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Palladium-catalyzed norbornene–carbon monoxide co-oligomerization initiated by aryl groups and terminated by double bond formation

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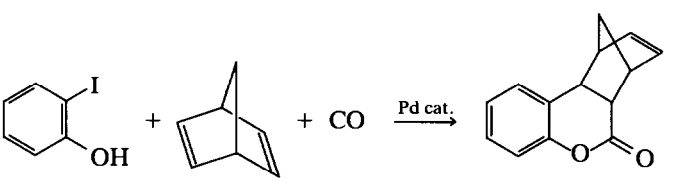
Abstract

The use of *m*-iodophenol as initiator in palladium-catalyzed norbornene–carbon monoxide oligomerization in the presence of potassium acetate unexpectedly leads to termination by double bond formation in spite of the limitations to β-H-*anti* elimination. The presence of *endo* products points to preliminary *exo*-to-*endo* isomerization through enolization. The X-ray structure of one stereoisomer (Ia) is given.

Introduction

In the course of our studies aimed at elucidating new methods of carbonylation of bifunctional systems in the presence of unsaturated compounds, we had previously reported new heterocyclic syntheses starting from *o*-iodophenols [1] (see, for example, eq. 1).



(1)

We wondered whether new olefin and carbon monoxide insertions could lead to rings larger than six-membered. To this end it appeared necessary to increase the distance between the hydroxide and iodide functions. We therefore started from *m*-iodophenol as the initiator of a norbornene–carbon monoxide co-oligomerization, which eventually would lead to cyclic products by reaction of an acylpalladium intermediate with the phenolic hydroxyl. Our previous experience [2] had, in

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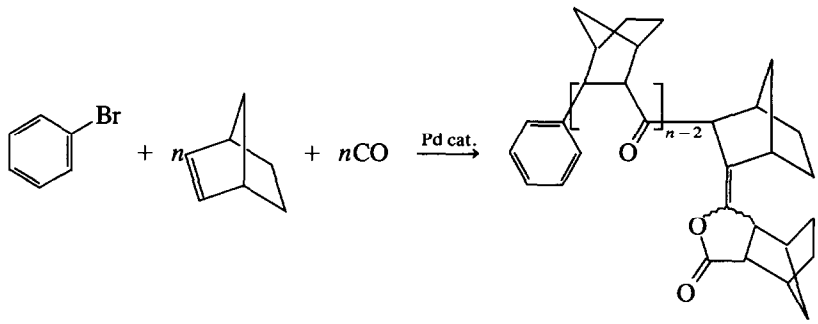
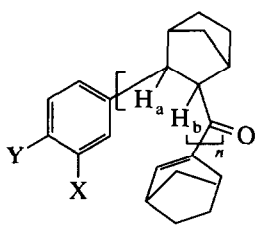
fact, shown that bromobenzene could start a norbornene–carbon monoxide co-oligomerization, which, in the absence of active hydrogen sources, terminated by formation of enol-lactones (eq. 2). β-Hydrogen elimination did not occur, as expected in view of the reluctance of the *cis,exo* acylnorbornylpalladium system to undergo *anti* elimination [3].



(2)

Results

m-Iodophenol was caused to react with norbornene and carbon monoxide in anisole as solvent at 80°C under atmospheric pressure in the presence of $[Pd(PPh_3)_4]$ as catalyst and of a stoichiometric amount of potassium acetate. Carbon monoxide was absorbed to an extent of *ca.* 250% of the stoichiometric amount for 1:1 reaction with iodophenol. Separation of the products by column chromatography with hexane/ethyl acetate 80/20 as eluent allowed the isolation of fractions containing a terminal norbornene unit of type I.



I X = OH; Y = H
III X = OMe; Y = H
IV X = H; Y = OH
V X = H; Y = H

a $n = 1$, H_a, H_b *endo*
b, c $n = 1$, H_a *endo*, H_b *exo*, two stereoisomers

The products I with $n = 1$ (Ia, Ib, c) could be isolated as a 1:1:0.5 mixture of three stereoisomers. Further separation led to isolation of a *cis,exo* isomer (Ia), the crystal structure of which is described below (Fig. 1). The other two isomers (Ib, c) were recognized by NMR spectroscopy as *exo,endo* products: both showed very similar absorptions and the characteristic coupling (J *ca.* 4 Hz) of the proton of the carbonyl-bonded carbon with the vicinal bridgehead proton. Ib and Ic must therefore correspond to diastereoisomers arising from the relative positions of the two alicyclic groups.

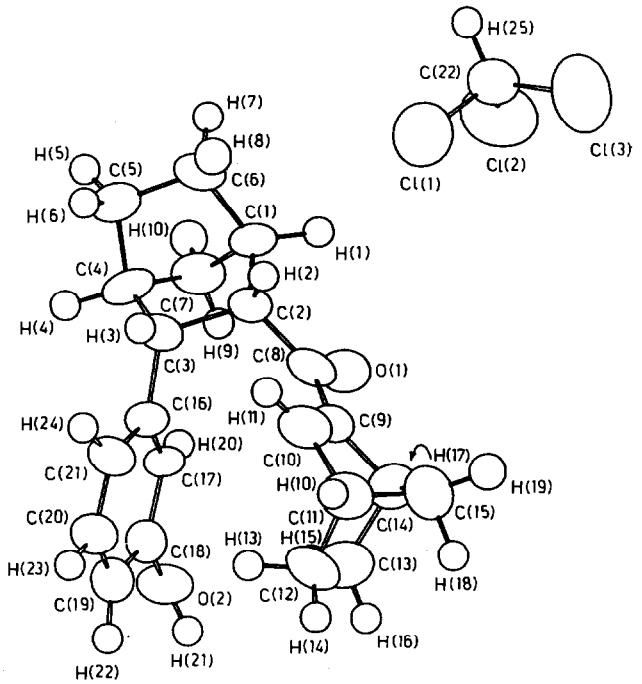
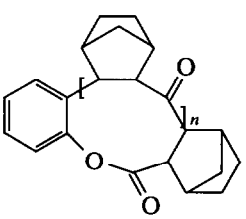


Fig. 1. X-Ray crystal structure of Ia·$CHCl_3$: perspective view of the molecule.

