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Full Paper

N-Heterocyclic Carbene Adducts of Cyclopalladated Ferrocenylpyridazine: Synthesis, Structural Characterization, and Application in α-Arylation of Ketones with Aryl Chlorides

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A new ferrocene-based ligand 3-chloro-6-pyridazinylferrocene **1** and its *N*-heterocyclic carbene adducts **2**–**3** were synthesized and characterized by ^{1}H NMR and IR spectroscopy, ESI-MS, and elemental analysis. Additionally, detailed structures of complexes **2**–**3** have been determined by single-crystal X-ray analysis. Complex **3** exhibited high catalytic activity for α-arylation of ketones with aryl chlorides. Typically, using 1 mol % catalyst in the presence of 1.5 equivalents of ^{t}BuOK as base in dioxane at 100°C provided coupled products in good yields.

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Introduction

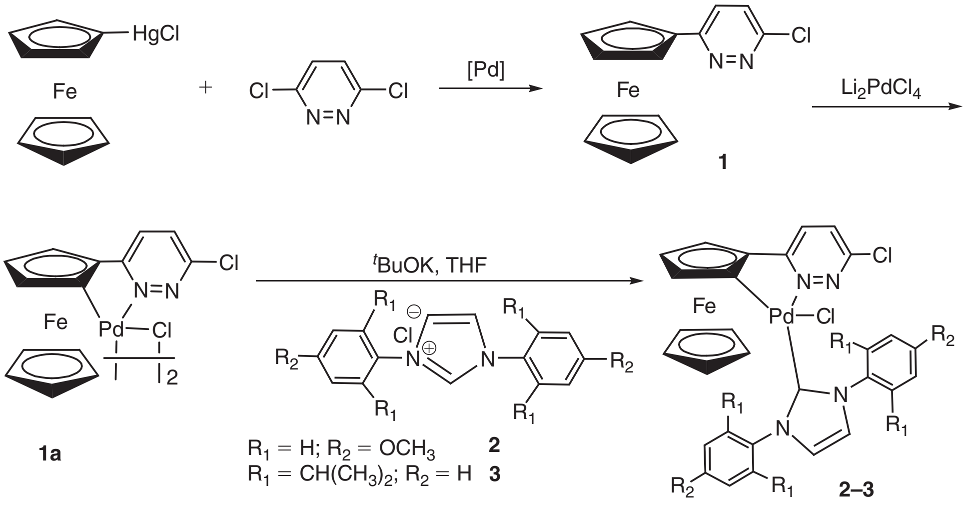
Since the first report by Buchwald, Hartwig and Miura in 1997,[1–3] palladium-catalyzed α-arylation of ketones with aryl halides has become an extremely powerful method in organic synthesis for the formation of C_{sp2}-C_{sp3} bonds.[4–7] Several Pd complexes derived from bulky and electron-rich alkylphosphine ligands are reported to be effective catalysts for the α-arylation of notoriously unreactive but relatively cheap aryl chlorides.[8–10] As an alternative, *N*-heterocyclic carbenes (NHCs) have become a paradigmatically new generation of strong σ-donor ligands and successfully used in palladium-catalyzed α-arylation.[11–15] Moreover, palladacycles are one of the most developed and studied classes of catalyst precursors because of their structural versatility and easy synthetic accessibility.[16,17] Among them, a wide variety of NHC adducts of palladacycles have been reported and successfully used in the coupling reactions.[18–23] However, only a few palladacycles have proved to be efficient for α-arylation of aryl chlorides.[24,25]

We have recently studied the monophosphine adducts of palladacycles containing the heterocyclic ring ferrocenyl ligand.[26–28] These adducts combine the stability induced by the presence of a palladacycle framework with the high activity commonly associated with phosphine ligands, and were far more active than the corresponding dimeric palladacycle. In addition, cyclopalladated ferrocene complexes are quite fascinating since ferrocene is an ideal framework on which planar chirality can be introduced. In view of these findings and our continuous interest in applications of chloromercuriferrocene,[26–29] we prepared a new ferrocene-based ligand 3-chloro-6-pyridazinylferrocene **1** and its carbene adducts of palladacycle **2**–**3** (Scheme 1) and examined their catalytic activity in the α-arylation of ketones. Here, we report that **3** is an extremely effective catalyst for the α-arylation of ketones with aryl chlorides.

