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Highly Active [Pd(μ-Cl)Cl(NHC)]$_2$ Complexes in the Mizoroki–Heck Reaction

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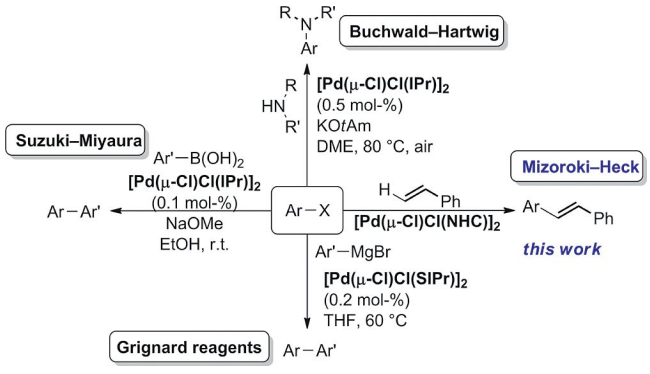
Keywords: Mizoroki–Heck reaction / Cross-coupling / Carbene ligands / Palladium

A series of Pd dimers bearing an N-heterocyclic carbene ligand was studied in the Mizoroki–Heck reaction. [Pd(μ-Cl)-Cl(SIPr)]$_2$ (SIPr = {*N*,*N*′-bis[2,6-(diisopropyl)phenyl]imidazolidin-2-ylidene}) was shown to be highly efficient in this cross-coupling for a range of aryl and heterocyclic bromides, with low palladium loading (20–200 ppm).

Introduction

Since Mizoroki and Heck independently reported the reaction of aryl halides with alkenes in the early 1970s,[1] the Mizoroki–Heck coupling has been employed in numerous applications, ranging from the synthesis of pharmaceuticals to that of fluorescent materials.[2] Although various metals are reported to catalyse the Mizoroki–Heck coupling,[3] Pd-based systems are the most commonly used because of their superior efficiency and selectivity.[4] Complexes based on N-heterocyclic carbene (NHC)[5] ligands have been extensively studied, leading to highly active catalysts.[6] Among them, complexes of the type [Pd(μ-Cl)Cl(NHC)]$_2$ are particularly attractive, as they are highly active, air- and moisture-stable and now commercially available.[7,8] Such systems have displayed outstanding performance in the Buchwald–Hartwig amination,[7a] in the Suzuki–Miyaura reaction at room temperature involving aryl chlorides,[7b] as well as in cross-coupling of Grignard reagents at low catalyst loadings (Scheme 1).[7c] In order to bring them a step closer to the category of "universal cross-coupling catalysts", we investigated their catalytic behaviour in the Mizoroki–Heck coupling.



Scheme 1. Dimeric palladium complexes in coupling reactions.

Results and Discussion

The coupling of 4-bromotoluene and styrene was first studied at 120 °C using 200 ppm Pd in the form of complex [Pd(μ-Cl)Cl(SIPr)]$_2$ (**1**) (Figure 1). Numerous bases and high-boiling-point solvents were tested. Whereas toluene and *N*-methylpyrrolidinone (NMP) gave poor conversions with K_2CO_3 as base (Table 1, entries 1 and 2), dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) rapidly emerged as the solvents of choice, affording the coupling product in quantitative conversions (Table 1, entries 3 and 4).

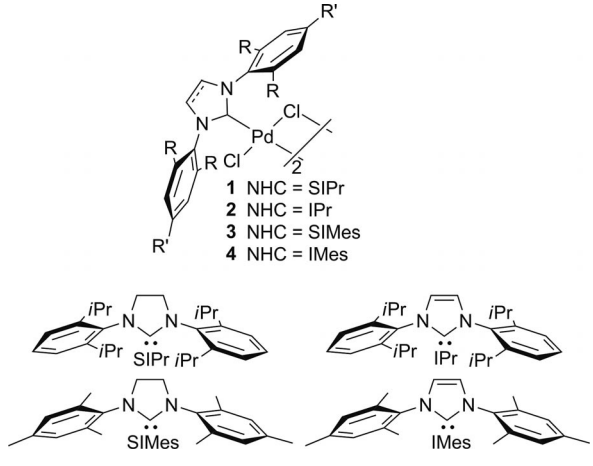


Figure 1. Dimeric complexes used in this study.

