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Palladium-catalyzed sequential reactions: a new termination step leading to spirocyclohexadienone formation from *p*-iodophenol and bicyclo[2.2.1]heptene

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Abstract

A new palladium-catalyzed sequence of C–C bond-forming steps is reported which terminates in an unprecedented way. It occurs under mild conditions with complete regio- and stereoselectivity starting from *p*-iodophenol and bicyclo[2.2.1]heptene. The process leads to the synthesis of complex molecules containing one cyclohexadienone and one or two phenolic functions.

Keywords: Palladium catalysis; Spirocyclohexadienones; Termination; Aromatic substitution; C–H activation

1. Introduction

Palladium complexes have proved to be very versatile catalysts for carbon–carbon forming organic synthesis allowing the construction of complex molecules through formation of several C–C bonds in one-pot reactions under mild conditions [1]. These reactions are characterised by an initiation step consisting of the formation of a palladium–carbon bond, followed by formation of C–C bonds in sequence and by a termination step which liberates the organic product from the metal. In the past years we described several palladium-catalyzed sequences [2], generally consisting of the oxidative addition of organic halides to palladium(0) as the initiation step, more than one C–C bond formation step, mainly involving insertion and aromatic substitution, and various types of termination. The most common terminations are β-hydrogen elimination, C–C coupling and nucleophilic attack on acyl functions. When the metal is liberated in the initial oxidation state the reaction becomes a catalytic one. The discovery of other types of termination is particularly important not only to work out new catalytic processes but also in view of the introduction of new functionalities in organic substrates. In the present paper we report a palladium-catalyzed reaction which terminates with the formation of a spirocyclohexadienone.

2. Results and discussion

Unusual molecules, containing one cyclohexadienone and one or two phenolic functions, were obtained from *p*-iodophenol (**1**) and bicyclo[2.2.1]heptene (**2**) (Scheme 1) via an extraordinary sequence of regio- and stereoselective elementary steps (including aromatic C–H activation), all occurring on a palladium catalyst under mild conditions.

Compound **1** readily reacts with **2** in DMF in the presence of $Pd(OAc)_2$ (10 mol% in respect to **1**) as catalyst and K_2CO_3 as a base at 60°C to give compounds **3** and **4** (the latter as a mixture of two diastereoisomers in 1:1 ratio) in a 41 and 29% isolated yield, respectively. The stereochemistry of the bicycloheptyl ring always is *exo*.

The *para* position of the hydroxyl group is critical because it gives rise to the cyclohexadienone group in the termination step. In principle this termination could

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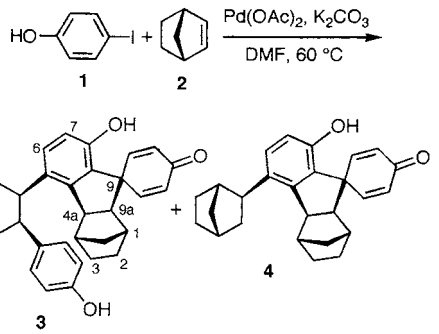
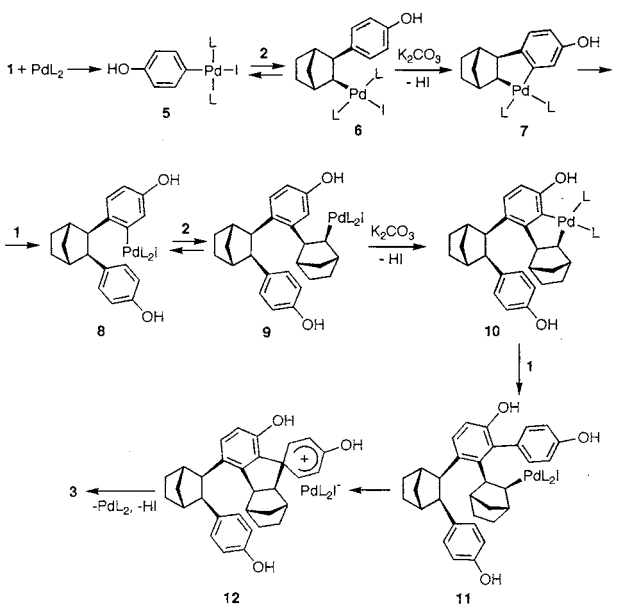


Scheme 1.

also occur with an *ortho* hydroxyl group but in this case ring closure to form a methanohexahydrodibenzofuran is preferred [3].

