for 1 h and then neutralized with 2 M NaOH. The aqueous layer was extracted twice with CH₂Cl₂ (20 mL each time), and the combined organic layers were dried with MgSO₄. After concentration in vacuo, the product was recrystallized from CH₂Cl₂/Et₂O to give a white solid (1.0 g, 70.4% based on the amount of **1**), m.p. 156–157 °C. ¹H NMR (CDCl₃): δ = 2.28 (s, 3 H, Me), 2.43 (s, 3 H, Me), 3.74 (s, 2 H, CH₂), 5.98 (s, 1 H, pyrazolyl), 6.91 (dd, *J* = 2.4, 6 Hz, 1 H, Py), 7.12–7.27 (m, 7 H, Ph), 7.41–7.44 7.12–7.27 (m, 3 H, Ph), 7.50–7.66 (m, 2 H, Py) ppm. ¹³C NMR (CDCl₃): δ = 13.70, 14.22, 47.50, 78.36, 109.33, 114.74, 122.11, 126.32, 126.78, 128.13, 139.28, 141.11, 146.89, 150.26, 152.30, 157.22 ppm. C₂₄H₂₃N₃O (369.46): calcd. C 78.02, H 6.27, N 11.37; found C 77.79, H 6.24, N 11.22.

[Pd(Cl){2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (3): A solution of **2** (0.11 g, 0.29 mmol) in thf (5 mL) was added to a stirred solution of [PdCl₂(PhCN)₂] (0.105 g, 0.27 mmol) in thf (10 mL) at about –80 °C. The mixture was warmed to room temperature and stirred for 10 h, then the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ and then filtered. Concentration of the filtrate afforded pale-yellow crystals (0.11 g, 80%), m.p. 293–295 °C. ¹H NMR (CDCl₃): δ = 2.54 (s, 3 H, Me), 2.59 (s, 3 H, Me), 3.97 (s, 2 H, CH₂), 6.01 (s, 1 H, pyrazolyl), 7.03 (d, *J* = 7.8 Hz, 1 H, Py), 7.12–7.25 (m, 7 H, Ph+Py), 7.62 (d, *J* = 8.1 Hz, 4 H, Ph), 7.80 (t, *J* = 8.4 Hz, 1 H, Py) ppm. C₂₄H₂₂Cl₂N₃OPd (510.32): calcd. C 56.49, H 4.35, N 8.23; found C 56.89, H 4.23, N 8.28.

[Ni(*o*-MeC₆H₄){2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (4a): A solution of **2** (0.22 g, 0.59 mmol) in thf (5 mL) was added to a stirred solution of [(Ph₃P)₂Ni(*o*-MeC₆H₄)Br] (0.44 g, 0.58 mmol) in thf (10 mL) at about –80 °C. The resultant solution was warmed to room temperature and stirred for 30 h, then the solvent was removed under vacuum and the residue was extracted with CH₂Cl₂. The solvent was removed from the extract under reduced pressure and the residual solid was recrystallized from thf to give red crystals (0.28 g, 92%), m.p. 203–204 °C. ¹H NMR (CDCl₃): δ = 1.16 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.78 (s, 3 H, Me), 3.49 (d, *J* = 14.4 Hz, 1 H, CH), 3.68 (d, *J* = 14.4 Hz, 1 H, CH), 5.74 (s, 1 H, pyrazolyl), 6.68–7.10 (m, 11 H, Ar), 7.37 (d, *J* = 6.3 Hz, 2 H, Ar), 7.61–7.70 (m, 4 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 13.50, 21.32, 24.97,

49.05, 77.27, 113.98, 122.05, 122.38, 124.83, 125.14, 125.36, 126.40, 126.59, 126.87, 127.08, 128.08, 128.27, 128.88, 136.72, 137.72, 147.52, 155.62, 159.87 ppm. C₃₁H₂₉N₃NiO (518.28): calcd. C 71.84, H 5.64, N 8.11; found C 71.76, H 5.51, N 8.19. Single crystals of complex **4a** suitable for an X-ray diffraction analysis were obtained by recrystallization of the sample from a mixture of thf and toluene.

