ORGANOMETALLICS

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Template-Directed Synthesis of Palladium(II) Sulfonate-NHC Complexes and Catalytic Studies in Aqueous Mizoroki−Heck Reactions

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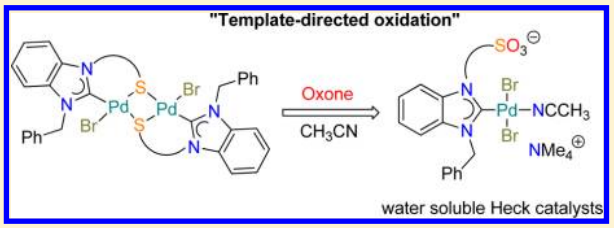
Supporting Information

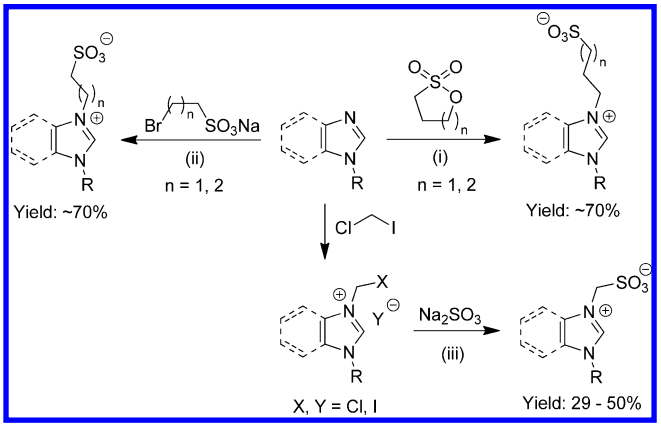
ABSTRACT: Oxidation of easily accessible thiolato-functionalized dinuclear Pd(II) NHC complexes **1**−**3** by Oxone gave rise to sulfonate-NHC complexes **4**−**6**. This represents the first template-directed approach to NHC complexes bearing sulfonate functions, where the sulfur atoms undergo a six-electron oxidation, changing their oxidation states from −II to +IV. The catalytic activities of water-soluble **4**−**6** were also tested in aqueous Mizoroki−Heck reactions.



INTRODUCTION

Sulfur-functionalized N-heterocyclic carbenes (NHCs) have attracted increasing attention due to their unique properties and versatile coordination chemistry, which has recently been reviewed.[1] Since the sulfur atom can easily adopt various stable oxidation states in its compounds ranging from −2 to +6, many different types of sulfur functions are available, which further diversifies the already rich NHC chemistry. Furthermore, complexes with sulfur-NHCs possess a versatile and diverse coordination chemistry with different bonding modes of the sulfur function, which is considered a useful prerequisite for a wide range of applications in catalysis.[1] Among various sulfur functions, there has been growing interest in the monoanionic alkyl or aryl sulfonate group,[2−5] especially in the field of green chemistry, mainly due to the fact that it can impart water solubility to complexes, making them suitable precatalysts in aqueous media.[6]

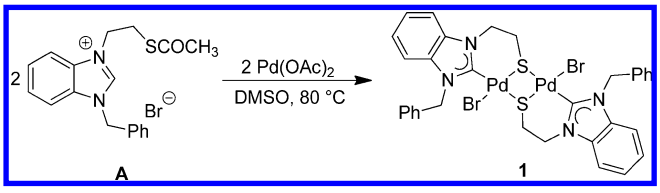
Scheme 1. Common Synthetic Routes to Azolium Salts Bearing Alkyl Sulfonate Groups



Synthetic methodologies to introduce an alkyl sulfonate group into carbene precursors usually involve (i) ring-opening reaction of sultones with azoles,[2] (ii) N-alkylation with haloalkyl sulfonates,[3] and (iii) reaction of *N*-haloalkylazolium salts with Na_2SO_3 (Scheme 1).[4] For method (i), only limited sultones are commercially available, e.g., 1,3-propanesultone and 1,4-butanesultone. As a result, azolium salts with certain length of the sulfonate tether (e.g., n = 2) are not accessible through this method. The choice of commercially available haloalkyl sulfonates is similarly limited for method (ii). The third method, on the other hand, suffers from low yields and the difficulty to separate the product from starting materials. Ag(I), Au(I), Rh(I), Ru(II), and Pd(II) NHC complexes bearing a sulfonate function have been synthesized,[2−5] and some of them have been tested in aqueous Suzuki−Miyaura[2f,5a,b] and Sonogashira[5b] reactions, showing good activities.

As our contribution to sulfur-NHC chemistry, we have developed a convenient method to synthesize thiolato-bridged dinuclear complexes of group 10 metals, which involves the *in situ* generation of thiols via the hydrolysis of thioester groups, as exemplified in Scheme 2 for complex **1**.[7] Reactivity studies of such dinuclear complexes bearing $[M_2S_2]$ (M = Ni, Pd, Pt)

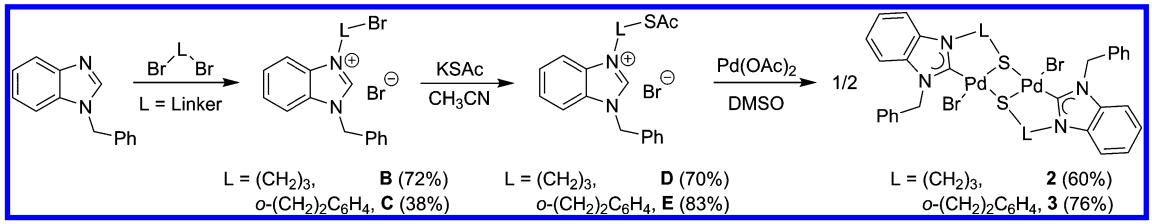
Scheme 2. Reported Synthesis of Thiolato-Bridged Pd(II) Dinuclear Complex 1[7a]



