Reactions of *trans*-5-Palladatricyclo[4.1.0.0^{2,4}]heptanes: Stereoselective Formation of Highly Substituted 1,1′-Bi(cyclopropyl) Compounds and (3*Z*)-1,3,5-Hexatrienes

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Abstract: The reaction of the racemic *trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptanes with hydrogen or $NaBH_4$ led to (1*R**,2*R**,1′*R**,2′*R**)-bi(cyclopropyl) compounds in a highly stereoselective reaction. Reactions with halogens, dibenzoyl peroxide, or cerium(IV) ammonium nitrate (CAN) afforded (3*Z*)-1,3,5-hexatrienes. The stereoselectivity was also high; the only exception was the reaction with bromine in dichloromethane, where small amounts of the corresponding (3*E*)-1,3,5-hexatrienes were observed as byproducts. The X-ray structure investigation of one bi(cyclopropyl) compound and one (3*Z*)-1,3,5-hexatriene proved the stereochemical assignments. On the other hand, extensive NMR investigations of two asymmetrical derivatives of the (3*Z*)-1,3,5-hexatrienes did not allow such an assignment of the double-bond geometry because of the spherical molecular shape of the (3*Z*)-1,3,5-hexatrienes. Both the reaction with hydrogen and the reaction with oxidants probably proceed through Pd^{IV} intermediates.

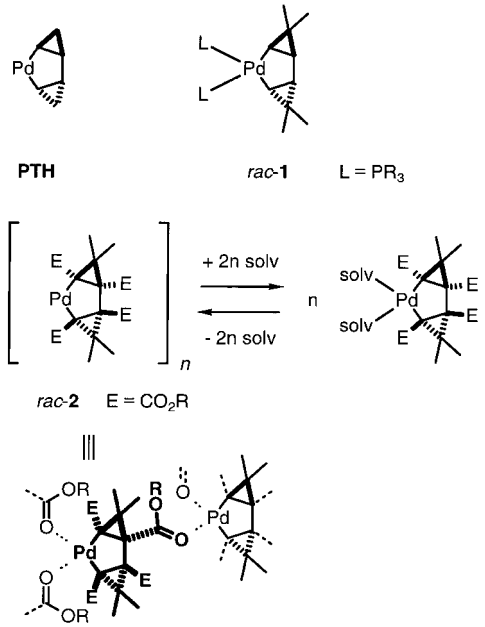
Keywords: alkenes · hydrogenations · metallacycles · oxidations · palladium

Introduction

Several *trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane (PTH) derivatives, either in form of complexes, *rac*-**1**, or as coordination polymers, *rac*-**2**, that dissolve readily in coordinating solvents, such as acetone or acetonitrile, have been prepared by Binger et al.[1] and by our group .[2] However, the reactivity of *rac*-**1** and *rac*-**2** has not been investigated in detail. The thermolysis of *rac*-**1** in decalin at 200 °C afforded 1,4-cyclohexadienes.[1] The ability of *rac*-**2** to act as a catalyst was proven by the cycloisomerization/dimerization[3] of allenyl ketones. No other stoichiometric reactions of *rac*-**1** or *rac*-**2** have been investigated yet. Here we present the results of investigations on the reactivity of *rac*-**2** PTHs in some stoichiometric reactions.

Results and Discussion

Reaction with hydrogen: Solutions of the *rac*-**2** complexes in acetone reacted readily with hydrogen (1 atm) at room temperature (Scheme 1). Either a palladium mirror or palladium black was formed. The supernatant solution contained one single product, the tetraalkyl (1*R**,2*R**,1′*R**,2′*R**)-3,3,3′,3′-tetramethyl-1,1′-bicyclopropyl-1,2,1′,2′-tetracarboxylates *rac*-**3** (Table 1). Under these conditions, *rac*-**3** was stable towards additional hydrogen, so no precautions were necessary in order to avoid an excess of hydrogen.[4]



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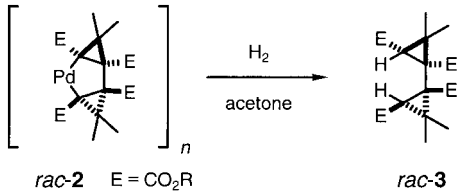


Scheme 1. Hydrogenation of *rac*-**2**.