Results and Discussion

*Synthesis and Characterization of Compounds **1**–**3***

The coupling reaction of chloromercuriferrocene and 3,6-dichloropyridazine readily afforded **1** according to the published procedures.[26–28] The following cyclopalladation reaction was carried out with **1** and 1.1 equivalents of Li_2PdCl_4 and NaOAc in methanol at room temperature for 24 h. The resulting red solids of **1a** were collected by filtration, washed several times with methanol, and were assigned as a chloride-bridged palladacyclic dimer.[26–28] Because of its poor solubility in all common organic solvents, **1a** was not characterized and was instead directly subjected to the following reaction. Two new carbene adducts of palladacycle **2**–**3** have been easily prepared in situ from the reaction of **1a** and 1,3-di-4-methoxyphenylimidazolium chloride or 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (IPrHCl) in THF at room temperature under a N_2 atmosphere. The one-pot synthesis avoids multi-step reactions employing free carbenes.[30] These new compounds were fully characterized by elemental analysis, ESI-MS, and IR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of compounds **1** and **2**–**3** are consistent with the proposed structures; **1** exhibits peaks for the Cp ring with a proton ratio of 2 : 2 : 5, while **2**–**3** exhibit those



Scheme 1. Synthesis of compounds **1**–**3**.

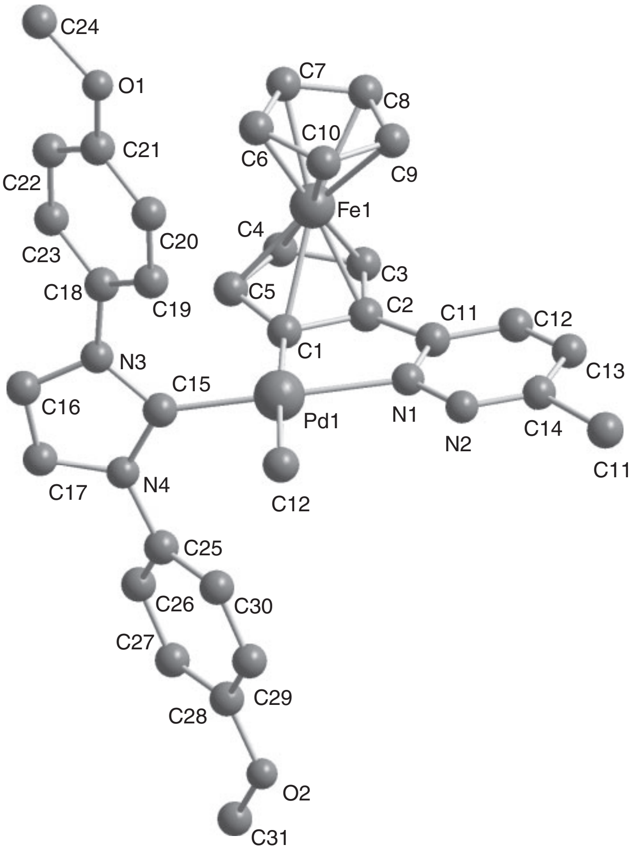


Fig. 1. Molecular structure of complex **2**. Displacement parameters are drawn at the 50 % level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.973(5), Pd(1)–N(1) 2.121(4), Pd(1)–C(15) 1.979(18), Pd(1)–Cl(2) 2.4037(13), and C(1)–Pd(1)–N(1) 80.24(18), N(1)–Pd(1)–Cl(2) 96.41(11), Cl(2)–Pd(1)–C(15) 94.38(14), C(1)–Pd(1)–C(15) 89.3(2).

