Applied
Organometallic
Chemistry

Received: 7 June 2012 Revised: 12 July 2012 Accepted: 29 July 2012

(wileyonlinelibrary.com) DOI 10.1002/aoc.2915

Chugaev-type bis(acyclic diaminocarbenes) as a new ligand class for the palladium-catalyzed Mizoroki–Heck reaction

Millicent O. Owusu, Sachin Handa and LeGrande M. Slaughter*

A series of differently substituted Chugaev-type palladium bis(acyclic diaminocarbene) complexes was screened to identify the most active catalyst for Mizoroki–Heck coupling reactions of aryl bromides with styrene. The best catalyst, which contains three methyl groups on the bis(carbene) ligand, gives excellent coupling yields at 120 °C for both activated and deactivated aryl bromides. However, activity with aryl chlorides is limited to electron-deficient examples. The optimized catalyst demonstrates limited air and moisture stability, giving reduced yields in couplings of activated aryl bromides in open-flask conditions. The modular synthesis of this class of catalysts should allow further fine-tuning of activity in Mizoroki–Heck and related coupling reactions. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: carbene ligands; acyclic diaminocarbenes; palladium; air-stable catalysts; Mizoroki–Heck reaction

Introduction

Among palladium-catalyzed carbon–carbon coupling reactions,[1] the Mizoroki-Heck reaction of aryl halides or triflates with alkenes occupies a special niche owing to its high atom economy and synthetic versatility.[2] As a result of its unique mechanism, which features β-hydrogen elimination from an alkylpalladium intermediate to release the coupled alkene product,[3] a vinylic C-H bond serves as the nucleophilic coupling partner, avoiding the need for costly and wasteful electropositive leaving groups such as boronic acid, trialkylsilyl or trialkylstannyl. However, effective Mizoroki–Heck catalysis typically requires harsher reaction conditions compared with other types of coupling reactions, and achieving broad substrate scope is more challenging. For example, Mizoroki–Heck couplings of electron-rich ('deactivated') aryl bromides, and even electron-deficient ('activated') aryl chlorides, often need temperatures of 120–180 °C to achieve reasonable yields,[4] whereas a number of palladium catalysts can accomplish Suzuki–Miyaura couplings of the same aryl halides at room temperature.[5,6] Therefore, identification of new ligand types that stabilize the palladium catalyst under demanding reaction conditions is an important goal.

Efforts to create more stable and effective Mizoroki–Heck catalysts have generally focused on ligands that are very strong donors and/or can chelate the palladium center. For example, bidentate phosphines[7] and phosphine-containing palladacycles[8] have been shown to provide superior activity over monodentate phosphines in couplings of aryl chlorides. This is in contrast to other types of coupling processes such as the Suzuki–Miyaura reaction, where mono-ligated species are thought to be the active intermediates and a 1:1 ligand:palladium ratio is usually optimal.[9] The improved activities observed with some chelate ligands may be due to an increase in thermal stability as well as enhanced rates of certain steps in the catalytic mechanism.[10] The use of strongly donating *N*-heterocyclic carbene (NHC) ligands (for reviews of NHC ligands, see references[11]) has also been investigated in the Mizoroki–Heck reaction,[12] as these ligands tend to bind the metal tightly and thus might prevent catalyst deactivation via ligand loss. Indeed, Mizoroki–Heck coupling was one of the very first reported catalytic applications of NHC complexes,[12a] and incorporation of NHCs into chelate ligands has been found to be advantageous in some cases.[12c–e,12g,12h,12k–m] Of note are Herrmann's polymer-bound bis(NHC) chelates **1a,b** (Fig. 1)[12c] and Crabtree's NCN pincer complexes **2a,b**,[12e,12h] all of which were found to give air-stable, recyclable Mizoroki–Heck catalysts. Despite the promising features of some of these catalysts, however, carbene ligands have not been investigated as widely in the Mizoroki–Heck reaction as they have in other types of coupling processes.[13]