Table 1. Reaction of *rac*-**2** with hydrogen.[a]

Entry	PTH	E	Product	Yield [%]
1	*rac*-**2a**	CO_2Me	*rac*-**3a**	72
2	*rac*-**2b**	CO_2tBu	*rac*-**3b**	88
3	*rac*-**2c**	CO_2Ph	*rac*-**3c**	51
4	*rac*-**2d**	$CO_2CH_2CO_2Me$	*rac*-**3d**	89
5	*rac*-**2e**	$CO_2CH_2C(Me)_2CO_2Me$	*rac*-**3e**	67
6	(1*S*,2*S*,4*S*,6*S*)-**2f**	(*S*)-$CO_2CH(Me)CO_2Et$	(1*R*,2*R*,1′*R*,2′*R*)-**3f**	99

[a] In acetone at room temperature.

The enantiomerically pure (1*S*,2*S*,4*S*,6*S*)-**2f** reacted to give an enantiomerically pure product (1*R*,2*R*,1′*R*,2′*R*)-**3f** (Table 1, entry 6). The change from the *S* to the *R* configuration originates not from an inversion but from the CIP-priority rules ("descriptor inversion").[5]

The constitution of **3** was deduced from the NMR spectra. The C_2 symmetry was retained in the product. In the ^1H NMR spectrum, a singlet at $\delta \approx 1.7$ was observed for the cyclopropyl hydrogen atom. A comparison of the ^{13}C NMR spectra of **2** and **3** indicated that only small changes in the chemical shift of the majority of the signals ($\Delta\delta \approx 1-5$ and for the C bearing the new H atom $\Delta\delta \approx 8$, which demonstrates nicely that Pd is essentially "NMR-neutral"). No diastereomers of (1*R**,2*R**,1′*R**,2′*R**)-**3** were observed; this proved that the new C–H bond was formed in a stereochemically defined manner. As observed in other hydrogenolytic cleavages of organopalladium compounds, we assumed a retention of configuration.[6] This was confirmed by the X-ray crystal structure analysis of *rac*-**3a** (Figure 1). Interestingly, in the solid state the two cyclopropane rings in *rac*-**3a** occupy a conformation similar to their relative arrangement in the PTH: the two newly introduced hydrogen atoms point towards each other. With respect to the PTH, the rotation around the C3–C3A bond is only 17.7(2)° (dihedral angle C1-C3-C3A-C1A). All bond lengths are quite similar to those observed in the PTHs.[2]

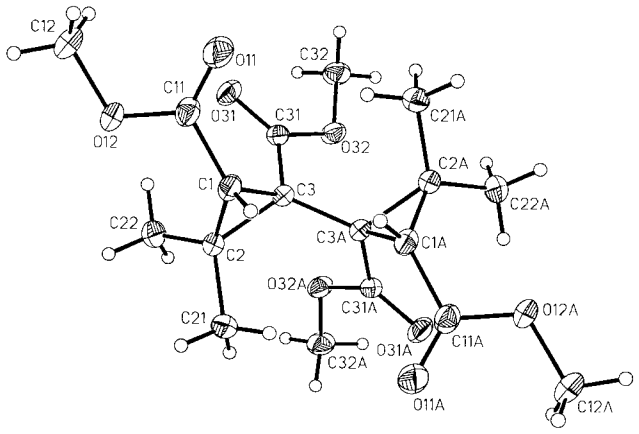
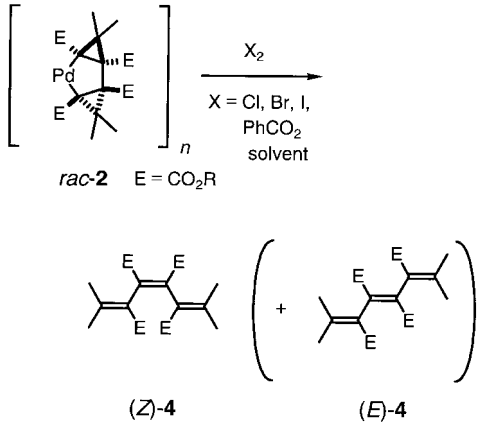


Figure 1. Molecular structure of *rac*-**3a** (ORTEP plot).

