Organometallics **2007,** *26,* 250−252

Synthesis of a Bis(N-heterocyclic carbene)palladium Complex via Oxidative Addition of a C−C Bond in a Biimidazolium Ion

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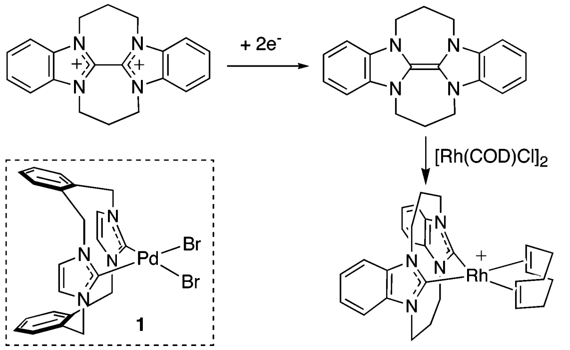
Received November 15, 2006

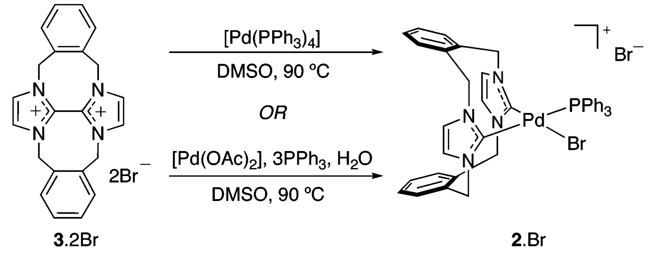
Summary: The formation of a cyclophane−NHC complex of Pd(II) via oxidative addition of a C−C bond in a bridged biimidazolium ion to Pd(0) is described. The active Pd(0) species appears to be $[Pd(PPh_3)_2Br]^-$. Simple (unbridged) biimidazolium ions do not form NHC complexes under similar conditions.

Complexes of N-heterocyclic carbenes (NHCs) have been of recent interest due to their ease of synthesis, high stability, and excellent catalytic properties toward a variety of reactions.[1−4] We are interested in xylyl-linked bis(imidazolium) cyclophanes[5,6] and their corresponding NHC metal complexes such as **1**[7] that have excellent catalytic ability in certain Heck reactions. Such complexes are similar to the Rh(I) cyclophane complex synthesized in two steps by Shi and Thummel[8] (Scheme 1), and we were intrigued by the possibility of synthesizing complexes such as **1** in a single step from a biimidazolium precursor. Here we report the synthesis of the NHC−Pd(II) cyclophane complex **2** via oxidative addition of a biimidazolium ion to Pd(0), a process that involves an unprecedented C−C bond cleavage in a biimidazolium ion that results in two NHC ligands (Scheme 2).

Scheme 1



Scheme 2



The reaction of the biimidazolium salt **3**·2Br with $[Pd(PPh_3)_4]$ in DMSO at 90 °C afforded the Pd(II) complex **2**·Br (Scheme 2). Under these conditions, a number of Pd(0) species, including $[Pd(PPh_3)_2]$ and $[Pd(PPh_3)_2Br]^-$, are plausible reactive intermediates. While $[Pd(PPh_3)_2]$ is commonly considered the active species in oxidative addition reactions involving $[Pd(PPh_3)_4]$, Amatore et al. have suggested that in the presence of halides $[Pd(PPh_3)_2X]^-$ is one of the active species.[9] The reaction of **3**·$2PF_6$ with $[Pd(PPh_3)_4]$, under the same conditions used for the reaction with **3**·2Br (Scheme 2), does not afford any oxidative addition product, but the reaction commences when NBu_4Br is added. This result is consistent with $[Pd(PPh_3)_2Br]^-$ being involved in the oxidative addition of the biimidazolium C−C bond.

