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C–H activations on a 1*H*-1,4-benzodiazepin-2(3*H*)-one template

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Abstract

Air stable benzodiazepine containing palladacycles were synthesized by a C–H activation reaction and studied by mass spectrometry and X-ray crystallography. Catalytic C–H functionalizations of 1-methyl-5-phenyl-1*H*-1,4-benzodiazepin-2(3*H*)-one with diphenyliodonium hexafluorophosphate led to a mixture, which included the starting material and the expected product 1-methyl-5-(2′-biphenyl)-1*H*-1,4-benzodiazepin-2(3*H*)-one.

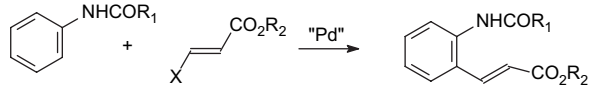
Keywords: Benzodiazepine; C–H activation; Palladium; Catalysis

1. Introduction

Palladacycles are a class of air stable organometallic complexes with interesting properties and applications in many areas of organic synthesis, especially in high turnover catalytic C–C bond forming reactions, such as Heck or Suzuki–Miyaura couplings. Palladacycles are typically five- or six-membered ring systems and are formed by a C–H activation reaction, assisted by coordination of the heteroatom of the ligand to the electrophilic Pd(II) species.[1] They are now established intermediates or precursors in *atom economical* C–H activations,[2] whereby a C–H bond is involved as one coupling partner as opposed to a C–X (X=Cl, Br, I) bond. Intramolecular coordination to the metal and the formation of palladacycles as either precatalysts or intermediates can promote the high *ortho*-regioselectivity observed in these synthetically powerful processes.[3]

We will report hereafter our recent findings on the stoichiometric and catalytic C–H activation of 1-methyl-5-phenyl-1*H*-1,4-benzodiazepin-2(3*H*)-one derivatives. In line with the nature of this Symposium-in-Print, we will initially provide an overview of selected publications in the burgeoning area of palladacycle mediated C–H activation chemistry, which will highlight these synthetically relevant transformations, benefiting from the unique properties of palladacycles including their facile synthesis by chelation-assisted C–H activation, their ease of handling/air stability as well as their well-defined chemistry and use as tools for the mechanistic investigations of carbon–carbon bond forming reactions.

Ambient temperature *ortho*-alkenylations and arylations of anilines and anilides catalyzed by palladium have been recently reported and are likely to involve palladacycle intermediates given the high degree of regioselectivity observed.[4] A number of catalytic alkenylations use an additional 1 equiv of a silver(I) salt and tolerate bromo substituents on the aryl coupling partner (Scheme 1).



Scheme 1. Catalytic palladium mediated vinylation reactions.

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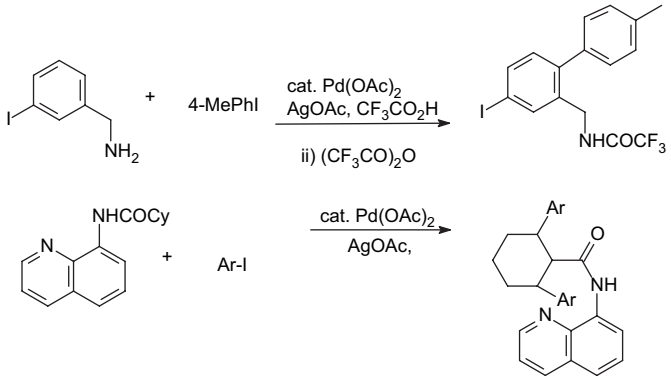
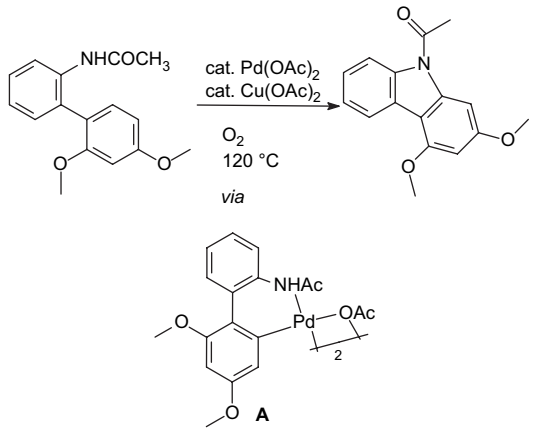
Related palladium catalyzed *ortho*-arylations of benzylamines tolerate an iodide group on the benzylamine coupling partner or a bromide on the aryl halide coupling partner (Scheme 2).[5] The activation of sp^3 C–H bonds is also possible by the use of a pyridine or quinoline tether, which coordinates to the metal and directs the C–H activation. In both instances (Scheme 3) a Pd(II)–Pd(IV) pathway is thought to operate.