Received: February 7, 2014
Published: March 21, 2014

   dx.doi.org/10.1021/om500140g | *Organometallics* 2014, 33, 1794−1800

Scheme 3. Synthesis of Thiolato-Bridged Pd(II) Dinuclear Complexes 2 and 3



cores revealed interesting results. For example, tetranuclear macrocyclic complexes formed after the halido ligands were removed by either Me_3OBF_4 or $NaSCH(CH_3)_2$.[7a,b] On the other hand, trinuclear complexes with capping sulfido or oxido ligands were obtained in reactions with Na_2S and NaOH, respectively.[7c] In the aforementioned studies, the oxidation states of the sulfur atoms remained unchanged. To further explore the reactivities of these thiolato-functionalized complexes, we investigated sulfur-centered oxidations by treatment of thiolato-bridged $[Pd_2S_2]$ dimers with oxidizing reagents with the aim to yield NHC complexes with sulfur functions of higher oxidation states. Herein, we report a novel template-directed approach to sulfonate-functionalized NHC complexes by oxidation of $[Pd_2S_2]$ complexes with Oxone and a preliminary catalytic study of the respective complexes in the aqueous Mizoroki–Heck reaction.

RESULTS AND DISCUSSION

Synthesis of Thiolato-Bridged Pd(II) NHC Complexes. Thiolato-functionalized dinuclear complexes **2** and **3** were synthesized in analogy to **1** (Scheme 3). Ligand precursors **D** and **E** were prepared from the reactions of KSAc with the bromopropyl- or bromo-*o*-xylenyl-substituted benzimidazolium salts **B** and **C**, which were in turn synthesized by reacting 1-benzylbenzimidazole with 1,3-dibromopropane or *o*-xylene dibromide. Subsequent reactions of **D** and **E** with $Pd(OAc)_2$ gave rise to complexes **2** and **3**, respectively, in yields of 60% and 76%. As expected, the *in situ* hydrolysis of the thioester group occurred in wet DMSO, and the resulting thiolato groups coordinated to the Pd(II) centers. In comparison, the synthesis of a thioester-functionalized complex could be achieved in an earlier study only through a postmodification approach,[8] in which a preformed Pd(II)-NHC complex bearing a bromopropyl arm was subjected to an S_N2 reaction with KSAc.

Similar to **1**, dinuclear complexes **2** and **3** show poor solubility in DMSO and precipitated from the reaction mixture. They were isolated as yellow powders after simple filtration and washing with H_2O. The solids are slightly soluble in CH_2Cl_2, $CHCl_3$, and DMF. Their formation is corroborated by positive ESI mass spectrometry, where predominant signals at m/z 856 and 979 are observed for their respective $[M - Br]^+$ fragments. The aliphatic protons become diastereotopic upon complex formation, which complicates their ^1H NMR spectra. Due to insufficient solubility, ^{13}C NMR spectra could not be obtained.

The identity of complex **3** was further confirmed by X-ray diffraction of a single crystal obtained via slow evaporation of a saturated $CHCl_3$/toluene solution. Both palladium centers are in a square planar environment coordinated by one terminal bromido ligand and one *o*-xylenyl-linked thiolato-NHC in a κ^2C,μ-S chelating and bridging mode (Figure 1). The carbene planes are twisted by ~60° out of the $[PdCS_2Br]$ coordination plane. The $[Pd_2S_2]$ core is significantly bent with a hinge angle of ca. 109°, which is smaller than that of complex **1** (119°).

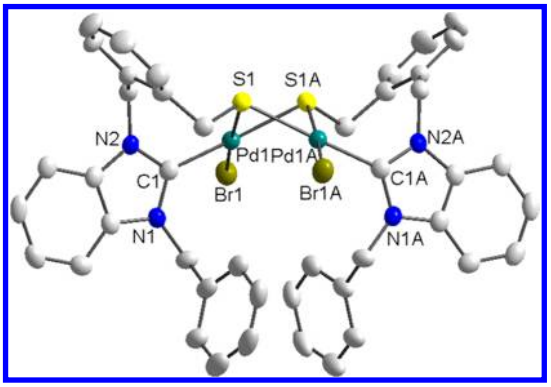


Figure 1. Molecular structure of **3** showing 50% probability ellipsoids; solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1–C1 2.002(8), Pd1–Br1 2.4641(12), Pd1–S1A 2.363(2), Pd1–S1 2.300(2); C1–Pd1–Br1 94.79(6), C1–Pd1–S1 92.2(2), Br1–Pd1–S1A 96.79(6), S1A–Pd1-S1 76.47(9), C1–Pd1–S1A 168.3(2), Br1–Pd1–S1 172.41 (6).

