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## 12 e<sup>-</sup> Pd(0): Cut 'em like butter



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surrogate



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# Swift C–C bond insertion by a 12-electron palladium(0) surrogate†

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The selective activation of C–C bonds holds vast promise for catalysis. So far, research has been primarily directed at rhodium and nickel under harsh reaction conditions. Herein, we report C–C insertion reactions of a 12-electron palladium(0) surrogate stabilized by a cyclic(alkyl)(amino) carbene (CAAC) ligand. Benzonitrile (1), biphenylene (2), benzocyclobutenone (3), and naphtho[b]cyclopropene (4) were studied. These substrates allow elucidation of the effect of ring strain as well as hybridization encompassing  $sp^3$ ,  $sp^2$  and  $sp$  hybridized carbon atoms. All reactions proceed quantitatively at or below room temperature. This work therefore outlines perspectives for mild C–C bond functionalization catalysis.

The functionalization of C–C bonds allows for the modification of organic molecules without the requirement for specific functional groups.<sup>1</sup> However, the elegance of this reaction-type is compromised by the strong and sterically shielded C–C bond, which renders the insertion step difficult. The most common transition metals used for catalytic transformations of C–C bonds are arguably rhodium and nickel. This is exemplified by the Rh-catalyzed cyclobutene ring opening<sup>2</sup> and the Ni-catalyzed transfer hydrocyanation.<sup>3</sup> However, also here, harsh reaction conditions, namely refluxing toluene or xylene solvents, are needed to break the C–C bond. These reactions may even take several days if not weeks to achieve high conversions.<sup>4,5</sup> As such, mild pathways to isolable, yet strained group-10 metallacycles are scarce as highlighted by Moret *et al.* for a nickelacyclobutane.<sup>6</sup>

So far, only a handful of C–C insertion products have been reported for platinum, and even fewer for palladium. Jones and colleagues pioneered the field and used nickel(0), palladium(0), and platinum(0) phosphine complexes for the activation of

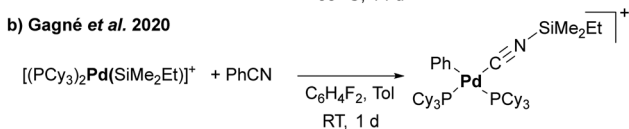
biphenylene (Scheme 1a),<sup>7–12</sup> as well as the photochemical activation of diphenylacetylene.<sup>13</sup> The insertion of the palladium(0) complex into biphenylene proceeded in reasonable yield only upon heating to 68 °C for 14 days.<sup>10,12,14</sup> Even for Ni(NHC)<sub>2</sub>, only a yield of 66% was obtained after stirring overnight.<sup>15,16</sup> The oxidative addition of benzonitrile with a bond dissociation energy (BDE) of 555 kJ mol<sup>−1</sup>, which considerably exceeds the one of the Ph–F bond (BDE = 485 kJ mol<sup>−1</sup>),<sup>17</sup> seems even more challenging.<sup>11,18</sup> Thus, it requires in the case of palladium the addition of Lewis-acids such as BEt<sub>3</sub><sup>19</sup> or silylium cations as studied by Gagné and coworkers (Scheme 1b).<sup>20,21</sup>