The reaction between **3**·2Br and $[Pd(PPh_3)_4]$ to form **2** (in DMSO at 90 °C) did not go to completion, even after 3 days, despite 40% conversion within 15 h. Under similar conditions but in the presence of 2 equiv of NBu_4Br the conversion was slightly improved (50%, 15 h), and in the presence of 1 equiv of CuBr (a known scavenger of PPh_3[10,11]) the conversion was substantially improved (80%, 18 h). These results are consistent with a situation where free PPh_3 evolved during the reaction inhibits formation of the coordinatively unsaturated Pd(0) intermediate (presumably $[Pd(PPh_3)_2Br]^-$) as the extent of conversion increases. Even though the complex **2** could be formed under these conditions, the long reaction times and complex mixtures precluded the use of this method as a practical preparative procedure.

Amatore et al. have shown that the reaction of $[Pd(OAc)_2]$ with 3 equiv of PPh_3 and a stoichiometric amount of water affords $[Pd(PPh_3)_2OAc]^-$, one of the active species that undergoes oxidative addition in Heck reactions involving catalysts based on $[Pd(OAc)_2]$ and PPh_3.[12] Treatment of the biimidazolium salt **3**·2Br with $[Pd(OAc)_2]$, 3 equiv of PPh_3, and water in DMSO at 90 °C afforded the palladium NHC

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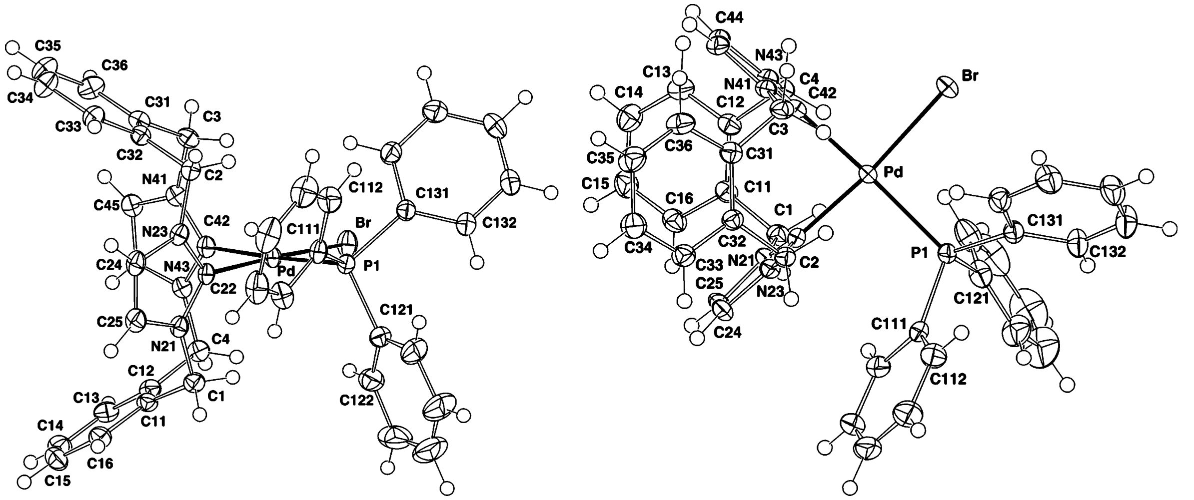
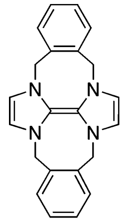


Figure 1. ORTEP projections of the cation of **2** showing non-hydrogen atoms with 50% probability amplitude displacement ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å. Selected bond distances (Å) and angles (deg): Pd−Br = 2.4610(4), Pd−P1 = 2.3380(10), Pd−C(22) = 1.999(3), Pd−C(42) = 2.022(4); Br−Pd−P1 = 92.65(3), Br−Pd−C(42) = 89.98(10), C(22)−Pd−C(42) = 84.26(13), P1−Pd−C(22) = 93.35(10).

