Palladacycles as intermediates in catalyzed processes to polycyclic hydrocarbons

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Abstract: Palladacycles are key intermediates of catalyzed
domino processes that lead from simple starting materials to
polycyclic hydrocarbons. Annulated fulvenes, sesquifulvalenes
and benzopleiadienes as well as various aryl annulated propel-
lanes are efficiently accessible by these processes.

Palladium-catalyzed reactions can open up short and efficient pathways from
simple starting materials to complex target molecules (ref. 1). Very often
palladacycles are key intermediates of these processes. In these cases the ring
size of the palladacycles is of special importance.
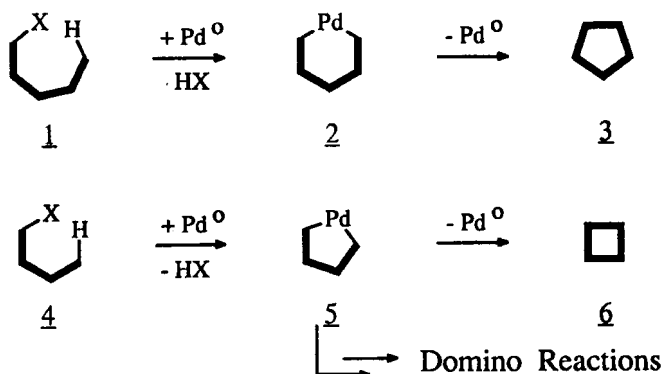
One of several ways (ref. 2) a palladacycle can be formed is the cyclopalla-
dation reaction of a substrate **1** with a reactive halogen atom X and a hydrogen
in a suitable distance. This is a very general reaction scheme: in principle the
centres connected with bold lines can be sp^2-hybridized as well as sp^3-hybri-
dized. Both, carbon atoms and heteroatoms are allowed, but in this brief over-
view we will focus on hydrocarbons exclusively.

A 6-membered palladacycle **2** rapidly transforms to a 5-membered ring **3** by re-
ductive elimination of Pd^0, that will reenter and therefore close the catalytic
cycle. 5-membered palladacycles **5** behave differently. The formation of 4-mem-
bered rings **6** is unfavourable, but not impossible as we will see below. The
5-membered palladacycles **5** can be very useful as reactive intermediates be-
cause they open up pathways to domino reactions (ref. 3) by reacting with a
second molecule of the substrate **4** or with added reagents. This becomes possible,
just because the competing reductive elimination is relatively slow. Various poly-
cyclic hydrocarbons and even propellanes are easily accessible by such processes.

The phenyl-substituted olefinic bromide <u>7</u> as well as the corresponding iodide is efficiently transformed by a Pd-catalyzed domino coupling process to the annulated fulvene <u>8</u>. 1 mol-% palladium acetate is sufficient. The active Pd⁰-catalyst is formed in situ under the reaction conditions. According to our mechanistic interpretation, a cyclometallation step leads to the 5-membered palladacycle <u>9</u> (Additional ligands are ommited for clarity). The reductive elimination of Pd⁰ is inhibited in this case, because the result would be a highly strained and antiaromatic benzocyclobutadiene. Instead, the palladacycle <u>9</u> adds another equivalent starting material presumably to give the Pd-intermediate <u>10</u> or its regioisomer with the palladium atom at the vinyl position. The final ring closure proceeds in the sense of an intramolecular Heck reaction (ref. 1).

