Diastereoselective Formation of a New Palladacycle and Organic Compounds Derived from Vinylcarbenoids as Side Products in the Synthesis of 5-Pallada-*trans*-tricyclo[4.1.0.0^{2,4}]heptanes from Acceptor-Substituted Cyclopropenes

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When a large excess of dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate was used in a reaction with $Pd_2(dba)_3$•$CHCl_3$, only reduced yields of tetramethyl 3,3,7,7-tetramethyl-5-pallada-*trans*-tricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate were obtained. One side product was the new palladacyle dimethyl 3-(3,4-bis(methoxycarbonyl)-5,5-dimethyl-5*H*-furan-2-ylidene)-1,1,4,4-tetramethyl-6-oxodihydro-5-oxa-2-palladacyclopropa[*c*]pentalene 1a,3a-dicarboxylate; its structure was proven by a crystal structure analysis of the bpy complex. The other side products are the 1,3,5-triene methyl (*Z*)-2-isopropylidene-3,4,5-tris-(methoxycarbonyl)-6-methylhepta-3,5-dienecarboxylate (**14**), the allyl alcohol dimethyl (*Z*)-2-(1-hydroxy-1-methylethyl)but-2-enedicarboxylate (**15**), the 1,3-diene dimethyl (*Z*)-2-isopropenylbut-2-enedicarboxylate (**16**), and the allyl ether dimethyl 2-isopropylidene-3-methoxysuccinate (**17**). The formation of most of these side products is interpreted as the reaction of a vinyl carbenoid species with O-nucleophiles.

Introduction

In reactions of transition metals (TM) with cyclopropenes **1** (Chart 1)[1] often an oxidative insertion of the metal into the C2−C3 or C1−C3 bond is observed. Thus, either metallacyclobutenes **2**[2] or the products of a subsequent ring opening, the vinyl carbenes **3**,[3] are formed. The latter compounds have recently received much attention as catalysts for olefin metathesis.[4] If β-hydrogen atoms are present in **2**, a β-hydrogen elimination followed by a reductive elimination leads to η^4-isoprene complexes **4**.[5]

There also exist a number of transition-metal-catalyzed reactions of cyclopropenes where the organic products suggest the intermediacy of vinyl carbene complexes.[6]

Inspired by the earlier work of Binger,[1a,7] we recently investigated the synthesis of 5-pallada-*trans*-tricylo-[4.1.0.0^{2,4}]heptanes (PTHs; **6**) by oxidative cyclization of two molecules of dialkyl 3,3-dimethylcyclopropene-1,2-dicarboxylate **5** on a Pd(0) center.[8] This method even allowed a highly stereoselective synthesis of enantio-

Chart 1

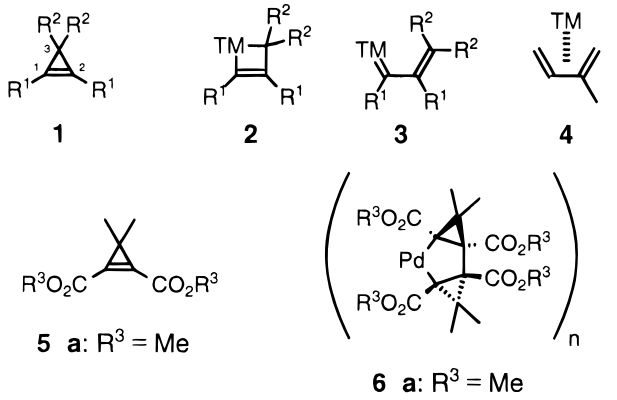

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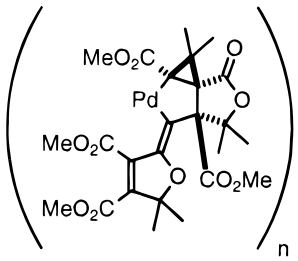
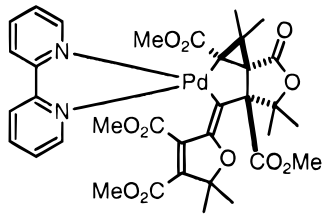
Chart 2



rac-**7** (5%)



rac-**8** (65%)

merically pure **6**.[9] These reactions provided high yields of **6**. Now we have reinvestigated the reaction of **5a** with Pd(0) in order to clarify the question whether any products derived from an insertion into the ring or a ring opening of the cyclopropene can be detected.