Scheme 2. Palladium mediated arylation of benzylamines.

A range of C–H activation/arylation processes have been developed, which employ a palladium catalyst with a stoichiometric amount of hypervalent iodine(III) arylating derivative. The proposed mechanism involves a chelation-assisted C–H activation (Y=coordinating group), oxidation of Pd(II) to Pd(IV) by the iodine(III) agent, and reductive elimination to furnish the arylated product.[6]

The Sanford group has also disclosed cross-couplings of aromatics via two C–H activations, involving palladacycles, (Scheme 4). No homocoupling products were observed for these reactions, which require stoichiometric amounts of silver salts and several equivalents of arene coupling partner.[6e]



Scheme 5. Carbazoles via C–H activation and C–N bond formation.

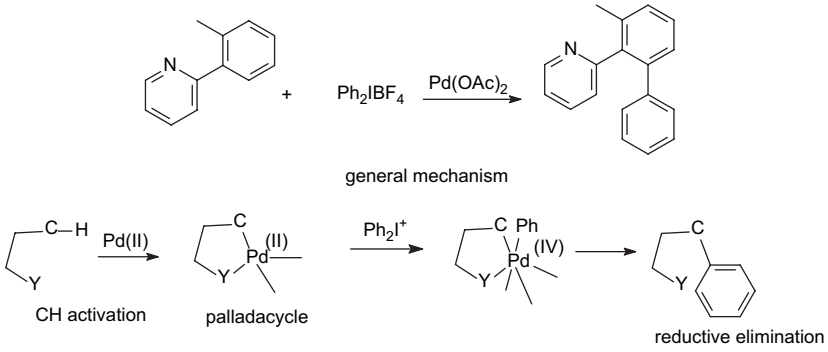
The regioselective synthesis of carbazoles involving C–H activation and C–N bond formation has recently been reported (Scheme 5). These processes are believed to involve a palladacycle intermediate such as **A**, which loses HOAc prior to a reductive elimination (C–N bond formation) step.[7]

Palladium catalyzed C–H activation, transmetallation processes have also been reported. A cyclic transition state (**B**, Scheme 6), involving a palladacycle intermediate has been postulated.[8]

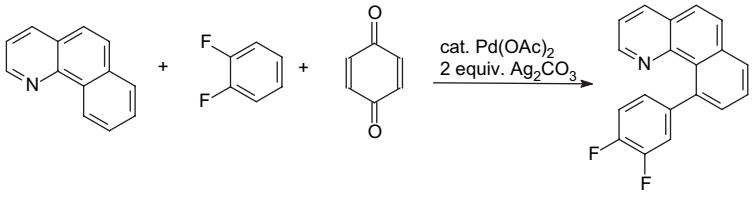
2. Results and discussion

2.1. Stoichiometric C–H activation

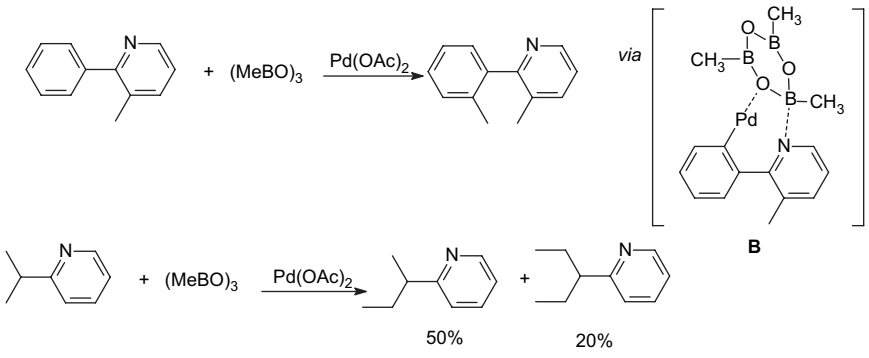
We recently disclosed the synthesis of a range of benzodiazepine-based palladacycles **2** and **3** by C–H activation and these were found to be effective precatalysts in a number of Heck and Suzuki reactions (Scheme 7).[9] The air stable dimeric complex