The $n = 1$ fraction of I accounted for *ca.* 45% of the total reaction product at 72% conversion of *m*-iodophenol. Higher homologues were also present in the following chromatographic fractions (20–25%, see Experimental) as shown by the mass spectrum (DCI: desorption chemical ionization), which revealed a series of oligomers, differing by 122 from each other with M^+ 1650 as the heaviest significant peak. The largest proportions, confirmed by SEC (size exclusion chromatography), had $n = 4$–7.

These fractions also contained a series of cyclic oligomers II of comparable amounts, with most having $n = 5$–7.



II

The residue (20–25%, eluted with ethyl acetate) contained higher members of the I and II series. Minor series were also found, however, one corresponding to open-chained oligomers, terminated by OH and COOH, and another with no aromatic ring. The last must have been initiated by H from HI or MeCOOH eliminated in the final step of the catalytic process, as previously observed [2].

Further analysis of the higher oligomeric fractions was carried out by SEC and HPLC–FDMS (field desorption mass spectrometry). The former technique con-

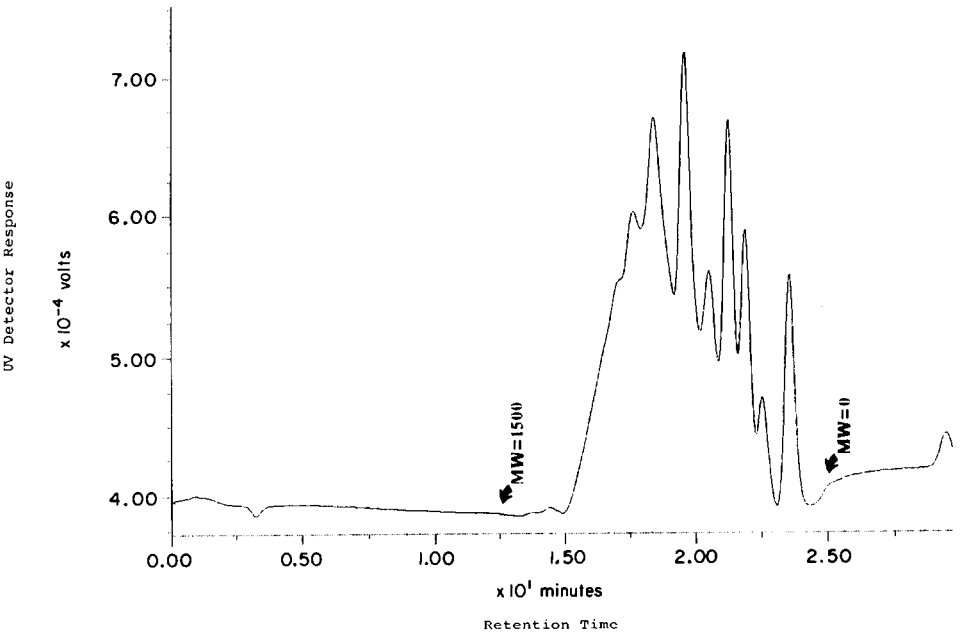
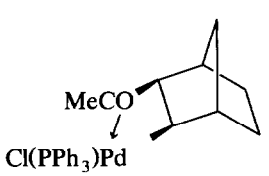


Fig. 2. SEC traces for I and II oligomeric series (methylcyclohexane fraction).

firmed the molecular weight distribution (Fig. 2). The latter allowed separation and identification of the first three members of the I and II series as isomeric mixtures. In a few cases some of these isomers (I, $n = 2, 3$) could be detected individually.

Other experiments were carried out in order to provide more information on the tendency to form double bonds in the termination step. Protection of the phenolic group as the methyl ether curtailed the formation of compounds III (methylated I). *p*-Iodophenol showed a behaviour similar to that of *m*-iodophenol (compounds IV). The addition of phenol to a reaction mixture containing iodobenzene in place of iodophenol led to oligomers of type I, although the stereoisomers corresponding to the first member (Va, b, c) were present only to a limited extent (6%). Benzoic anhydride was found as a by-product, and arose from the mixed benzoic acetic anhydride. Double bond formation did not occur in the absence of phenol.

The acetylnorbornylpalladium complex VI [4], chosen as a model compound, did not give elimination to acetylnorbornene, even upon treatment with a stoichiometric amount of potassium iodide, but it did do so when a stoichiometric amount of potassium acetate was added. Further addition of phenol (1 : 1 : 1) gave the same result, but in a shorter time (30 min rather than 3 h).



VI

Table 1

Bond distances (Å) and angles (°) with e.s.d.s in parentheses.