The course of the reaction leading to **3** can be viewed as shown in Scheme 2.

The first step of the catalytic cycle, consisting of oxidative addition of **1** to the in situ generated palladium(0) to form **5**, is followed by insertion of **2** to afford the *cis*,*exo*-arylbicycloheptylpalladium(II) species **6**. In the presence of a suitable base, such as K_2CO_3, complex **6** readily undergoes ring closure with C–H activation of the aryl nucleus to the five-membered alkylaromatic palladacycle **7**. The arylpalladium species **8** resulting from reaction of **7** with a second molecule of *p*-iodophenol (**1**) further inserts **2** thus yielding an arylbicycloheptylpalladium complex **9**, which forms a new alkylaromatic palladacycle **10**, again by activation of an aromatic C–H bond in the same way as **6** gives **7**. Species **11**, obtained by reaction of **10** with a third molecule of **1**, evolves to **3** likely through **12**. The last step leading to spirocyclohexadienone formation is unprecedented in palladium chemistry [4]. An arenonium complex **12**, formed by C-attack on the substituted 4-carbon of a phenolic group is likely to be the intermediate. Arenonium complexes of Pt [5a] and Rh [5b] have been isolated by van Koten and Milstein.

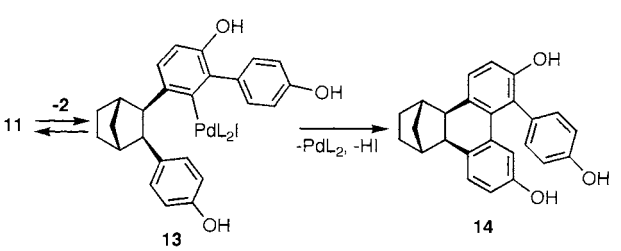


Scheme 2.

All complexes involved in the **1**–**7** and **8**–**10** sequences were proven to be present in reactions with iodobenzene derivatives under similar conditions [6a–q]. Oxidative addition of **1** to palladium(0) is a well known general process [6a]. Bicycloheptene and bicycloheptadiene insertion into arylpalladium bonds has also been previously described [6b–d]. Palladacycle formation is in agreement with the process of electrophilic aromatic substitution observed for type **6** complexes [6e–g], where a Wheland-type intermediate might be involved [6h]. The reaction of *p*-iodophenol (**1**) with the alkylaromatic palladacycle **7** leading to **8** might involve a palladium(IV) intermediate [6i–q], analogous to that observed with allyl and benzyl halides [6j–k]. Evidence for the intermediacy of species **8**–**10** was obtained for differently substituted compounds of the same class by isolating the reductive elimination product of type **10** complexes (a benzocyclobutene derivative [6n]).

According to our previous experience referring to a new method of aromatic functionalization in the *o*,*o*′-positions via palladacycles [7], we should have expected bicycloheptene expulsion from **11** to **13** as shown in Scheme 3.

This process, which corresponds to the reverse bicycloheptene insertion equilibrium, is triggered by the steric hindrance generated by the two substituents in the *ortho* positions of the aromatic ring. The expected reaction, however, did not occur working at 60°C, the presence of the OH group in the *para* position making the spirocyclic ring formation the preferred pathway. Only on raising the temperature were we able to observe it, although to a limited extent. Accordingly, when the reaction was carried out at 105°C compound **14** was formed in a 15% yield along with other by-products (Scheme 3) [8]. The latter is particularly significant because it necessarily derives from **13**, which in its turn results from the bicycloheptyl-bonded palladium complex **11** through bicycloheptene deinsertion [9]. That an isomer of **11**, deriving from reaction of the *p*-hydroxyphenyl group with the bicycloheptyl rather than the aryl site of the metallacycle **10** is a possible intermediate



Scheme 3.

to **3**, in the same way observed for the conversion of **7** into **8**, can be ruled out on the ground that recent observations by ourselves [7c] have shown that the presence of an alkyl or aryl substituent in *ortho* to the C–C bond of an alkylaromatic palladacycle shifts phenyl migration from the bicycloheptyl to the aryl moiety.

To confirm the structure of the spirocyclohexadienone the crystal structure of **3** was solved and is depicted in Fig. 1. The cyclohexadienone ring forms a dihedral angle of 90.7(1)° with the five-membered ring. The molecules in the unit cell are joined together by strong O–H···O= hydrogen bonds. Disordered water molecules were also found.