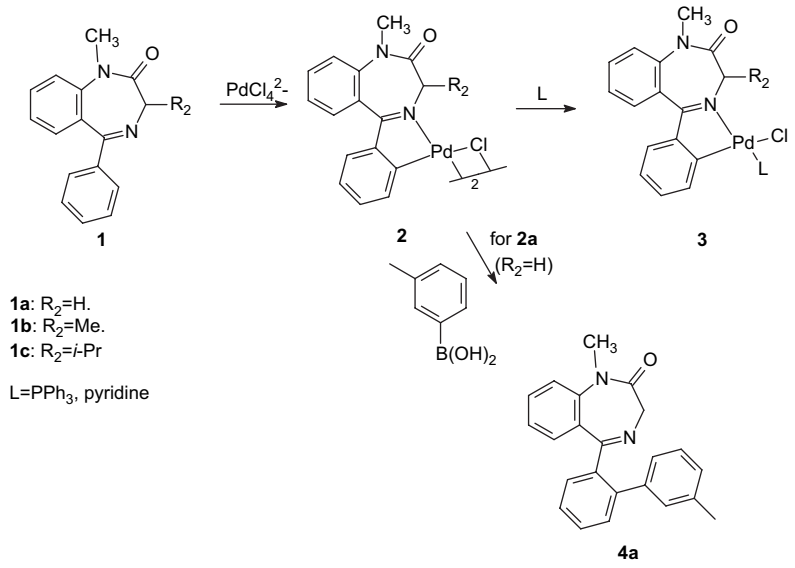
Scheme 3. C–H activation/arylations with iodonium salts.



Scheme 4. Cross-couplings involving double C–H activations and a postulated palladacycle intermediate.



Scheme 6. C–H activation/transmetallation via a palladacycle.



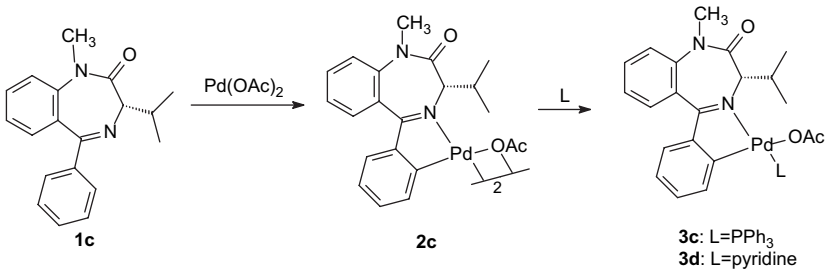
Scheme 7. Reactions of benzodiazepine containing palladacycles.

2a reacted with triphenylphosphine to afford the monomeric complex **3a** (L=PPh_3) and underwent a stoichiometric reaction with an arylboronic acid to afford the *ortho*-substituted benzodiazepine **4a**.[10]

We were aware of two major limitations to the chemistry depicted in Scheme 7.

(i) The ligands **1** and complexes **2** and **3** are mainly derived from glycine and are hence achiral (i.e., **1a**–**3a**, R_2=H). With the plethora of amino acid starting materials available from the chiral pool we wanted to synthesize benzodiazepine containing ligands as well as palladacycles containing a stereogenic centre i.e., with $R_2 \neq H$.
(ii) The synthesis of **4** involved stoichiometric amounts of the palladacycle **2a**. We wished to synthesize analogues related to **4** employing C–H activation chemistry.