Acyclic diaminocarbenes (ADCs, e.g. Fig. 2)[14] have received much less attention as ancillary ligands in catalysis compared with NHCs,[15] (for selected examples of the use of ADC ligands in catalysis, see references[16]) despite having similar electronic stabilization and potentially stronger donor abilities.[17] In two very limited reports of Mizoroki–Heck coupling with palladium catalysts containing monodentate ADC ligands (e.g., Fig. 2),[18] no particular advantages were noted and no useful activity with aryl chlorides was achieved. In 2006, our group reported that a series of modular chelated palladium bis(ADC) complexes with different nitrogen substituents could be rapidly prepared (Scheme 1) and catalytically screened to identify a Suzuki–Miyaura coupling catalyst that gave good yields at 120 °C for a range of aryl bromides, as well as activated aryl chlorides, with little loss of activity under open-flask conditions in air in the case of aryl bromides.[19] The synthesis of **3a–e** and **4a–e** involves simple addition of alkylisocyanides and hydrazines to aqueous solutions of Pd^{II} under benchtop conditions.

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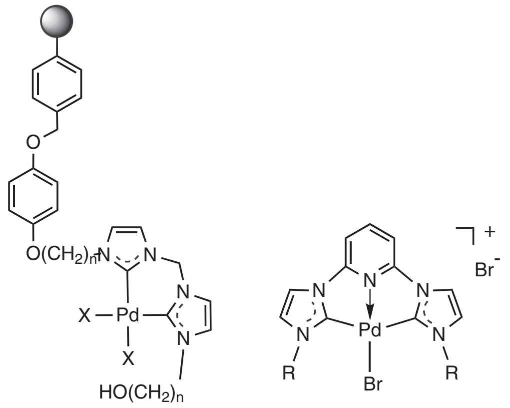


1a (n = 3, X = Br)
1b (n = 2, X = I)

2a (R = Me)
2b (R = nPr)

Figure 1. Examples of robust Mizoroki–Heck catalysts containing NHC chelate ligands.

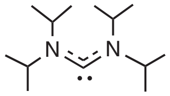
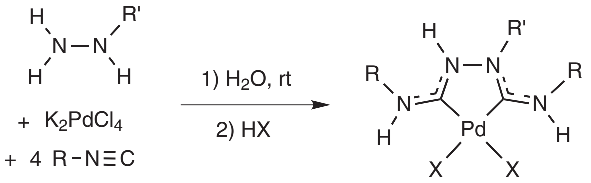


Figure 2. An acyclic diaminocarbene (ADC).



R' = H: R = Me (a), iPr (b), Cy (c), tBu (d)
R' = Me, R = Me (e)

3a-e X = Cl
4a-e X = Br

Scheme 1. Modular synthesis of Chugaev-type palladium bis(ADC) complexes.

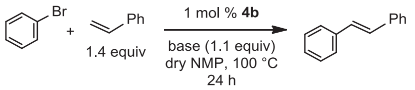
The platinum analogue of **3a** was prepared as early as 1915 by Chugaev,[20] although its structure was not recognized until 1970.[21] Subsequent to our initial reports, we and others have further developed the metal-templated addition of amines to isocyanides as a strategy for the preparation and optimization of structurally diverse ADC ligands in various catalytic reactions involving palladium(II)[22] and gold(I).[23] However, the Chugaev-type complexes **3a–e** and **4a–e** have not been investigated in any reaction type other than Suzuki–Miyaura coupling. Furthermore, no studies of Mizoroki–Heck coupling with ADC-containing chelate complexes have appeared. (For an example of the use of mixed chelate ligands containing phosphines tethered to ADCs or other acyclic carbenes in Pd-catalyzed Sonogashira coupling reactions, see Eberhard *et al.*[24]) Given the advantages associated with strongly donating chelate ligands, and the relative scarcity of studies on catalytic applications of ADC-ligated complexes, we felt that it was important to investigate the utility of Chugaev-type complexes **3a–e** and **4a–e** as catalysts in the Mizoroki–Heck reaction. Herein we present the results of this study.

