DOI: 10.1002/adsc.200800768

A Lutidine-Bridged Bis-Perimidinium Salt: Synthesis and Application as a Precursor in Palladium-Catalyzed Cross-Coupling Reactions

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Received: December 11, 2008; Revised: March 23, 2009; Published online: May 5, 2009

Dedicated to Prof. Armin de Meijere on the occasion of his 70th birthday.

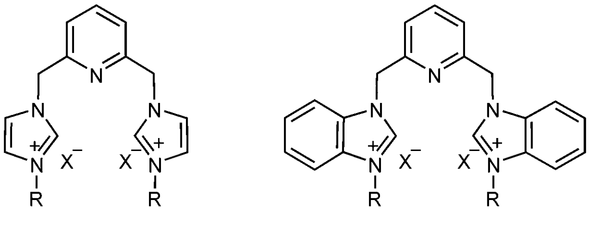
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200800768.

Abstract: A novel lutidine-bridged bis-perimidinium dibromide **3** was synthesized in quantitative yield from cheap commercial starting materials. The bisylidene prepared therefrom *in situ* upon deprotonation is a potent precatalyst in palladium-catalyzed Heck and Suzuki cross-coupling reactions under aerobic conditions, and is efficient even with a ppm scale catalyst loading. Its stronger σ-donor character is held to be responsible for its superior catalytic performance compared with imidazole- and benzimidazole-based analogues bearing the same skeleton precursors.

Keywords: carbenes; Heck reaction; palladium; perimidinium salts; Suzuki coupling

N-Heterocyclic carbenes (NHCs) are known as strong σ-donor and weak π-acceptor ligands, and as such their metal complexes are widely applied in catalysis and material sciences.[1] They increasingly compete successfully with phosphines in terms of compatibility with aerobic conditions, thermostability and environmental friendliness.[2] In this respect, ylidenes derived from five-membered heterocycles such as imidazolium (**1**) and benzimidazolium salts (**2**), have been developed as typical skeletons of stable NHCs, and have been successfully applied as ligands in transition metal-catalyzed reactions (Scheme 1).[1–3] Ylidenes derived from perimidinium salts (**3**) provide arene-fused six-membered heterocycles and, thus, represent a novel type of NHC framework which results in a stronger σ-donor ability in comparison with N-heterocyclic carbenes derived from (benz)imidazolium salts.[4a,d] Therefore, we started to exploit the potential of perimidine-based NHCs in transition metal-catalyzed transformations, an approach which has been paid less attention to so far.[4b,c]

Due to their robustness, activity and variability, pincer-type ligands and their metal complexes attract increasing interest in catalysis, the development of molecular devices and soft matter.[5] As widely utilized pincer skeletons, lutidine/pyridine-bridged NHCs and their metal complexes proved to efficiently catalyze C–C and C–N bond formation as well as olefin metathesis.[5b–d,6] Recently, we reported that bis-imidazol-2-ylidene palladium pincer complexes and their benzo analogues efficiently gelate a wide variety of organic solvents and ionic liquids.[7] We disclosed



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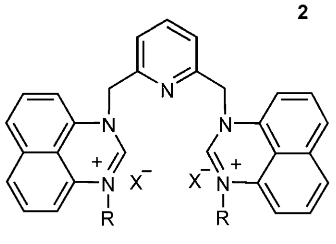

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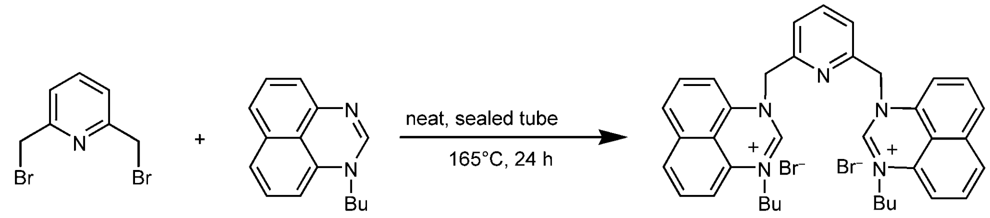
Scheme 1. Lutidine-bridged imidazole-, benzimidazole- and perimidine-based NHC precursors **1**–**3**.