To address (i), we synthesized the ligands **1b** and **1c** using standard synthetic protocols and alanine and valine-based starting materials, respectively.[11] The attempted C–H activation of **1b** with Na_2PdCl_4, followed by treatment with PPh_3 and recryztallisation afforded X-ray quality crystals, which were found to be $PdCl_2(PPh_3)_2$ indicating that the original C–H activation reaction had not taken place and a coordination complex of the type $(L-H)_2PdCl_2$, where L–H=**1b**, had been formed. Treatment of the purported coordination complex with PPh_3 presumably leads to displacement of L–H from palladium. The attempted C–H activation of **1c** using these conditions was also unsuccessful although using $Pd(OAc)_2$ as the metallating agent led presumably to **2c**. The latter was not isolated as such dimeric complexes are usually insoluble for NMR measurements and exist as mixtures of isomers in solution. Treatment of the purported complex **2c** with either PPh_3 or pyridine led to the palladacycles **3c** and **3d**, respectively (Scheme 8). Unfortunately, the treatment of **1b** with $Pd(OAc)_2$ did not lead to the expected **2b**. Complex **3c** was characterized in solution by ^1H and ^{31}P spectroscopy and in the solid phase by X-ray diffraction (Fig. 1). X-ray analysis of crystals of **3d** obtained from CH_2Cl_2/hexane led to the characterization of the *trans*-isomer (Fig. 2). Bond lengths and angles (Tables 1 and 2) are comparable to similar complexes already reported in the literature.[9]



Scheme 8. Formation of palladacycles containing a remote stereogenic centre.

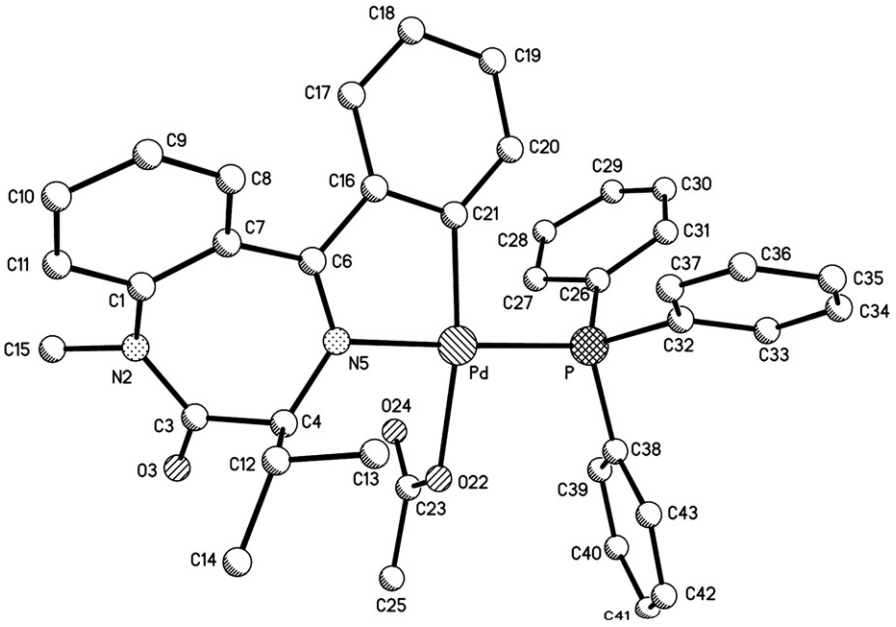


Figure 1. Ortep plot of complex **3c**.