The course of the reaction leading to compound **4** differs from that shown in Scheme 2 in that the acidity of the phenolic group allows cleavage of the initial palladacycle (**7**) with protonation of the bicycloheptyl moiety and palladation of the aryl moiety (Scheme 4). This process was also previously observed [6h, 7c, 10] and recently reported for a different palladacycle [11]. The subsequent steps then occur according to the same pattern shown in Scheme 2.

In conclusion, the discovery of a new termination step has allowed us to gain access to unusual structures containing both cyclohexadienone and phenolic groups through a catalytic reaction from *p*-iodophenol and bicycloheptene. Although mechanistically quite complex, the reaction offers a tool for the synthesis of functionalized molecules through catalytic sequences. The scope of the reaction is currently investigated.

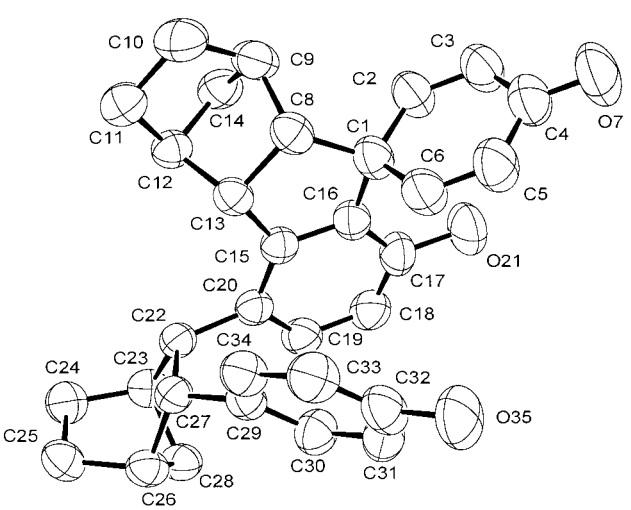
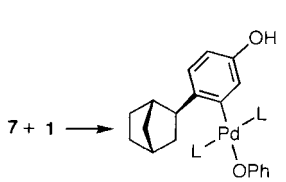


Fig. 1. Crystal structure of **3**.



Scheme 4.

3. Experimental

All reactions were carried out under nitrogen by using standard Schlenk techniques. DMF was dried over 4 Å molecular sieves. Melting points were determined by the capillary method on an electrothermal apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 20°C on a Brucker AC 300 spectrometer at 300.1 and 75.5 MHz, respectively. Proton and carbon assignments are based on ^{1}H-^{1}H and ^{13}C-^{1}H correlation experiments. The IR spectra were recorded on a Nicolet 5PC FT-IR spectrophotometer. Mass spectra were obtained with a Finnigan MAT SSQ10 spectrometer. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

3.1. General procedure

To a solution of palladium acetate (40 mg, 0.18 mmol) and potassium carbonate (250 mg, 1.8 mmol) in dry dimethylformamide (2 ml) was added *p*-iodophenol (400 mg, 1.82 mmol) and bicyclo[2.2.1]heptene (170 mg, 1.81 mmol) dissolved in dry DMF (2 ml). After stirring at 60°C for 20 h, the mixture was diluted with CH_2Cl_2, washed with 5% H_2SO_4, dried over Na_2SO_4, filtered and concentrated. Flash chromatography (9:1 hexane–ethyl acetate) afforded 115 mg (41%) of **3** and 98 mg (29%) of **4**, the latter as a mixture of two diastereoisomers in a 1:1 ratio (determined by NMR). Compound **3**, after isolation by flash chromatography, was crystallized from a mixture of hexane and acetone (ca. 3:1) and gave clear, colorless crystals suitable for X-ray determination.

One pure diastereoisomer of **4** readily crystallized from CH_2Cl_2.

3.1.1. exo-2,3,4,4a,9,9a-Hexahydro-8-hydroxy-5-{2″-[3″-(p-hydroxyphenyl)]exo-bicyclo[2.2.1]heptyl}spiro[1-H-1,4-methanofluorene-9,4′-cyclo-2′,5′-hexadien-1′-one] (3)