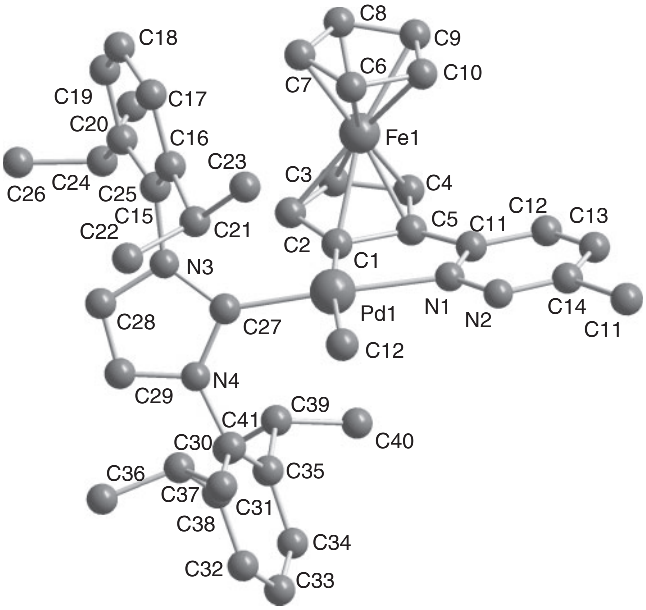


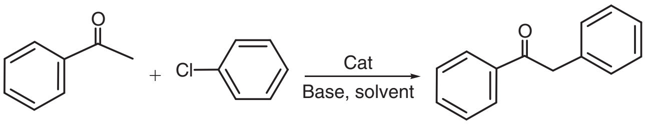
Fig. 2. Molecular structure of complex **3**·CH_2Cl_2 (representation of one of the two independent crystal structures). Displacement parameters are drawn at the 50 % level. CH_2Cl_2 and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.974(5), Pd(1)–N(1) 2.148(4), Pd(1)–C(27) 1.991(11), Pd(1)–Cl(2) 2.3853(15), and C(1)–Pd(1)–N(1) 80.48(19), N(1)–Pd(1)–Cl(2) 93.01(13), Cl(2)–Pd(1)–C(27) 94.82(13), C(1)–Pd(1)–C(27) 91.82(19).

corresponding peaks with a proton ratio of 1 : 1 : 1 : 5, clearly showing that they were *ortho*-cyclopalladated products. The ^{1}H NMR spectra of **2**–**3** showed only one set of signals in a symmetrical environment indicating the exclusive formation of the isomer. In the mass spectra of **2**–**3**, the most intense peak was attributed to $[M–Cl]^+$. In order to further investigate the structures of these complexes, their detailed structures have been determined by X-ray single-crystal diffraction.

*Crystal Structures of Complexes **2**–**3**·CH_2Cl_2*

The crystals were obtained by recrystallization from CH_2Cl_2/petroleum ether solution at room temperature. The molecules are shown in Figs 1–2. The bicyclic system formed by the palladacycle and the C_5H_3 moiety is approximately coplanar (dihedral angles of 6.8° and 6.7° for complexes **2**–**3**·CH_2Cl_2, respectively). The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the C atom of

Table 1. Optimization of reaction conditions for the α-arylation of acetophenone with phenyl chloride[A]



Entry	Catalyst [mol %]	Base	Solvent	Yield [%][B]
1	**3** (1)	K_2CO_3	Dioxane	16
2	**3** (1)	NaH	Dioxane	56
3	**3** (1)	^{t}BuONa	Dioxane	78
4	**3** (1)	^{t}BuOK	Dioxane	90
5	**3** (1)	^{t}BuOK	Toluene	86
6	**3** (1)	^{t}BuOK	THF	60
7	**3** (1)	^{t}BuOK	DMF	46
8	**2** (1)	^{t}BuOK	Dioxane	Trace
9	**1a** (0.5)	^{t}BuOK	Dioxane	Trace
10[C]	**1a**/IPrHCl (0.5/2)	^{t}BuOK	Dioxane	52

[A] Reaction conditions: phenyl chloride (1.0 mmol), acetophenone (1.2 mmol), base (1.5 mmol), solvent (3 mL), reflux temperature, 3h.

[B] Isolated yields (average of two experiments).

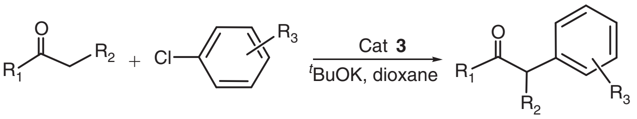
[C] ^{t}BuOK (3.0 mmol).