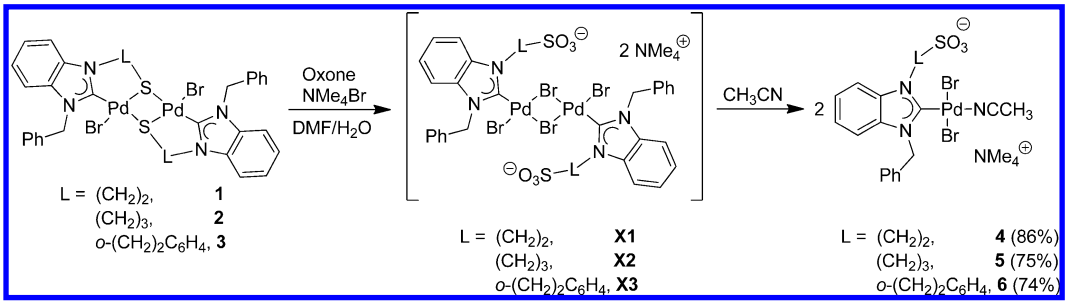
Reactions with Oxidants. The oxidation of the thiolato-bridges of **1** may lead to the formation of a dinuclear or mononuclear complex bearing sulfur donors of higher oxidation states, such as sulfinate, sulfenate, or sulfonate. Oxidation of the thiolato group of a Ni(II) complex to the sulfinate ligand by aerial oxygen or H_2O_2 has been reported.[9] Our previous study also showed that the thioether function of a dibenzimidazolium salt was easily oxidized to a sulfoxide group by 3 equiv of H_2O_2 in acetic acid at ambient temperature.[10] Complex **1** was therefore treated with the same reagents, and DMF was added to ensure a homogeneous reaction. However, the compound remained intact below 70 °C and started to decompose to palladium black at higher temperatures. The fact that **1** is resistant to oxidation by H_2O_2 may be ascribed to the lower electron density at the sulfur atoms in the bridging mode, which calls for a stronger oxidant.[7a]

Indeed, thiolato to sulfonate oxidation occurs with complex **1** when Oxone ($KHSO_5$) is used, which is a cheap and strong oxidant. The reaction proceeds smoothly at ambient temperature with 3 equiv of Oxone in a DMF/H_2O mixture with excess of NMe_4Br, which provides additional bromido ligands as well as a suitable countercation (Scheme 4). Other alkali or ammonium salts proved less suitable for the isolation and crystallization of the product. In comparison, the reaction did not even occur in boiling CH_2Cl_2 due to the insolubility of the oxidant. With 2 equiv of Oxone a lower yield of the sulfonate species was obtained, and no sulfinate or sulfenate intermediates could be detected. In contrast, Oxone was reported to be a chemoselective reagent for the oxidation of organic sulfides to sulfoxides and further to sulfones.[11]

The negative ion ESI mass spectrum of the oxidation product of **1** shows a predominant signal at m/z 581 corresponding to a monoanionic Pd(II) complex fragment bearing a sulfonate-

dx.doi.org/10.1021/om500140g | Organometallics 2014, 33, 1794–1800

Scheme 4. Synthesis of Sulfonate Complexes 4−6



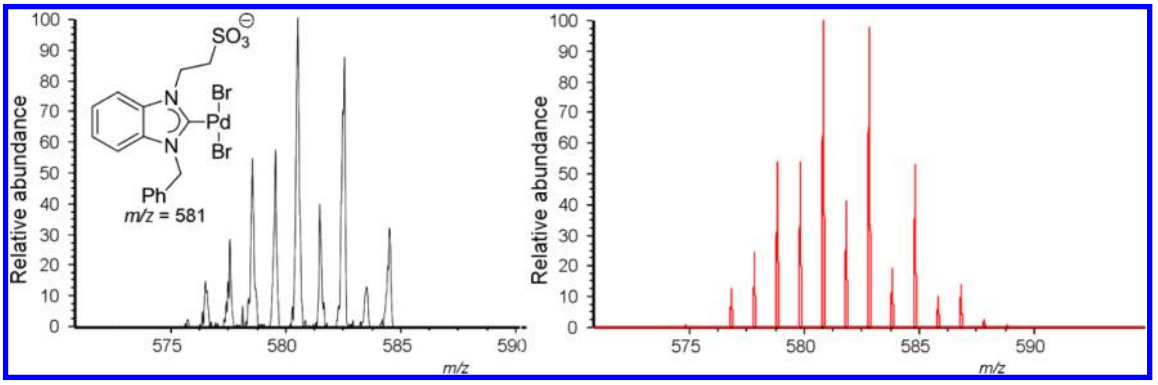


Figure 2. Isotopic pattern of the fragment from **X1**/**4** in the negative ESI mass spectrum (left) and a simulated pattern (right).

NHC ligand and two bromido ligands (Figure 2). In solution, formation of solvates or dimerization to **X1** is proposed. Indeed, the solvate **4** can be isolated in a good yield of 86% when the crude product is treated with CH_3CN. Complex **4** is a yellow powder, which is soluble in DMF, CH_3CN, and DMSO, slightly soluble in H_2O, but insoluble in diethyl ether and hexane. The negative ion ESI mass spectrum of **4** is identical with the one discussed earlier, i.e., **X1**. The ^{1}H NMR spectrum recorded in CD_3CN shows a singlet at 6.03 ppm for the benzylic protons. Two multiplets centered at 5.10 and 3.32 ppm are assigned to the two methylene groups of the tether. All three signals do not show the diastereotopic patterns typical of **1**, implying a pendant sulfonate moiety. A singlet at 3.10 ppm attributed to NMe_4^+ supports the successful incorporation of the ammonium cation. Moreover, a triplet was observed for the cation at 56.0 ppm in the ^{13}C NMR spectrum due to the coupling with the NMR-active ^{14}N nucleus. The carbene carbon atom resonates at 161.4 ppm, which is shifted upfield in comparison to that of **1**.

The identity of **4** was also confirmed by X-ray analysis on single crystals obtained from diffusion of diethyl ether into a concentrated CH_3CN solution. The molecular structure depicted in Figure 3 shows that the Pd(II) center is coordinated by one carbene carrying a pendant sulfonate function and two bromido ligands *trans* to each other. The fourth coordination site is completed by a CH_3CN molecule from the solvent used for crystallization. The negative charge of the complex is balanced by an NMe_4^+ countercation. The Pd(II) center adopts a slightly distorted square planar geometry, and the dihedral angle between the [$PdCNBr_2$] coordination plane and the carbene plane measures 89°.