M.p. (hexane–acetone) 265–266°C (dec.); ^{1}H-NMR (acetone-d_6): δ 7.92 (s, 1H, OH (C4‴)), 7.69 (s, 1H, OH (C8)), 7.12 (dd, $J = 10.2, 2.8$, 1H, H3′), 6.90 (d, $J = 8.3$, 1H, H6), 6.68 (part AA′ of an AA′BB′ system, 2H, H2‴, H6‴), 6.43 (part BB′ of an AA′BB′ system, 2H, H3‴, H5‴), 6.37 (d, $J = 8.3$, 1H, H7), 6.17 (dd, $J = 10.2, 1.9$, 1H, H2′), 5.91 (dd, $J = 9.8, 2.8$, 1H, H5′), 5.78 (dd, $J = 9.8, 1.9$, 1H, H6′), 3.54 (br d, $J \sim 9.3$, 1H, H2″), 3.26 (br d, $J \sim 9.7$, 1H, H3″), 3.21 (d, $J = 7.5$, 1H, H4a), 2.59 (m, 1H, H1″), 2.50 (m, 1H, H4), 2.31 (m,

1H, H4″), 2.23 (d quintets, $J = 10.0$, 1.9, 1H, H7″ *syn*), 2.19 (m, 1H, H1), 2.01 (d, $J = 7.5$ Hz, 1H, H9a), 1.80–1.38 (m, 8H, 2H5″, 2H6″, 2H3, H2 *exo*, H7″ *anti* centred at 1.44, $J = 10.0$, 1.5), 1.21 (d quintets, $J = 10.0$, 1.8, 1H, H10 *syn*), 1.15–1.08 (m, 1H, H2 *endo*), 1.06 (d quintets, $J = 10.0$, 1.5, 1H, H10 *anti*); ^{13}C-NMR (acetone-d_6): δ 186.2 (CO), 155.7 (q), 155.2 (C5′), 152.5 (q), 151.9 (C3′), 147.0 (q), 135.1 (q), 131.8 (q), 130.5 (C2‴, C6‴), 128.7 (C2′), 128.6 (q), 128.4 (C6), 124.2 (C6′), 114.7 (C3‴, C5‴), 114.2 (C7), 56.4 (C9a), 55.8 (C4a), 55.1 (C9), 54.9 (C3″), 50.4 (C2″), 44.5 (C4″), 41.8 (C1″), 41.5 (C4), 41.3 (C1), 37.5 (C7″), 34.5 (C10), 31.4, 31.2, 29.9, 29.5; IR (KBr, cm^{-1}) ν 3337, 1654, 1605; MS (CI), $[M + H^+]$ 465. Anal. Calc. for $C_{32}H_{32}O_3$: C, 82.73; H, 6.94. Found: C, 82.43; H, 6.97%.

*3.1.2. exo-5-(2″-exo-Bicyclo[2.2.1]heptyl)-2,3,4,4a,9,9a-hexahydro-8-hydroxyspiro[1-H-1,4-methanofluorene-9,-4′-cyclo-2′,5′-hexadien-1′-one] (**4**)*

A mixture of two diastereoisomers: ^{1}H-NMR ($CDCl_3$): δ 7.31, 7.28 (2dd, $J = 10.2$, 2.9, 1H, H3′), 7.10, 7.09 (2d, $J = 8.3$, 1H, H6), 6.70 (dd, $J = 9.8$, 2.9, 1H, H5′), 6.58 (d, $J = 8.3$, 1H, H7), 6.51, 6.50 (2dd, $J =$ 10.2, 1.9, 1H, H2′), 6.18 (dd, $J = 9.8$, 1.9, 1H, H6′), 4.53 (brs, 1H, OH), 3.45, 3.44 (2d, $J = 7.7$, 1H, H4a), 2.85 (m, 1H, H2″), 2.62, 2.59 (2m, 1H, H4), 2.39 (m, 2H, H9a, H4″), 2.30 (m, 1H, H1), 2.26, 2.19 (2m, 1H, H1″), 1.85–1.50 (m, 9H, H3″ *endo*, H7″ *syn*, 2H5″, 2H6″, H3 *exo*, H2 *exo*, H3″ *exo*), 1.45–1.11 (m, 5H, H3 *endo*, H10 *syn*, H2 *endo*, H7″ *anti*, H10 *anti*); IR (KBr, cm^{-1}): ν 3337, 1653, 1609; MS (CI), $M + H^+$ 373. Anal. Calc. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.62; H, 7.60%. (**4**) Pure diastereoisomer from CH_2Cl_2: m.p. 273–274°C (dec.); ^{1}H-NMR ($CDCl_3$): δ 7.28 (dd, $J = 10.2$, 2.9, 1H, H3′), 7.09 (d, $J = 8.3$, 1H, H6), 6.70 (dd, $J = 9.8$, 2.9, 1H, H5′), 6.58 (d, $J = 8.3$, 1H, H7), 6.50 (dd, $J = 10.2$, 1.9, 1H, H2′), 6.18 (dd, $J = 9.8$, 1.9, 1H, H6′), 4.53 (s, 1H, OH), 3.44 (d, $J = 7.7$, 1H, H4a), 2.83 (dd, $J = 8.8$, 5.5, 1H, H2″), 2.62 (m, 1H, H4), 2.38 (m, 2H, H9a, H4″), 2.30 (m, 1H, H1), 2.26 (m, 1H, H1″), 1.81 (ddd, $J = 11.5$, 8.8, 2.1, 1H, H3″ *endo*), 1.68 (1H partly overlapped, H7″*syn*), 1.66–1.51 (m, 7H, 2H5″, 2H6″, H3 *exo*, H2 *exo*, H3″ *exo*), 1.45–1.29 (m, 2H, H3 *endo*, H10 *syn* centred at 1.32), 1.25–1.11 (m, 3H, H2 *endo*, H7″ *anti* centred at 1.23, H10 *anti* centred at 1.16); ^{13}C-NMR ($CDCl_3$): δ 185.6, 154.2, 151.0, 150.7, 145.6, 137.3, 129.7, 129.6, 127.6, 124.9, 114.9, 56.2, 55.5, 54.5, 43.5, 43.1, 40.7, 40.6, 40.1, 36.8, 36.1, 34.0, 30.7, 29.5, 28.7, 28.5.

