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Pd−PEPPSI-Type Expanded Ring N-Heterocyclic Carbene Complexes: Synthesis, Characterization, and Catalytic Activity in Suzuki−Miyaura Cross Coupling

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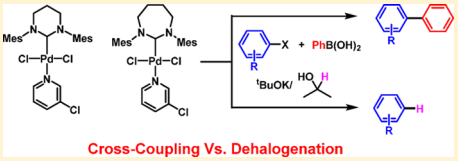
Supporting Information

ABSTRACT: The synthesis and characterization of the new six- and seven-membered Pd−PEPPSI-type N-heterocyclic carbene (NHC) complexes **3** and **4** is described. Complexes of the general formula [Pd(NHC)(3ClPy)Cl_2] (NHC = 6- or 7-Mes, 3ClPy = 3-chloropyridine) are accessed via the oxidation of the well-defined parent palladium(0) complexes **1** and **2**. Complexes **3** and **4** have been employed in Suzuki−Miyaura cross-coupling and catalytic dehalogenation of a range of aryl halide substrates.



N-heterocyclic carbenes (NHCs) have been utilized extensively as ligands in organometallic chemistry and homogeneous catalysis since the isolation of the first stable free NHC species by Arduengo and co-workers in 1991.[1] The rate of expansion within the field in the following two decades has been phenomenal, and as a consequence there are a number of excellent reviews which detail the progress to date.[2] More recently a new class of NHC ligand architecture has emerged within the literature: the expanded ring NHC.[3] Expanded ring NHCs are analogous to traditional imidazol-2-ylidene-[4] and 4,5-dihydroimidazol-2-ylidene-based[5] systems, with the exception of the increase in ring size of the heterocycle backbone. To date, a number of examples of six-, seven-, and eight-membered-ring systems have been prepared.[6] Increasing the NHC heterocycle ring size and thus the corresponding N−C_{NHC}−N bond angle affords markedly different steric and electronic properties, in comparison with those of their traditional five-membered counterparts.[3] Our group and others have previously reported the application of a number of expanded ring NHC complexes of the late transition metals in a range of catalytic transformations with encouraging results.[3] With this in mind, we are looking to expand the scope for the utilization of such ancillary ligands in other important transition-metal-mediated transformations. We became interested in a series of publications by Organ et al. that describe the synthesis of a series of NHC complexes coined Pd−PEPPSI compounds (PEPPSI = pyridine, enhanced, precatalyst, preparation, stabilization, initiation).[7,8] To date, this family of complexes has been employed to great effect in a number of C−C,[9] C−N,[10] and C−S[11] cross-coupling transformations in terms of the catalytic activity rendered under mild conditions, the broad substrate scope applicable, and the functional group tolerance afforded. In recent reviews of these (NHC)−Pd−PEPPSI type systems[12] the authors conclude that the catalytic activity of this family of complexes in cross-coupling transformations is derived from both the large σ-donor function of the ancillary NHC ligands and the degree of steric hindrance imparted by the bulky *N*-aryl substituents employed (in particular the IPr[7] and IPent[9] systems (IPr = 2,6-diisopropylphenyl, IPent = 2,6-bis(pentan-3-yl)phenyl). Considering the above criteria, it would seem to be a logical progression to utilize the unique steric and electronic properties of expanded ring NHC ligands in the development of new (NHC)−Pd−PEPPSI systems for cross-coupling applications. Herein, we describe the synthesis and characterization of novel six- and seven-membered (NHC)−Pd−PEPPSI type complexes and a preliminary evaluation of their effectiveness in Suzuki−Miyaura cross coupling.