complex **2** in 75% yield (by NMR) within 3 h (Scheme 2). Complex **2** was readily isolated in 50% yield (based on **3**·2Br) as the tetraphenylborate salt **2**·BPh_4 via salt metathesis with $NaBPh_4$ in methanol.[13] The salt **2**·BPh_4 has been characterized by ^1H, ^{13}C, and ^{31}P NMR studies, microanalysis, FAB-MS, and a single-crystal X-ray crystallographic study[14] (see Figure 1 and the Supporting Information). The treatment of **3**·$2PF_6$ with [Pd-$(OAc)_2$], PPh_3 (3 equiv), and water in DMSO at 90 °C did not afford an oxidative addition product, though a significant amount of black precipitate formed. Upon addition of NBu_4Br, however, formation of **2** commenced immediately, consistent with the notion that the reactive Pd(0) species involved in the oxidative addition is $[Pd(PPh_3)_2Br]^-$ rather than $[Pd(PPh_3)_2OAc]^-$.

The formation of **2**·Br may proceed via a concerted oxidative addition of the central C−C bond in the biimidazolium cation **3** to a Pd(0) center. Alternatively, the biimidazolium cation **3** could be reduced by Pd(0) to the corresponding carbene dimer **3′**, which is expected to exist in equilibrium with the bis(NHC) species **3″**;[15] formation of **2** would then proceed via simple coordination of the NHC groups in **3″** to Pd(II). Mechanisms between these extremes can also be envisaged, which may involve single-electron transfer from Pd(0) to **3** prior to cleavage of the central C−C bond. The results of cyclic voltammetric studies make us disinclined to favor mechanisms that involve reduction of **3** by Pd(0). Oxidation potentials for $[Pd(PPh_3)_2X]^-$ (X = OAc, Br) and $[Pd(PPh_3)_n]$ ($n = 2-4$) fall in the range 0 to +0.4 V (vs SCE; Pt or Au electrode, 0.3 M Bu_4NBF_4 in DMF or THF).[9,16] Biimidazolium cations have quite low reduction potentials,[17] and we have found that **3** undergoes two single-electron, irreversible reductions at −1.14 and −1.22 V (vs Ag/AgCl; Pt electrode, 0.1 M Bu_4NClO_4 in DMSO). These results suggest that Pd(0) species likely to be present in our reaction mixtures are unlikely to be sufficiently strong reducing agents to reduce the biimidazolium cation **3** to species such as **3′** and **3″**, and with this in mind we tentatively suggest that **2** is formed via a concerted oxidative addition of the central C−C bond to a Pd(0) center.



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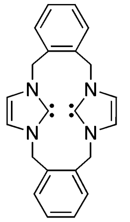

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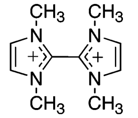