The generality and versatility of this new template-assisted approach was tested in the oxidations of **2** and **3**, which afforded complexes **5** and **6** as yellow solids (Scheme 2) in yields of 75% and 74%, respectively. They show similar

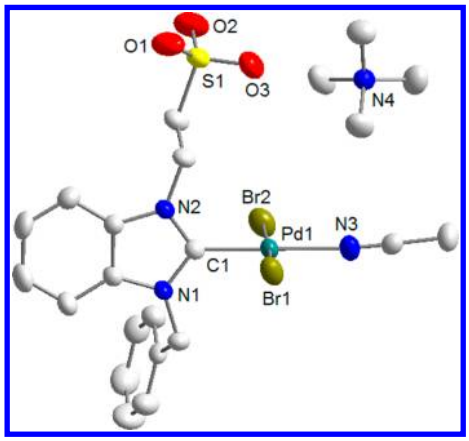


Figure 3. Molecular structure of **4** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−C1 1.959(4), Pd1−Br1 2.4295(11), Pd1−N3 2.099(3), Pd1−Br2 2.4210(10); C1−Pd1−Br1 89.18(11), C1−Pd1−Br2 87.74(11), Br1−Pd1−N3 92.35(10), Br2−Pd1−N3 90.70(10), C1−Pd1−N3 178.33(15), Br1−Pd1−Br2 175.95(2). $PdCNBr_2$/NHC dihedral angle 89.1°.

solubility to that of **4**. In their negative ESI mass spectra, isotopic patterns centered at m/z 595 or 659 for their [M − NMe_4 − CH_3CN]$^-$ complex fragments support the formation of the desired sulfonate complexes. A singlet resonating at 6.05 assignable to the benzylic protons and three multiplets located in the range 4.99−2.47 ppm corresponding to the methylene groups of the arm were observed in the ^{1}H NMR spectrum of **5**. For complex **6**, three singlets were recorded at 6.41, 6.13, and 4.17 ppm due to the SCH_2 protons and the two sets of NCH_2 protons. The singlets for the NMe_4 cations appear at ∼3.1 ppm of both complexes. In their ^{13}C NMR spectrum, the chemical shifts of the carbene carbon atoms are found at 160.8 and 162.6 ppm, respectively.

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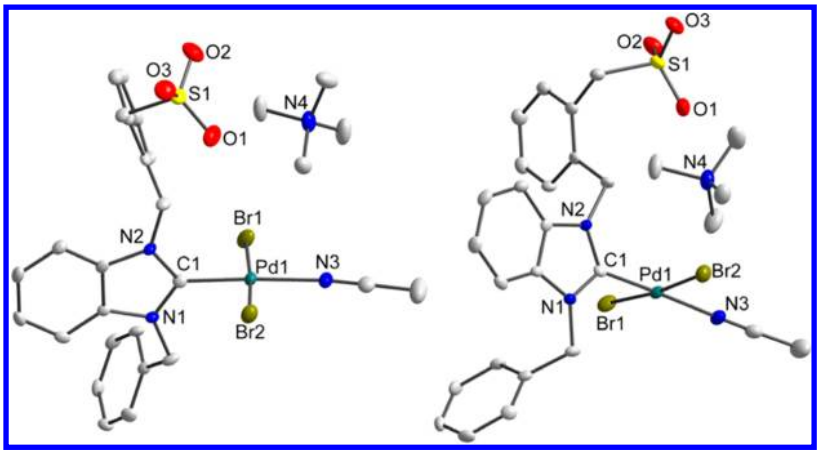


Figure 4. Molecular structure of **6** (different views) showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−C1 1.949(5), Pd1−Br1 2.4280(10), Pd1−N3 2.077(5), Pd1−Br2 2.4409(10); C1−Pd1−Br1 88.23(15), C1−Pd1−Br2 88.03(15), Br1−Pd1−N3 93.45(15), Br2−Pd1−N3 90.44(15), C1−Pd1−N3 177.28(2), Br1−Pd1−Br2 174.52(2). $PdCNBr_2$/NHC dihedral angle 85.7(8)°.

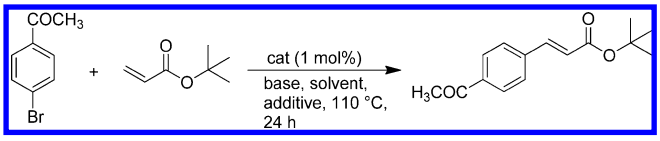
In analogy to **4**, single crystals of complex **6** were obtained by diffusion of diethyl ether to a CH_3CN solution. Figure 4 shows the expected molecular structure of complex **6**. The dihedral angle between the [$PdCNBr_2$] coordination plane and the carbene plane measures ∼86°, which is smaller than that of complex **4**. This may be due to the less flexible *o*-xylenyl linker in complex **6**, which prevents the carbene ring from rotating to the ideal perpendicular position. The phenyl ring of the linker was almost perpendicular to the carbene ring with a dihedral angle of 89°. Notably, complex **6** is not accessible via any of the general routes (i)−(iii) mentioned above.