C(1)–C(2)	1.53(1)	C(10)–C(11)	1.50(2)
C(1)–C(6)	1.55(1)	C(11)–C(12)	1.53(2)
C(1)–C(7)	1.55(1)	C(11)–C(15)	1.53(1)
C(2)–C(3)	1.60(1)	C(12)–C(13)	1.50(2)
C(2)–C(8)	1.54(1)	C(13)–C(14)	1.55(2)
C(3)–C(4)	1.53(1)	C(14)–C(15)	1.57(1)
C(3)–C(16)	1.51(1)	C(16)–C(17)	1.39(1)
C(4)–C(5)	1.51(2)	C(17)–C(18)	1.40(1)
C(4)–C(7)	1.51(1)	C(18)–C(19)	1.38(1)
C(5)–C(6)	1.57(1)	C(18)–O(2)	1.37(1)
O(1)–C(8)	1.20(1)	C(19)–C(20)	1.40(1)
C(8)–C(9)	1.48(1)	C(20)–C(21)	1.37(1)
C(9)–C(10)	1.30(1)	C(22)–C(1)	1.74(1)
C(9)–C(14)	1.51(1)	C(22)–Cl(2)	1.74(1)
		C(22)–Cl(3)	1.71(1)
C(6)–C(1)–C(7)	100.0(9)	C(10)–C(11)–C(15)	99.8(1.0)
C(2)–C(1)–C(7)	101.3(8)	C(10)–C(11)–C(12)	106.4(1.0)
C(2)–C(1)–C(6)	108.4(9)	C(12)–C(11)–C(15)	100.9(1.1)
C(1)–C(2)–C(8)	112.1(8)	C(11)–C(12)–C(13)	102.8(1.1)
C(1)–C(2)–C(3)	103.3(8)	C(12)–C(13)–C(14)	105.3(1.3)
C(3)–C(2)–C(8)	116.5(8)	C(9)–C(14)–C(13)	105.0(1.1)
C(2)–C(3)–C(16)	117.0(9)	C(13)–C(14)–C(15)	98.0(1.1)
C(2)–C(3)–C(4)	101.3(8)	C(9)–C(14)–C(15)	98.6(1.0)
C(4)–C(3)–C(16)	115.6(9)	C(11)–C(15)–C(14)	93.4(1.0)
C(3)–C(4)–C(7)	105.6(9)	C(3)–C(16)–C(21)	120.1(9)
C(3)–C(4)–C(5)	107.8(1.0)	C(3)–C(16)–C(17)	121.8(9)
C(5)–C(4)–C(7)	100.3(1.0)	C(17)–C(16)–C(21)	118.1(9)
C(4)–C(5)–C(6)	102.8(1.0)	C(16)–C(17)–C(18)	120.1(9)
C(1)–C(6)–C(5)	102.9(1.0)	O(2)–C(18)–C(17)	119.9(9)
C(1)–C(7)–C(4)	94.9(8)	C(17)–C(18)–C(19)	122.0(1.0)
O(1)–C(8)–C(2)	120.7(9)	O(2)–C(18)–C(19)	118.2(9)
C(2)–C(8)–C(9)	118.9(9)	C(18)–C(19)–C(20)	117.2(9)
O(1)–C(8)–C(9)	120.4(1.1)	C(19)–C(20)–C(21)	121.5(9)
C(8)–C(9)–C(14)	121.3(9)	C(16)–C(21)–C(20)	121.0(1.0)
C(8)–C(9)–C(10)	129.8(1.1)	Cl(1)–C(22)–Cl(2)	110.4(6)
C(10)–C(9)–C(14)	108.9(1.0)	Cl(1)–C(22)–Cl(3)	110.2(6)
C(9)–C(10)–C(11)	108.1(1.1)	Cl(2)–C(22)–Cl(3)	110.6(7)

X-Ray structure of cis-exo Ia (n = 1).

In Fig. 1 is depicted the asymmetric unit, consisting of the title compound and one solvate chloroform molecule. The two bicyclic rings display a set of C(sp^3)–C(sp^3) bond distances ranging from 1.50(1)–1.60(1) Å (Table 1). In spite of the wide range, most of these values are in agreement with those previously reported [5,6] and larger variations can be rationalized by the lower accuracy of the data. Bond angles are typical of norbornane derivatives, in particular, at the bridging carbons C(7), 94.9(8)° and C(15), 93.4(1.0)°. The values larger than the tetrahedral involving C(2) and C(3) can be ascribed to steric hindrance between adjacent rings. The double bonds C(9)–C(10) and C(8)–O(1), 1.30(1) and 1.20(1) Å, respectively, are normal; the system of atoms C(2), C(8), O(1), C(9), C(10), C(11), C(14), H(11) shows only small displacements from planarity and the phenyl ring, including O(2),

Table 2

Possible hydrogen bonds (Å and °).

Donor-H	Donor · · · Acceptor	H · · · Acceptor	Donor-H · · · Acceptor
O(2)–H(21)	O(2) · · · O(1^{i})	H(21) · · · O(1^{i})	O(2)–H(21) · · · O(1^{i})
1.14	2.74(1)	1.92	125
C(17)–H(20)	C(17) · · · O(1^{i})	H(20) · · · O(1^{i})	C(17)–H(20) · · · O(1^{i})
1.01(9)	3.21(1)	2.37(8)	140(7)
C(22)–H(25)	C(22) · · · O(2^{ii})	H(25) · · · O(2^{i})	C(22)–H(252/O(2^{ii})
0.99(11)	3.19(2)	2.26(11)	156(7)

Equivalent positions: (*i*) $-x, -y, 1-z$; (*ii*) $x, y, z-1$.

is planar. The organic molecule is folded in such a way that the atoms C(8), C(9), C(10), C(12), and C(13) are located close to the phenyl ring: the shortest C · · · H contacts are C(20) · · · H(13) 3.05(9) Å and C(18) · · · H(15) 3.04(9) Å. This is in agreement with the low-frequency NMR shifts observed for H(13) and H(15). The molecules show Van der Waals contacts and hydrogen bonds (Table 2) involving both oxygen atoms and the chloroform molecule.