While $NaBH_4$ in methanol also reduced *rac*-**2a** to give *rac*-**3a** (87% yield; with $NaBD_4/D_2$-*rac*-**3a** was formed),[7] we were unable to achieve a hydrogen transfer from 1,4-cyclohexadiene.

Reactions with halogens or dibenzoyl peroxide: We then turned to reactions with halogens. Since they cannot be used in acetone, suspensions of *rac*-**2** in dichloromethane (CH_2Cl_2) or solutions in acetonitrile were treated with solutions of the halogen in CH_2Cl_2 or acetonitrile at 0 °C (Scheme 2). The



Scheme 2. Reactions of *rac*-**2** with halogens.

reaction mixtures immediately turned dark and a precipitate formed (presumably PdX_2). With bromine in CH_2Cl_2, both *rac*-**2a** and *rac*-**2d** led to two products: a major (*Z*) and a minor (*E*) diastereomer of the dialkyl 2,5-diisopropylidene-3,4-bis(alkoxycarbonyl)hex-3-enedioates **4a** and **4d**, respectively, were isolated (Table 2, entries 1 and 5). With bromine in acetonitrile only (*Z*)-**4** was observed (Table 2, entry 7).

Again, an excess of the reagent could be used: with 10 equiv of bromine in CH_2Cl_2 the identical ratio of (*Z*)-**4a**:(*E*)-**4a** of 4.5:1.0 was obtained (Table 2, entry 2). The electron-poor 1,3,5-hexatriene did not add any additional bromine: no significant addition or isomerization was visible in the NMR spectra of (*Z*)-**4d** and excess bromine in $CDCl_3$ recorded at room temperature.

On the other hand, treatment of *rac*-**2** with iodine under the same conditions as above led exclusively to (*Z*)-**4**, even in CH_2Cl_2 (Table 2, entries 3, 4, 6, 8, and 10). Bubbling chlorine through a suspension of **2d** in CH_2Cl_2 also gave only (*Z*)-**4d** (Table 2, entry 9).

The elucidation of the double-bond geometry was not trivial. Finally, we obtained crystals of (*Z*)-**4e** that were suitable for an X-ray crystal structure determination (Figure 2),[8] and were thus able to prove the (*Z*)-configuration of the central double bond. Each olefinic double bond is almost perpendicular (twist angles = 75° and 96°) to the neighboring C=C bond. The shape of the whole molecule is spherical, which explains the failure of most efforts to crystallize **4** (with the exception of **4e**, all derivatives were isolated as oils).

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Table 2. Reaction of *rac*-**2** with halogens.[a]

Entry	PTH	E	Equiv	Reagent/Solvent	Ratio (*Z*)-**4**:(*E*)-**4**	Yield [%] (*Z*)-**4** + (*E*)-**4**
1	*rac*-**2a**	CO_2Me	1	Br_2/CH_2Cl_2	4.5:1.0	86
2	*rac*-**2a**	CO_2Me	10	Br_2/CH_2Cl_2	4.5:1.0	79
3	*rac*-**2a**	CO_2Me	1	I_2/CH_2Cl_2	1:–	80
4	*rac*-**2b**	CO_2tBu	1	I_2/MeCN	1:–	84
5	*rac*-**2d**	$CO_2CH_2CO_2Me$	1	Br_2/CH_2Cl_2	11:1	94
6	*rac*-**2d**	$CO_2CH_2CO_2Me$	1	I_2/CH_2Cl_2	1:–	97
7	*rac*-**2d**	$CO_2CH_2CO_2Me$	1	Br_2/MeCN	1:–	95
8	*rac*-**2d**	$CO_2CH_2CO_2Me$	1	I_2/MeCN	1:–	95
9	*rac*-**2d**	$CO_2CH_2CO_2Me$	[b]	Cl_2/CH_2Cl_2	1:–	98
10	*rac*-**2e**	$CO_2CH_2C(Me)_2CO_2Me$	1	I_2/CH_2Cl_2	1:–	96
11	*rac*-**2d**	$CO_2CH_2CO_2Me$	1	$(PhCO_2)_2/CH_2Cl_2$	1:–	95

[a] At 0 °C. [b] Excess; however, the amount was not determined.