[Ni(1-C₁₀H₇){2-[OC(Ph)₂CH₂]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (4b): A solution of **2** (0.08 g, 0.21 mmol) in thf (5 mL) was added to a stirred solution of [(Ph₃P)₂Ni(naphthyl)Br] (0.17 g, 0.22 mmol) in thf (10 mL) at about –80 °C. The mixture was warmed to room temperature and stirred for 30 h, then the solvent was removed under vacuum and the residue extracted with CH₂Cl₂. The extract was filtered and then concentrated to dryness to give a red solid, which was recrystallized from a mixture of CH₂Cl₂/hexane (1:1) to afford red crystals (0.11 g, 83%), m.p. 171–173 °C. ¹H NMR (CDCl₃): δ = 0.72 (s, 3 H, Me), 2.32 (s, MeC₆H₅), 2.38 (s, 3 H, Me), 3.54 (d, *J* = 15.3 Hz, 1 H, CH), 3.81 (d, *J* = 15.3 Hz, 1 H, CH), 5.63 (s, 1 H, pyrazolyl), 6.90–6.98 (m, 4 H, Ar), 7.06–7.15 (m, 6 H, Ar), 7.20–7.31 (m, 5 H, Ar), 7.37 (d, *J* = 7.2 Hz, 3 H, Ar), 7.60 (d, *J* = 7.2 Hz, 3 H, Ar), 7.70 (t, *J* = 8.1 Hz, 1 H, Ar), 8.00 (d, *J* = 6.9 Hz, 1 H, Ar), 9.29–9.32 (m, 1 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 13.86, 21.58, 49.32, 77.27, 107.16, 114.41, 122.19, 122.74, 123.70, 123.79, 123.92, 125.08, 125.24, 125.43, 125.96, 126.72, 127.42, 127.61, 128.02, 128.36, 129.17, 132.75, 133.54, 133.89, 138.02, 139.14, 140.23, 141.68, 151.77, 151.82, 156.11, 156.97, 160.38 ppm. C₃₄H₂₉N₃NiO·0.8C₇H₈ (628.02): calcd. C 75.73, H 5.68, N 6.69; found C 75.75, H 5.75, N 6.67.

2-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)pyridin-2-yl]-1-phenylethanone (5): A solution of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (0.48 g, 2.57 mmol) in thf (10 mL) was cooled to about –60 °C and a solution of LDA in Et₂O [prepared from diisopropylamine (0.29 g, 2.8 mmol) and *n*BuLi (1.2 mL of a 2.5 M solution in hexane, 3 mmol) in Et₂O] was added with stirring. The mixture was stirred at –20 °C for 20 min and was then added dropwise to PhCN (0.30 g, 2.91 mmol) at about –80 °C. The resultant solution was stirred at –20 °C for 30 min and at room temperature for 10 h. A 2 M aqueous solution of H₂SO₄ (10 mL) was then added at 0 °C. The mixture was stirred at room temperature for 10 h and then neutralized with NaOH solution. The organic layer was separated and the aqueous layer was extracted twice with diethyl ether (20 mL each time). The combined ether solutions were dried with Na₂SO₄, then the Na₂SO₄ was removed by filtration and the filtrate was concentrated to give pale-yellow crystals (0.49 g, 66%), m.p. 80–81 °C. ¹H NMR (CDCl₃): δ = 2.19 (s, 3 H, Me), 2.41 (s, 3 H, Me), 4.37 (s, 2 H, CH₂), 5.86 (s, 1 H, pyrazolyl), 7.07 (t, *J* = 4.2 Hz, 1 H, Ar), 7.32–7.50 (m, 3 H, Ar), 7.65 (d, *J* = 4.2 Hz, 2 H, Ar), 7.94–7.97 (m, 2 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 13.67, 14.64, 47.89, 109.05, 113.66, 120.71, 125.44, 128.43, 128.66, 128.85, 133.31, 136.59, 138.90, 141.68, 149.81, 153.28, 153.68, 196.73 ppm. C₁₈H₁₇N₃O (291.35): calcd. C 74.20, H 5.88, N 14.42; found C 74.28, H 5.58, N 14.26.

[Na{2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (6): A mixture of **5** (0.60 g, 2.06 mmol) and NaH (0.08 g, 3.3 mmol) in thf (20 mL) was refluxed for 12 h, then the mixture was filtered and the solvent removed from the filtrate under vacuum. The residue was recrystallized from a mixture of thf/hexane (1:1) to give pale-yellow crystals (0.50 g, 77%), m.p. 245–247 °C. ¹H NMR (C₆D₆): δ = 1.76 (s, 3 H, Me), 1.86 (s, 3 H, Me), 5.30 (s, 1 H, pyrazolyl), 5.67 (s, 1 H, CH), 5.92 (d, *J* = 7.5 Hz, 1 H, Py), 6.42–6.45 (m, 1 H, Py), 6.82–7.16 (m, 4 H, Ph + Py), 7.99 (t, *J* = 7.8 Hz, 1 H, Py), 6.62–6.67 (m, 4 H, Ph), 7.79 (d, *J* = 7.2 Hz, 2 H, Ph) ppm. ¹³C NMR (C₆D₆): δ = 13.57, 13.70, 95.16, 106.15, 108.68, 119.64, 127.02, 127.60,

128.23, 135.73, 139.06, 147.35, 150.19, 150.37, 161.98, 173.33 ppm. $C_{18}H_{16}N_3NaO$ (313.33): calcd. C 69.00, H 5.15, N 13.41; found C 69.32, H 5.11, N 13.75.