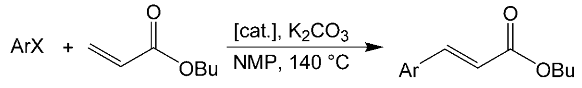
4 **3**

Scheme 2. Synthesis of lutidine-bridged bis-perimidinium dibromide **3**.

their high catalytic activities in homogeneous (such as Heck and Suzuki coupling reactions with a ppm scale catalyst loading)[8] and heterogeneous (Michael addition in the gel state)[7b] transformations, and also reported on bis-benzimidazolium salts – precursors of the pincer ligands – as efficient gelators for organic, especially alcoholic, solvents and catalysts for phase-transfer alkylations.[9] In an extension of this work, we incorporated the perimidine ring, a stronger σ-donor with an increased π-size in comparison to the (benz)-imidazole heterocycles, into pincer-type NHCs in order to explore their potential in catalysis and soft materials. We now report on a novel lutidine-bridged bis-perimidinium salt which is easily accessible from cheap commercial starting materials, and on its role as a precatalyst in palladium-catalyzed Heck and Suzuki cross-coupling reactions.

Lutidine-bridged bis-perimidinum dibromide **3** is accessible as a bright yellow solid in almost quantitative yield by *N*-alkylation of *N*-butylperimidine **4** with 2,6-bis(bromomethyl)pyridine in a sealed tube (Scheme 2). *N*-Butylperimidine **4** was obtained in 86% isolated yield by dropwise addition of *n*-butyl bromide to a solution of perimidine – deprotonated by oil-free NaH in THF at room temperature – and subsequent warming of the mixture to reflux.[10]

Within our programme aiming at the development of NHCs and Fischer carbenes towards application in catalysis and soft material sciences,[7–9,11] we addressed the role of a strong σ-donor in a six-membered heterocycle on the catalytic activity and tested bis-perimidinium salt **3** in palladium-catalyzed Heck and Suzuki cross-coupling reactions. To simplify the catalytic protocol we aimed at an *in situ* formation of the catalyst[4d,6d] and used bis-perimidinium dibromide **3** in the presence of equimolar amounts of $Pd(OAc)_2$. The Heck coupling of aromatic halides and *n*-butyl acrylate was chosen as a model reaction. A 2 mol% catalyst loading [equimolar amounts of **3** and $Pd(OAc)_2$] in 1-methyl-2-piperidone (NMP) at 140 °C using K_2CO_3 as a base gave the best results for iodobenzene (98% after 60 min) (Scheme 3). A slightly lower yield was observed for bromobenzene (93% after 90 min). Identical results were obtained under aerobic conditions indicating that the pincer palladium complex intermediate formed *in situ* tolerates higher temperatures and the presence of air and moisture.



5a – j

PhI: 2 mol% [cat.], 1 h, 98% yield (**5a**)
PhBr: 2 mol% [cat.], 1.5 h, 93% yield (**5a**)

Scheme 3. Cross-coupling of halobenzenes and *n*-butyl acrylate catalyzed by bis-perimidinium dibromide **3**/$Pd(OAc)_2$ [catalyst prepared *in situ* from equimolar amounts of **3** and $Pd(OAc)_2$].

If the reaction time is extended to 42 h under these standard conditions, the catalyst loading can be dramatically reduced to 2 ppm resulting in only moderately decreased yields of *n*-butyl cinnamate **5a** (82% for iodobenzene and 71% for bromobenzene; Table 1, entries 1 and 2). In order to investigate the scope of the protocol and, in particular, the electronic and steric implications of the substrates, we tested a variety of iodoarenes under our 2 ppm catalyst loading standard conditions (Table 1). For monosubstituted iodoarenes, the catalyst tolerates additional substituents with different electronic and steric properties and allowed for moderate to good isolated yields of biphenyl derivatives **5b–i** (Table 1, entries 3–11). Compared with their *meta*-isomer the coupling of *ortho*- and *para*-iodotoluenes resulted in higher conversions and yields (88% and 92% *versus* 74%) and in turnover numbers (TON) up to 4.62×10^5 (Table 1, entries 3–5); a lower yield and TON were again observed with *para*-bromotoluene (77%, 3.85×10^5; Table 1, entry 6). Donor-substitution increases the yield and TON of the *β*-aryl acrylate as shown for *para*-iodoanisole (4.51×10^5, Table 1, entry 7). Moderate yields and TONs result from acceptor and sterically more demanding substitution patterns (Table 1, entries 8–12). 1-Iodo-3,5-dimethylbenzene still afforded a 62% yield (Table 1, entry 12), whereas no coupling product at all, even at extended reaction times, was observed for the strong acceptor analogue 1-iodo-3,5-

Table 1. Heck cross-coupling reactions of haloarenes with *n*-butyl acrylate catalyzed by lutidine-bridged N-heterocyclic dibromides **1–3** and $Pd(OAc)_2$.[a]