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[13] A mixture of **3**·2Br (102 mg, 0.2 mmol), palladium acetate (46 mg, 0.2 mmol), triphenylphosphine (160 mg, 0.61 mmol), and water (4 μL, 0.22 mmol) in dry DMSO (ca. 8 mL) was stirred at 90 °C for 15 h. The solution was cooled, the solvent was removed under vacuum (ca. 50 °C), and the residue was extracted with methanol (ca. 6 mL). A solution of sodium tetraphenylborate (103 mg, 0.3 mmol) in methanol (ca. 2 mL) was added, and the resulting mixture was stirred at room temperature for 10 min. The solid was collected, washed with methanol, and recrystallized by layering a concentrated solution of the complex in dichloromethane with methanol, to yield pale orange crystals (110 mg, 50 %). Anal. Calcd for $C_{64}H_{55}N_4$-$BPBrPd\cdot 1.5CH_2Cl_2\cdot CH_3OH$: C, 63.01; H, 4.93; N, 4.42. Found: C, 63.09; H, 4.78; N, 4.51. ^1H NMR (600.13 MHz, d_6-DMSO): δ 4.57 (2H, d, J = 14 Hz, 2 × benzylic C*H*H), 5.24 (2H, d, J = 14 Hz, 2 × benzylic C*H*H), 5.98 (2H, d, J = 14 Hz, 2 × benzylic C*H*H), 6.33 (2H, d, J = 14 Hz, 2 × benzylic C*H*H), 6.79 (4H, d, J = 7.2 Hz, *para* BPh_4), 6.92 (8H, t, J = 7.4 Hz, *meta* BPh_4), 7.18 (10H, m, *ortho* BPh_4 and imidazolyl H4′ and H5′), 7.36 (2H, dt, J = 1.4 and 7.5 Hz, 2 × xylyl H), 7.40 (2H, dt, J = 1.4 and 7.5 Hz, 2 × xylyl H), 7.52 (2H, d, $^4J_{H-P}$ = 1.2 Hz, imidazolyl H4 and H5), 7.53 (6H, m, *meta* PPh_3), 7.59 (3H, dt, J = 1.7 and 7.4 Hz, *para* PPh_3), 7.67 (8H, m, *ortho* PPh_3 and 2 × xylyl H), 7.83 (2H, dt, J = 1.1 and 7.5 Hz, 2 × xylyl H). ^{13}C NMR (150.90 MHz, d_6-DMSO): δ 50.5 (CH_2), 50.8 (CH_2), 121.9 (BPh_4 CH_{para}), 122.4 (d, $^4J_{C-P}$ = 5 Hz, imidazolyl C4 and C5), 122.7 (imidazolyl C4′ and C5′), 125.3 (q, $^2J_{C-B}$ = 2.7 Hz, BPh_4 CH_{meta}), 129.0 (d, $^3J_{C-P}$ = 10 Hz, PPh_3 CH_{meta}), 129.53 (d, $^1J_{C-P}$ = 45 Hz, PPh_3 C_{ipso}), 129.56 (xylyl CH), 129.7 (xylyl CH), 131.1 (PPh_3 CH_{para}), 132.15 (xylyl CH), 132.27 (xylyl CH), 133.8 (d, $^2J_{C-P}$ = 12 Hz, PPh_3 CH_{ortho}), 134.9 (xylyl C), 135.51 (BPh_4 CH_{ortho}), 135.58 (xylyl C), 159.5 (d, $^2J_{C-P}$ = 8 Hz, imidazolyl C2′), 163.28 (d, $^2J_{C-P}$ = 160 Hz, imidazolyl C2), 163.30 (q, $^1J_{C-B}$ = 49 Hz, BPh_4 C_{ipso}). ^{31}P NMR (121.5 MHz, d_6-DMSO): δ 19.44. Mass spectrum (FAB): *m/z* 787.081 818 ($C_{40}H_{35}N_4P^{79}$-$Br^{106}Pd$ requires 787.081 747), 789.081 645 ($C_{40}H_{35}N_4P^{81}Br^{106}Pd$ requires 789.079 701), 791.079 384 ($C_{40}H_{35}N_4P^{81}Br^{108}Pd$ requires 791.080 120).

[14] Crystal/refinement data for **2**·$BPh_4\cdot 1.80CH_2Cl_2$ ($\equiv C_{65.8}H_{58.6}$-$BBrCl_{3.6}N_4PPd$): M_r = 1261.1, orthorhombic, space group *Fdd*2 (C_{2v}[19], No. 43), a = 38.434(2) Å, b = 48.007(3) Å, c = 12.7080(7) Å, V = 23448 Å^3. $D_c(Z = 16) = 1.43_2$ g cm^{-3}, μ_{Mo} = 1.24 mm^{-1}, specimen 0.48 × 0.42 × 0.36 mm, "T"$_{min/max}$ = 0.91. $2\theta_{max}$ = 68°, N_t = 86 281, N = 22 236 (R_{int} = 0.034), N_o = 19 090, R1 = 0.037, wR2 = 0.034 (n_w = 0.04), GOF = 1.05, $|\Delta\rho_{max}|$ = 0.77 e Å^{-3}, $x_{abs} = -0.012(4)$. Solvent residues were modeled in terms of one molecule of CH_2Cl_2, full site occupancy, and a second with site occupancy refined to 0.801(3).