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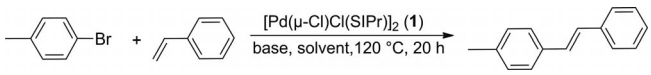
Table 1. Optimisation of the Mizoroki–Heck reaction conditions.[a]



Entry	Solvent	Base	Pd loading [ppm]	Conv.[b] [%]	TON[c]
1	Toluene	K_2CO_3	200	6	300
2	NMP	K_2CO_3	200	8	400
3	DMA	K_2CO_3	200	98	4900
4	DMF	K_2CO_3	200	99	4950
5	DMF/H_2O	K_2CO_3	200	76	3800
6	DMF	$KHCO_3$	200	99	4950
7	DMF	K_3PO_4	200	88	4400
8	DMF	KOMe	200	<1[d]	<50
9	DMF	Cs_2CO_3	200	4	200
10	DMF	KO*t*Bu	200	<1[d]	<50
11	DMF	CsF	200	58	2900
12	DMF	Cy_2NMe	200	10	500
13	DMF	NaOAc	200	21	1050
14	DMF	$KHCO_3$	200	69[e]	3450
15	DMF	K_2CO_3	20	25	12500
16	DMA	K_2CO_3	20	18	9000
17	**DMF**	**$KHCO_3$**	**20**	**83**	**41500**
18	**DMF**	**$KHCO_3$**	**20**	**99[f]**	**49500**

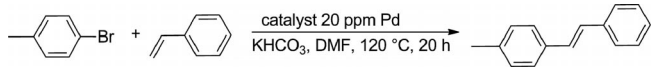
[a] Reaction conditions: 4-bromotoluene (0.5 mmol), styrene (0.75 mmol), base (1 mmol), solvent (2 mL), 120 °C, 20 h. [b] Conversion to coupling product, based on 4-bromotoluene, determined by GC, minimum average of two runs. [c] Mol product/mol Pd. [d] Unidentified side-products were observed in GC. [e] 100 °C. [f] 140 °C.

The use of a mixture of DMF and H_2O (DMF/H_2O 1:1) induced a slight decrease in the conversion, indicating that the presence of water is slightly detrimental to the reaction (Table 1, entry 5). A screening of bases was next carried out in DMF. Whereas $KHCO_3$ also led to the quantitative formation of the desired product (Table 1, entry 6), K_3PO_4, Cs_2CO_3, CsF, alkoxide bases and dicyclohexylmethylamine only led to poor/moderate conversions (Table 1, entries 7–13). In the case of alkoxide bases, some unidentified side-products were observed (Table 1, entries 8 and 10). The optimisation of the base was also performed in all solvents previously tested, but no further improvement of the optimal combination solvent/base was found (see Table S1). Lowering the temperature to 100 °C with $KHCO_3$ in DMF proved to be detrimental to catalyst efficiency (Table 1, entry 14). At a catalyst loading of 20 ppm of Pd, the combination of DMF and $KHCO_3$ was found to be optimal, leading to an 83% conversion of 4-bromotoluene (Table 1, entry 17). Increasing the temperature to 140 °C allowed full conversion with a turnover number (TON) of nearly 50000, thus competing with highly active systems reported in the literature (Table 1, entry 18; see Table S2 for an extensive low-catalyst-loading study).[4a,4b]

A comparative study of NHC-based dimer precatalysts was then carried out {Figure 1; IMes = *N*,*N*′-bis[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene, SIMes = *N*,*N*′-bis[2,4,6-(trimethyl)phenyl]imidazolidin-2-ylidene and IPr = *N*,*N*′-bis[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene}.

The catalytic activity of the four congeners was investigated at 120 °C with a catalyst loading of 20 ppm Pd (Table 2). The conversions obtained range from modest (59%) to good (83%), and the system based on SIPr shows a slightly higher activity (Table 2, entries 1–4). The saturated NHC ligands SIMes and SIPr were found to exhibit better activity than those of their unsaturated counterparts IMes and IPr (Table 2, entries 1,3 and 2,4).