Catalytic Studies. Since sulfonate complexes **4**−**6** are soluble in H_2O, their catalytic activities were tested in aqueous reactions. Although Mizoroki−Heck reactions catalyzed by Pd(II) complexes have been extensively investigated,[12] not many studies focused on reactions in aqueous media, which still remains a challenge.[13] Reported studies also suffer from some limitations. For example, good yields were obtained only with aryl iodides,[13c,f] and organic solvents such as DMF had to be added to water.[13b,i,m]

The catalytic activity of precatalyst **4** was first tested in the reaction of 4-bromoacetophone and *tert*-butyl acrylate in 1 mL of H_2O with 1.5 equiv of NaOAc and 1 mol % of **4** at 110 °C for 24 h. A low yield of 13% was obtained (Table 1, entry 1). In comparison, a more diluted reaction with 3 mL of H_2O gave no conversion (entry 2). The addition of 1.5 equiv of TBAB did not lead to higher yields (entries 3 and 4).[14] Moreover, no conversion was detected from the reaction in boiling ^{i}PrOH (entry 5). To modify the reaction conditions, the base was changed to 1.5 equiv of NEt_3, and the reaction in H_2O (1 mL) gave an improved yield of 25% (entry 6). In comparison, an increased loading of NEt_3 (2.5 equiv) did not lead to an improvement (entry 7). However, in the presence of 1.5 equiv of TBAB, a good yield of 86% was obtained in 1 mL of H_2O (entry 8). The reaction in a diluted mixture dropped to 26% (entry 9). When the reaction was carried out in 1 mL of H_2O in the presence of 1.5 equiv of NEt_3, 1.5 equiv of TBAB, and 1 mol % of **5**, a slightly better yield of 88% was obtained (entry 10). Complex **6**, with the more bulky *o*-xylene linker, showed the best activity, affording an excellent yield of 97% (entry 11) under the same conditions. Shortening of the reaction time to 2 h led to a drop of yield (58%, entry 12). When the solvent volume was decreased to 0.5 mL, the yield remained essentially unchanged when catalyzed by **5** (86%, entry 13), while it slightly dropped when catalyzed by **4** and **6** (entries 14 and 15). Notably, no sign of decomposition was observed in all the runs. To evaluate the thermal stability under the optimized conditions further, complex **6** was heated without substrates *ceteris paribus* for a prolonged time (24 h), and again no decomposition was observed. In comparison, 1 mol % $Pd(OAc)_2$ also gave a good yield of ∼80% under the same conditions. However, almost immediate formation of palladium black was observed in this case.

Having identified the suitable reaction condition for the aqueous Heck reaction, the scope of the reaction was then

Table 1. Mizoroki−Heck Coupling Reactions[a] Catalyzed by Complexes 4−6



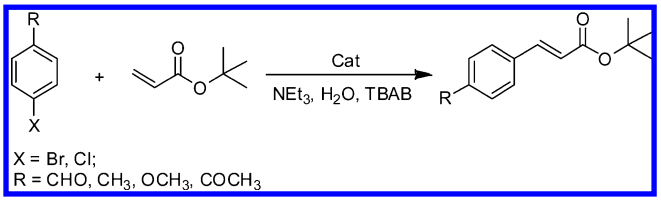
entry	precatalyst	base	temp [°C]	solvent	additive	yield [%][b]
1	**4**	NaOAc	110	H_2O (1 mL)		13
2	**4**	NaOAc	110	H_2O (3 mL)		0
3	**4**	NaOAc	110	H_2O (1 mL)	TBAB	9
4	**4**	NaOAc	110	H_2O (3 mL)	TBAB	11
5	**4**	NaOAc	100	^{i}PrOH (1 mL)		0
6	**4**	NEt_3	110	H_2O (1 mL)		25
7	**4**	NEt_3 (2.5 equiv)	110	H_2O (1 mL)		25
8	**4**	NEt_3	110	H_2O (1 mL)	TBAB	86
9	**4**	NEt_3	110	H_2O (3 mL)	TBAB	26
10	**5**	NEt_3	110	H_2O (1 mL)	TBAB	88
11	**6**	NEt_3	110	H_2O (1 mL)	TBAB	97
12	**6**	NEt_3	110	H_2O (1 mL)	TBAB	58[c]
13	**4**	NEt_3	110	H_2O (0.5 mL)	TBAB	86
14	**5**	NEt_3	110	H_2O (0.5 mL)	TBAB	86
15	**6**	NEt_3	110	H_2O (0.5 mL)	TBAB	96

[a]Reaction conditions: 0.3 mmol of 4-bromoacetophenone; 0.42 mmol of *tert*-butyl acrylate; 0.45 mmol of base; TBAB (0.45 mmol when necessary); 1 mol % of precatalyst. [b]Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c]Reaction was heated for 2 h instead.

dx.doi.org/10.1021/om500140g | *Organometallics* 2014, 33, 1794−1800

explored with complexes **4** and **6**. In the coupling of the activated substrate of 4-bromobenzaldehyde, both catalysts give excellent yields. Again, complex **6** outperforms **4** (>99% vs 92%, Table 2, entries 1 and 2) and even gives quantitative yield

Table 2. Mizoroki–Heck Coupling Reactions[a] Catalyzed by Complexes 4 and 6



entry	cat.	cat. loading	aryl halide	time	yield [%][b]
1	**4**	1 mol %	4-bromobenzaldehyde	24 h	92
2	**6**	1 mol %	4-bromobenzaldehyde	24 h	>99
3	**6**	1 mol %	4-bromobenzaldehyde	2 h	>99
4	**6**	0.5 mol %	4-bromobenzaldehyde	2 h	99
5	**6**	0.1 mol %	4-bromobenzaldehyde	2 h	70
6	**6**	0.1 mol %	4-bromobenzaldehyde	24 h	>99
7	**6**	0.05 mol %	4-bromobenzaldehyde	2 h	48
8	**6**	0.05 mol %	4-bromobenzaldehyde	24 h	>99
9	**6**	0.01 mol %	4-bromobenzaldehyde	2 h	17
10	**6**	0.01 mol %	4-bromobenzaldehyde	24 h	56
11	**4**	1 mol %	4-bromotoluene	24 h	6
12	**6**	1 mol %	4-bromotoluene	24 h	25
13	**4**	1 mol %	4-bromoanisole	24 h	5
14	**6**	1 mol %	4-bromoanisole	24 h	6
15	**4/6**	1 mol %	4-chloroacetophone	24 h	0
16	**4/6**	1 mol %	4-chlorobenzaldehyde	24 h	0
17	**6**	1 mol %	4-chlorobenzaldehyde	4 h	0[c]