Results and Discussion

For initial optimization of catalytic conditions, we chose to use isopropyl-substituted catalyst **4b**. In our previous study of Suzuki–Miyaura coupling reactions, **4b** was found to be a moderately active catalyst, but not the most active of the series.[19] Because Mizoroki–Heck coupling catalysts are often highly sensitive to the nature of the base additive, the base was the first experimental parameter to be varied. The coupling of 'unactivated' bromobenzene with styrene was used as a screening reaction, and a relatively moderate temperature of 100 °C was used to ensure that differences in catalytic activity would be readily observable. With a catalyst loading of 1 mol% **4b** in *N*-methyl-2-pyrollidone (NMP) as a solvent, the mild base NaOAc provided the best results, affording a 94% yield of *trans*-stilbene after 24 h (Table 1, entry 1). Anhydrous K_3PO_4 and Cs_2CO_3 were only slightly less effective as base additives (entries 3 and 4). The use of NEt_3 led to much poorer activity, with only a 21% yield of the stilbene product (entry 2). Although amines have been found to be excellent bases with Mizoroki–Heck coupling catalysts bearing electron-rich phosphine ligands (for an example of a catalytic system that is effective for Mizoroki–Heck couplings of activated aryl chlorides at room temperature, see Littke and Fu[6]), poor activity with NEt_3 has also been noted in NHC-based catalyst systems.[12f,12g] Notably, Nolan's *in situ*-generated Pd–NHC catalysts require the more expensive base Cs_2CO_3 and are ineffective with NaOAc,[12f,12g] although pre-formed NHC–palladium complexes have shown useful Mizoroki–Heck activity with NaOAc.[12a,12d,12i–m] Only an 11% yield of stilbene was obtained in a control reaction with no added base (entry 5), confirming that the additive is essential for useful catalytic activity. The higher activity observed with NaOAc prompted us to select it as the base of choice for Mizoroki–Heck reactions catalyzed by palladium bis(ADC) complexes.

With the optimal base additive identified, we next examined the effect of catalyst structure on activity. The Chugaev-type palladium bis (ADC) catalysts contain three sites of variation: the isocyanide-derived

Table 1. Optimization of the base for the catalytic Mizoroki–Heck coupling reaction[a]



Entry	Base	Yield (%)[b]
1	NaOAc	94
2	NEt_3	21
3	K_3PO_4	92
4	Cs_2CO_3	90
5	None	11

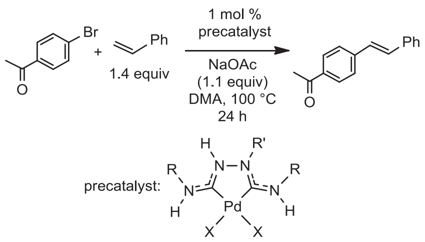
[a] Reaction conditions: 0.017 mmol **4b**, 1.7 mmol PhBr, 2.4 mmol styrene, 1.87 mmol base, anhydrous NMP, 100 °C, 24 h; reaction times not optimized.

[b] Yields determined by ^{1}H NMR.

substituent R (Me, *i*Pr, Cy, or *t*Bu), the hydrazine substituent R′ (H or Me), and the labile halide ligand X$^-$ (Cl$^-$ or Br$^-$). For this phase of optimization, the relatively less challenging coupling of 4-bromoacetophenone with styrene was examined, as this 'activated' substrate allowed measurable yields to be obtained with all catalysts. Screening the entire library of ten precatalysts with a palladium loading of 1 mol% at 100 °C revealed large variations in catalytic activity as a function of catalyst structure, with yields of the stilbene product ranging from 16% to 98% (Table 2). Precatalysts **4a–e**, which contain bromide ligands, gave significantly higher yields than chloride-containing **3a–e**, possibly as a result of the higher lability of bromide under catalytic conditions. Among the bromide-ligated precatalysts, dimethyl-substituted bis(ADC) complex **4a** gave the poorest yield of stilbene product (entry 2), whereas catalysts **4b–d**, each bearing a secondary or tertiary alkyl group, afforded substantially better yields (entries 4, 6, 8). Complex **4e**, containing a trimethyl-substituted bis(ADC) ligand, proved to be the best precatalyst, producing a nearly quantitative yield (98%) of the stilbene product (entry 10).