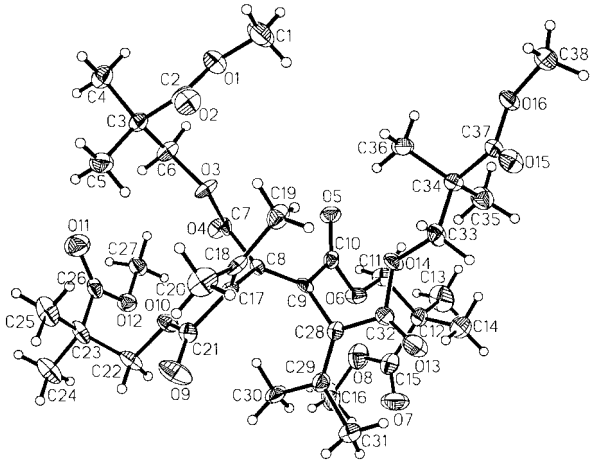
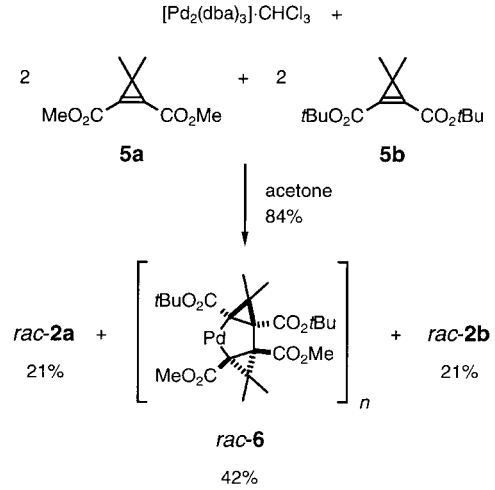


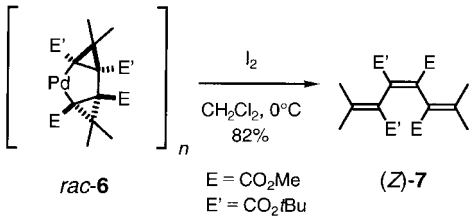
Figure 2. Molecular structure of (*Z*)-**4e** (ORTEP plot).

This spherical shape also explained our difficulties in the assignment of the double-bond geometry by NMR spectroscopy. For this purpose we synthesized the "mixed" PTH *rac*-**6** by the statistical reaction of equimolar amounts of the cyclopropenes **5a** and **5b** with $[Pd_2(dba)_3]\cdot CHCl_3$ (Scheme 3).

In the reaction of *rac*-**6** with iodine only (*Z*)-**7** was formed (Scheme 4). In (*Z*)-**7** the substituents on the central double

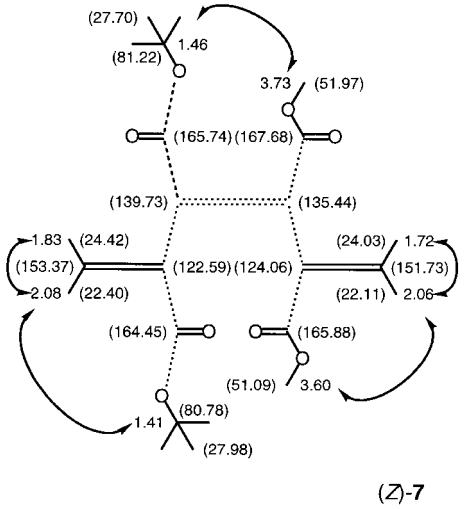


Scheme 3. Synthesis of the "mixed" PTH *rac*-**6**.