a : 1 Mol - % Pd(OAc)₂ , K₂CO₃ , n-Bu₄NBr ,
   DMF , N₂ , 3 d , 100 °C .
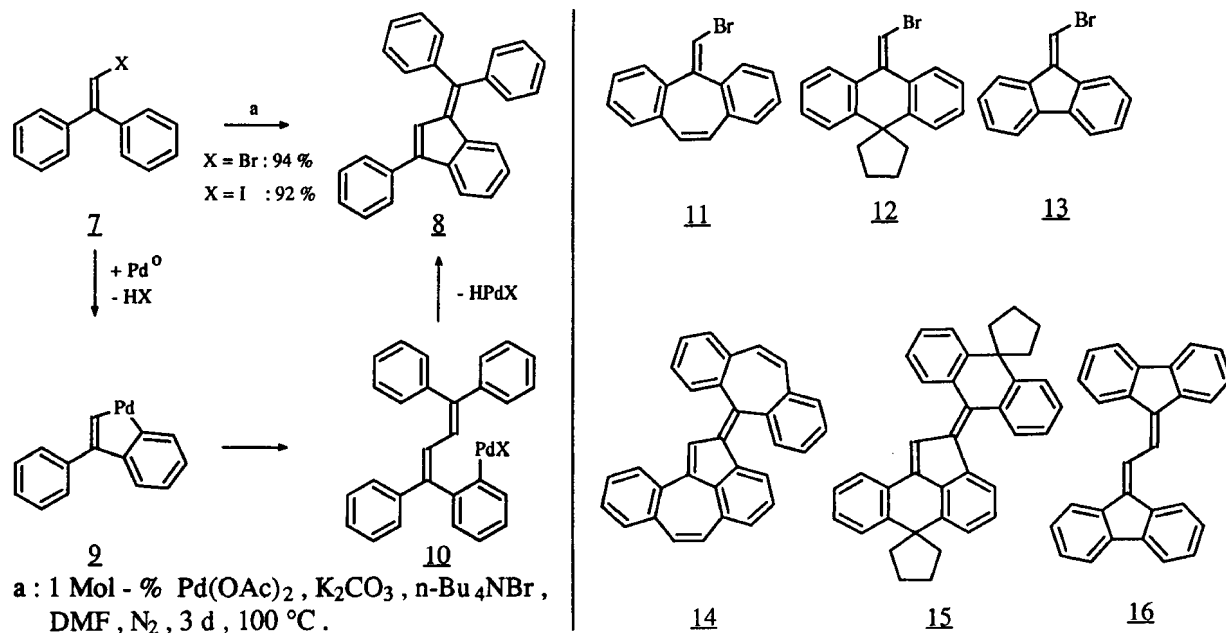
We have tested scope and limitations of this new synthesis for annulated fulvenes by introducing a bridge between the phenyl substituents. The substrates <u>11</u> and <u>12</u> with seven-membered and six-membered central rings give the same reaction and lead to the annulated fulvenes <u>14</u> and <u>15</u> with excellent yields in the range of 90 %. With the fluorenone derived substrate <u>13</u> we have finally reached the limit of the new annulation reaction. In this case the formation of an especially strained fulvene does not occur, probably because the cyclopalladation step is inhibited. Instead, a palladium catalyzed Ullmann coupling reaction (ref. 4) takes place leading to product <u>16</u>.

Through cross coupling reactions of olefinic bromides with substituted alkynes (for comparison: ref. 5) some interesting products become easily accessible. By the condensation of the suberenone derived substrate <u>11</u> with diphenylacetylene two main products are formed, the sesquifulvalene <u>17</u> and the benzopleiadiene <u>18</u>. The product ratio is strongly influenced by the reaction conditions. A higher concentration of the bromide <u>11</u> with an excess of the alkyne leads mainly to the formation of product <u>17</u> (64 %). A higher dilution and a one to one ratio of the coupling components, conditions that favour the cyclopalladation to <u>20</u>, are giving rise to the formation of the annulation product <u>18</u>. In the latter case <u>18</u> is isolated with 57 % yield, whereas <u>17</u> is a byproduct with less than 3 % yield.

The reaction of the fluorene system <u>13</u> is once again a special case. Surprisingly the spirocycle <u>19</u> is the main product confirmed by a x-ray structure. On the first glimpse this substituted cyclopentadiene looks rather complicate, but with palladacycles like <u>21</u> as reactive intermediates its formation is easily explained. According to semiempirical calculations <u>19</u> is indeed the thermodynamically most stable of the five double bond isomers.