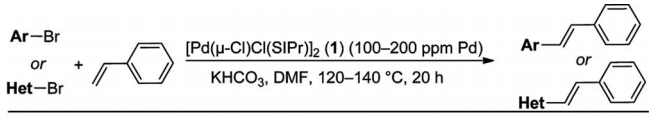
Table 2. Catalyst screening.[a]

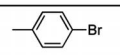
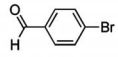
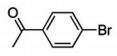
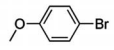
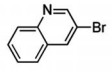


Entry	Catalyst	Conversion[b] [%]	TON[c]
1	$[Pd(\mu\text{-}Cl)Cl(SIPr)]_2$ (**1**)	83	41500
2	$[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ (**2**)	75	37500
3	$[Pd(\mu\text{-}Cl)Cl(SIMes)]_2$ (**3**)	73	36500
4	$[Pd(\mu\text{-}Cl)Cl(IMes)]_2$ (**4**)	59	29500

[a] Reaction conditions: 4-bromotoluene (0.5 mmol), styrene (0.75 mmol), $KHCO_3$ (1 mmol), DMF (2 mL), catalyst (20 ppm Pd), 120 °C, 20 h. [b] Conversion to coupling product, based on 4-bromotoluene, determined by GC, minimum average of two runs. [c] Mol product/mol Pd.

Table 3. Coupling of styrene with aryl and heterocyclic bromides.[a]



Entry	Substrate	*T* [°C]	Pd loading [ppm]	Yield[b] [%]	TON[c]
1		120	100	94	9400
2		120	100	> 99	> 9900
3		140	100	96	9600
4		140	100	91	9100
5		140	100	93	9300
6		140	100	96	9600
7		140	200	78	3900
8		140	200	> 99	> 4950
9		140	200	66	3300
10		140	200	42	2100

[a] Reaction conditions: Ar-Br or Het-Br (0.5 mmol), styrene (0.75 mmol), $KHCO_3$ (1 mmol), DMF (2 mL), $[Pd(\mu\text{-}Cl)Cl(SIPr)]_2$ (**1**), 120–140 °C, 20 h. [b] Isolated yield, minimum average of two reactions. [c] Mol product/mol Pd.

The scope of the reaction with the optimised reaction conditions and amounts of reactants was next evaluated in the coupling of a range of aryl bromides and heterocyclic bromides with styrene, with [Pd(μ-Cl)Cl(SIPr)]$_2$ (**1**) as precatalyst (Table 3).

Complex **1** was found to be highly efficient for reactions involving electronically activated and deactivated as well as sterically hindered aryl bromides. Quantitative conversions of coupling products were reached with a Pd loading of only *100 ppm* (Table 3, entries 1–6). Indeed, *p*-bromotoluene and activated *p*-bromobenzaldehyde were coupled with styrene in high isolated yields of 94% and 99%, respectively (Table 3, entries 1 and 2). Reaction of deactivated substrates 4-bromoanisole and 4-bromoacetophenone required 140 °C in order to efficiently proceed to completion (Table 3, entries 3 and 4). The catalyst system is also efficient with *ortho*-substituted aryl bromides. Indeed, 2-bromotoluene and 1-bromonaphthalene reacted with styrene to furnish the desired products in 93 and 96% yields, respectively (Table 3, entries 5 and 6). Heteroaromatic moieties are fragments of interest to the pharmaceutical industry. Hence, heteroaromatic bromides, which are known to be difficult coupling partners, were next evaluated. In order to reach good conversion, the catalyst loading was increased to 200 ppm. Thus, precatalyst [Pd(μ-Cl)Cl(SIPr)]$_2$ (**1**) was able to couple 3-bromopyridine and 3-bromoquinoline in good to excellent yields (Table 3, entries 7 and 8). Finally, 2-bromothiophene and 3-bromothiophene were treated with styrene in modest yields, 66% and 42% (Table 3, entries 9 and 10), respectively.