Discussion

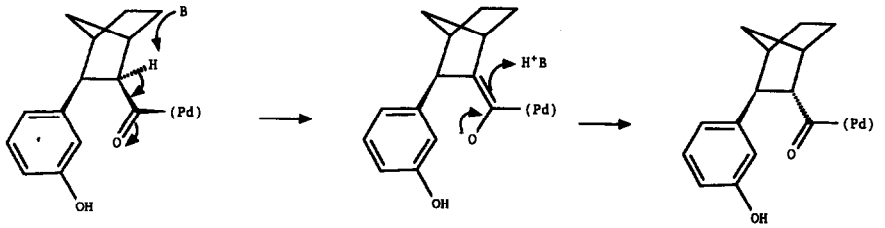
Although olefin–carbon monoxide radical [7] or coordination [8–10] copolymerizations have been studied for several years, until recently little was known about the initiation and termination steps and the detailed stereochemistry of the process. Palladium-catalyzed norbornene–carbon monoxide copolymerization was recently studied by Sen [9], who proposed a new catalytic system, based on cationic Pd. Another type of catalyst enabled us to clarify the course of a Pd-catalyzed norbornene–carbon monoxide cooligomerization (eq. 2) [2]. Styrene–carbon monoxide copolymerization with a cationic Pd catalyst was recently shown to be diastereoselective [10].

On the basis of our previous results [2] we expected that in the presence of a phenolic group in the growing chain, copolymerization should terminate with the formation of esters.

Although our experiments led in part to cyclic oligomers II, the most curious result was the termination type by double bond formation (as in oligomers I) which was also unexpected on the basis of literature [3]. However, the concomitant formation of *exo,exo* (Ia) and *exo,endo* (Ib, c) products throws light on the process involved. *Exo* to *endo* isomerization most likely occurs by enolization, according to Scheme 1.

The acetate anion (B) should attack the proton of the first norbornane unit α to the carbonyl group. Enolization [11] and re-protonation at the *exo* position lead to the *endo* form.

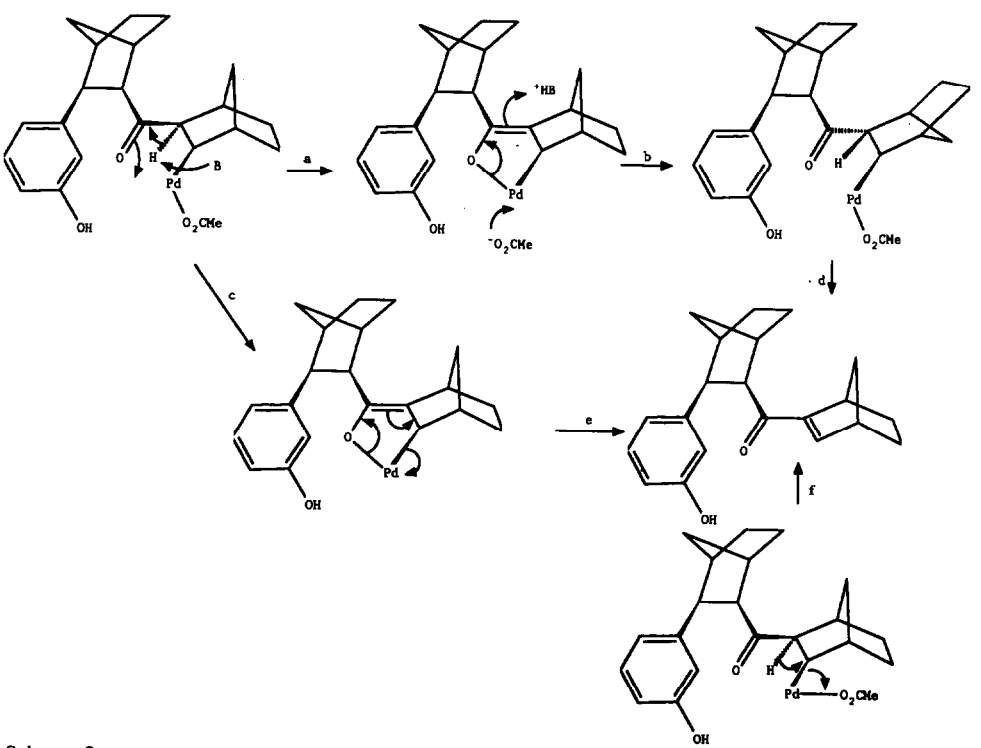
To justify elimination by double bond formation it seems reasonable to apply the same process to the proton of the terminal norbornene unit α to the carbonyl group (Scheme 2). Enolization through path a, promoted by palladacycle formation, and re-protonation would lead to the *syn* arrangement required for the



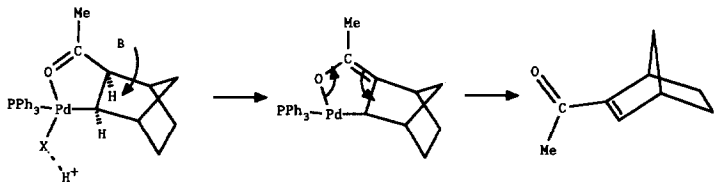
(Pd) = $Pd(PPh_3)O_2CMe$

Scheme 1.

favoured type of elimination (path b, d). Direct elimination from the palladacycle (path c, e) is a possible alternative. Support is provided by the elimination reaction of the model palladium complex VI (Scheme 3). Finally, the disfavoured elimination process (Scheme 2, path f) might have some relevance, depending on the degree of association of the base system [12]. In our case, the system that is responsible for enolization is based on potassium acetate. Its activity is increased by the presence of phenolic groups, as shown in the reaction of the model complex VI. Our interpretation is that there is a concerted action of the acetate anion on



Scheme 2.



X = Cl or O_2CMe

Scheme 3.

the norbornyl proton α to the carbonyl and of the phenolic group on the X leaving group (halide or acetate) (Scheme 3).