Results and Discussion

When, instead of the immediate addition of 2 equiv, an excess (2.5 equiv) of cyclopropene **5a** was added stepwise to $Pd_2dba_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) in the PTH synthesis, we observed the formation of the deep red colored side product **7** (Chart 2). In thin-layer chromatography on silica gel **7** was less polar than

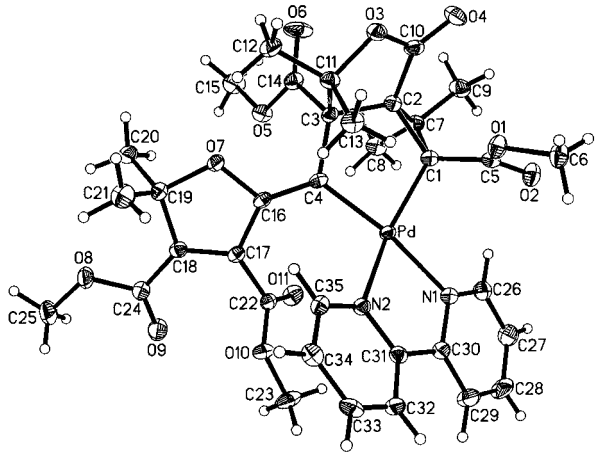


Figure 1. ORTEP plot of **8**.

the PTH **6a**, indicating that again a palladium−organic compound had been formed but more than two cyclopropenes were involved. This was further supported by the ^1H NMR, where in noncoordinating solvents such as $CDCl_3$ only broad signals were visible, while in coordinating solvents such as acetonitrile and acetone well-defined signals were obtained. Nevertheless, the NMR and MS data obtained from **7** in acetone did not allow a reliable structural assignment. Thus, we prepared the bpy complex **8**. Fortunately, crystals suitable for a X-ray crystal structure elucidation could be obtained from acetone (the ORTEP plot of **8** is depicted in Figure 1).

8 contains an interesting tricyclic palladacycloalkane substructure that is connected to a dihydrofuran ring by a C=C double bond. The formation of **8** is highly stereoselective; the double bond between the two subunits is formed in an *E* configuration only. Furthermore, forced by the *cis* fusion of the five-membered lactone ring and the central palladacyclopentane ring, the relative configuration of the stereogenic center at C3 and the two stereogenic centers at the ring fusion of the three- and the central five-membered ring is well defined, the cyclopropane being cis to the CO_2CH_3 group. Due to the rigid structure one ester group on the dihydrofuran ring suffers severe steric interaction with the bpy ligand; thus, the square-planar coodination at Pd(II) is heavily distorted. The angle between the N1−Pd−N2 plane and the C1−Pd−C4 plane is 27.7°. For Pd(II)−bpy complexes this interplanar angle reaches a record value. Due to the popularity of the bpy ligand in the Cambridge Crystallographic Database about 80 Pd(II)−bpy species are registered. While most of these show a distortion of less than 10°, only 6 complexes reach values between 10 and 20° (11.0,[10] 11.3,[11] 14.3,[12] 15.2,[13] 15.6,[14] and 15.9°[15]) and only 4 reach values over

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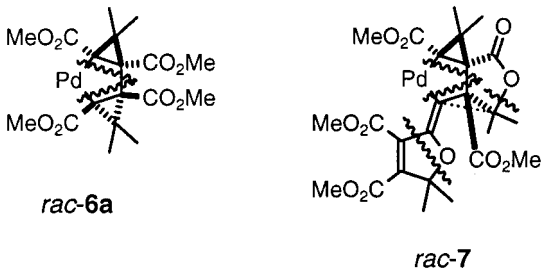
Chart 3



20° (23.6,[16] 24.1,[17] 24.6,[18] and 25.4°[19]). The last 4 structures contain bis(bipyridyl)palladium or (biphenylene)(bipyridyl)palladium complexes that show repulsive C−H···H−C interactions. The nonplanarity in **8** is required to avoid the following short intramolecular repulsive interactions: N2···O10 = 2.89 Å, N2···C22 = 3.07 Å, C35···O10 = 3.01 Å, C26···O2 = 3.07 Å ,and H26···O2 = 2.42 Å. These steric interactions may also be responsible for the nonplanarity of the C4−C16 double bond; the torsion angle Pd−C4−C16−C17 is −23.2(3)°. The bipyridyl group is nonplanar: the angle between the planes of the two pyridyl groups is 17.5°. The Pd−C4 bond of 1.999(2) Å, involving the planar C atom, is significantly shorter than the Pd−C1 bond of 2.041(2) Å, as one would expect. The Pd−N bond lengths of 2.118(2) and 2.122(2) Å show no significant differences.