[Pd(Cl){2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (7): A solution of **6** (0.13 g, 0.42 mmol) in thf (5 mL) was added to a stirred solution of [PdCl₂(PhCN)₂] (0.13 g, 0.34 mmol) in thf (10 mL) at about -80 °C. The mixture was stirred at room temperature overnight, then the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ and then filtered. Concentration of the filtrate afforded red crystals of **7** (0.10 g, 68%), m.p. 293–295 °C. ¹H NMR (CDCl₃): δ = 2.58 (s, 3 H, Me), 2.62 (s, 3 H, Me), 5.93 (s, 1 H, CH), 6.04 (s, 1 H, pyrazolyl), 6.86 (d, *J* = 8.1 Hz, 1 H, Py), 6.91 (d, *J* = 8.1 Hz, 1 H, Py), 7.27–7.32 (m, 3 H, Ph), 7.53 (t, *J* = 8.1 Hz, 1 H, Py), 7.80–7.83 (m, 2 H, Ph) ppm. ¹³C NMR (CDCl₃+C₅D₅N): δ = 14.19, 14.35, 77.37, 112.15, 118.83, 119.16, 119.48, 121.46, 122.84, 124.39, 126.02, 127.26, 127.29, 128.07, 134.95, 147.42, 147.78, 157.20 ppm. $C_{18}H_{16}ClN_3OPd$ (432.21): calcd. C 50.02, H 3.73, N 9.72; found C 50.00, H 3.64, N 9.64.

[Ni(*o*-MeC₆H₄){2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (8a): A solution of **6** (0.15 g, 0.48 mmol) in thf (5 mL) was added to a stirred solution of [(PPh₃)₂Ni(*o*-MeC₆H₄)Br] (0.33 g, 0.43 mmol) in thf (10 mL) at about -80 °C. The solution was warmed to room temperature and stirred for 30 h, then the solvent was removed under vacuum and the residue extracted with CH₂Cl₂. The solvent was removed from the extract under vacuum and the residual solid was recrystallized from a 1:1 mixture of thf/toluene to afford brown crystals of **8a** (0.16 g, 85%), m.p. 247–248 °C. ¹H NMR (CDCl₃): δ = 1.17 (s, 3 H, Me), 2.37 (s, 3 H, Me), 3.00 (s, 3 H, Me), 5.75 (s, 1 H, pyrazolyl), 5.98 (s, 1 H, CH), 6.63 (d, *J* = 7.8 Hz, Py), 6.73–6.75 (m, 4 H, C₆H₄+Py), 7.11–7.15 (m, 3 H, Ph), 7.45 (t, *J* = 8.1 Hz, 1 H, Py), 7.51–7.54 (m, 2 H, Ph), 7.67–7.71 (m, 1 H, C₆H₄) ppm. ¹³C NMR (CDCl₃): δ = 14.13, 15.19, 25.16, 92.96, 99.66, 113.76, 119.46, 122.67, 122.74, 122.47, 126.47, 127.89, 128.64, 136.05, 136.46, 139.93, 140.12, 144.27, 146.15, 152.67, 153.56, 155.04, 169.88 ppm. $C_{25}H_{23}N_3NiO$ (440.16): calcd. C 68.22, H

5.27, N 9.55; found C 68.42, H 5.42, N 9.49. Single crystals for X-ray diffraction analysis were obtained by recrystallization of the sample from a mixture of thf and benzene.

[Ni(1-C₁₀H₇){2-[OC(Ph)=CH]-6-(3,5-Me₂C₃HN₂)C₅H₃N}] (8b): A solution of **5** (0.17 g, 0.54 mmol) in thf (5 mL) was added to a stirred solution of [(PPh₃)₂Ni(naphthyl)Br] (0.40 g, 0.51 mmol) in thf (10 mL) at about -80 °C. The resultant solution was warmed to room temperature and stirred for 30 h, then the solvent was removed under vacuum and the residue dissolved in CH₂Cl₂. The mixture was filtered and the filtrate was concentrated to give red crystals of **8b** (0.17 g, 71%), m.p. 239–240 °C. ¹H NMR (CDCl₃): δ = 0.84 (s, 3 H, Me), 2.48 (s, 3 H, Me), 5.76 (s, 1 H, pyrazolyl), 6.08 (s, 1 H, CH), 6.75 (d, *J* = 7.8 Hz, 1 H, Py), 6.84 (d, *J* = 8.1 Hz, 1 H, Py), 7.01–7.15 (m, 5 H, Ar), 7.27–7.43 (m, 5 H, Ar), 7.53 (t, *J* = 8.1 Hz, 1 H, Py), 7.58–7.62 (m, 1 H, Ar), 7.89 (d, *J* = 6.6 Hz, 1 H, Ar), 9.66 (d, *J* = 7.8 Hz, 1 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 14.39, 15.27, 93.11, 99.56, 113.89, 119.66, 122.72, 123.56, 123.77, 124.23, 126.59, 127.82, 127.86, 128.38, 128.70, 129.19, 132.86, 133.16, 133.88, 136.17, 139.77, 140.18, 141.97, 146.45, 153.84, 155.16, 155.32, 170.23 ppm. $C_{28}H_{23}N_3NiO$ (476.20): calcd. C 70.62, H 4.87, N 8.82; found C 70.46, H 4.81, N 9.07.