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Intriguingly, under conditions used for the reaction of **3** with $[Pd(PPh_3)_4]$ or $[Pd(OAc)_2]/PPh_3/H_2O$ (in DMSO at 90 °C), the simple (nonbridged) biimidazolium ion **4** does not react to form Pd−NHC complexes; indeed, **4**·2Br and **4**·2I are inert toward these reagents. There are significant differences between the biimidazolium cations **3** and **4** that may account for this difference in reactivity. Spectroscopic and crystallographic studies (see the Supporting Information) suggest that the dihedral angle between the imidazolium groups is substantially larger in **4** than in **3**. X-ray studies reveal a dihedral angle of 56.2(1)° in **3**, which, given the bridged structure within this cation, we would expect to be retained in solution. While X-ray studies of salts of **4** reveal dihedral angles of 59−80° (see the Supporting Information and ref 18), a theoretical study suggests that the most favored conformation of this cation has a dihedral angle of 90°.[18] Studies of numerous bridged biimidazolium salts and their 2,2′-bipyridinium analogues found that the wavelength of the lowest energy UV absorption increased as the dihedral angle decreased.[17,19,20] The lowest energy absorptions for **3** and **4** (280 and <260 nm, respectively) also suggest a smaller average dihedral angle for the bridged cation **3** compared to that of its nonbridged analogue **4**. It may be that the smaller dihedral angle in **3** (i.e., more nearly planar biimidazolium structure) allows for easier approach of a metal to the central biimidazolium C−C bond, thus facilitating the reaction of **3** compared to **4**. X-ray studies suggest the existence of considerable strain associated within the bridging groups within the cation **3** (see Figure S7 in the Supporting Information). The strain within **3** may serve to activate this cation toward reaction with Pd(0). Perhaps as a consequence of its larger dihedral angle,[17,19,20] the cation **4** is more difficult to reduce ($E^{p}_{Red} = -1.41$ V vs Ag/AgCl; Pt electrode, 0.1 M Bu_4NClO_4 in DMSO) than **3**, a characteristic that may disfavor the reaction of **4** with Pd(0). We are currently studying reactions of a range of electron-rich metal sources and biimidazolium salts with different bridging groups to gain insight into these issues.

NHC complexes are usually synthesized via one of four methods: (i) treatment of azolium salts with a base to form a free carbene (which may or may not be isolated) followed by addition of a metal source,[21−23] (ii) a one-pot procedure involving the reaction of an azolium salt with a base and a metal source,[24] (iii) carbene-transfer reactions, usually involving transfer of the NHC from Ag(I) to another metal,[25] and (iv) reaction of tetraaminoethylenes ("carbene dimers") with metal centers (Scheme 1).[26,27] Less commonly used methods include (v) oxidative addition of the C2−Z bond (Z = halide,[28−30] H,[30−33] SR[34,35]) in imidazolium ions to low-valent metal centers (which results in both the NHC and X fragments bound to the metal center) and (vi) multistep oxidative cleavage of the C2−R bond (R = Me, Et, Bn) in 2-alkylimidazolium ions mediated by Ag(I) (where the NHC fragment binds to the metal center while the R group is oxidized to a carboxylic acid).[36] While the possibility of oxidative addition of the $C2-CH_3$ bond in the 1,2,3-trimethylimidazolium ion to Ni(0), Pd(0), and Pt(0) has been explored by computational methods,[30] to the best of our knowledge case vi represents the only prior report of C−C bond activation of a imidazolium cation to form an isolable NHC−metal complex. The oxidative addition of biimidazolium ions such as **3** to Pd(0) provides an interesting new route to cyclophane−NHC complexes, and we are currently exploring the scope of this reaction.

Acknowledgment. We thank both the Australian Research Council and The University of Western Australia for financial support.

Supporting Information Available: Full experimental details for the synthesis and characterization of **2**·BPh_4, **3**·2Br, **4**·2I, and **4**·2Br, including cyclic voltammetry, UV−vis, and crystallographic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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