Entry	ArX	Salt	Product	Yield (%)[b]	TON
1	Iodobenzene	**3**	**5a**	82	4.10×10^5
2	Bromobenzene	**3**	**5a**	71	3.55×10^5
3	2-Iodotoluene	**3**	**5b**	88	4.41×10^5
4	3-Iodotoluene	**3**	**5c**	74	3.71×10^5
5	4-Iodotoluene	**3**	**5d**	92	4.62×10^5
6	4-Bromotoluene	**3**	**5d**	77	3.85×10^5
7	4-Iodoanisole	**3**	**5e**	90	4.51×10^5
8	4-Iodoacetophenone	**3**	**5f**	69	3.45×10^5
9	1-Iodo-2-(trifluoromethyl)benzene	**3**	**5g**	71	3.57×10^5
10	1-Iodo-4-(trifluoromethyl)benzene	**3**	**5h**	73	3.63×10^5
11	1-Iodonaphthalene	**3**	**5i**	73	3.66×10^5
12	1-Iodo-3,5-dimethylbenzene	**3**	**5j**	62	3.08×10^5
13	4-Iodotoluene	**2**	**5d**	69	3.44×10^5
14	4-Iodotoluene	**1**	**5d**	46	2.30×10^5

[a] *Reaction conditions:* 2 mmol haloarene, 2.4 mmol *n*-butyl acrylate and 3 mmol K_2CO_3 in 3 mL NMP at 140 °C for 42 h with 2 ppm catalyst [prepared *in situ* from equimolar amounts of lutidine-bridged *N*-heterocyclic dibromide and $Pd(OAc)_2$].

[b] Isolated yield.

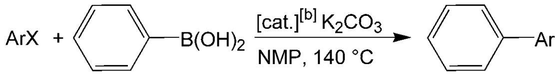
bis(trifluoromethyl)benzene indicating a pronounced stereoelectronic effect.

A comparison between the lutidine-bridged bis-perimidinium dibromide **3** and its imidazole and benzimidazole analogues (**1** and **2**, $R=n$-Bu and $X=Br$) suggests that their catalytic performance increases with the σ-donor ability of the NHC ligand present in the active palladium catalyst. Under the standard conditions of 2 ppm catalyst loading applied to the coupling of *para*-iodotoluenes with *n*-butyl acrylate, the less efficient benzimidazolium (**2**) and imidazolium (**1**) analogues afford reduced yields of 69 and 46%, respectively (Table 1, entries 13 and 14). Major amounts of starting materials were recovered in the both cases, strictly contrasting the full conversion observed with bis-perimidinium dibromide **3** as precatalyst (Table 1, entry 5). These results underline the role of σ-donation of the NHC ligand in palladium catalysis.

In order to characterize the nature of the catalytic species generated from $Pd(OAc)_2$ and salt **3** *in situ* we performed the mercury test which has been reported to allow a discrimination between molecular and nanoparticle/colloidal catalysis.[12–15] A set of reactions using iodobenzene, butyl acrylate, 1 mol% catalyst in the presence of excess mercury (with respect to the palladium source) added after 0, 15, 30 and 45 min was run at 140 °C in NMP and monitored by TLC and GC-MS. In all four cases a full conversion to butyl cinnamate and an isolated yield of 98% identical with that known for the reaction without mercury was observed suggesting a molecular catalytically active species containing the CNC ligand similar to that previously reported by Crabtree.[15] To demonstrate the thermal stability of the catalyst we synthesized the bis-perimidinylidene pincer palladium complex under the conditions applied in the catalytic reactions but in the absence of any substrate (for details, see Supporting Information).

The bis-perimidinium salt **3** is equally effective in Suzuki coupling reactions and allows for remarkably low catalyst loading (Table 2). Under similar conditions as applied for the Heck cross-coupling, but with a catalyst loading reduced to 0.2 mol%, bromobenzene reacted with phenylboronic acid to give biphenyl **6a** in a 95% yield after 6 h (Table 2, entry 1); reducing the catalyst concentration by another order of magnitude still resulted in an 82% yield (Table 2, entry 2). A study of the amount of catalyst required for a synthetically useful protocol was carried out for a selection of donor- and acceptor-substituted iodoarenes. The balance of catalyst concentration and reaction time is demonstrated for iodobenzene (Table 2, entries 3–5). With a catalyst loading of 0.02 mol%, 92% of biphenyl **6a** was isolated after warming a NMP solution at 140 °C for 5 h (Table 2, entry 3). To secure a similar high yield the amount of catalyst can be even reduced to 5 ppm if the reaction is allowed to proceed for 48 h. A further reduction of the catalyst loading to 2 ppm resulted in a 63% yield of **6a** after 36 h and a TON of 3.15×10^5 while a considerable amount of starting material was recovered (Table 1, entry 4). Since running the reactions in NMP to 140 °C for 48 h in the presence of 5 ppm catalyst turned out to be the overall optimum conditions they were applied to a comparative study demonstrating the scope of the protocol and influences of electronic and steric prop-