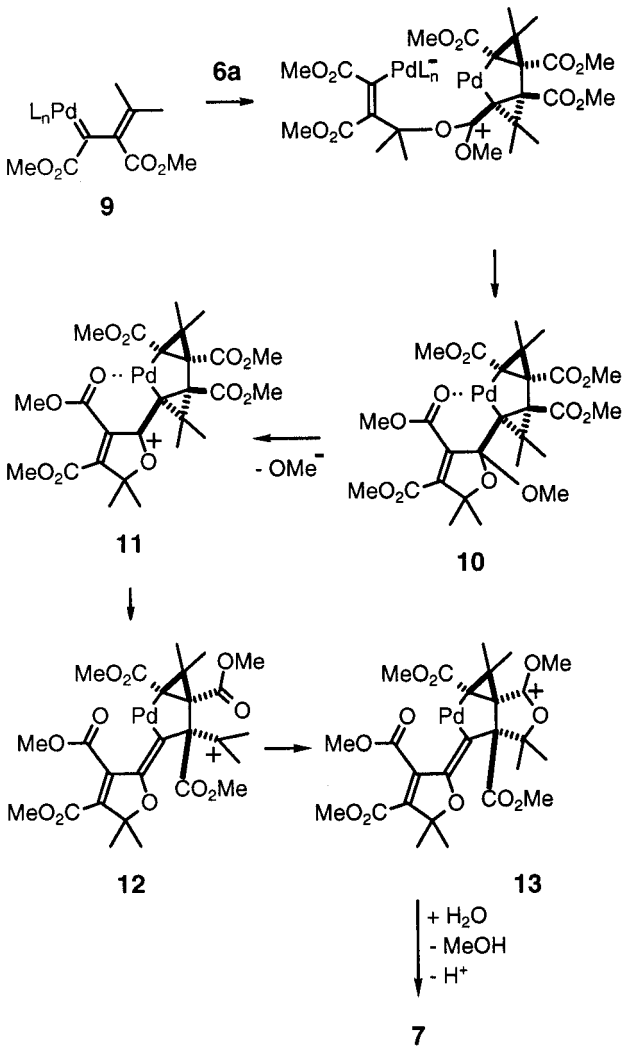
The fused lactone ring labeled C2, C3, C11, O3, and C10 approximately adopts an envelope conformation with the atom C3 0.46 Å outside the plane through atoms C2, C10, O3, and C11. The C3−C11 bond of 1.579(3) Å is slightly lengthened compared to a single C−C bond of 1.54 Å. The five-membered ring labeled O7, C16, C17, C18, and C19 is almost planar; C18 lies 0.06 Å outside the plane through O7, C16, C17, and C19.

The molecule is stabilized by a number of very weak, intramolecular C−H···O interactions, namely H9A···O4 = 2.45 Å, H12B···O7 = 2.43 Å, H12C···O6 = 2.45 Å, H13B···O1 = 2.52 Å, H20C···O8 = 2.55 Å, and H26···O2 = 2.42 Å. The crystal packing shows a number of intermolecular C−H···O interactions with H···O distances of about 2.6 Å. The acetone molecule in the lattice shows four intermolecular C−H···O interactions with the atoms of the main molecule.

An analysis of the structure of **7** strongly suggests that the latter is formed from **6a** (Chart 3); the connectivity of the carbon framework and the relative configuration at the stereogenic centers of the tricyclic palladacycle can be traced back to that of **6a**. The differences are the cleavage of one of the cyclopropane rings that leads to the exocyclic double bond and the lactone formation, which is accompanied by the loss of one methoxy group.

We could not find a reasonable mechanistic proposal for the formation of **7** from a seven-membered metallacycle (such species have been observed for Rh)[20] generated by the insertion of a third cyclopropene into one C−Pd bond of **6a** and a subsequent rearrangement. Since, as discussed in the Introduction, in the presence of transition metals cyclopropenes can also form vinyl carbenoids, we suggest a reaction pathway involving such species. This is supported by the dihydrofuran ring, which contains three carbon atoms from a third cyclopropene molecule as an open chain, being reminiscent of a vinyl carbene or carbenoid.