Crystal Structure Determination: Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected with a Siemens CCD area detector with graphite-monochromated Mo-*K*_α radiation (*λ* = 0.71073 Å). The structure was solved by direct methods using SHELXS-97^[16] and refined against *F*² by full-matrix least squares using SHELXL-97.^[17] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 3. CCDC-641763 and -641764 (for **4b**-C₇H₈ and **8a**-0.5C₆H₆, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Summary of crystal data for complexes **4b** and **8a**.

	4b -C ₇ H ₈	8a -0.5C ₆ H ₆
Empirical formula	C ₄₁ H ₃₇ N ₃ NiO	C ₂₈ H ₂₆ N ₃ NiO
Formula mass	646.45	479.23
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	15.609(2)	20.171(3)
<i>b</i> [Å]	11.1736(15)	13.841(2)
<i>c</i> [Å]	19.144(3)	18.560(3)
<i>β</i> [°]	95.792(2)	96.873(2)
<i>V</i> [Å ³]	3321.7(8)	5144.5(14)
<i>Z</i>	4	8
<i>T</i> [K]	294(2)	298(2)
<i>D</i> _{calcd.} [g cm ⁻³]	1.293	1.237
<i>F</i> (000)	1360	2008
<i>μ</i> [mm ⁻¹]	0.621	0.777
<i>θ</i> range for data collection [°]	1.77–26.40	2.03–25.01
Absorption correction	semiempirical from equivalents	semiempirical from equivalents
No. of reflections collected	18266	12474
No. of independent reflections (<i>R</i> _{int})	6767 (<i>R</i> _{int} = 0.0493)	4477 (<i>R</i> _{int} = 0.0531)
No. of data/restraints/parameters	6767/92/457	4477/102/325
Goodness of fit on <i>F</i> ²	1.000	1.001
Final <i>R</i> indices ^[a] [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.0962	<i>R</i> ₁ = 0.0695, <i>wR</i> ₂ = 0.1775
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1007, <i>wR</i> ₂ = 0.1202	<i>R</i> ₁ = 0.1352, <i>wR</i> ₂ = 0.2258
Largest diff peak/hole [e Å ⁻³]	0.328/−0.239	0.571/−0.589

[a] *R*₁ = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|; *wR*₂ = [Σ*w*(*F*_o² − *F*_c²)/Σ*w*(*F*_o⁴)]^{1/2}.

General Procedure for the Heck Reactions: A Schlenk tube was charged with aryl halide (2 mmol), butyl acrylate or styrene (3 mmol), a base (3 mmol), the pre-catalyst, and solvent (6 mL) and the mixture was stirred at the appropriate temperature for the specified period of time. The mixture was then cooled to room temperature and quenched with a 1 M aqueous solution of hydrochloric acid (3 mL). The aqueous phase was extracted with CH_2Cl_2 (3×5 mL), then the combined organic layers were washed with water (10 mL) and dried with Na_2SO_4 . The NaSO_4 was removed by filtration and the filtrate was concentrated. The residue was purified by column chromatography.

General Procedure for the Kumada Reactions: A Schlenk tube was charged with aryl halide (2 mmol), pre-catalyst, solvent (4 mL), and a magnetic stir bar, then a thf solution of $p\text{-MeC}_6\text{H}_4\text{MgBr}$ (prepared from 2.4 mmol of $p\text{-MeC}_6\text{H}_4\text{Br}$ and 3 mmol of Mg in thf) was added dropwise at room temperature with stirring. The reaction mixture was stirred at the appropriate temperature for the specified period of time. After the mixture had been cooled to room temperature, the reaction was quenched with water. The aqueous phase was extracted with CH_2Cl_2 (3×5 mL) and the combined organic layers were dried with MgSO_4 . The MgSO_4 was removed by filtration and the filtrate was concentrated. The residue was purified by column chromatography.

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