Table 2. Suzuki-coupling of haloarenes with phenyl boronic acid catalyzed by lutidine-bridged dibromides **1–3** and $Pd(OAc)_2$.[a]



6a – l

Entry	ArX	Salt	Catalyst [mol%]	Time [h]	Product	Yield[c] [%]	TON
1	Bromobenzene	**3**	0.2	6	**6a**	95	475
2	Bromobenzene	**3**	0.02	6	**6a**	82	4120
3	Iodobenzene	**3**	0.02	5	**6a**	92	4600
4	Iodobenzene	**3**	0.0002	36	**6a**	63	3.15×10^{5}
5	Iodobenzene	**3**	0.0005	48	**6a**	91 (81[d])	1.83×10^{5}
6	2-Iodotoluene	**3**	0.0005	48	**6b**	89	1.79×10^{5}
7	3-Iodotoluene	**3**	0.0005	48	**6c**	74	1.48×10^{5}
8	4-Iodotoluene	**3**	0.0005	48	**6d**	93	1.87×10^{5}
9	4-Iodoanisole	**3**	0.0005	48	**6e**	89	1.77×10^{5}
10	4-Iodoacetophenone	**3**	0.0005	48	**6f**	71	1.43×10^{5}
11	1-Iodo-4-(trifluoromethyl)benzene	**3**	0.0005	48	**6g**	82	1.64×10^{5}
12	1-Iodo-2-(trifluoromethyl)benzene	**3**	0.0005	48	**6h**	83	1.66×10^{5}
13	1-Fluoro-2-iodobenzene	**3**	0.0005	48	**6i**	76	1.53×10^{5}
14	1-Iodonaphthalene	**3**	0.0005	48	**6j**	73	1.45×10^{5}
15	2-Iodopyridine	**3**	0.0005	48	**6k**	67	1.34×10^{5}
16	1-Iodo-3,5-dimethylbenzene	**3**	0.0005	48	**6l**	61	1.22×10^{5}
17	4-Iodotoluene	**2**	0.0005	48	**6d**	70	1.41×10^{5}
18	4-Iodotoluene	**1**	0.0005	48	**6d**	49	9.72×10^{4}

[a] *Reaction conditions:* 2 mmol haloarene, 2.2 mmol phenyl boronic acid and 2.4 mmol K_2CO_3 in 3 mL NMP at 140 °C.
[b] Catalyst prepared *in situ* from equimolar amounts of **1–3** and $Pd(OAc)_2$.
[c] Isolated yield.
[d] Reaction for 36 h.

erties of the substrates. As observed for the Heck reactions (*vide supra*) *ortho-* and *para*-iodotoluenes are more reactive (yields of 89 and 93% for **6b** and **6d**, respectively) than their *meta*-isomer **6c** (74%, Table 2, entries 6–8). The examples outlined in Table 2, entries 9–14, are characterized by moderate to good yields (71–89%) and indicate that no obvious electronic or steric effects are operative allowing for a rather broad monosubstitution pattern of the biaryl target molecules. The coupling reactions of 2-iodopyridine (67% of **6k**, Table 2, entry 15) and disubstituted iodoarenes such as 1-iodo-3,5-dimethylbenzene (61% of **6l**, Table 2, entry 16) turned out to be less efficient. As observed for the Heck reaction its electron-poor fluoro analogue, 1-iodo-3,5-bis(trifluoromethyl)benzene, was totally unreactive under our standard conditions, and the starting materials were completely recovered.

The phenylation of iodotoluene was chosen as a model reaction for a comparative study of the lutidine-bridged salts **1–3** as precatalysts for the Suzuki reaction. The yields obtained for the resulting 4-phenyltoluene **6d** increased from 49% to 70% and 93% in the series of bis-imidazolium (**1**), bis-benzimidazolium (**2**) and bis-perimidinium dibromide (**3**), respectively (Table 2, entries 17, 18 and 8) confirming the trend observed for the Heck reaction that the efficiency of the precatalyst increases with the σ-donor ability of the respective NHC ligand formed in the presence of base and attached to palladium in the active catalyst.