Scheme 1



Therefore, we propose that first the vinyl carbenoid **9** is formed by insertion of Pd into a single bond of the cyclopropene ring followed by ring opening (Scheme 1). Since **5a** bears two substituents on the double bond, the C2−C3 and the C1−C3 bonds are sterically less accessible; thus, with only 2 equiv of cyclopropene the cyclization to **6a** is faster. **9** reacts as an electrophile and attacks the nucleophilic oxygen atom of the ester group in **6a** α to Pd. Then the ring is closed and the intermediate **10** is formed. In **10** an internal coordination of one ester group on the dihydrofuran ring to Pd should be feasible, and this would nicely explain the observed double-bond geometry. The formation of the latter double bond is now initiated by the loss of the

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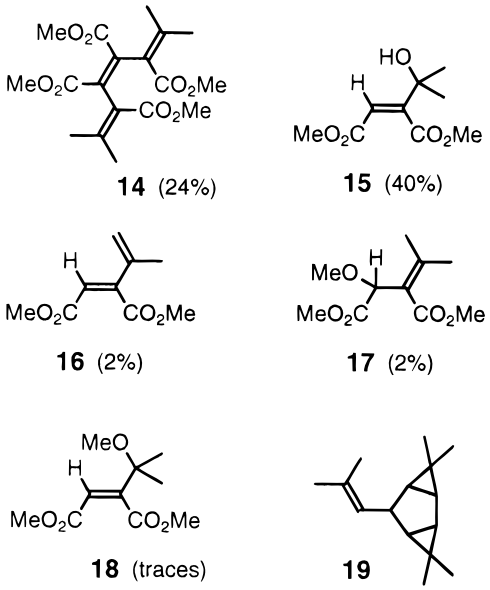
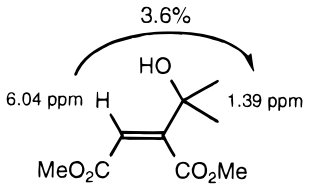
Chart 4



methoxy group at the lactal leading to **11**. This loss is supported by the neighboring oxygen atom, double bond, and cyclopropyl ring. Then the cyclopropyl ring opens (releasing the ring strain), and so the new double bond and a tertiary carbenium ion in **12** are formed. This electrophilic carbon atom now attacks the ester group located in the direct neighborhood, giving the intermediate **13**. Finally a reaction with external water (different from most of the other investigations in this field, the synthesis of **6** is possible in the presence of water; therefore, we used normal reagent-grade acetone) and loss of a second molecule of methanol delivers **7**. Overall, **7** is the product of the reaction of Pd(0) with three molecules of **5a** and one molecule of water accompanied by the loss of two molecules of methanol—this explains our difficulties in elucidating the structure from NMR and MS data.

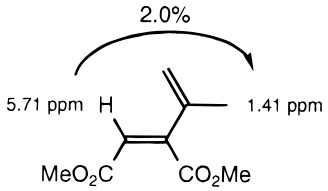
If this mechanistic proposal is true and a vinyl carbenoid as key intermediate is formed, this intermediate should be able to react with other nucleophiles present in the solution such as water and—as the reaction leading to **7** proceeds—small amounts of the more nucleophilic methanol. Thus, we repeated the reaction and changed the workup, now also focusing on organic products. After this change we indeed could isolate the products **14**−**17** (Chart 4).

1,3,5-Trienes such as **14** have been observed in transition-metal-catalyzed reactions of cyclopropenes before and have been interpreted as products of a dimerization of vinyl carbenoids.[6a,k,21] Since we have observed **14** before,[22] the assignment of a *Z* geometry is unambiguous. **15** is the product of the addition of water as a nucleophile, the position of the addition (1,3-addition of H−OH) corresponding to our mechanistic proposals for the formation of **7** quite well. The double-bond geometry was assigned by a NOE difference spectrum (Figure 2).



15

Figure 2. NOE observed in the NOE difference spectra of **15**.



16

Figure 3. NOE observed in the NOE difference spectra of **16**.