A similar trend of catalytic activity as a function of bis(ADC) substitution pattern was observed in our study of Suzuki–Miyaura coupling with this precatalyst library, although chloride-ligated complexes were slightly more effective in that reaction.[19] The trend is best explained as a consequence of electronic rather than steric effects. Strongly donating ligands are known to enhance the rate of oxidative addition of the aryl halide, which can be the turnover-limiting step of the Mizoroki–Heck reaction, as well as preventing ligand dissociation that can lead to catalyst deactivation.[9] The larger alkyl substituents of **4b–d** increase the electron richness of the bis(ADC) ligand compared with methyl groups, due to their stronger inductive effects, thus boosting the donor ability of the chelate ligand and improving catalytic activity relative to **4a**. The presence of three rather than two alkyl substituents on the bis (ADC) framework of **4e** evidently endows this ligand with the strongest donor ability of the series, despite the weaker inductive donor ability of a methyl group compared with the larger alkyl groups. The somewhat anomalous decrease in catalytic activity for bis(ADC) complexes **3d** and **4d**, which contain larger *tert*-butyl substituents, compared with those having secondary alkyl groups (e.g. **4b** and **4c**) also parallels our previous results in Suzuki–Miyaura coupling reactions with these catalysts.[19] This is possibly due to the greater polarizability of the *tert*-butyl group,[25] which could result in *tert*-butyl exhibiting a weaker inductive donor effect than cyclohexyl or isopropyl if there is a buildup of electron density at palladium in key steps of the catalytic mechanism. This is likely to be the case, given that we have observed rapid deprotonation of the acidic backbone N-H groups of Chugaev-type bis(ADC) ligands in the presence of base.[15a] This could result in an anionic active Pd^0 species, consistent with the Amatore–Jutand mechanism for the Mizoroki–Heck reaction.[26]

Table 2. Selection of the optimal precatalyst for the Mizoroki-Heck coupling reaction[a]



Entry	Precatalyst	R	R′	X	Yield (%)[b]
1	**3a**	Me	H	Cl	16
2	**4a**	Me	H	Br	36
3	**3b**	*i*Pr	H	Cl	69
4	**4b**	*i*Pr	H	Br	93
5	**3c**	Cy	H	Cl	48
6	**4c**	Cy	H	Br	93
7	**3d**	*t*Bu	H	Cl	43
8	**4d**	*t*Bu	H	Br	68
9	**3e**	Me	Me	Cl	59
10	**4e**	Me	Me	Br	98

[a] Reaction conditions: 0.017 mmol precatalyst, 1.7 mmol 4-bromoacetophenone, 2.4 mmol styrene, 1.87 mmol NaOAc, anhydrous DMA, 100 °C, 24 h; reaction times not optimized.

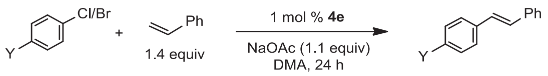
[b] Yields determined by ^{1}H NMR.

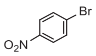
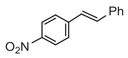
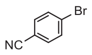
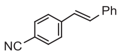
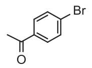
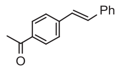
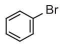
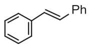
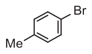
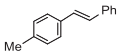
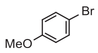
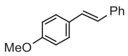
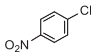
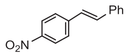
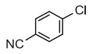
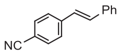
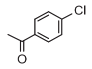
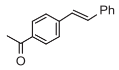
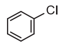
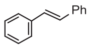
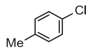
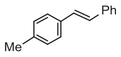
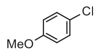
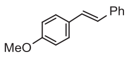
It should be mentioned that anhydrous dimethylacetamide (DMA) was used as the solvent for screening differently substituted precatalysts, because initial trials with **4b** suggested slightly better activity in DMA versus NMP. However, it was noted during precatalyst screening that a reddish-brown color developed during the course of the reaction for several precatalysts (especially **3a**, **4a** and **3d**), whereas very little colorization was observed when NMP was used. As these color changes in DMA could indicate decomposition of the catalyst into nanoparticulate or unligated forms of Pd^0,[27] we chose to use NMP as the solvent for further catalytic studies.