RESULTS AND DISCUSSION

In search of a suitable synthetic approach toward expanded ring (NHC)−Pd−PEPPSI type complexes, an important consideration is the relative acidity of the NC*H*N proton in expanded ring NHC salts. This proton is considerably less acidic than in related imidazolium-based derivatives.[13] With this in mind the one-pot methodology of Organ et al. employing K_2CO_3 as the base to deprotonate expanded ring NHC·HX salts in the presence of $PdCl_2$ in 3-chloropyridine[7] is not applicable. Also, due to the propensity for larger ring NHC species to generate their corresponding "ring opened" hydrolysis products[3d] without the exclusion of both air and moisture, employment of stronger bases (KHMDS or ^{t}BuOK) under conditions analogous to those of Organ et al. failed during initial attempts.[14] In search of a suitable alternate route to such compounds, we turned to a number of palladium(0) complexes bearing expanded ring NHC ancillary ligand architectures which we had previously reported, [Pd(NHC)(dvtms)] (dvtms = divinyltetramethyldisiloxane).[15] These [Pd(NHC)(dvtms)] systems were found to undergo facile coligand exchange protocols with maleic anhydride to afford new expanded ring NHC palladium(0) complexes of the general formulas [Pd(NHC)$(MA)_n$] (MA = maleic anhydride, n = 1, 2).[16] In light of these previous observations we were

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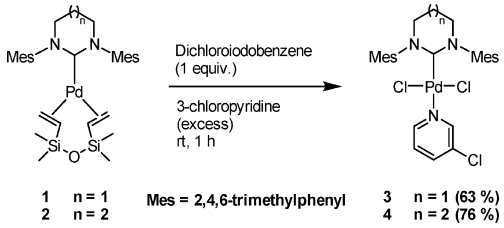
interested in whether [Pd(NHC)(dvtms)] systems would also allow access to novel palladium(II) complexes of the general formula [Pd(NHC)(3ClPy)Cl_2] via their oxidation in the presence of 3-chloropyridine. Importantly, the addition of 1 equiv of dichloroiodobenzene to a stirred 3-chloropyridine solution of either **1** or **2** at ambient temperature, with no precautions taken to exclude air/moisture provided access to the desired expanded ring (NHC)−Pd−PEPPSI type complexes **3** and **4** as air- and moisture-stable yellow microcrystalline solids after workup (Scheme 1).[17]

Scheme 1. Synthesis of Expanded Ring (NHC)−Pd−PEPPSI Complexes 3 and 4



The ^{1}H NMR spectra for compounds **3** and **4** reveal the disappearance of the characteristic axial and equatorial SiCH_3 and vinylic resonances of the dvtms coligand from the parent [Pd(NHC)(dvtms)] complexes.[15] The $^{13}C\{^1H\}$ NMR spectra demonstrate a trend of increasing downfield shift of the carbenic carbon (N−C_{NHC}−N) with increasing heterocycle ring size from five- to six- to seven-membered derivatives. This observation is consistent with previous studies of late-transition-metal complexes bearing expanded ring NHC ligands.[15,16] However, the extent of the carbenic carbon shift is less pronounced than those observed in the corresponding parent palladium(0) complexes:[15] for example, the $^{13}C\{^1H\}$ N−C_{NHC}−N shifts of **1** and **3**, which are 230.4 and 178.4 ppm, respectively. This difference in $^{13}C\{^1H\}$ NMR shift is attributed to both the change in oxidation state of the palladium center and the modulation of the coligand donor set.

Single crystals of **3** and **4** suitable for X-ray diffraction were obtained by layering concentrated dichloromethane solutions with *n*-pentane at ambient temperature (Figure 1). A comparison

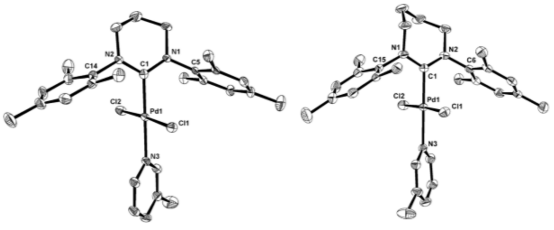


Figure 1. ORTEP[19] representations of (left) **3** and (right) **4**. Thermal ellipsoids are shown at 50% probability with all solvent molecules and hydrogen atoms omitted for clarity.

of bond metrics with those of other previously reported five-membered Pd−PEPPSI systems reveals C_{NHC}−Pd bond distances to be relatively similar across the series, regardless of the steric demand or relative *σ*-donor function exerted by the ancillary NHC ligand in question (Table 1). The Pd−N_{Py} bond distances are also found to be broadly comparable. The obvious differences when comparing structural metrics, as expected, come in the form of the N−C_{NHC}−N and C_{NHC}−N−C_{Aryl} bond