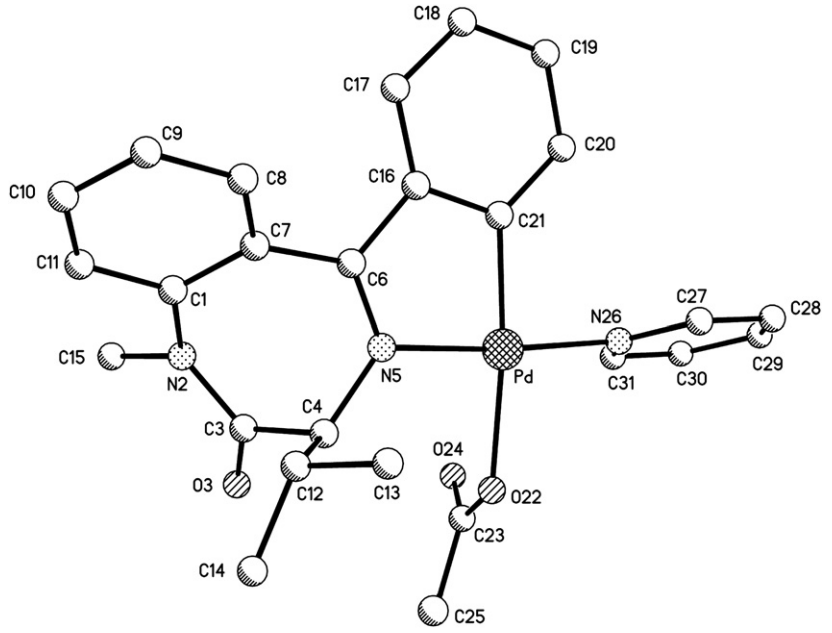


Figure 2. Ortep plot of complex **3d**.

Table 1
Selected bond lengths (Å) and angles (°) for **3c**

Pd–C(21)	2.015(6)
Pd–N(5)	2.085(4)
Pd–O(22)	2.102(4)
Pd–P	2.2620(16)
C(21)–Pd–N(5)	81.1(2)
C(21)–Pd–O(22)	171.10(18)
N(5)–Pd–O(22)	90.94(17)
C(21)–Pd–P	96.30(15)
N(5)–Pd–P	173.21(13)
O(22)–Pd–P	92.08(12)
C(32)–P–Pd	115.3(2)
C(26)–P–Pd	114.8(2)
C(38)–P–Pd	110.98(19)

Symmetry transformations used to generate equivalent atoms.

Table 2
Selected bond lengths (Å) and angles (°) for **3d**

Pd–C(21)	1.980(4)
Pd–N(5)	2.025(3)
Pd–N(26)	2.058(4)
Pd–O(22)	2.117(3)
C(21)–Pd–N(5)	80.90(15)
C(21)–Pd–N(26)	94.77(17)
N(5)–Pd–N(26)	175.67(15)
C(21)–Pd–O(22)	173.08(14)
N(5)–Pd–O(22)	92.18(12)
N(26)–Pd–O(22)	92.15(14)
C(20)–C(21)–Pd	129.2(3)
C(16)–C(21)–Pd	113.2(3)
C(23)–O(22)–Pd	124.6(3)
C(31)–N(26)–Pd	118.5(4)
C(27)–N(26)–Pd	122.3(4)

Symmetry transformations used to generate equivalent atoms.

The analysis of palladacycles and their fragmentation by mass spectrometry is a promising area of current interest.[12] The spectra for complexes **3a** and **3c** are shown in Figure 3. Species containing acetate and chloride residues both lose these as anions and were detected as the counter cations. Moreover, an acetonitrile adduct was observed for the cation of **3a**. An apparent sensitivity of the compounds to elevated temperatures meant that the ion source conditions were maintained at a value as low as possible.

2.2. Catalytic C–H activation

Given the impressive use of palladacycles in catalytic C–H activation chemistry, we have undertaken preliminary steps towards the synthesis of the *ortho*-arylated benzodiazepine **4b** employing hypervalent iodonium salts as the arylating agent (Table 3). A typical reaction was performed at 100 °C for 12 h, using 1.5 equiv Ph_2IBF_4, 5 mol % $Pd(OAc)_2$ in HOAc in a sealed tube and the worked-up reaction mixture was analyzed by ^{1}H NMR. The best conditions were found to be when using a large excess of iodonium salt (2.5 equiv) or long reaction times (64 h) (entries 2–4) where conversions reached ca. 60%. The use of microwave energy (entry 5) or additives such as silver salts[3a] (entries 7 and 8) or PPh_3 (entry 6) did not improve the yield. However, the product, starting material and further potential side products have thus far proven to be inseparable by standard column chromatography. Therefore, the synthesis and separation of **4b** and analogues are ongoing theme in our laboratory.

3. Conclusion

Chelation-assisted C–H activations of an aryl group is readily achieved using palladium in both stoichiometric and catalytic amounts. Mechanistically relevant palladacycles are easily isolated and can be characterized in solution and in the solid state.