## Previously reported:

### a) Jones *et al.* 1998



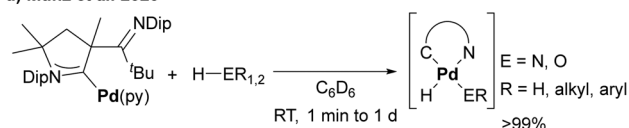
### b) Gagné *et al.* 2020



### c) Murakami *et al.* 2017



### d) Munz *et al.* 2020



## This work:



**Scheme 1** Insertion into C–C and H–E (E = N, O) bonds by palladium(0) complexes.

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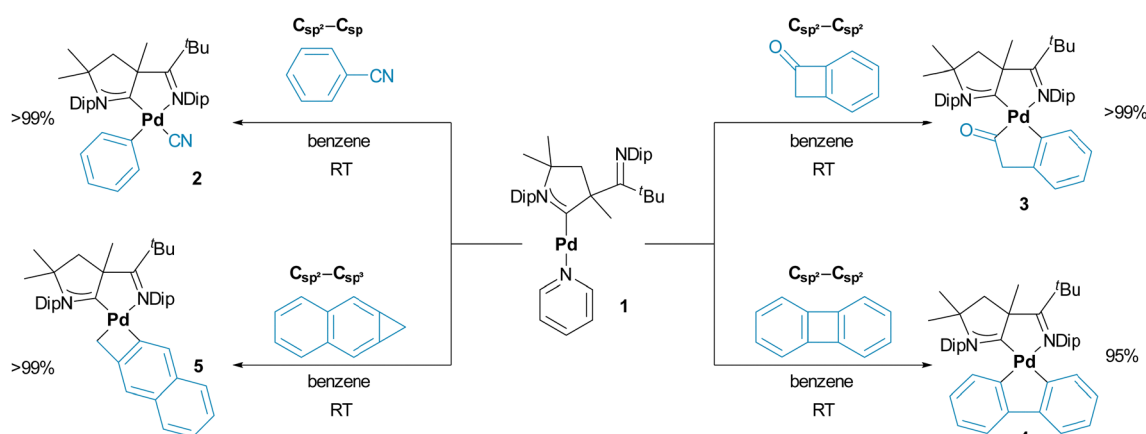
† Electronic supplementary information (ESI) available. CCDC 2288556–2288560. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3cc03964a>



Single crystals suitable for XRD analysis were obtained directly from the reaction in case of **3** and **5**, *via* slow evaporation of a concentrated solution of **2** in pyridine, or through diffusion techniques (pentane/pyridine) at  $-30\text{ }^{\circ}\text{C}$  for **4** (Fig. 1). Comparing the bond lengths of the Pd-C<sub>Ar</sub> bonds between the

In the case of **2**, this bond is even shorter with 1.9847(17) Å due to the *trans*-influence of the cyanido ligand. The palladacycles **4** and **5** are almost planar with the sum of the internal angles being close to the ideal (**4**, 538.5° vs. 540°; **5**, 359.2° vs. 360°). In contrast, palladacycle **3** is significantly bent (522.2° vs. 540°) and the carbonyl group is twisted out of plane with a short distance of approximately 3.1 Å to the mean plane of the phenyl ring of the diisopropylphenyl group. Small inter-ligand distances are also found for the phenylene groups in **3** and **4**. These palladacycle–CAAC interactions parallel the stability of complexes **3**, **4** and **5**. While **5** is perfectly stable in pyridine, solutions of **4** turn colorless within 2 h, thereby depositing insoluble needles. SC-XRD analysis identified these crystals as the di(pyridine) complex **6** (Fig. 2). In case of **3**, this transformation requires heating to 80 °C overnight (ESI<sup>†</sup>). Substitution reactions of CAACs are very unusual, and Pd<sup>II</sup>(CAAC) complexes are usually inert towards strong nucleophiles, including phosphines and other carbene-ligands.<sup>36,37</sup> We therefore propose that the loss of the CAAC ligand is due to steric congestion.

The ease of C-C activation may be understood by the interplay of ring strain and carbon atom hybridization. No ring strain is required for the oxidative addition into the  $C_{sp^2}-C_{sp}$  bond of benzonitrile (**2**) despite the high BDE of 555 kJ mol<sup>-1</sup>.<sup>11</sup> Although lower *s*-character of the C-C bond reduces the BDE

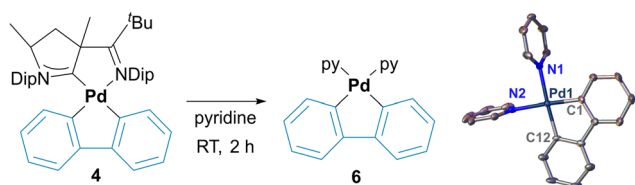


**Scheme 2** Insertion of complex **1** into C<sub>sp2</sub>–C<sub>sp</sub>, C<sub>sp2</sub>–C<sub>sp2</sub> and C<sub>sp2</sub>–C<sub>sp3</sub> bonds.





**Fig. 1** Solid state structures of complexes **2**, **3**, **4** and **5**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths [Å] and (torsion) angles [°]: **2**: Pd1–N2, 2.1846(14); Pd1–C1, 1.9847(17); Pd1–C37, 2.0182(18); Pd1–C38, 2.0107(17). **3**: Pd1–N1, 2.2460(15); Pd1–C1, 2.0565(18); Pd1–C33, 1.970(2); Pd1–C36, 2.0859(19); N2–C1–C36–C35, 39.3. **4**: Pd1–N2, 2.210(4); Pd1–C1, 2.044(4); Pd1–C37, 2.085(4); Pd1–C48, 1.990(4); N1–C1–C37–C42, 76.3. **5**: Pd1–N1, 2.175(6); Pd1–C1, 2.011(7); Pd1–C37, 2.062(6); Pd1–C38, 2.049(7); N2–C1–C38–C39, 18.9.