17 18 19 20 21
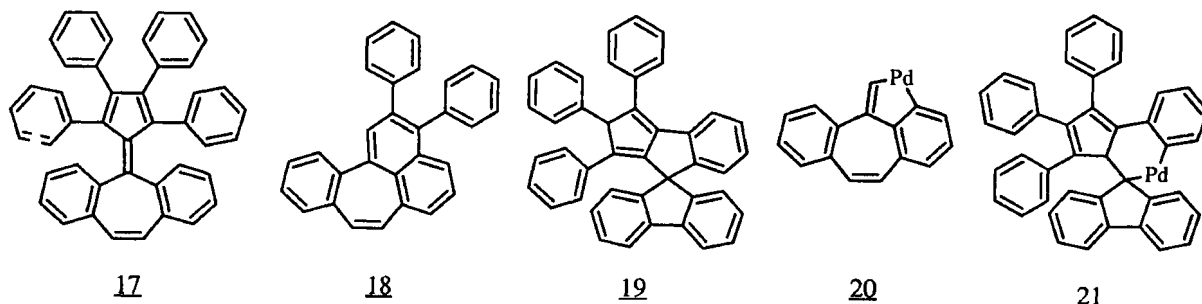
As an interesting target molecule for palladium catalyzed processes we have chosen the annulated pentalene system **25**. Because of the tedious and rather inefficient literature procedure (ref. 6) for its synthesis not much was known about the reactivity of this molecule. We have found that it can be synthesized in a single preparative step by coupling acenaphthylene **22** with 1,8-diiodonaphthalene **23**. Also in this case a palladacyle (**24**) is assumed as an intermediate.

cat. Pd⁰

22 23 24 25
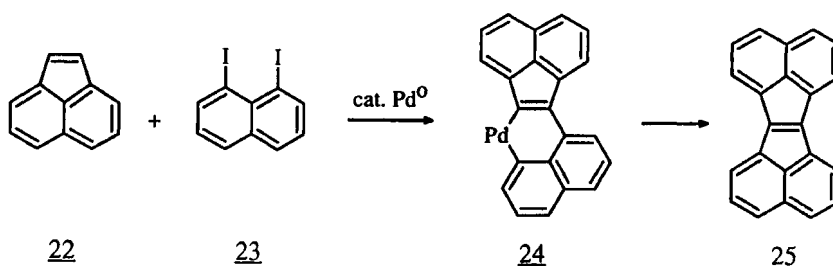
The central double bond of **25** offers opportunities for the construction of propellanes by various cycloaddition reactions. Surprisingly this double bond is reactive enough to take part in palladium-catalyzed annulation reactions (ref. 7). The purple hexacyclic hydrocarbon **25** reacts with iodobenzene under palladium catalysis to give the [4.3.3]propellane **26** with 72 % yield. This is quite an unusual reaction, in fact its the first example of an intermolecular Heck-type reaction at a tetrasubstituted double bond. Presumably a phenyl-palladium-species adds to the double bond of **25**, followed by a cyclometallation to the palladapropellane **29**. Addition of a second equivalent of iodobenzene finally leads to **26**.

26 27 28 29 30 31
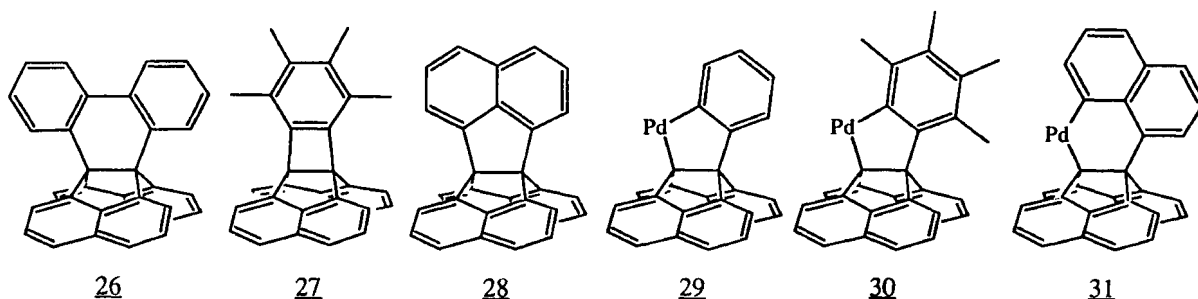
The reaction with iodoprehnitene (1-iodo-2,3,4,5-tetramethylbenzene) takes a surprizing course; as the only isolated product we obtained the [3.3.2]propellane **27** in 22 % yield. Presumably because of steric hindrance the addition of a second molecule aryl iodide to the palladapropellane intermediate **30** is inhibited. In this special case reductive elimination to the four-membered ring occurs.