[a]Reaction conditions: 0.3 mmol of 4-bromoacetophenone; 0.42 mmol of *tert*-butyl acrylate; 0.45 mmol of base; H_2O (1 mL); TBAB (0.45 mmol). [b]Yields were determined by ^1H NMR spectroscopy for an average of two runs. [c]Microwave reaction at 160 °C.

in 2 h (entry 3). Quantitative yield after 2 h was also obtained when the loading of catalyst **6** was lowered to 0.5 mol % (entry 4). Further reduction of the catalyst loading to 0.1, 0.05, and 0.01 mol % resulted in lower yields ranging from 70% to 17% (entries 5, 7, and 9). These reactions required longer reaction time to give high yields (entries 6, 8, and 10). Both catalysts gave low conversions in the reactions with deactivated substrates such as 4-bromotoluene and 4-bromoanisole (entries 11–14). No reaction occurred with the more challenging aryl chlorides (entries 15 and 16) even under microwave irradiation (entry 17), which shows the limitations of this catalyst system in aqueous catalysis.

A concentration/time diagram was recorded on the coupling of the most active substrate, 4-bromobenzaldehyde, employing 1 mol % catalyst **6** (Figure 5). The diagram indicates that the coupling occurred almost immediately after the catalyst was added, and no induction period was observed in such time intervals. The reaction was fastest in the first 20 min, reaching a yield of 62% and finally completing at 120 min.

CONCLUSION

In conclusion, we reported the first versatile template-directed approach to water-soluble NHC–SO_3^- complexes **4**–**6** by easy oxidation of dinuclear thiolato-NHC Pd(II) complexes **1**–**3** with Oxone. The solid-state molecular structures of **3**, **4**, and **6**

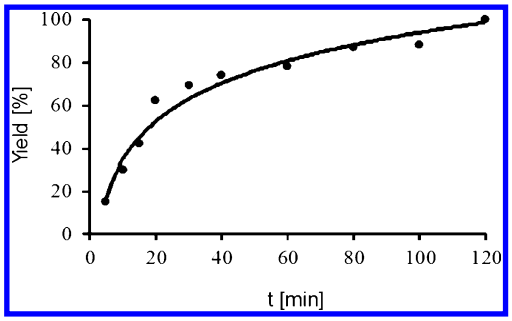


Figure 5. Concentration/time profile for the coupling reaction of 4-bromobenzaldehyde with *tert*-butyl acrylate catalyzed by complex **6**.

are described. In comparison to other known catalytic Pd systems, complexes **4**–**6** are well active in aqueous Mizoroki–Heck reactions of aryl bromides, with complex **6** being the best performer. However, the more difficult coupling of aryl chlorides in aqueous media remains a challenge to be tackled in the future. Research in our lab is currently on going to extend this new synthetic strategy to other transition metals and to further investigate the catalytic activities of NHC–SO_3^- complexes in aqueous reactions.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. Salt **B** has been synthesized according to a reported procedure.[15] The chemical shifts (δ) for the ^1H and ^{13}C NMR spectra were internally referenced to the residual solvent signals relative to tetramethylsilane.

Salt C. α,α'-Dibromo-*o*-xylene (5.3 g, 20 mmol) and benzylbenzimidazole (208 mg, 1 mmol) were dissolved in toluene (50 mL) and stirred at 50 °C overnight, resulting in a suspension. The white solid was collected by centrifuging and washed with toluene (3 × 10 mL) and diethyl ether (3 × 10 mL). The solid was redissolved in CH_2Cl_2 and filtered. Slow evaporation of the filtrate gave the product as a white crystalline solid (179 mg, 0.38 mmol, 38%). ^1H NMR (500 MHz, $CDCl_3$): δ 11.44 (s, 1 H, NCHN), 7.58 (d, 1 H, Ar–H), 7.54–7.42 (m, 5 H, Ar–H), 7.35–7.28 (m, 6 H, Ar–H), 7.18 (d, 1 H, Ar–H), 6.11 (s, 2 H, NCH_2Ph), 5.82 (s, 2 H, NCH_2Ph), 4.70 (s, 2 H, CH_2Br). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 144.0 (NCHN), 136.9, 133.1, 132.33, 132.25, 131.9, 131.7, 130.4, 129.9, 129.83, 129.76, 129.0, 128.9, 127.83, 127.82, 114.6, 114.5 (Ar–C), 52.4, 49.6 (NCH_2Ph), 32.0 (CH_2Br). MS (ESI): m/z 391 $[M - Br]^+$.