Similar products of a 1,1-addition of H−OH, not of a 1,3-addition, have also been observed in related reactions before.[6a] **16** corresponds to the products observed by Butenschön[5] and is probably formed by an analogous mechanism. In our case it is remarkable that only the isomer with the *Z* configuration at the trisubstituted double bond is formed. Again the assignment was possible by a NOE difference spectrum (Figure 3). **17** is the product of a 1,1-addition of H−OMe to the vinyl carbenoid analogue to the previously reported water adduct mentioned above.[6a]

In the ^{1}H NMR we also observed traces of another side product, to which we assigned the structure **18**, the 1,3-addition product of H−OMe. Interestingly, we observed no products of an insertion of the vinyl carbenoid into a Pd−C bond of **6a**; no products analogous to the compounds **19** obtained by Binger[6c,d,e,j] could be isolated.

This is in accordance with the low tendency of the Pd−C bonds in **6** to undergo even intramolecular insertion reactions.[23]

Conclusion

We have demonstrated that in the reaction of cyclopropenes **5** the formation of **6** is clearly the main reaction; only with an excess of **5** are products derived from vinyl carbenoids obtained. In the case of our electron-poor substrates the addition of different nucleophiles to these vinyl carbenoids was observed. The reason for the different regioselectivities of these additions is still unclear. The formation of **7** is an example of an unprecedented reaction of cyclopropenes.

Experimental Section

Preparative HPLC: programmable pump Waters 590 with Perfusor VI injector, peak-separator 2150, R 401 differential refractometer, column 250 × 16 mm internal diameter, Macherey-Nagel Nucleosil 50−10, flow 10 mL/min. **5a**[8c] and Pd_2dba_3·$CHCl_3$[24] were prepared as described previously.

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Abbreviations: hexane (H), acetone (A), ethyl acetate (EA), methyl acetate (MA), and dichloromethane (DCM). The assignments s (C_{quat}), d (CH), t (CH_2), and q (CH_3) for the ^{13}C NMR signals are based on DEPT 135 and DEPT 90 spectra.

Synthesis of 7. A 2.00 g (10.9 mmol) amount of cyclopropene **5a**[8c] was added to a suspension of 2.24 g (2.17 mmol) of $Pd_2dba_3{\cdot}CHCl_3$ in 100 mL of acetone and the mixture stirred at room temperature. More **5a** was added after 12 h (400 mg, 2.17 mmol), 14 h (400 mg, 2.17 mmol), and 16 h (200 mg, 1.09 mmol). After 18 h the solvent was removed in vacuo and the remaining deep red residue was worked up by column chromatography on silica gel to afford 750 mg (36%) of PTH **6a** and 110 mg (5%) of **7**. R_f(H:A = 3:2) = 0.16. ^1H NMR (acetone-d_6, 250 MHz): δ 3.89 (s, 3 H), 3.85 (s, 3 H), 3.61 (s, 3 H), 3.41 (s, 3 H), 1.70 (s, 3 H), 1.61 (s, 3 H), 1.52 (s, 3 H), 1.45 (s, 6 H), 1.37 (s, 3 H). ^{13}C NMR (acetone-d_6, 64.9 MHz): δ 18.8 (q), 25.5 (q), 26.9 (q), 27.1 (q), 28.0 (q), 30.3 (q), 33.8 (s), 44.3 (s), 50.4 (s), 50.8 (q), 51.2 (q), 53.0 (q), 55.4 (q), 79.9 (s), 85.3 (s), 90.0 (s), 118.5 (s), 126.9 (s), 146.1 (s), 152.8 (s), 165.1 (s), 168.8 (s), 172.6 (s), 173.2 (s), 174.7 (s).