With **4e** selected as the best precatalyst for Mizoroki–Heck coupling reactions, we next investigated the ability of this catalyst to tolerate different functional groups on the aryl halide. For reactions performed under a nitrogen atmosphere, the optimized catalytic system demonstrated excellent substrate scope in couplings of aryl bromides with styrene, affording stilbene products in 92–99% yield when either electron-withdrawing or electron-donating substituents were present (Table 3, entries 1–6a). An increase of the reaction temperature to 120 °C was necessary to obtain maximum yields in most cases. Unfortunately, generally poor catalytic activity was obtained with aryl chlorides. Although an excellent yield was obtained with the strongly electron-withdrawing *p*-nitro substituent (entry 7), aryl chlorides with more weakly activating cyano and acetyl groups gave only moderate yields (entries 8 and 9). No stilbene product at all was detected when unactivated or electron-rich chlorobenzene derivatives were used (entries 10–12). For all reactions that gave a yield, the *trans*-stilbene product was formed exclusively. We did not detect any of the geminal coupling product, which is sometimes a significant byproduct in Mizoroki-Heck reactions of styrene.[12m]

We also investigated the tolerance of precatalyst **4e** to air and moisture by repeating Mizoroki–Heck couplings of aryl bromides with styrene in undried NMP under open-flask conditions. For activated aryl bromides, yields of the stilbene products dropped 34–40% compared with reactions performed under nitrogen in dry NMP (Table 3, entries 1–3b). Much greater drops in yield were observed for electron-neutral and electron-rich aryl bromides (entries 4–6b). Given that a palladium catalyst containing the same bis(ADC) ligand (i.e. **3e**) gave almost identical yields in Suzuki–Miyaura couplings of electron-poor and electron-neutral aryl bromides performed under open-flask conditions compared

Table 3. Aryl halide scope and air/moisture tolerance of Mizoroki–Heck coupling reactions with optimized precatalyst **4e**[a]



Entry	Aryl halide	Product	Atmosphere[b]	Temperature (°C)	yield (%)[c]
1a 1b			N_2 air	120 120	97 58
2a 2b			N_2 air	120 120	97 57
3a 3b			N_2 air	100 120	98 64
4a 4b			N_2 air	120 120	99 13
5a 5b			N_2 air	120 120	93 18
6a 6b			N_2 air	120 120	92 9
7			N_2	120	96
8			N_2	120	45
9			N_2	120	40
10			N_2	120	-[d]
11			N_2	120	-[d]
12			N_2	120	-[d]

[a] Reaction conditions: 0.017 mmol **4e**, 1.7 mmol aryl halide, 2.4 mmol styrene, 1.87 mmol NaOAc, NMP, 24 h; reaction times not optimized.

[b] Reactions under N_2 conducted in anhydrous NMP; reactions under air conducted open to atmosphere in undried NMP.

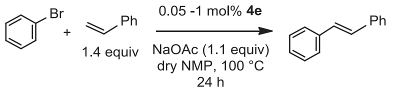
[c] Yields determined by ^{1}H NMR.

[d] No product detected.

with dry, degassed conditions,[19] it seems likely that the limited air tolerance observed in the present study results from aspects of the Mizoroki–Heck reaction rather than from the catalyst itself. Specifically, alkenes are susceptible to oxidation,[28] and we postulate that palladium-bound styrene intermediates, or styrene itself, might undergo oxidative degradation at rates competitive with catalysis at temperatures needed for coupling activity in this system.

Finally, we studied the activity of optimized catalyst **4e** at lower catalyst loadings. In couplings of the unactivated substrate bromobenzene with styrene at a relatively moderate temperature of 100 °C, only a slight drop in yield was seen upon decreasing the catalyst loading from 1.0 mol% to 0.5 mol% (Table 4, entries 1 and 2). At Pd loadings of 0.25, 0.1, and 0.05 mol%, yields were significantly lower, although turnover numbers (TON) continued to increase (entries 3–5), reaching 940 TON at 0.05 mol% **4e**.