Salt D. A mixture of salt **B** (892 mg, 2.17 mmol) and $KSCOCH_3$ (371 mg, 3.25 mmol) in CH_3CN (20 mL) was stirred at 70 °C overnight. The resulting suspension was filtered, and the solvent of the filtrate was removed *in vacuo*. The resulting solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 5:1) to give the product as an off-white solid (616 mg, 1.52 mmol, 70%). ^1H NMR (500 MHz, $CDCl_3$): δ 11.55 (s, 1 H, NCHN), 7.70 (d, 1 H, Ar–H), 7.56–7.48 (m, 5 H, Ar–H), 7.35–7.31 (m, 3 H, Ar–H), 5.85 (s, 2 H, NCH_2Ph), 4.71 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 3.00 (t, ^3J(H,H) = 7.0 Hz, 2 H, CH_2S), 2.40 (m, 2 H, CH_2), 2.27 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 195.9 (CO), 144.3 (NCHN), 133.3, 132.2, 131.8, 130.0, 129.9, 129.0, 127.8, 114.5, 113.7 (Ar–C), 52.2 (NCH_2Ph), 46.9 (NCH_2), 31.3 (CH_2S), 30.0 (CH_2), 26.4 (CH_3). One signal for an aromatic carbon atom was not observed due to accidental overlap. MS (ESI): m/z 325 $[M - Br]^+$.

Salt E. A mixture of salt **C** (63 mg, 0.13 mmol) and $KSCOCH_3$ (18 mg, 0.16 mmol) in CH_3CN (20 mL) was stirred overnight. The solvent of the mixture was removed *in vacuo* before CH_2Cl_2 (30 mL) was added. The resulting suspension was filtered and dried under reduced pressure to afford the product as an off-white oil (50 mg, 0.11 mmol, 83%). ^1H NMR (300 MHz, $CDCl_3$): δ 11.15 (s, 1 H, NCHN), 7.64–7.61 (m, 1 H, Ar–H), 7.50–7.39 (m, 5 H, Ar–H), 7.32–7.11

dx.doi.org/10.1021/om500140g | *Organometallics* 2014, 33, 1794–1800

(m, 7 H, Ar−H), 5.92 (s, 2 H, NCH_2Ph), 5.85 (s, 2 H, NCH_2Ph), 4.18 (s, 2 H, CH_2S), 2.13 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 195.1 (CO), 143.6 (NCHN), 136.3, 133.2, 132.0, 131.81, 131.79, 131.0, 130.1, 129.7, 129.6, 129.4, 129.1, 129.0, 127.8, 127.7, 114.5, 114.3 (Ar−C), 52.1, 49.5 (NCH_2Ph), 31.2 (CH_2S), 30.8 (CH_3). One signal for an aromatic carbon atom is not observed due to accidental overlap. MS (ESI): m/z 387 $[M - Br]^+$.

Dinuclear Complexes 2 and 3. A mixture of salt **D**/**E** (405/467 mg, 1.0 mmol) and $Pd(OAc)_2$ (224 mg, 1.0 mmol) in DMSO (5 mL) was stirred at 80 °C overnight. The resulting suspension was filtered, and the yellow solid was washed with H_2O (3 × 20 mL) and dried to give the products. Complex **2**: 277 mg, 0.3 mmol, 60%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50−7.19 (m, 18 H, Ar−H), 6.44 (d, ^2J(H,H) = 15.6 Hz, 2 H, NC*H*HPh), 5.37 (d, ^2J(H,H) = 15.6 Hz, 2 H, NCH*H*Ph), 4.83−4.77 (m, 2 H, NC*H*H), 3.10−2.91 (m, 4 H, CH_2), 2.26 (br s, 2 H, CH_2). Signals for another two CH_2 groups were not resolved. Anal. Calcd for $C_{34}H_{34}Br_2N_4Pd_2S_2$: C, 43.66; H, 3.66; N, 5.99. Found: C, 43.61; H, 4.07; N, 5.52. MS (ESI): m/z 856 $[M - Br]^+$. Complex **3**: 403 mg, 0.38 mmol, 76%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, 2 H, Ar−H), 7.43−7.39 (m, 4 H, Ar−H), 7.35−7.32 (m, 8 H, Ar−H), 7.22−7.09 (m, 12 H, Ar−H and NC*H*HPh), 7.07−7.06 (m, 2 H, Ar−H), 6.96−6.88 (m, 2 H, NC*H*H), 5.32 (d, 2 H, NCH*H*Ph), 4.91−4.81 (m, 2 H, NCH*H*), 4.39 (d, ^2J(H,H) = 15.1 Hz, 1 H, NC*H*HS), 4.22 (d, ^2J(H,H) = 15.1 Hz, 1 H, NC*H*HS), 2.63 (d, ^2J(H,H) = 15.1 Hz, 2 H, NCH*H*S). Anal. Calcd for $C_{44}H_{38}Br_2N_4Pd_2S_2{\cdot}H_2O$: C, 49.04; H, 3.74; N, 5.20. Found: C, 48.72; H, 3.48; N, 5.05%. MS (ESI): m/z 979 $[M - Br]^+$. The ^{13}C NMR spectra of complexes **2** and **3** could not be obtained due to poor solubility.