When the phenolic group is not contained in the aromatic iodide, as with the reaction of iodobenzene with norbornene and CO, a similar effect can be observed on adding phenol in the presence of potassium acetate. The latter alone does not cause double-bond formation, however, as far as we could ascertain. A subtle balance of factors, including acetate solubility and the coordination power of the phenolic oxygen seems responsible for the observed effects.

The isolation of trimers I suggests some stereochemical considerations. Only one (*syn*) of the two possible *exo,exo* isomers (Ia) was obtained, while two (*syn* and *anti*) forms of the *exo,endo* isomer were found (Ib, c). These results can be rationalized in terms of steric hindrance to the coordination of one face of norbornene in the former case, which results in the stereoselective formation of the *syn* isomer only, while in the latter case the *trans* arrangement of the phenyl and carbonyl groups removes the steric hindrance to coordination of either face of norbornene. It is tempting to hypothesize that in the absence of an enolization process the subsequent norbornene units react with the same face, so the *exo,exo* members would correspond to an isotactic polymerization.

In conclusion, our catalytic method effects β-hydrogen elimination in hindered systems. The results reported here may have practical significance in so far that β-hydrogen elimination could be used to control chain length in polyketones as well as in other polymers, and in general to favour the formation of olefinic compounds in competition with other reactions.

Experimental

All reactions were conducted under dinitrogen. ACS grade reagents were used without further purification, with the exception of acetyl chloride which was distilled prior to use. All solvents were dried over 4 Å molecular sieves [13], except for benzene, which was dried over sodium benzophenone ketyl. Once dry and deoxygenated, the solvents were stored under dinitrogen over 4 Å molecular sieves. Column chromatography and flash chromatography were performed on silica gel 60 (Merck, 70–230 and 230–400 mesh ASTM respectively). Analytical TLC was carried out on precoated Merck silica gel 60 plates. Capillary GLC analyses were carried out with a Dani 3900 instrument equipped with a flame ionization detector, using Supelco SPB-1 columns. HPLC analyses were carried out on a Perkin–Elmer Series 2 Liquid Chromatograph equipped with a Perkin–

Elmer 75 UV detector (set at 232 nm), using a Spherisorb ODS-2 column (15 cm × 0.4 cm). The flow rate was 1.0 ml/min. SEC analyses were conducted on a Waters 510 instrument equipped with a Waters 486 UV detector (set at 254 nm), using two Ultrastyragel 100 Å columns connected in series (Millipore, range of separation 50–1500 Da, 30 cm × 0.8 cm). ^{1}H and ^{13}C-NMR spectra were recorded respectively on Bruker AMX-400 and AC-100 spectrometers at 400 and 25.2 MHz. Chemical shifts are given in parts per million ($\delta_{TMS} = 0$) using as internal reference the solvent peak referred to TMS (^{1}H-NMR: 7.25 ppm for chloroform, 7.20 ppm for benzene-d_5; ^{13}C-NMR: 77.1 ppm for chloroform-d). GC-MS and DCI-MS spectra were recorded on a Finnigan 1020 and a Finnigan-MAT 8400 spectrometer, respectively. HPLC-FDMS spectra were recorded on a Varian-MAT 311-A spectrometer. Infrared spectra were taken on a Nicolet 5PC FTIR instrument. Melting points were measured on an Electrothermal apparatus and are uncorrected. The X-ray crystal structure was determined using a Siemens AED single crystal automated diffractometer.

General experimental procedure

[$Pd(PPh_3)_4$] 54 mg (0.047 mmol) and potassium acetate, 228 mg (2.32 mmol) were mixed under dinitrogen with *m*-iodophenol, 445 mg (2.02 mmol) and norbornene, 579 mg (6.15 mmol) in 5 ml of anisole. Dinitrogen was replaced by CO and the mixture was heated for 7 h at 80°C with stirring. CO absorption amounted to 120 ml. Addition of water, and extraction with dichloromethane, followed by drying over sodium sulphate and solvent evaporation afforded 986 mg of product in the form of a red, gummy solid. Flash chromatography on silica (hexane/ethyl acetate 80/20) gave the following products: unreacted *m*-iodophenol (126 mg); Ia, b, c ($n = 1$, 206 mg); higher oligomers ($n \geq 2$, 278 mg), divided in two fractions (115 and 163 mg).

The residue (205 mg, eluted with ethyl acetate) also contained higher oligomers ($n \geq 3$). The yield of the three isomers Ia, b, c was 46%, based on converted *m*-iodophenol. Further purification by column chromatography (silica gel, eluent dichloromethane/ethyl acetate 95/5) gave 115 mg of Ib + Ic (Ib : Ic = 2 : 1) and 77 mg of Ia. Ia: mp = 180°C (from $CHCl_3$); GC-MS (70 eV): *m/e* 308 (M^+, 10), 241(20), 213(10), 121(100), 107(30), 93(75), 77(20), 65(60); FTIR ($CHCl_3$): 3350, 1650, 1598 cm^{-1}.