Table 1. Comparison of Bond Lengths (Å), Bond Angles (deg), and Percent Buried Volume (%V_{bur}) Values of the Pd−PEPPSI Complexes [Pd(NHC)(3ClPy)Cl_2][a]

complex	Pd−C_{NHC}	Pd−N_{Py}	N−C_{NHC}−N	%V_{bur}
[Pd(IMes)(3ClPy)Cl_2]	1.962(4)	2.117(3)	105.1(3)	34.2
[Pd(IPr)(3ClPy)Cl_2]	1.969(3)	2.137(2)	105.4(3)	34.3
[Pd(IPent)(3ClPy)Cl_2]	1.974(3)	2.097(3)	105.4(3)	37.9
[Pd(IPr*)(3ClPy)Cl_2]	1.974(6)	2.132(6)	105.7(5)	43.1
[Pd(6-Mes)(3ClPy)Cl_2]	**1.983(3)**	**2.101(2)**	**118.4(2)**	**37.4**
[Pd(7-Mes)(3ClPy)Cl_2]	**1.984(2)**	**2.103(2)**	**120.5(2)**	**39.4**

[a]Percent buried volume values (%V_{bur}) calculated using the SambVca software.[20]

angles in the six- and seven-membered derivatives **3** and **4**, where the N−C_{NHC}−N bond angles are 118.4(2) and 120.5(2)°, respectively. The C_{NHC}−N−C_{Aryl} bond angles are also increasingly acute by comparison to the related five-membered systems.[7−9] The increase in N−C_{NHC}−N and decrease in C_{NHC}−N−C_{Aryl} bond angles of the expanded ring NHC derivatives **3** and **4** afford increasingly hindered palladium coordination spheres; this feature is noteworthy in that it has been postulated to be of importance in the catalytic application of such Pd−PEPPSI type systems in cross-coupling transformations.[12] Quantifying the steric constraint imparted by **3** and **4** by the percent buried volume (%V_{bur}) analysis[18] provides an insight into where these systems lie in terms of the steric demand imparted. By comparison of **3** and **4** to other Pd−PEPPSI derivatives (Table 1) it may be observed that **3** and **4** (37.4 and 39.4) are significantly more sterically imposing than their five-membered counterpart, IMes (34.2). Complexes **3** and **4** also generate steric environments greater than those of the IPr (34.3) and IPent (37.9) systems of Organ et al. To the best of our knowledge, the only Pd−PEPPSI system reported to date with a %V_{bur} value larger than that of **4** is the extremely bulky IPr* system recently reported by Nolan and co-workers.[8h] The impact of increasing heterocycle ring size and importantly the corresponding N−C_{NHC}−N bond angle, therefore, has a dramatic effect on the steric constraint imparted by the 6- and 7-Mes ligands in relation to five-membered systems incorporating much larger *N*-aryl substituents.

Given that the steric parameters of the expanded ring NHC derivatives **3** and **4** have been demonstrated to be significantly different from those of the related five-membered Pd-PEPPSI system (IMes) and comparable with those of other sterically hindered Pd-PEPPSI systems, we were interested in the implications this would have (in combination with the enhanced *σ*-donor function of expanded ring NHCs) in C−C cross-coupling transformations. The Suzuki−Miyaura cross-coupling reaction[21] was selected as an archetypal transformation to test the efficiency of the new six- and seven-membered complexes **3** and **4**.