Conclusions

[Pd(μ-Cl)Cl(SIPr)]$_2$ (**1**) has been shown to be an excellent precatalyst for the Mizoroki–Heck reaction involving aryl and heterocyclic bromides at catalyst loadings in the ppm range. The catalytic behaviour of this commercially available complex adds one more important cross-coupling reaction to the arsenal of this family of complexes. Ongoing work in our laboratory aims to further extend the reaction chemistry of this very useful catalyst family not only to other cross-coupling reactions but also to other bond-forming transformations.

Experimental Section

General Remarks: All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system from Innovative Technology. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded, at 300 and 75 MHz, respectively, with a Bruker Spectrospin 300 MHz spectrometer operating at 298 K. Proton and carbon chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ [δ = 7.26 and 77.16 ppm, respectively]. Gas chromatography (GC) analyses were performed with an Agilent 7890A apparatus equipped with a flame ionisation detector and a (5%-phenyl)methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). Palladium complexes **1**–**4**[7,9] (Table 2) were prepared according to published procedures.

General Procedure for the Mizoroki–Heck Reaction: In a glovebox, a vial was charged with the base (1 mmol), the required amount of catalyst (stock solution), the aryl bromide (if solid, 0.5 mmol) and the solvent (2 mL). Outside the glovebox, the aryl bromide (if liquid, 0.5 mmol) and styrene (0.75 mmol) were injected through the septum. The mixture was then stirred at the indicated temperature for 20 h. The reaction mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (7 mL). A saturated aqueous solution of NH_4Cl (20 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried with $MgSO_4$. After filtration through cotton wool, the solvent was evaporated. The crude product was purified by flash column (pentane/diethyl ether) chromatography.

Preparation of the Catalysts Stock Solutions: The palladium complex (5 μmol) was weighed into a vial, dissolved with DMF (1 mL). Aliquots (100 μL) of this solution were diluted to 1 mL to decrease the catalyst concentration ten times (Pd concentration 0.5–1 μmol mL^{-1}).

4-Methylstilbene (Table 3, entry 1):[10] Eluent: C_5H_{12}/Et_2O 99:1. Colourless solid, yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.3 Hz, 2 H), 7.35 (d, J = 8.2 Hz, 2 H), 7.29 (t, J = 7.3 Hz, 2 H), 7.19 (m, 1 H), 7.11 (d, J = 8.2 Hz, 2 H), 7.05 (d, J = 16.4 Hz, 1 H), 7.00 (d, J = 16.4 Hz, 1 H), 2.30 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.7, 134.7, 129.5, 128.8, 127.8, 127.5, 126.57, 126.54, 21.4 ppm.

4-Styrylbenzaldehyde (Table 3, entry 2):[11] Eluent: C_5H_{12}/Et_2O 9:1. Pale yellow solid, yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.89 (s, 1 H, CHO), 7.77 (d, J = 8.2 Hz, 2 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 7.2 Hz, 2 H), 7.29–7.13 (m, 4 H), 7.05 (d, J = 16.3 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 191.8, 143.6, 136.7, 135.5, 132.3, 130.4, 129.0, 128.6, 127.5, 127.0 ppm.

1-(4-styrylphenyl)ethanone (Table 3, entry 3):[10] Eluent: C_5H_{12}/Et_2O 4:1. Colourless solid, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 2 H), 7.60–7.53 (m, 4 H), 7.39 (t, J = 7.3 Hz, 2 H), 7.30–7.16 (m, 3 H), 2.61 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 197.7, 142.2, 136.8, 136.1, 131.6, 129.02, 128.94, 128.5, 127.6, 127.0, 126.6, 26.7 ppm.

4-Methoxystilbene (Table 3, entry 4):[10] Eluent: C_5H_{12}/Et_2O 4:1. Colourless solid, yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 4 H), 7.28 (t, J = 7.6 Hz, 2 H), 7.18 (m, 1 H), 7.01 (d, J = 16.3 Hz, 1 H), 6.90 (d, J = 16.3 Hz, 1 H), 6.84 (d, J = 8.6 Hz, 2 H), 3.76 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 159.4, 137.8, 130.3, 128.8, 128.3, 127.9, 127.4, 126.8, 126.4, 114.3, 55.5 ppm.