NHC, the chlorine atom, the nitrogen atom and the C atom of the ferrocenyl moiety. The Pd–C_{carb} [1.991(11) Å] bond length of complex **3**·CH_2Cl_2 is similar to those of related carbene adducts [1.992–1.998 Å],[20,22,24] while it is longer than those of related complex **2** [1.979(18) Å] possibly owing to the steric bulk of the IPr ligand. In addition, The Pd–N [2.148(4) Å] bond length of complex **3**·CH_2Cl_2 is also longer than that of complex **2** [2.121 (4) Å]. The imidazole ring plane of NHC is almost perpendicular to the square plane formed by the Pd(II) centre (dihedral angles of 91.7°, 72.7° for complexes **2**–**3**·CH_2Cl_2, respectively). In this type of arrangement, the *N*-substituents of NHC reduce the steric interaction with palladacyclic ligand.

Application in α-Arylation of Ketones

Our initial exploration of reaction conditions focussed on the coupling of acetophenone with phenyl chloride in the presence of 1 mol % carbene adduct of palladacycle **3**. After screening a variety of bases (e.g. K_2CO_3, NaH, ^{t}BuONa and ^{t}BuOK) (Table 1, entries 1–4), ^{t}BuOK was found to give the best result (90 % yield) and ^{t}BuONa displayed moderate efficiency (78 % yield). Then, a quick survey of solvents indicated that dioxane was much better than other solvents such as toluene, THF and DMF (entries 5–7). Toluene also afforded good coupled product yield (86 %). Furthermore, the activities of several related catalytic systems in the same model reaction were investigated. Complex **2** was found to be an inactive precatalyst (entry 8). The dimeric complex **1a** was also inactive under the same reaction conditions (entry 9) and the yield was greatly improved by the addition of carbene precursor IPrHCl (52 %, entry 10) suggesting that carbene IPr participated in the catalytic cycles. However, the activity of **1a**/IPrHCl system was still obviously lower than that of the preformed IPr adduct of cyclopalladated ferrocenylpyridazine. On the basis of these results, we propose that the carbene ligand may promote the release of the 'real catalyst' species from palladacycle and the coupling reaction catalyzed by palladacycle proceeded through a Pd^0/Pd^{II} cycle.[23,28]

Table 2. α-Arylation of ketones with aryl chlorides catalyzed by complex 3[A]



Entry	R_1	R_2	R_3	Yield[B] [%]
1	Ph	H	*p*-Me	92
2	Ph	H	*m*-OMe	91
3	Ph	H	*p*-OMe	93
4	Ph	H	*p*-CF_3	68
5	Ph	H	*p*-NO_2	Trace
6	Ph	H	*o*-Me	93
7	Ph	H	*o*-OMe	95
8	Ph	H	1,3-dimethyl	96
9	Ph	CH_3	*p*-OMe	90
10	Ph	CH_3	*o*-OMe	92
11	Ph	CH_3	1,3-dimethyl	94
12	Ph	CH_3	*p*-CF_3	70
13	4-OMe-Ph	H	*o*-Me	89
14	4-OMe-Ph	H	*p*-OMe	87
15	*o*-Me-Ph	H	*o*-Me	85
16	*o*-Me-Ph	H	*p*-OMe	82

[A] Reaction conditions: aryl chlorides (1.0 mmol), ketones (1.2 mmol), ^{t}BuOK (1.5 mmol), dioxane (3 mL), 100°C, 3 h.

[B] Isolated yields (average of two experiments).

Under the optimized reaction conditions (**3**, ^{t}BuOK, dioxane), α-arylation of ketones with a variety of electronically and structurally diverse aryl chlorides were carried out to explore the scope of this system (Table 2). Reactions of electron-rich aryl chlorides such as 4-chlorotoluene, 3- and 4-chloroanisoles also gave very high yields (92, 91 and 93 %, respectively, entries 1–3). However, for electron-deficient aryl chlorides such as 4-triflurormethyl chlorobenzene, the yield decreased noticeably (68 %, entry 4). In the case of 4-nitrochlorobenzene, **3** was almost inactive under the similar reaction conditions (entry 5). These results represent an interesting trend, the oxidative addition does not affect the overall rate of the reaction and is not the rate determining step.[31,32] It was noteworthy that the coupling of hindered aryl chlorides with acetophenone gave the desired products in excellent yields (entries 6–8), which shows that the steric hindrances have no deleterious effect on these reactions. The scope of the α-arylation was further investigated by varying the aromatic ketones under the same condition. Similar to the results for acetophenone, good yields were also obtained in the case of propiophenone (entries 9–12). In cases of *p*-methoxyacetophenone and *o*-methylacetophenone, the electronic and steric effects have no significant influence on the reaction (entries 13–16).