After a brief catalyst optimization study,[22,23] the initial substrate range applicable to **3** and **4** was tested in the cross-coupling of a number of aryl bromide substrates with phenylboronic acid (Table 2). Employment of **3** at ambient temperature led to the efficient coupling of a variety of activated, neutral, and deactivated aryl bromide substrates within 1 h, with measured percentage conversions ranging from 88 to 100% (Table 2, entries 1, 3, 5, and 7). However, the employment of hindered aryl bromide substrates in the ortho position(s) led to a change in catalytic behavior, with the observation of the corresponding catalytic dehalogenation products as well as the

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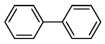
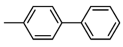
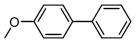
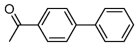
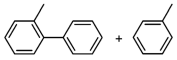
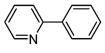
Table 2. Suzuki–Miyaura Cross-Coupling of Aryl Bromide Substrates with Phenylboronic Acid[a]

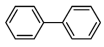
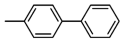
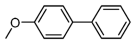
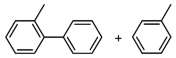
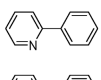
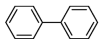
Entry	Complex	Aryl Bromide	Product	% Conv.[b]
1	3			94
2	4			79
3	3			95
4	4			81
5	3			88
6	4			26
7	3			100
8	4			100
9	3			82[c]
10	4			15[c]
11	3			15[d]
12	4			2[d]
13	3			56
14	4			42

[a]Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.2 mmol), ^{t}BuOK (1.3 mmol), decane (1 mmol, internal standard), iPrOH (2 mL), catalyst (1 mol %), ambient temperature, 1 h. [b]Percentage conversion determined from consumption of aryl bromide substrate by GCMS analysis. [c]Percentage consumption of 2-bromotoluene; >80% of the product observed by GCMS is toluene. [d]No cross-coupled observed by GCMS.

desired cross-coupled products. For example, 2-bromotoluene (Table 2, entry 9) gave the expected biaryl cross-coupled product (4-phenyltoluene) along with >80% of the corresponding dehalogenation product, toluene.[24] Changing the aryl bromide substrate to 2-bromo-*m*-xylene, a more sterically demanding example, led exclusively to the catalytic dehalogenation product, *m*-xylene, albeit in low yield (15%) (Table 2, entry 11). The increasingly sterically demanding seven-membered complex **4** led to a decrease in catalytic activity in the majority of cases, most notably in the conversion of deactivated and hindered aryl bromide substrates (Table 2, entries 6, 10, and 12).

Considering the activities observed in the aryl bromide cross-coupling studies (Table 2), complexes **3** and **4** were also tested in the Suzuki–Miyaura cross-coupling of aryl chlorides under analogous conditions (Table 3). A trend inverse to that obtained for the cross-coupling of aryl bromide substrates, with regard to the influence of NHC ring size on catalytic activity, is observed. The seven-membered derivative **4** outperforms its six-membered analogue **3** in all cases, with the exception of entries 7 and 8. The reversal in percentage conversions in the cases of entries 7 and 8 may be derived from a combination of the ortho-substitution pattern of the substrate and the steric constraint imparted by the seven-membered ancillary ligand. Activities at ambient temperature are reduced (Table 3, entries 1–10) in comparison with those of the corresponding aryl bromide substrates. 4-Chloroanisole and 2-chloropyridine give the highest percentage conversions with little difference between the six- and seven-membered NHC derivatives **3** and **4** (Table 3, entries 5, 6, 9, and 10). With neutral and hindered substrates some difference in catalytic activity between complexes **3** and **4** is apparent. The corresponding dehalogenation product (toluene) is also observed in entries 7 and 8.[24] Increasing the reaction temperature to 80 °C in the cross-coupling of chlorobenzene and phenylboronic acid affords a near-quantitative conversion (96%) after 1 h (Table 3, entry 11).

Table 3. Suzuki–Miyaura Cross-Coupling of Aryl Chloride Substrates with Phenylboronic Acid[a]

Entry	Complex	Aryl Chloride	Product	% Conv.[b]
1	3			84
2	4			100
3	3			63
4	4			93
5	3			94
6	4			95
7	3			93[e]
8	4			83[e]
9	3			100[d]
10	4			100[d]
11	3			96[e]

[a]Reaction conditions (unless stated otherwise): aryl chloride (1 mmol), phenylboronic acid (1.2 mmol), ^{t}BuOK (1.3 mmol), decane (1 mmol, internal standard), iPrOH (2 mL), catalyst (1 mol %), ambient temperature, 7 h. [b]Percentage conversion determined from consumption of aryl chloride substrate by GCMS analysis. [c]Percentage consumption of 2-chlorotoluene; >80% of the product observed by GCMS is toluene. [d]5 h. [e]80 °C, 1 h.