Table 4. Mizoroki-Heck coupling of bromobenzene with styrene at different catalyst loadings[a]



Entry	mol% **4e**	Yield (%)[b]	TON
1	1.0	98	98
2	0.5	96	192
3	0.25	62	248
4	0.1	49	490
5	0.05	47	940

[a] Reaction conditions: 1.7 mmol PhBr, 2.4 mmol styrene, 1.87 mmol base, anhydrous NMP, 100 °C, 24 h; reaction times not optimized.

[b] Yields determined by ^1H NMR.

Significantly, only a few reported Pd–NHC catalyst systems have achieved comparable or higher TON with unactivated or electron-rich aryl bromides, and temperatures higher than 100 °C were used in each case.[12a,12d,12k]

Conclusion

This study demonstrates that Chugaev-type palladium bis(ADC) complexes can be structurally optimized to provide excellent catalysts for Mizoroki–Heck coupling reactions of aryl bromides with styrene. The substrate scope of the best catalyst encompasses electron-poor and electron-rich aryl bromides, and the reaction temperatures of 100–120 °C are relatively moderate compared to the majority of published catalyst systems.[4] The activity of the optimized catalyst with aryl chlorides is limited to electron-deficient examples, but this is similar to the substrate scope that has been observed for most NHC-containing Mizoroki–Heck catalysts.[12] Even the best Pd–NHC catalysts have only achieved moderate yields in Mizoroki–Heck couplings of electron-rich aryl chlorides.[12i,12m] The air and moisture tolerance of the optimized catalytic system is limited, but this may be due to the fact that catalysis was performed below solvent reflux temperature. Notably, it was reported that **2b** only gave reasonable coupling activities under open-flask conditions when the DMA solvent was refluxing, which may result in solvent vapor purging the flask of oxygen.[12h] Overall, this study suggests that bis(ADC) ligands are potentially competitive with NHCs in their ability to promote catalytic Mizoroki–Heck coupling reactions. The facile synthesis of these acyclic carbene ligands should allow further catalyst fine-tuning that may lead to improved activities and reaction scope.

Experimental

General Considerations

Palladium bis(ADC) complexes **3a–e** and **4a–e** were synthesized by our published procedure.[19] Mizoroki–Heck substrates 4-bromoacetophenone (Aldrich), 4-bromonitrobenzene (Eastman) and bromobenzene (Aldrich) were purified by literature procedures[29] from samples that had been in use >4 years. All other reagents were purchased from Aldrich or Acros at the highest available purity and used as received. Anhydrous DMA and NMP were purchased from Acros in septum-sealed bottles and used as received for Mizoroki–Heck reactions performed under nitrogen. Undried NMP (Acros, 99 + %) was used as received for reactions done in open-flask conditions. NMR spectra were recorded on a Varian Unity INOVA 400 MHz spectrometer using $CDCl_3$ (Cambridge Isotope Laboratories, 99.8%) as a solvent.

Catalytic Mizoroki–Heck Reactions

Base (1.87 mmol), aryl halide (1.7 mmol), and styrene (2.4 mmol, 275 ml) were added successively to a reaction vessel, followed by a solution of precatalyst (0.85–17 μmol) in the appropriate solvent (5 ml). For reactions done under inert conditions, reagents were loaded into a sealable reaction vessel in a nitrogen glovebox, and the vessel was closed with a PTFE stopcock. For reactions done in open-flask conditions, all reagents were loaded under air into a round-bottom flask, which was then attached to a reflux condenser open to air. The reaction vessel was placed in a preheated oil bath, and the mixture was stirred vigorously for 24 h. The reaction mixture was allowed to cool, and 100 μl of diethylene glycol dibutyl ether was added to the flask as an NMR internal standard. A 200 μl aliquot of the mixture was withdrawn and diluted with 10 ml dichloromethane. The organic layer was extracted four times with 10 ml portions of water, dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy. Reaction yields were determined by comparing ^1H NMR integrations of product peaks with those of the internal standard.

Acknowledgments

We thank the Donors of the American Chemical Society Petroleum Research Fund (grant #40196-G1) for financial support of this research.

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