*3.1.3. exo-7,10-Dihydroxy-1,2,3,4,4a,12b-hexahydro-8-(p-hydroxyphenyl)-1,4-methanotriphenylene (**14**)*

^{1}H-NMR (acetone-d_6): δ 8.36 (s, 1H, OH), 7.57 (s, 1H, OH), 7.26 (vbr dd, 1H), 7.15 (s, 1H, OH), 7.06 (brd, $J = 8.3$, 1H, H5), 6.94 (br d, $J = 8.2$, 1H, H12), 6.92 (vbr d, 1H), 6.90 (vbr d, 1H), 6.82 (d, $J = 8.3$, H6), 6.80 (vbr d, 1H), 6.51 (dd, $J = 8.2$, 2.5, 1H, H11), 6.47 (d, $J = 2.5$, 1H, H9), 3.20 (br d, $J = 9.8$, 1H, H4a), 3.04 (br d, $J = 9.8$, 1H, H12b), 2.26 (m, 1H, H1), 2.17 (m, 1H, H4), 1.69–1.56 (m, 4H, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.43 (d quintets, $J = 9.7$, 1.7, 1H, H13 *syn*), 0.99 (d quintets, $J = 9.7$, 1.4, 1H, H13 *anti*); MS (CI), $[M + H^+]$ 371. Anal. Calc. for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 80.88; H, 6.00%.

3.2. Molecular structure determination

Crystal structure analysis of **3** was performed on an Enraf–Nonius CAD4 diffractometer equipped with a PC. Data collection was at room temperature with Cu–K_α radiation. Corrections for Lorentz and polarisation effects were applied. The structure was solved with direct methods with SIR97 [12] and refined with the CRYSRULER package [13] using SHELX93 [14]. Most H atoms were found in a ΔF map; the remainder were put in their calculated positions and all refined isotropically. Crystal dimension: $0.09 \times 0.14 \times 0.29$ mm; crystal system monoclinic; space group $C2/c$; unit cell dimensions and volume, $a = 18.366(3)$, $b = 10.253(3)$, $c =$ 30.881(3) Å, $\beta = 91.97(3)°$, $V = 5811.7$ Å^3; $Z = 8$, $F(000) = 2240$, λ(Cu–K_α) = 1.5418 Å; scan type $\varpi - 2\theta$; scan speed range = 0.5–16° min^{-1}; θ range for data collection = 3–70°; recorded reflections = 5504; observed reflections ($\geq 2\sigma I$) = 2519; $R = 0.049$ $R_w =$ 0.20, $w = 1/[2\sigma^2 F_o^2 + (aP)^2 + bP]$, $a = 0.1148$, $b = 0.96$, $P = [\max(F_o^2, 0) + F_c^2]/3$; GOF = 1.038; $\Delta\rho_{min/max} =$ $-0.16/0.29$ e Å^{-3}.

Atomic coordinates of atoms and a complete listing of bond distances and angles are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

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[8] At 105°C compounds **3** (28%), **4** (12%) and **14** (15%) were formed together with small amounts of other products corresponding to different sequences. They have been characterized but are not reported here for reasons of clarity.

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