CONCLUSION

The two novel six- and seven-membered expanded ring N-heterocyclic carbene Pd–PEPPSI type complexes **3** and **4** have been synthesized via the oxidation of well-defined parent palladium(0) precursors **1** and **2**. The 6- and 7-Mes ancillary ligands in **3** and **4** have been noted to generate steric environments around the palladium center which are far greater than those reported for the IMes derivative and are also comparable to those of a number of other previously reported Pd–PEPPSI systems bearing considerably larger *N*-aryl substituents (iPr, iPent). The efficiency of complexes **3** and **4** in Suzuki–Miyaura cross-coupling of aryl bromide and chloride substrates was examined, as well as the catalytic dehalogenation of aryl chloride substrates.[23]

EXPERIMENTAL SECTION

Synthesis of 3 and 4. A screw-cap vial was charged with **1** or **2** (1 equiv) and 3-chloropyridine (2 mL), and the solution was stirred for ca. 5 min at ambient temperature. Dichloroiodobenzene (1 equiv) was added quickly in one portion to afford a bright yellow solution, the vial was sealed, and stirring was continued for 1 h. The excess 3-chloropyridine was removed by vacuum distillation after this time, and the resultant yellow residue was triturated with *n*-pentane to yield yellow solids isolable by filtration. Recrystalilzation from dichloromethane and *n*-pentane afforded **3** and **4** as yellow microcrystalline solids.

*[Pd(6-Mes)(3ClPy)Cl$_2$] (**3**).* Yellow microcrystalline solid (63%, 63 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.04 (1H, d, J = 2.2 Hz, *o*-CHPy); 7.98 (1H, dd, J = 5.4, 1.3 Hz, *o*-CH Py); 7.47 (1H, m, *m*-CH Py); 7.04 (4H, s, *m*-CH Mes); 6.97 (1H, dd, J = 8.3, 5.4 Hz, *p*-CH Py); 3.58 (4H, t, J = 5.8 Hz, NCH_2); 2.55 (12H, s, *o*-CH_3 Mes); 2.35 (6H, s, *p*-CH_3 Mes); 2.31 (3H, m, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ 178.4; 150.0; 149.0; 141.0; 138.0; 137.0; 136.8; 131.8; 129.5; 124.3; 48.1; 21.1; 21.0; 19.9. Anal. Calcd for $C_{27}H_{32}N_3PdCl_3 \cdot 1.5CH_2Cl_2$: C, 46.34; H, 4.78; N, 5.69. Found: C, 46.25; H, 4.61; N, 5.95.

*[Pd(7-Mes)(3ClPy)Cl$_2$] (**4**).* Yellow microcrystalline solid, yield 76%, 76 mg. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.97 (1H, d, J = 2.3 Hz, *o*-CH Py); 7.93 (1H, dd, J = 5.4, 1.2 Hz, *o*-CH Py); 7.46 (1H, m, *m*-CH Py); 7.04 (4H, s, *m*-CH Mes); 6.69 (1H, dd, J = 8.2, 5.5 Hz, *p*-CH Py); 3.98 (4H, bt, NCH_2); 2.62 (12H, s, *o*-CH_3 Mes); 2.34 (6H, s, *p*-CH_3

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Mes); 2.26 (4H, m, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3, 298 K): δ 188.7; 149.9; 148.9; 142.7; 137.9; 136.9; 136.7; 131.9; 129.6; 124.3; 55.5; 24.8; 21.0; 20.5. Anal. Calcd for $C_{28}H_{34}N_3PdCl_3$: C, 53.78; H, 5.48; N, 6.72. Found: C, 53.31; H, 5.34; N, 6.24.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving catalyst optimization data, deuterium labeling/catalytic dehalogenation data, additional experimental data, and crystallographic data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available free of charge from the CCDC under file numbers 988948 and 988949.

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The manuscript was written through contributions of both authors. Both authors have given approval to the final version.

Notes

The authors declare no competing financial interest.

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