A fascinating target is of course the symmetrical [3.3.3]propellane **28**. As it turned out, it is easily synthesized by the palladium-catalyzed reaction with 1-iodonaphthalene (37 % yield). In this case the six-membered palladacycle **31** is probably an intermediate.

The ring strain of the [3.3.3]propellane 28 is illustrated by the x-ray structure with bond angles of 109° at sp²-hybridized carbon centres and an elongated central bond with a length of 162 pm, compared to 154 pm of a normal C-C single bond. Figure 1 gives impressions of the crystal packing of 28: a perspective of the three-dimensional lattice and an overview of a space filling mono layer. Two of three naphthalene units have parallel slightly shifted neighbours in the distance of 350 pm, the typical van-der-Waals distance. The third one is directed to the axis of the next molecule. Despite of the impressive bond length of the central single bond the [3.3.3]propellane 28 is thermodynamically very stable. Until 400 °C no change of the colourless crystals occurs. Currently the reactivity of the synthesized propellanes is studied, especially with regard to the strained central single bond.
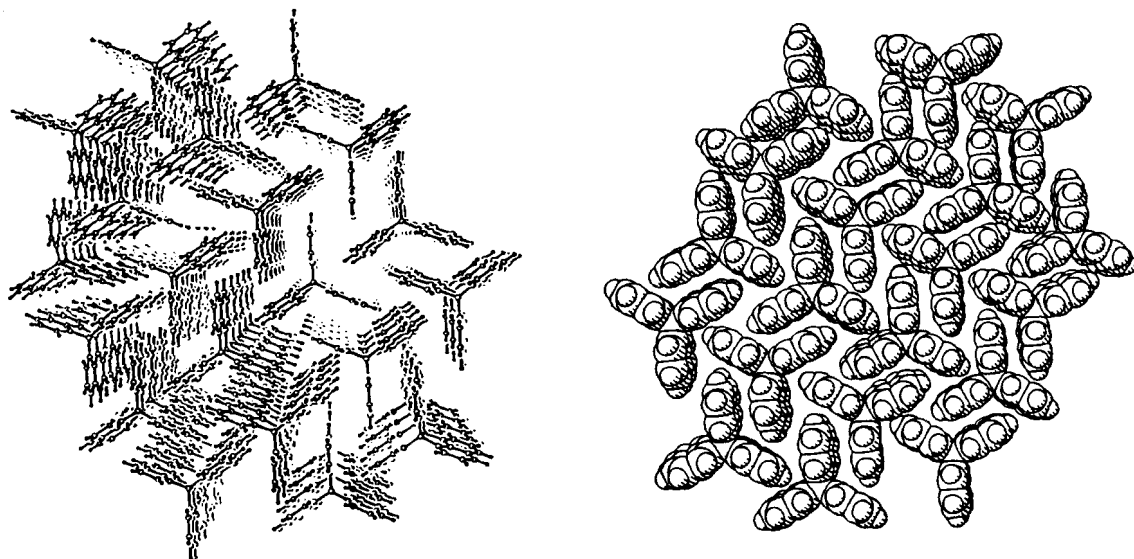

Fig. 1: Impressions of the crystal packing of the [3.3.3]propellane 28.

In summarization, we have described some domino coupling processes with palladacycles as reactive intermediates. These processes are useful for the construction of annulated 4-, 5- and 6-membered rings with special emphasis on fulvenes, sesquifulvalenes and benzopleiadienes. Finally we have introduced a new entry to strained propellanes.

ACKNOWLEDGEMENT

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