In conclusion, lutidine-bridged bis-perimidinium bromide **3** which is accessible from cheap commercial starting materials in a nearly quantitative reaction is an efficient precatalyst in combination with palladium acetate for Heck and Suzuki cross-coupling reactions under aerobic conditions. This protocol is characterized by good yields even with very low catalyst loadings down to the ppm scale. It is compatible with a broad selection of functional groups in the haloarene varying in their electronic and steric properties. In comparison with bis-imidazolium and bis-benzimidazolium dibromide congeners the deprotonation of bis-perimidinium dibromide generates an NHC ligand with increased σ-donor ability improving the efficiency of the palladium catalyst formed *in situ* in the series of bis-imidazolium, bis-benzimidazolium and bis-perimidinium dibromide precatalysts. These results render the perimidine skeleton a promising target for further development and optimization of transition metal based catalysts.

Experimental Section

General Remarks

Commercial reagents and solvents were used without further purification. All reactions were carried under the air unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 DRX/300 DPX spectrometers. ESI mass spectra were recorded on a Bruker Daltonics Announces Autoflex ESI mass spectrometer. GC-MS analyses were obtained from a HP 5890 Series II. Lutidine-bridged bis-imidazolium dibromide **1** and its bis-benzimidazolium analogue **2** ($R = n$-Bu and $X = Br$) were synthesized according to literature procedures.[6d,16]

Synthesis of Lutidine-Bridged Bis-perimidinium Dibromide 3

A mixture of 2,6-dibromolutidine (265 mg, 1 mmol) and *N*-butylperimidine[10] (500 mg, 2.2 mmol) was heated to 165 °C under stirring in a sealed tube for 24 h. Then the mixture was cooled to room temperature, the residue was dissolved in $CHCl_3$ and reprecipitated upon addition of cold Et_2O to give NMR-pure bis-perimidinium dibromide **3** as a bright yellow powder in almost quantitative yield. ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): $\delta = 8.44$ (s, 2H), 7.21 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 2H), 6.62–6.69 (m, 4H), 6.47 (d, $J = 8.3$ Hz, 2H), 6.13–6.18 (m, 4H), 5.72 (d, $J = 7.5$ Hz, 2H), 4.52 (s, 4H), 2.97 (t, $J = 7.5$ Hz, 4H), 0.83–0.92 (m, 4H), 0.61 (sextet, $J = 7.5$ Hz, 4H), 0.12 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz): $\delta = 153.63$, 152.18, 138.73, 134.05, 133.40, 132.23, 131.87, 130.87, 129.54, 128.31, 127.52, 124.03, 123.36, 122.49, 120.58, 108.15, 108.06, 54.70, 50.95, 27.91, 19.00, 13.55; MS (ESI): $m/z = 634.3$ $[M-Br]^{+}$, 588.3, 329.2, 276.7 $[M-2Br]^{2+}$, 224.1; HR-MS (ESI): $m/z = 632.2383$, calcd. for $[M-Br]^{+}$: 632.2383; anal. calcd. for $C_{37}H_{39}Br_2N_5 \cdot 2H_2O$: C 59.29, H 5.78, N 9.34; found: C 59.04, H 5.71, N 9.25.

General Procedure for the Heck Reactions

To a suspension of K_2CO_3 (414 mg, 3 mmol.) in 10 mL NMP, haloarene (2 mmol), *n*-butyl acrylate (307 mg, 2.4 mmol) and the catalyst [prepared from equimolar amounts of $Pd(OAc)_2$ and bis-perimidinium bromide **3** in NMP] were added. The reaction mixture was heated at 140 °C (monitored by GC-MS) and then allowed to cool to room temperature after the reaction was finished. Then the reaction mixture was diluted with water, and the product was extracted with ether (3×20 mL). The combined extracts were dried over $MgSO_4$, the organic phase was concentrated under vacuum and the crude product was purified by flash column chromatography (hexane/EtOAc = 100/1).

General Procedure for the Suzuki Reactions

To a suspension of K_2CO_3 (331 mg, 2.4 mmol.) in 3 mL NMP, haloarene (2 mmol), phenylboronic acid (258 mg, 2.2 mmol) and catalyst [prepared from equimolar amounts of $Pd(OAc)_2$ and bis-perimidinium bromide **3** in NMP] were added. The reaction mixture was heated at 140 °C (monitored by GC-MS and TLC) and then allowed to cool to room temperature. The work-up of the reaction was performed as described above for the Heck reaction.

Supporting Information

Detailed synthetic procedures and spectroscopic data for the bis-perimidinylidene palladium complex are given in the Supporting Information.

Acknowledgements

We thank the referees for suggesting the mercury test. T.T. thanks the Alexander-von-Humboldt-Foundation for a research fellowship. J. M. thanks the Konrad-Adenauer-Foundation for a PhD grant. Financial support from the DFG (SFB 624 "Templates") is gratefully acknowledged.

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