Scheme 4. Reaction of *rac*-**6** with iodine

bond are now different. On account of the presence of only isolated ^1H spin systems, which are separated by an array of twelve quarternary C atoms and four O atoms, a complete assignment of all signals was not possible from the $^{13}C,^1H$-COSY, $^{13}C,^1H$-HMBC, and ROESY[9] spectra. We were only able to determine the connectivity of partial structures; however, we were not able to relate these segments (Scheme 5).



Scheme 5. ^1H and ^{13}C (numbers in parentheses) assignments in (*Z*)-**7** as derived from $^{13}C,^1H$-COSY, $^{13}C,^1H$-HMBC spectra, and strong ROESY-crosspeaks (arrows). The dotted lines show just *one possible* connection of the segments.

Molecular modeling revealed that the crosspeaks provided by the ROESY spectrum would not allow the determination of the double-bond geometry in an unequivocal manner. The conformers of lowest energy show quite different dihedral

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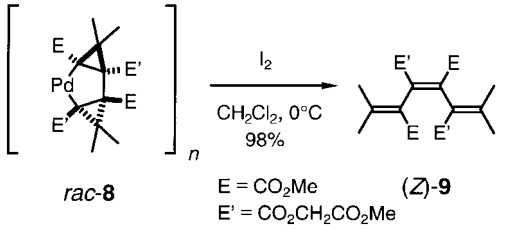
angles and thus a different molecular shape with different distances between the methyl groups on the surface of the molecule (with the quarternary carbons and the carboxyl groups in the core) for both the *Z* and the *E* isomers of **7** (Figure 3).[10]

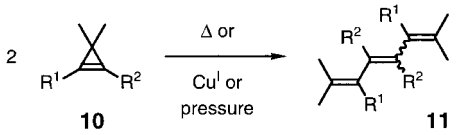
We also converted the asymmetrical PTH *rac*-**8** to (*Z*)-**9** (Scheme 6). Here, NMR-based assignments similar to those for (*Z*)-**7** were possible; however, for similar reasons it was impossible to prove the double-bond geometry by NMR spectroscopy.



Scheme 6. Reaction of the asymmetrical PTH *rac*-**8** with iodine.

The absorption maxima in the UV spectrum of (*Z*)-**4d** [$\lambda_{max} = 210$ nm (hexane, lg $\varepsilon = 4.467$)], (*Z*)-**4e** [$\lambda_{max} = 215$ nm (hexane, lg $\varepsilon = 4.595$)], and (*Z*)-**9** [$\lambda_{max} = 214$ nm (hexane, lg $\varepsilon = 4.510$)] are quite untypical for conjugated trienes. Considering the conformation of (*Z*)-**4e** (Figure 2), it becomes clear that the three olefin-subunits of the highly congested 1,3,5-hexatriene system are no longer coplanar. This is not only true in the solid state but also in solution. The conformations of lowest energy calculated by molecular modeling[10] show the three C=C bonds are almost orthogonal to each other. This loss of conjugation readily explains the UV absorptions of about 215 nm.[11] For a conjugated 1,3,5-hexatriene one would expect a value of at least 270 nm (depending on further substituents).

Since the PTHs are prepared from two cyclopropenes, the sequence PTH-formation/ reaction with halogen is related to the ring-opening/dimerization process of cyclopropenes **10** to 1,3,5-hexatrienes **11**. The latter reactions are either copper-catalyzed, thermal, or are initiated by high pressure (Scheme 7.[12]



Scheme 7. Ring-opening/dimerization process of cyclopropenes **10**.

However, in these reactions usually a mixture of *E*/*Z* stereoisomers was isolated; that is, the diastereoselectivity was low. When only one stereoisomer was formed the configuration of the central double bond was proven to be *E* by an X-ray crystal structure determination.[13] So our *Z*-selective formation of the 1,3,5-hexatrienes would nicely contrast the reactions mentioned before.