Conclusions

In summary, we have prepared and characterized a new ferrocene-based ligand **1** and its NHC adducts of palladacycle **2**–**3**. Their detailed structures have been determined by X-ray single-crystal diffraction. Complex **3** was found to be an efficient catalyst for α-arylation of ketones with aryl chlorides.

Experimental

General Procedures

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled before use. All other chemicals were commercially available expect for chloromercuriferrocene, which was prepared according to the published procedures.[33] Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. Crystallographic data were collected on a Bruker SMART APEX-II CCD diffractometer.

Synthesis of 3-Chloro-6-pyridazinylferrocene **1**

In a flask equipped with reflux condenser and gas inlet, chloromercuriferrocene (1 mmol), 3,6-dichloropyridazine (1.1 mmol), NaI (2 mmol), $Pd(PPh_3)_4$ (0.05 mmol), 18 mL absolute THF and 12 mL absolute Me_2CO were placed under an N_2 atmosphere. The reaction mixture was then placed in an oil bath and heated at 70°C for 6 h, cooled and quenched with water. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The second band was collected, which afforded the red solid **1**, yield 55 %. ν_{max} (KBr)/cm^{-1} 2923, 1574, 1480, 1436, 1389, 1280, 1157, 1110, 1035, 998, 822, 745, 687. δ_H (400 MHz, $CDCl_3$) 7.46 (d, *J* 8.8, 1H, ArH), 7.35 (s, 1H, *J* 8.8, ArH), 5.01 (s, 2H, C_5H_4), 4.52 (s, 2H, C_5H_4), 4.08 (s, 5H, C_5H_5). *m/z* (ESI) 299.6 $[M+H]^+$. Anal. Calc. for $C_{14}H_{11}ClFeN_2$: C 56.3, H 3.7, N 9.4. Found: C 56.6, H 3.5, N 9.6 %.

General Procedure for the Synthesis of Carbene Adducts of Cyclopalladated Ferrocenylpyridazines **2–3**

A mixture of **1** (1 mmol), Li_2PdCl_4 (1.1 mmol) and NaOAc (1 mmol) in 20 mL dry methanol was stirred for 24 h at room temperature. The red solid **1a** (yield: 89 %) was collected by filtration and washed several times with methanol. Without further purification, it was directly subjected to the following reaction. A Schlenk tube was charged with **1a** (0.5 mmol), the corresponding imidazolium salt (1.25 mmol) and ^{t}BuOK (2.5 mmol) under nitrogen. Dry THF was added by a cannula and stirred at room temperature for 2 h. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The second band was collected, which afforded the corresponding carbene adduct **2** or **3**.

$[PdCl\{[(\eta^5\text{-}C_5H_5)]Fe[(\eta^5\text{-}C_5H_3)\text{-}N_2C_4H_2\text{-}Cl]\}(C_3N_2H_2)(C_6H_4\text{-}OCH_3)_2]$ (**2**): Red solid, yield 90 %. ν_{max} (KBr)/cm^{-1} 2933, 1509, 1467, 1375, 1289, 1160, 1148, 1009, 842, 818, 770, 692. δ_H (400 MHz, $CDCl_3$) 8.39 (d, *J* 8.8, 2H, ArH), 7.86 (d, *J* 8.8, 2H, ArH), 7.52 (d, *J* 8.8, 1H, ArH), 7.42 (s, 1H, NCHCHN), 7.35 (s, 1H, NCHCHN), 7.29 (d, *J* 8.8, 1H, ArH), 7.17 (d, *J* 8.8, 2H, ArH), 6.86 (d, *J* 8.8, 2H, ArH), 4.38 (s, 1H, C_5H_3), 4.22 (s, 1H, C_5H_3), 3.91 (s, 1H, C_5H_3), 3.81 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.49 (s, 5H, C_5H_5). *m/z* (ESI) 684.3 $[M^+\text{–}Cl]$. Anal. Calc. for $C_{31}H_{26}Cl_2FeN_4O_2Pd$: C 51.7, H 3.6, N 7.8. Found: C 51.5, H 3.3, N 8.1 %.