4. Experimental section

4.1. General

All reactions were carried out in air and commercial grade solvents and materials were used except where specified. NMR spectra were measured on a Jeol EX270 spectrometer at 270 MHz (^{1}H) and 109 MHz (^{31}P). Electrospray Ionization (ESI) mass spectra were obtained on a model 300MSMS (Applied Biosystems, Warrington, UK) instrument. A TurboIon source was employed in positive ion mode with minimum heating. Samples containing 1 μg/μl were introduced as loop injections into a flow of 50:50 v/v acetonitrile/0.05% aqueous formic acid. The spectra and the theoretical isotope distributions were obtained with MassLynx v3.5 (Waters Associates, UK). The X-ray structure data for **3c** and **3d** have been deposited at the Cambridge Crystallographic Data Centre (CCDC 658227: **3c**; CCDC 658228: **3d**).

4.2. 3-Isopropyl-5-phenyl-1H-1,4-benzodiazepin-2(3H)-one[12]

2-Aminobenzophenone (1.97 g, 10.00 mmol), EEDQ (2.47 g, 10.00 mmol) and (L)-Boc–Gly–OH (2.17 g. 10.00 mmol) were combined in CH_2Cl_2 (20 ml) and stirred overnight at room temperature. The organic layer was washed successively with HCl (20 ml, 10% solution) and Na_2CO_3 (50 ml, saturated), dried over $MgSO_4$, filtered, and concentrated. The crude product was dissolved in TFA (30 ml) and DCM (20 ml) and allowed to stir for 2.5 h at room temperature. After concentration, the resulting oil was dissolved in CH_2Cl_2 (20 ml) and reconcentrated then redissolved in CH_2Cl_2 (20 ml). The organic layer was washed with Na_2CO_3 (50 ml, saturated), dried ($MgSO_4$ as above) and concentrated. Thereafter, to the resulting oil were added ammonium acetate (4.00 g, 51.89 mmol) and AcOH (30 ml) and the reaction mixture was stirred at room temperature overnight then concentrated under reduced pressure to afford an oil. The latter was dissolved in ethyl acetate (30 ml) and washed with a saturated solution of Na_2CO_3 (3×30 ml). The organic layer was dried over $MgSO_4$ and filtered. After concentration of the solvent and flash chromatography (10:1:1 DCM/ethyl acetate/hexane) a yellow solid was obtained (1.97 g, 71%). ^{1}H NMR ($CDCl_3$) δ 9.58 (1H, br s), 7.50–7.24 (9H, m), 3.12 (1H, d), 2.75 (1H, m), 1.17 (3H, d), 1.08 (3H, d).