Synthesis of 8. A 100 mg (170 μmol) amount of **7** was dissolved in 10 mL of dichloromethane, and 28.0 mg (180 μmol) of 2,2′-bipyridyl in 2 mL of dichloromethane was added at room temperature. The mixture was stirred for 1 h; then the solvent was removed in vacuo. The remaining oily crude product still contained traces of DCM that prevented precipitation. Therefore, with stirring, a few drops of hexane were added which induced the precipitation of the product. After removal of the hexane in vacuo the remaining bright red solid was washed with two 2 mL portions of a cold hexane/ethyl acetate mixture (1:1) to afford 85 mg (65%) of **8**. First crystals of **8** were obtained by slow evaporation of a solution in DCM, but the crystals contained DCM and were of low quality and the X-ray crystal structure investigation gave unsatisfactory results. Therefore, they were dissolved in acetone and the solution was evaporated very slowly at 4 °C. Now single crystals of a better quality were obtained. Mp (from acetone): 152 °C. IR (film, NaCl; cm^{-1}): 3112, 3058, 2980, 2946, 1739, 1707, 1686, 1602, 1491, 1473, 1458, 1433, 1376, 1368, 1345, 1291, 1245, 1214, 1137, 1099, 1056, 1036, 1004, 982, 964, 895, 821, 768, 734, 702, 652. ^1H NMR (CD_2Cl_2, 250 MHz): δ 9.03 (d, $^2J_{HH}$ = 4.5 Hz, 1 H), 8.94 (d, $^2J_{HH}$ = 4.7 Hz, 1 H), 8.35 (d, $^2J_{HH}$ = 8.0 Hz, 1 H), 8.10−7.94 (m, 3 H), 7.52−7.51 (m, 2 H), 3.67 (s, 3 H), 3.63 (s, 3 H), 3.40 (s, 3 H), 3.23 (s, 3 H), 1.79 (s, 3 H), 1.67 (s, 3 H), 1.62 (s, 3 H), 1.53 (s, 3 H), 1.51 (s, 3 H), 1.49 (s, 3 H). ^{13}C NMR (CD_2Cl_2, 64.9 MHz): δ 19.5 (q), 25.0 (q), 26.8 (q), 27.5 (q), 28.0 (q), 29.3 (q), 36.0 (s), 43.6 (s), 51.0 (q), 51.4 (q), 51.9 (s), 52.2 (q), 52.6 (q), 79.3 (s), 86.0 (s), 88.9 (s), 122.7 (d), 122.9 (d), 126.0 (d), 126.2 (d), 132.2 (s), 137.5 (s), 138.1 (s), 138.3 (d), 138.7 (d), 141.4 (s), 150.0 (s), 151.3 (d), 151.6 (d), 155.9 (s), 163.7 (s), 165.9 (s), 172.9 (s), 174.5 (s), 175.7 (s). MS (FAB; *m*/*z* (%)): 769 (4) [M^+ + H], 753 (1) [$M^+ - CH_3$], 737 (4) [$M^+ - H_3CO$]. Anal. Calcd for $C_{35}H_{38}N_2O_{11}Pd$ (769.11): C, 54.66; H, 4.98; N, 3.64. Found: C, 54.62; H, 5.37; N, 3.62.

Crystal Structure Analysis of 8: Siemens SMART CCD three-circle diffractometer, Mo Kα, 0.710 73 Å, ω-scans, empirical absorption correction with SADABS.[25] The structure was determined by direct methods[26] and refined with SHELXL 96[27] by full-matrix least-squares methods against F^2. Hydrogen atoms were taken from a difference Fourier synthesis and refined with isotropic displacement parameters. Crystal data are summarized in Table 1. The asymmetric unit contains a solvent molecule. A total of 77.1% of the solvent sites contain acetone, and 22.9% of the solvent sites contain dichloromethane. The solvent has been refined with a split atom model. H atoms at the solvent were placed at ideal positions. Crystallographic data in CIF format (excluding structure factors) for **8** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145723. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223−336033; e-mail, deposit@ccdc.cam.ac.uk). Structure factors can be obtained from the authors.

Table 1. Crystallographic Data for 8

mol formula	$C_{35}H_{38}N_2O_{11}Pd{\cdot}0.77C_3H_6O{\cdot}0.23CH_2Cl_2$
fw	833.33
temp, K	137
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.520(1)
b, Å	22.911(3)
c, Å	14.086(2)
β, deg	101.521(7)
V, Å^3	3642.7(7)
Z	4
D_{calcd}, g cm^{-3}	1.519
μ, mm^{-1}	0.610
cryst size, mm	0.10 × 0.15 × 1.04
cryst color, shape	yellow, rod
θ range, deg	1.7−32.4
max indices, *h*, *k*, *l*	16, 33, 20
abs cor range	0.744−1.000
no. of rflns measd	43 545
no. of unique rflns	11 723
no. of rflns with $F^2 > 2\sigma(F^2)$	8340
$R(I)_{int}$	0.061
no. of params	645
R indices ($I > 2\sigma(I)$)	R1 = 0.043, wR2 = 0.085
R indices (all data)	R1 = 0.078, wR2 = 0.095
largest diff peak and hole, e Å^{-3}	1.18 and −1.37