^{1}H-NMR spectrum (benzene-d_6, numbering according to Fig. 1): δ 0.30 (m, 1H, H_{13}), 0.53 (m, 1H, H_{15}), 0.83 (dd, further split, 1H, H_{19}, $J = 12.8$ Hz, $J = 0.9$ Hz), 1.08 (m, 1H, H_8), 1.16–1.22 (m, 2H, $H_6 + H_{18}$), 1.29–1.35 (m, 2H, $H_{14} + H_{16}$), 1.38 (bd, 1H, H_{10}, $J = 10.2$ Hz), 1.44–1.53 (m, 2H, $H_5 + H_7$), 2.24 (bd, 1H, H_1, $J = 1.4$ Hz), 2.63 (m, 1H, H_{17}), 2.67 (bd, 1H, H_4, $J = 2.5$ Hz), 2.72 (dt, 1H, H_9, $J = 10.2$ Hz, $J = 1.7$ Hz), 2.85 (d, 1H, H_2, $J = 10.2$ Hz), 3.10 (dd, 1H, H_3, $J = 10.2$ Hz, $J = 1.4$ Hz), 3.37 (bs, 1H, H_{12}), 6.11 (bs, 1H, OH), 6.29 (d, 1H, H_{11}, $J = 3.3$ Hz), 6.52 (bd, 1H, H_{22}, $J = 7.6$ Hz), 6.64 (ddd, 1H, H_{24}, $J = 8.1$ Hz, $J = 2.5$ Hz, $J = 1.0$ Hz), 6.72 (t, 1H, H_{20}, $J = 2.1$ Hz), 6.90 (t, 1H, H_{23}, $J = 7.8$ Hz).

In $CDCl_3$ the signals of H_{13} and H_{15}, indicative of the *syn,exo* isomer Ia, are found at lower frequencies: δ −0.04 (H_{13}), 0.50 (H_{15}). ^{13}C-NMR spectrum ($CDCl_3$) and DEPT: Positive (CH) and negative (CH_2) phases are indicated by + and − respectively; & indicates that the signal (quaternary carbon) disappears: δ 23.5(−), 25.0(−), 28.9(−), 31.3(−), 37.5(−), 39.0(+), 39.8(+), 43.8(+), 43.9(+),

47.6(−), 54.9(+), 55.7(+), 113.3(+), 115.3(+), 121.2(+), 129.0(+), 144.3(&), 148.3(+), 149.8(&), 155.7(&), 199.0(&).

Ib: GC-MS (70 eV): *m/e* 308 (M^+, 20), 241(30), 213(20), 121(40), 107(45), 93(90), 77(35), 65(100).

Ic: GC-MS (70 eV, ⋆): *m/e* 308 (M^+, 15), 241(25), 213(20), 121(30), 107(40), 93(80), 77(30), 65(100).

Ib, c: FTIR ($CHCl_3$): 3450, 1705, 1652 cm^{-1}.

^{1}H-NMR spectrum (benzene-d_6, numbering analogous to that of Fig. 1; the signals due to the minor isomer are indicated by an asterisk): δ 0.78 (m, H_{13}), 0.82–0.91 (m, $H_8 + H_{19}$ both isomers + H_{13}⋆), 0.99 (m, H_{14} both isomers), 1.10 (m, H_{15}), 1.20–1.65 (m, $H_5 + H_6 + H_7 + H_{10} + H_{16} + H_{18}$ both isomers + H_{15}⋆), 1.84 (bd, H_9 both isomers, $J = 10.1$ Hz), 2.31 (bs, H_1), 2.46 (bs, H_4 both isomers), 2.47 (m, H_1⋆), 2.61 (bs, H_{17} both isomers), 3.28 (ddd, H_2⋆, $J = 5.7$ Hz, $J = 4.1$ Hz, $J = 1.7$ Hz), 3.33 (ddd, H_2, $J = 5.7$ Hz, $J = 4.1$ Hz, $J = 1.7$ Hz), 3.50 (s, H_{12}⋆), 3.60 (s, H_{12}), 3.72 (d, H_3, $J = 5.7$ Hz), 3.75 (d, H_3⋆, $J = 5.7$ Hz), 6.25 (d, H_{11}⋆, $J = 3.3$ Hz), 6.35 (d, H_{11}, $J = 3.3$ Hz), 6.58 (m, H_{24} both isomers), 6.70 (t, H_{20}, $J = 2.0$ Hz), 6.75 (t, H_{20}⋆, $J = 2.0$ Hz), 6.85 (m, H_{22} both isomers), 7.06 (t, H_{23}⋆, $J = 7.9$ Hz), 7.07 (t, H_{23}, $J = 7.9$ Hz).

^{13}C-NMR spectrum ($CDCl_3$): δ 23.5(−), 23.7(−, ⋆), 24.5(−, both isomers), 24.9(−), 25.1(−, ⋆), 29.6(−), 29.9(−, ⋆), 39.3(−, ⋆), 39.4(−), 40.6(+), 41.3(+, ⋆), 42.7(+, both isomers), 43.3(+, ⋆), 43.7(+), 43.8(+), 43.9(+, ⋆), 46.5(+), 47.1(+), 47.6(−, ⋆), 47.7(−), 59.3(+), 59.7(+, ⋆), 112.7(+, both isomers), 114.1(+), 114.2(+, ⋆), 118.6(+, both isomers), 129.5(+, both isomers), 147.0(+, ⋆), 147.3(+), 148.3(&), 148.4(&, ⋆), 149.5(&), 150.0(&, ⋆), 156.3(&, both isomers), 198.1(&), 199.1(&, ⋆).

For crystal structure determination of Ia, the crystal was sealed in a glass capillary in the presence of the mother liquid ($CHCl_3$) and mounted in a random orientation on the diffractometer. The resulting crystal data and details concerning data collection and refinements are quoted in Table 3. After the usual data reduction, an empirical correction was applied using Walker and Stuart's method [14]. The structure was solved by direct methods and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms; hydrogen were located from a ΔF map and introduced in the last refinement cycles, only H(21) was not refined. The final atomic coordinates are quoted in Table 4, the atomic scattering factors were taken from *International Tables* [15]. The calculations were performed on a Gould 33/77 with SHELX [16], ORTEP [17] and PARST [18] programs. As consequence of thermal motion and disordering effects of the chlorine atoms of chloroform, the final R index (0.0845) was rather high.