2-Methylstilbene (Table 3, entry 5):[10] Eluent: C_5H_{12}/Et_2O 99:1. Colourless liquid, yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 6.7 Hz, 1 H), 7.60 (d, J = 7.6 Hz, 2 H), 7.36–7.25 (m, 7 H), 7.07 (d, J = 16.2 Hz, 1 H), 2.51 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.8, 136.5, 135.9, 130.5, 130.1, 128.8, 127.69, 127.67, 126.7, 126.3, 125.5, 20.0 ppm.

1-Styrylnaphthalene (Table 3, entry 6):[10] Eluent: C_5H_{12}/Et_2O 90:5. Pale yellow liquid, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, J = 7.4 Hz, 1 H), 7.93–7.86 (m, 2 H), 7.81 (d, J = 8.2 Hz, 1 H), 7.76 (d, J = 7.2 Hz, 1 H), 7.62 (d, J = 8.5 Hz, 2 H), 7.56–7.47 (m, 3 H), 7.44–7.39 (m, 2 H), 7.34–7.31 (m, 1 H), 7.16 (d, J = 16.3 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.8, 135.2, 133.9, 131.9, 131.5, 128.9, 128.8, 128.2, 127.9, 126.8, 126.2, 126.0, 125.8, 123.9, 123.8 ppm.

3-Styrylpyridine (Table 3, entry 7):[12] Eluent: C_5H_{12}/Et_2O 70:30. Colourless solid, yield 78%. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.73 (d, J = 2.2 Hz, 1 H), 8.48 (dd, J = 3.2, 1.6 Hz, 1 H), 7.84 (dt, J = 8, 2.2 Hz, 1 H), 7.53 (d, J = 7.3 Hz, 2 H), 7.39 (t, J = 7.3 Hz, 2 H), 7.33–7.26 (m, 2 H), 7.18 (d, J = 16.5 Hz, 1 H), 7.5 (d, J = 16.5 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 148.7, 136.7, 133.1, 132.7, 130.9, 128.9, 128.3, 126.8, 125.0, 123.6 ppm.

3-Styrylquinoline (Table 3, entry 8):[12] Eluent: C_5H_{12}/Et_2O 85:15. Pale yellow solid, yield 99%. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.10 (d, J = 2.1 Hz, 1 H), 8.13 (d, J = 2 Hz, 1 H), 8.07 (d, J = 8.5 Hz, 1 H), 7.79 (dd, J = 8.1, 1.2 Hz, 1 H), 7.67–7.62 (m, 1 H), 7.56–7.48 (m, 3 H), 7.40–7.25 (m, 4 H), 7.20 (d, J = 16.6 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 149.6, 147.6, 136.9, 132.4, 131.1, 130.4, 129.4, 129.3, 129.0, 128.4, 128.2, 128.0, 127.1, 126.8, 125.3 ppm.

2-Styrylthiophene (Table 3, entry 9):[12] Eluent: C_5H_{12}/Et_2O 85:15. Pale yellow solid, yield 66%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 2 H), 7.38–7.33 (m, 2 H), 7.28–7.19 (m, 3 H), 7.08 (m, 1 H), 7.03–7.00 (m, 1 H), 6.94 (d, J = 16.1 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.0, 137.1, 131.0, 128.8, 128.5, 127.7, 126.4, 126.2, 124.5, 121.9 ppm.

3-Styrylthiophene (Table 3, entry 10):[10] Eluent: C_5H_{12}/Et_2O 85:15. Pale yellow solid, yield 42%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 2 H), 7.36–7.30 (m, 4 H), 7.26–7.21 (m, 2 H), 7.12 (d, J = 16.3 Hz, 1 H), 6.95 (d, J = 16.3 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 140.3, 137.5, 128.8, 127.6, 126.4, 126.3, 125.1, 123.0, 122.5 ppm.

Supporting Information (see footnote on the first page of this article): Solvent and base screening, experiments with low catalyst loading, ^1H and $^{13}C\{^1H\}$ NMR spectra of all biaryl products.

Acknowledgments

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