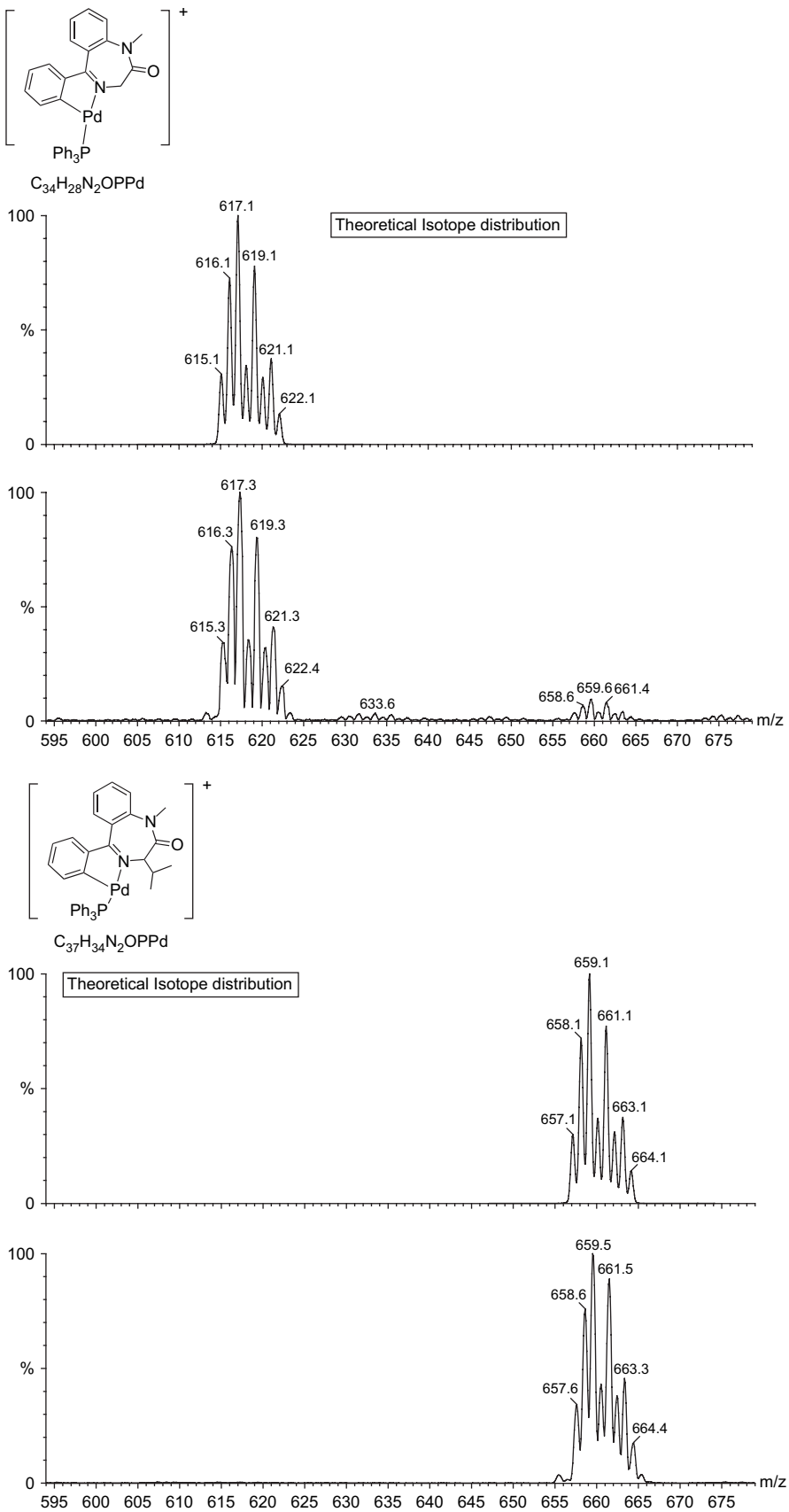
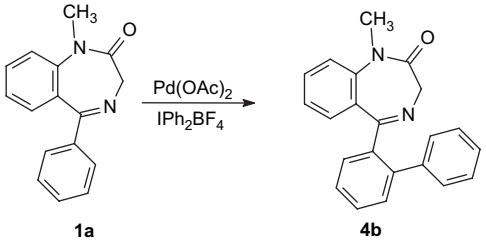


Figure 3. ESI of palladacycles **3a** and **3c**, showing both theoretical and experimentally derived values for the isotopomeric cluster of Pd^{+} ions.

Table 3
Attempted *ortho*-arylation of **1a**



1a **4b**

Entry	Ph_2IBF_4 (equiv)	Time (h)	Temp (°C)	Conversion (%)
1	1.5	12	100	40
2	2.5	12	100	59
3	1.5	64	100	61
4	2.5	60	100	61
5[a]	1.5	0.25	200	<10
6[b]	1.5	12	100	<10
7[c]	1.5	12	100	<10
8[d]	1.5	48	120	29

[a] In microwave.
[b] PPh_3 added (1 equiv).
[c] $AgBF_4$ added (1 equiv).
[d] AgOAc added (1 equiv).

4.3. 1-Methyl-3-(isopropyl)-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepin-2-one, *1c*

This was made on 1.19 mmol scale by stirring the product from previous step (297 mg, 1.19 mmol) with NaH (60 mg, 1.5 mmol of a 60% suspension in mineral oil) in DMF for 30 min under Ar. Methyl iodide (132 μl, 2.11 mmol) was added to the reaction mixture, which was stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate (20 ml) and washed with brine (3×20 ml), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Compound **1c** was obtained as yellow solid (314 mg, 74%). ^{1}H NMR ($CDCl_3$) δ 7.59–7.24 (9H, m), 3.41(3H, s), 3.08 (1H, d), 1.16 (3H, d), 1.02 (3H, d). ^{13}C ($CDCl_3$) δ 169.6, 167.6, 143.9, 138.9, 131.1, 130.2, 130.2, 129.6, 129.1, 128.1, 123.6, 121.3, 69.7, 35.0, 29.5, 20.3, 19.2. HRMS calcd 291.1492; $C_{19}H_{20}N_2O$ requires 291.1490.