The two fractions containing higher oligomers were characterized by DCI-MS. In the former (115 mg, ≈ 12% yield calculated for a $\overline{PM}$ corresponding to $n = 4$, based on converted *m*-iodophenol) both linear (I) and cyclic (II) oligomers were present with the following distribution: $2 \leq n \leq 8$ for I with the major peak (100%) corresponding to $n = 4$; $1 \leq n \leq 9$ for II with the major peaks (70%) for $n = 4, 5$. Linear type I oligomers were more abundant than cyclic type II ones.

The last fraction (163 mg, ≈ 11% yield calculated for a $\overline{PM}$ corresponding to $n = 7$) also contained linear and cyclic oligomers, but with a different distribution: $2 \leq n \leq 9$ with the major peaks for $n = 7$ for both I and II, with the same intensity.

DCI-MS of the residue (205 mg, ≈ 10% yield calculated for a $\overline{PM}$ correspond-

Table 3

Experimental data from the crystallographic analysis

Formula	$C_{22}H_{25}Cl_3O_2$
MW	427.8
Space group	$P2_1ln$
a, Å	15.240(7)
b, Å	10.192(5)
c, Å	14.384(6)
β, °	107.94(7)
U, Å^3	2125(2)
Z	4
D_c	1.337
D_m	1.36
Reflections for lattice parameters number	25
θ range	22.6–40.1
$F(000)$	896
Temperature, K	294
Diffractometer	Siemens AED
Crystal size, mm	0.49×0.85×0.95
μ, cm^{-1}	40.91
Scan speed, ° min^{-1}	4–12
Scan width, °	1.3+0.35tgθ
θ range, °	3–65
h, range	−20,20
k, range	0,14
l, range	0,19
Standard reflection	2 0 −8
Max. intensity variation, %	4
Scan mode	ω–2θ
No. of reflections measured	3581
No. of reflections used in the refinement	1689
No. of refined parameters	323
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0845
$R' = [\Sigma w(\Delta F^2)/\Sigma wF^2{}_o]^{1/2}$	0.0895
k, g in $w = k/[\sigma^2(F_o) + gF_o{}^2]$	1.25,3.37×10^{-4}
Max., min. height in final ΔF map, eÅ^{-3}	0.35, −0.22

ing to $n = 10$) showed that it was composed mainly of the two kind of oligomers with few impurities. Their distribution was the following: $3 \leq n \leq 12$ for I with the major peak (50%) for $n = 9$; $2 \leq n \leq 13$ for II with the major peak (100%) for $n = 10$. In this case the cyclic oligomers were dominatant to the linear ones.

Extraction of the crude product obtained from the general procedure described above was also carried out using hexane and methylcyclohexane (30 ml each) in sequence at refluxing temperature for 2 h. The methylcyclohexane fraction (282 mg, white powder) contained most of the oligomers with only small amounts of residual *m*-iodophenol and triphenylphosphine oxide, while the hexane fraction (297 mg) mainly consisted of *m*-iodophenol and light oligomeric fractions. The methylcyclohexane fraction was analyzed using three different techniques:

DCI-MS: both linear and cyclic oligomers were present with $1 \leq n \leq 9$ for I and $2 \leq n \leq 9$ for II, with maximum intensity at $n = 4$ for I and $n = 3$ for II.

Table 4

Fractional atomic coordinates with e.s.d.s in parentheses

Atom	x	y	z
Cl(1)	−0.0463(3)	0.1911(5)	−0.0163(3)
Cl(2)	−0.1601(4)	0.3280(4)	−0.1831(3)
Cl(3)	−0.1730(4)	0.0516(5)	−0.1699(4)
O(1)	0.0177(5)	−0.1776(7)	0.4676(5)
O(2)	0.0353(5)	0.1399(7)	0.7302(5)
C(1)	0.1920(7)	−0.1839(12)	0.4459(8)
C(2)	0.1751(7)	−0.2411(11)	0.5372(7)
C(3)	0.2420(8)	−0.1565(11)	0.6240(8)
C(4)	0.2770(7)	−0.0526(12)	0.5666(9)
C(5)	0.3501(9)	−0.1159(15)	0.5305(11)
C(6)	0.2928(8)	−0.2142(14)	0.4503(8)
C(7)	0.2005(9)	−0.0355(11)	0.4709(8)
C(8)	0.0724(8)	−0.2411(10)	0.5296(7)
C(9)	0.0410(7)	−0.3235(9)	0.5978(7)
C(10)	0.0878(8)	−0.4025(11)	0.6662(8)
C(11)	0.0226(9)	−0.4611(12)	0.7147(8)
C(12)	−0.0044(12)	−0.3497(15)	0.7721(10)
C(13)	−0.0589(12)	−0.2591(18)	0.6927(12)
C(14)	−0.0585(9)	−0.3250(12)	0.5955(9)
C(15)	−0.0645(10)	−0.4713(12)	0.6264(10)
C(16)	0.2017(6)	−0.1039(9)	0.7003(7)
C(17)	0.1345(6)	−0.0064(10)	0.6787(7)
C(18)	0.1014(7)	0.0433(10)	0.7520(7)
C(19)	0.1341(7)	−0.0001(12)	0.8470(7)
C(20)	0.2023(7)	−0.0977(11)	0.8679(7)
C(21)	0.2345(9)	−0.1489(11)	0.7964(7)
C(22)	−0.1003(9)	0.1836(11)	−0.1417(8)

SEC: 15 mg of the methylcyclohexane extract were dissolved in 3 ml of tetrahydrofuran and 5 μl of such solution were analyzed by SEC. The various oligomers were partially separated (Fig. 2), and a molecular weight distribution comparable to that measured by DCI-MS (200÷1100 Da) was obtained.