$[PdCl\{[(\eta^5\text{-}C_5H_5)]Fe[(\eta^5\text{-}C_5H_3)\text{-}N_2C_4H_2\text{-}Cl]\}(C_3N_2H_2)(C_6H_3\text{-}2C_3H_7)_2]$ (**3**): Red solid, yield 87 %. ν_{max} (KBr)/cm^{-1} 2960, 1583, 1514, 1469, 1379, 1329, 1253, 1106, 1038, 800, 756, 700. δ_H (400 MHz, $CDCl_3$) 7.45–7.50 (m, 3H, $NCHCHN^+ArH$), 7.16–7.32 (m, 6H, ArH), 7.04 (d, *J* 8.8, 1H, ArH), 4.66 (m, 1H, CH), 4.48 (s, 1H, C_5H_3), 4.35 (s, 1H, C_5H_3), 3.98 (s, 1H, C_5H_3), 3.40 (s, 5H, C_5H_5), 3.20 (m, 1H, CH), 2.90–2.97 (m, 2H, CH), 1.61 (s, 6H, CH_3), 1.54 (d, *J* 6.4, 3H, CH_3), 1.42 (d, *J* 6.4, 3H, CH_3), 1.17 (d, *J* 6.4, 3H, CH_3), 0.97 (d, *J* 6.4, 3H, CH_3), 0.85 (d, *J* 6.4, 3H, CH_3), 0.58 (d, *J* 6.4, 3H, CH_3). *m/z* (ESI) 792.5 $[M^+\text{–}Cl]$. Anal. Calc. for $C_{41}H_{46}Cl_2FeN_4Pd$: C 59.5, H 5.6, N 6.8. Found: C 59.7, H 5.3, N 7.1 %.

Table 3. Crystallographic data and structure refinement for 2–3·CH_2Cl_2

Compound	**2**	**3**·CH_2Cl_2
Empirical formula	$C_{31}H_{26}Cl_2FeN_4O_2Pd$	$C_{83}H_{94}Cl_6Fe_2N_8Pd_2$
Formula weight	719.71	1740.86
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Crystal size [mm]	0.26 × 0.21 × 0.14	0.39 × 0.27 × 0.16
a [Å]	11.0551(15)	14.019(2)
b [Å]	11.4501(15)	16.262(3)
c [Å]	13.900(3)	20.503(3)
α [°]	111.740(2)	78.153(2)
β [°]	92.674(2)	70.538(2)
γ [°]	117.2520(10)	81.476(2)
V [Å^3]	1402.2(4)	4296.9(11)
D_c [g cm^{-3}]	1.705	1.346
Z	2	2
GOF(on F^2)	1.010	0.942
Reflections collected	10451	31135
Reflections unique	5171	15531
R_1, wR_2 [$I > 2\sigma(I)$]	0.0435, 0.1134	0.0565, 0.1017

General Procedure for the α-Arylation of Ketones

In a Schlenk tube, a mixture of catalyst (0.01 mmol), aryl chloride (1.0 mmol), ketone (1.2 mmol) and the selected base (1.5 mmol) in solvent (3 mL) was evacuated and charged with nitrogen. The reaction mixture was then placed in an oil bath and heated at reflux temperature for 3 h, then cooled and quenched with water. The reaction mixture was extracted three times with CH_2Cl_2, the combined organic layers were washed with water, dried ($MgSO_4$), and evaporated to dryness. The pure products were isolated by flash chromatography on silica gel and identified by comparing melting points or ^{1}H NMR spectra with those found in the literature.[2,10,12,31,32]

Single Crystal X-Ray Structure Determination

Crystallographic data for complexes **2** and **3**·CH_2Cl_2 were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromator at 296 K using Mo-Ka radiation ($\lambda = 0.071073$ Å). The data were corrected for Lorentz polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the *SHELX-97* program.[34] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. Crystal data and structure refinements are summarized in Table 3. CCDC reference numbers 857945 and 857946 for **2** and **3**·CH_2Cl_2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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