**Fig. 2** Solid state structures for the di(pyridine) complexes **6**. Thermal ellipsoids at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths [Å]: Pd1–N1, 2.127(3); Pd1–N2, 2.128(3); Pd1–C1, 2.002(3); Pd1–C12, 2.002(3).

(Ph–Ph, BDE = 418 kJ mol<sup>−1</sup>),<sup>17</sup> it renders these compounds kinetically more stable (*vide infra*). As such, ring strain is required (**3**, computed at 116 kJ mol<sup>−1</sup>, Table S2; **4**,<sup>38</sup> 222 kJ mol<sup>−1</sup>) for the oxidative addition. In the case of **3**, selective insertion into C(O)–C<sub>sp</sub> was obtained, although the C(O)–C<sub>sp</sub> bond (CH<sub>3</sub>C(O)–Et, BDE = 349 kJ mol<sup>−1</sup> vs. CH<sub>3</sub>C(O)–Ph, BDE = 413 kJ mol<sup>−1</sup>)<sup>39</sup> is weaker. Compound **5** showcases that even C<sub>sp</sub>–C<sub>sp</sub> bonds (Ph–Et, BDE = 427.6 kJ mol<sup>−1</sup>)<sup>39</sup> may be activated in the presence of substantial ring-strain (computed at 291 kJ mol<sup>−1</sup>, Table S2 (ESI<sup>†</sup>); literature values benzocyclopropenes, 285–300 kJ mol<sup>−1</sup>).<sup>40</sup> Indeed, we did not observe a room-temperature reaction with benzocyclobutene, which features a C<sub>sp</sub>–C<sub>sp</sub> bond with a considerably reduced strain of 136 kJ mol<sup>−1</sup>.<sup>40</sup>

It is intriguing to note that the observed reactivity aligns with computational predictions by Ananikov, Musaev, and Morokuma.<sup>41</sup> Based on the calculation of oxidative addition transition states for CH<sub>3</sub>–CH<sub>3</sub>, Ph–Ph and HC<sub>2</sub>–C<sub>2</sub>H with Pd(PMe<sub>3</sub>)<sub>2</sub>, the authors proposed that low barriers, *viz.* fast reactions, are due to enhanced s-character in the transition state. The BDEs of the Pd–R and C–C bonds, which *both* follow the trend HC<sub>2</sub> > Ph > CH<sub>3</sub>, play a secondary role in the Bell–Evans–Polanyi (Hammond's postulate, respectively) sense. It was furthermore shown that ground state inhibition through the formation of  $\pi$ -complexes in the case of olefins and especially alkynes somehow compromises this general trend. This

matches perfectly with the slow formation of **2** pending the formation of an intermediate (*vide supra*). We furthermore would like to highlight that the reactivity trend also coincides with the oxidative addition of organic (pseudo)halides, which has been attributed to both the higher stability of the forming Pd–C bonds as well as  $\pi$ -backbonding.<sup>42</sup>

In summary, we present the oxidative addition of biphenylene, benzonitrile, naphtho[*b*]cyclopropene, and benzocyclobutenone to a palladium(0) complex. These insertion reactions proceed swiftly in (cold) benzene and, hence, under unprecedented mild conditions. Further, we report that complex **4** undergoes the unusual substitution of the CAAC ligand in pyridine. The ease of C–C bond insertion correlates with ring-strain and hybridization. Current efforts are targeting catalysis with stronger C–C bonds at elevated temperatures.

K.B.; investigation (synthesis and characterization **3**, **5** and **6**, computations), formal analysis, visualization, writing – original draft. A.G.; investigation (synthesis **2** and **4**). P.M.; characterization **4** and determination of all reaction times (investigation). F.D., crystallographic analysis **3**, **5** (investigation), contribution to writing – original draft; F.W.H. crystallographic analysis **2**, **4**, **6** (investigation). D.M.; conceptualization, funding acquisition, project administration, supervision, writing – review and editing.

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## Conflicts of interest

There are no conflicts to declare.



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