Formation of 14−17. A 160 mg (870 μmol) amount of cyclopropene **5a** was added to a suspension of 150 mg (145 μmol) of $Pd_2dba_3{\cdot}CHCl_3$ in 7 mL of acetone and stirred at room temperature. More **5a** was added after 17 h (27.0 mg, 147 μmol), after 19 h (27.0 mg, 147 μmol), and after 21 h (14.0 mg, 73.1 μmol). After 23 h the solvent was removed in vacuo and the remaining deep red residue worked up by column chromatography on silica gel. Then the fractions containing the organic products were purified by HPLC (H/MA/DCM = 10/4/7). Thus, 38.4 mg (24%) of **14**,[22] 70.3 mg (40%) of **15**, 3.5 mg (2%) of **16**, and 3.8 mg (2%) of **17** were obtained. A few fractions of **16** contained small amounts of an impurity, according to the ^1H NMR probably **18**.

15: R_f (H:A = 5:1) = 0.13. IR (film, NaCl; cm^{-1}): 3492, 2982, 2955, 1728, 1649, 1437, 1347, 1260, 1195, 1170, 1046, 1020, 970, 908, 889, 856, 823, 739, 714, 696. ^1H NMR ($CDCl_3$, 250 MHz): δ 6.04 (s, 1 H), 3.78 (s, 3 H), 3.66 (s, 3 H), 2.46 (br s, 1 H), 1.39 (s, 6H). ^{13}C NMR ($CDCl_3$, 64.9 MHz): δ 28.9 (q, 2 C), 51.8 (q), 52.3 (q), 71.6 (s), 116.8 (d), 157.6 (s), 165.4 (s), 168.3 (s). Anal. Calcd for $C_9H_{14}O_5$ (202.21): C, 53.46; H, 6.98. Found: C, 53.25; H, 7.05.

16: R_f (H:EA = 10:1) = 0.11. IR (film, NaCl; cm^{-1}): 2954, 1741, 1724, 1654, 1610, 1560, 1437, 1387, 1364, 1304, 1247, 1197, 1171, 1075, 1026, 872. ^1H NMR (C_6D_6, 250 MHz): δ 5.71 (s, 1 H), 5.29 (s, 1 H), 5.01 (s, 1 H), 3.61 (s, 3 H), 3.27 (s, 3 H), 1.41 (s, 3 H). ^{13}C NMR ($CDCl_3$, 64.9 MHz): δ 19.3 (q), 51.8 (q), 52.4 (q), 116.3 (d), 122.7 (t), 137.7 (s), 149.8 (s), 165.5 (s), 168.2 (s). MS (70 eV; *m*/*z* (%)): 184 (100), 169 (55), 153 (50), 125 (49). HRMS (80 eV): calcd for $C_9H_{12}O_4$, 184.072 34; found, 184.073 56.

17: R_f (H:A = 5:1) = 0.22. IR (film, NaCl; cm^{-1}): 2996, 2953, 2830, 1759, 1724, 1654, 1637, 1436, 1376, 1311, 1282, 1226, 1195, 1106, 1092, 1015, 913. ^1H NMR ($CDCl_3$, 250 MHz): δ 4.76 (s, 1 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.43 (s, 3 H), 2.08 (s,

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3 H), 1.97 (s, 3 H). ^{13}C NMR ($CDCl_3$, 64.9 MHz): δ 22.4 (q), 23.4 (q), 51.7 (q), 52.3 (q), 57.6 (q), 77.5 (d), 125.0 (s), 150.0 (s), 167.6 (s), 171.0 (s). MS (70 eV; *m*/*z* (%)): 216 (2), 157 (100), 125 (42), 75 (30). HRMS (80 eV): calcd for $C_8H_{13}O_3$ ($M^+ - C_2H_3O_2$), 157.087 82; found, 157.086 47.

18 (from mixture with **15**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.93 (s, 1 H), 3.78 (s, 3 H), 3.67 (s, 3 H), 3.14 (s, 3 H), 1.33 (s, 6 H).

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Supporting Information Available: Tables giving X-ray crystallographic data and figures giving an additional view of the molecule and a packing diagram for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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