Sulfonate Complex 4. Complex **1** (45 mg, 0.05 mmol), Oxone (92 mg, 0.15 mmol), and NMe_4Br (39 mg, 0.25 mmol) in DMF (5 mL) and H_2O (2 mL) were stirred at ambient temperature overnight. After the solvent was removed, the resulting solid was triturated with CH_3CN (3 × 5 mL) and the suspension filtered. The solvent of the filtrate was removed, and the residue was washed with H_2O (3 × 3 mL) and redissolved in CH_3CN (5 mL). Removal of the solvent gave the product as a yellow powder. A second batch was obtained by removing the solvent of the aqueous solution, washing the residue with a little H_2O (3 × 1 mL), and recrystallization in CH_3CN (5 mL) (60 mg, 0.086 mmol, 86%). ^1H NMR (500 MHz, CD_3CN): δ 7.62 (d, 1 H, Ar−H), 7.54 (d, 2 H, Ar−H), 7.53−7.30 (m, 4 H, Ar−H), 7.17−7.14 (m, 2 H, Ar−H), 6.04 (s, 2 H, NCH_2Ph), 5.12−5.09 (m, 2 H, NCH_2), 3.34−3.31 (m, 2 H, CH_2SO_3), 3.10 (s, 12 H, NMe_4), 1.96 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_3CN): δ 161.4 (NCN), 135.9, 135.1, 134.6, 129.4, 128.89, 128.87, 124.5, 124.2 (Ar−C), 118.3 (CN), 112.2, 111.9 (Ar−C), 56.0 (t, ^1J(C,N) = 4.1 Hz, NMe_4), 53.6 (NCH_2Ph), 50.8 (NCH_2), 46.4 (CH_2SO_3), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Anal. Calcd for $C_{22}H_{30}Br_2N_4O_3PdS$: C, 37.92; H, 4.34; N, 8.04. Found: C, 37.52; H, 4.38; N, 8.12. MS (ESI): m/z 74 NMe_4^+, −581 $[M - NMe_4 - CH_3CN]^-$.

Sulfonate Complexes 5 and 6. Complexes **5** and **6** were synthesized in analogy to **4** from **2**/**3** (187/212 mg, 0.2 mmol), Oxone (369 mg, 0.6 mmol), and NMe_4Br (154 mg, 1.0 mmol). Complex **5**: 214 mg, 0.3 mmol, 75%. ^1H NMR (300 MHz, CD_3CN): δ 7.80 (d, 1 H, Ar−H), 7.53−7.52 (m, 2 H, Ar−H), 7.33−7.29 (m, 4 H, Ar−H), 7.15−7.13 (m, 2 H, Ar−H), 6.05 (s, 2 H, CH_2Ph), 4.99 (ps t, 2 H, NCH_2), 3.10 (s, 12 H, NMe_4), 2.78 (ps t, 2 H,CH_2SO_3), 2.54−2.47 (m, 2 H, CH_2), 1.96 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 160.8 (NCN), 136.0, 135.4, 134.5, 129.3, 128.8, 124.4, 124.1(Ar−C), 118.1 (CN), 112.2, 112.1 (Ar−C), 55.9 (t, ^1J(C,N) = 4.1 Hz, NMe_4), 53.5 (NCH_2Ph), 49.1 (NCH_2), 48.5 (CH_2SO_3), 26.1 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Two signals accidently overlap at 128.8 ppm. Anal. Calcd for $C_{23}H_{32}Br_2N_4O_3PdS$: C, 38.86; H, 4.54; N, 7.88. Found: C, 38.56; H, 4.60; N, 7.90. MS (ESI): m/z 74 $[NMe_4]^+$, −595 $[M - NMe_4 - CH_3CN]^-$. Complex **6**: 231 mg, 0.3 mmol, 74%. ^1H NMR (500 MHz, CD_3CN): δ 7.59 (d, 2 H, Ar−H), 7.41−7.33 (m, 4 H, Ar−H), 7.22 (t, 1 H, Ar−H), 7.17−7.11 (m, 4 H, Ar−H), 7.04 (t, 1 H, Ar−H), 6.86 (d, 1 H, Ar−H), 6.41 (s, 2 H, NCH_2Ph), 6.13 (s, 2 H, NCH_2Ph), 4.17 (s, 2 H,CH_2SO_3), 3.06 (s, 12 H, NMe_4), 1.96 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_3CN): δ 162.6 (NCN), 136.1, 135.4, 135.2, 134.9, 133.5, 133.2, 129.6, 129.03, 128.96, 128.2, 128.0, 127.8, 124.5, 124.4 (Ar−C), 118.1 (CN), 113.1, 112.4 (Ar−C), 56.1 (t, ^1J(C,N) = 3.7 Hz, NMe_4), 55.5, 53.8 (NCH_2Ph), 51.0 (CH_2SO_3), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Two signals accidently overlap at 128.8 ppm. Anal. Calcd for $C_{28}H_{34}Br_2N_4O_3PdS$: C, 43.51; H, 4.43; N, 7.25. Found: C, 43.23; H, 4.49; N, 7.24. MS (ESI): m/z 74 $[NMe_4]^+$, −659 $[M - NMe_4 - CH_3CN]^-$.

Aqueous Mizoroki−Heck Catalysis. In a typical run, a reaction tube was charged with a mixture of aryl halide (0.3 mmol), base (0.45 mmol), *tert*-butyl acrylate (0.42 mmol), catalyst (0.003 mmol), TBAB (0.45 mmol when necessary), and solvent. The reaction was stirred at 110 °C for the desired time. After the mixture was cooled to ambient temperature, dichloromethane (2 mL) was added. The organic layer was then washed with water (6 × 8 mL) and dried over Na_2SO_4. The solvent was allowed to evaporate, and the residue was analyzed by ^1H NMR spectroscopy.

X-ray Diffraction Studies. X-ray data for **3**, **4**, and **6** were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs.[16] Data were processed and corrected for Lorentz and polarization effects with SAINT[17] and for absorption effect with SADABS.[18] Structural solution and refinement were carried out with the SHELXTL suite of programs.[19] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **3**, **4**, and **6** (CCDC 977882−977884) as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National University of Singapore and the Singapore Ministry of Education (MOE) for financial support (WBS R-143-000-483-112). Technical support from staff at the CMMAC of our department is appreciated. In particular, we thank Ms. Geok Kheng Tan and Prof. Lip Lin Koh for determining the X-ray molecular structures.

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