4.4. Palladacycle *2c*

Palladacycle **2c** was made from **1c** on a 0.18 mmol scale by stirring with $Pd(OAc)_2$ (40 mg, 0.18 mmol) in AcOH (5 ml) for 1 h under reflux. The reaction was cooled, filtered (Celite) and the solvent was concentrated in vacuo. The resulting solid was dissolved in CH_2Cl_2 (10 ml) and the reaction mixture was reconcentrated. This was repeated twice. After reconcentration with diethyl ether, a red solid was obtained.

4.5. Formation of *3d* by reaction of *2c* with pyridine

Two drops of pyridine were added to a suspension of **2c** (185 mg, 0.18 mmol) in CH_2Cl_2 (5 ml) in a small glass vial. After 2 h, the organic layer was washed with water (5 ml), dried over $MgSO_4$ then filtered over Celite. Hexane was allowed to slowly diffuse into the CH_2Cl_2 solution and black crystals were obtained (0.054 g, 56%). ^{1}H NMR ($CDCl_3$) δ 9.07 (2H, d), 7.8–7.24 (8H, m), 6.21 (1H, d), 4.95 (1H, d), 3.40 (4H, m), 1.04 (3H, d), 0.76 (3H, d). Found: C, 57.74; H, 5.02; N, 7.63. ($C_{26}H_{27}N_3O_3Pd\cdot 0.5H_2O$ requires C, 57.31; H, 5.18; N, 7.71).

4.6. Reaction of *2c* with triphenylphosphine, *3c*

Compound **2c** was prepared on a 0.68 mmol scale and treated with triphenylphosphine (178 mg, 0.68 mmol) and stirred overnight in CH_2Cl_2 (10 ml). Thereafter, the reaction mixture was concentrated. Orange crystals were obtained from dichloromethane/hexane (196 mg, 42%). ^{1}H NMR ($CDCl_3$): δ 7.79 (6H, m), 7.56 (2H, m), 7.36 (11H, m), 7.10 (1H, m), 6.83 (1H, m), 6.55 (2H, m), 4.99 (1H, d), 3.46 (3H, s), 1.56 (3H, br s), 1.20 (1H, d), 0.96 (3H, d), 0.72 (3H, d). ^{31}P ($CDCl_3$): δ 40.69. Found: C, 62.11; H, 5.07; N, 3.51. ($C_{39}H_{37}N_2O_3PPd\cdot 0.5CH_2Cl_2$ requires C, 62.29; H, 5.03; N, 3.68).

4.7. Arylation reactions: attempted formation of *4b*

A mixture of **1a** (78 mg, 0.33 mmol), Ph_2IBF_4 (180 mg, 0.49 mmol)[13] and $Pd(OAc)_2$ (3 mg, 5 mol %) in AcOH (5 ml) was stirred for 64 h at 100 °C. Thereafter, the cooled reaction mixture was filtered over Celite and concentrated under reduced pressure. The resulting crude product was dissolved in CH_2Cl_2, washed with Na_2CO_3 then brine. The separated organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. (Selected regions) ^{1}H NMR for **1a** ($CDCl_3$) δ 4.76(1H, d), 3.69(1H, d), 3.39 (NMe). ^{1}H NMR for **1a/4b** mixture ($CDCl_3$) δ 4.11 (1H, d), 3.65 (1H, d), 3.12 (NMe) (assumed to be **4b**); 4.76 (1H, d), 3.69 (1H, d), 3.39 (NMe) (**1a**). EI *m/z* mixture of 326 and 250 amu for **4b** and **1a**, respectively. HRMS calcd 327.1492; $C_{22}H_{18}N_2O$ requires 327.1495.

Acknowledgements

Johnson Matthey is thanked for a generous loan of Pd salts. Dr. Matthew Gaunt (University of Cambridge) is thanked for useful discussions and for providing an initial sample of IPh_2BF_4. The EPSRC Mass Spectrometry Service Centre (Swansea) is thanked for the HRMS measurements.

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