HPLC-FDMS: an analytical HPLC separation of the various components was carried out using the following gradient programme: acetonitrile/water from 60/40 to 90/10 with a 2%/min^{-1} increase of acetonitrile. For HPLC-FDMS determinations a few drops of a 0.05 M solution of ammonium acetate/acetic acid were added to the eluting solvent as ion source. In this way several components of the mixture were identified as MH^+: linear oligomers having m/e 309 ($n = 1$), 431 ($n = 2$), 553 ($n = 3$), 675 ($n = 4$); cyclic oligomers having m/e 337 ($n = 1$), 459 ($n = 2$), 581 ($n = 3$).

IIIa, b, c. [$Pd(PPh_3)_4$] 241 mg (0.208 mmol) and potassium acetate, 1.02 g (10.4 mmol) were mixed under dinitrogen with m-iodoanisole, 1.23 ml (10.4 mmol), and norbornene, 1.22 g (12.9 mmol) in 10 ml of anisole. Dinitrogen was replaced by CO and the mixture was heated for 4 h at 80°C with stirring. CO absorption amounted to 240 ml. Using the work-up procedure described above, 3.4 g of a red oil were obtained. Purification of the crude product by flash chromatography on silica

Table 5

Significant MS and ^1H NMR spectroscopic data for compounds III-Va, b, c

Compound	GC-MS (20 eV)	^1H NMR ($CDCl_3$)
IIIa	*m/e* 322 (M^+, 50), 294(15), 255(80), 227(20), 121(100), 93(70), 77(30), 65(50).	δ −0.15 (m, 1H, H_{13}), 0.48 (m, 1H, H_{15}), 3.70 (s, 3H, OCH_3)
IIIb, c	*m/e* 322 (M^+, 75), 294(20), 255(100), 227(40), 121(30), 93(75), 77(35), 65(70). *m/e* 322 (M^+, 70), 294(30), 255(90), 227(30), 122(30), 93(60), 77(40), 65(100).	δ 0.88 (m, H_{13}, both isomers), 3.66 (s, OCH_3, *), 3.68 (s, OCH_3)
IVa	*m/e* 308 (M^+, 20), 252(40), 241(70), 121(90), 107(100), 93(60), 77(40), 65(90).	δ −0.15 (m, 1H, H_{13})
IVb, c	*m/e* 308(M^+, 35), 252(80), 241(40), 121(40), 107(90), 93(100), 76(30), 65(90). *m/e* 308 (M^+, 30), 252(85), 241(40), 121(80), 107(100), 93(60), 77(60), 65(75).	
Va	*m/e* 292 (M^+, 10), 225(60), 197(30), 121(100), 93(45), 91(75), 77(30), 65(60).	
Vb, c	*m/e* 292 (M^+, 25), 225(80), 197(35), 121(30), 93(55), 91(100), 77(35), 65(90). *m/e* 292 (M^+, 15), 225(60), 197(45), 121(30), 93(55), 91(100), 77(30), 65(90).	

(hexane/dichloromethane 50/50) afforded 335 mg of a mixture of IIIa, b, c (yield 10%, Table 5).

IVa, b, c. [$Pd(PPh_3)_4$] 58 mg (0.05 mmol) and potassium acetate, 203 mg (2.06 mmol), were mixed under dinitrogen with *p*-iodophenol, 444 mg (2.02 mmol) and norbornene, 611 mg (6.49 mmol) in 6 ml of anisole. Dinitrogen was replaced by CO and the mixture was heated for 4 h at 80°C with stirring. CO absorption amounted to 144 ml. Using the work-up procedure described above, 1.19 g of a red solid were obtained. Purification of the crude product by flash chromatography on silica (hexane/ethylacetate 80/20) afforded 232 mg of a mixture of IVa, b, c (Table 5) and 54 mg of unreacted *p*-iodophenol. Yield 43% based on converted *p*-iodophenol.

Va, b, c. [$Pd(PPh_3)_4$] 47 mg (0.04 mmol) and potassium acetate, 344 mg (3.50 mmol), were mixed under dinitrogen with iodobenzene, 340 μl (3.00 mmol), phenol, 288 mg (3.06 mmol) and norbornene, 330 mg (3.50 mmol) in 9 ml of anisole. Dinitrogen was replaced by CO and the mixture was heated for 12 h at 80°C with stirring. CO absorption amounted to 90 ml. Using the same work-up procedure as above, 418 mg of a red solid were obtained. Purification of the crude by flash chromatography on silica (dichloromethane as eluent) afforded 56 mg of a mixture of Va, b, c (Table 5, 6% yield) and 19 mg of benzoic anhydride.

The acetylnorbornyl palladium complex VI was prepared according to a published procedure [4].

Treatment of VI with potassium acetate: to VI (54 mg, 0.1 mmol) dissolved in 3 ml of benzene were added 80 μl of a benzene solution of hexadecane (0.0137 mmol) as internal standard. To this solution, stirred under dinitrogen at 25°C, 10 mg (0.1 mmol) of potassium acetate were added, and the reaction was then followed by GLC. The solution slowly turned brown with the formation of a suspension of palladium particles. After 3 h the amount of 2-acetylnorbornene

detected was 95% of the theoretically available and did not change further with time. Only two reaction products were detected by GLC and identified by GC-MS: 2-acetylnorbornene [19] and biphenyl ($\approx$ 20% with respect to 2-acetylnorbornene).

Treatment of VI with potassium acetate/phenol: the reaction was conducted under exactly the same conditions as above, adding 10 mg (0.1 mmol) of phenol to the solution. The reaction was complete in 30 min. The products detected were the same as above with the addition of phenyl acetate as byproduct ($\approx$ 50% with respect to 2-acetylnorbornene).

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