Oxidants unable to undergo oxidative addition: Reactions of **2a** with CAN[14] in acetonitrile or with ferrocenium tetrafluoroborate in THF[15] also only gave (*Z*)-**4a** in 99% and 82% yield, respectively.

Related reactions and possible mechanisms

Reaction with hydrogen: Although the hydrogenolytic cleavage of the Pd–C bond was already observed some time ago,[6] there are only two important publications of relevance for the PTHs. Elsevier et al. investigated the reaction of palladoles **12** which bear chelating nitrogen ligands.[16] Unlike the case with *rac*-**3**, which are stable towards additional hydrogen, they observed only small amounts (<10%) of the expected 1,3-butadienes **13** accompanied by a mixture of by-products that

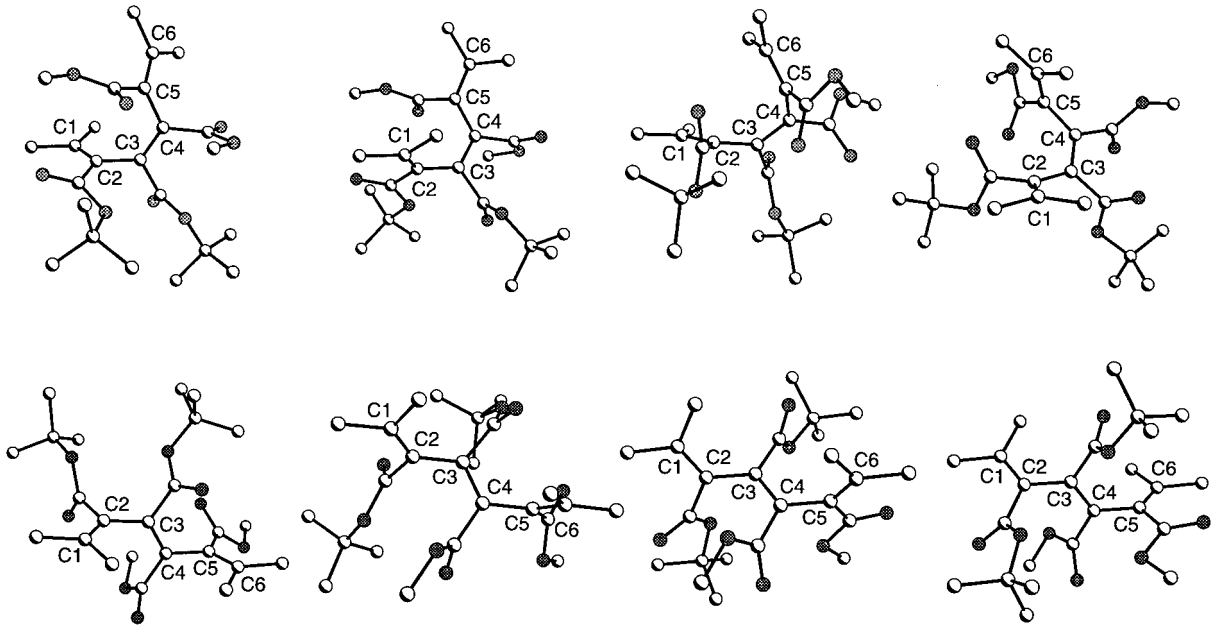
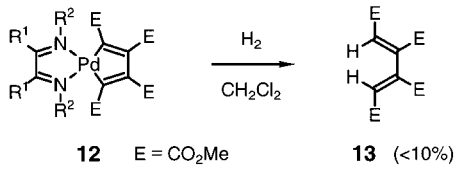
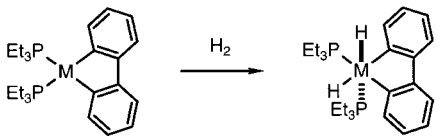


Figure 3. Various low-energy conformers of (*Z*)-**7** (upper row) and (*E*)-**7** (lower row).

arise from heterogeneous hydrogenation caused by the palladium precipitate (Scheme 8). Jones et al. suggested the Pt^{IV} and Pd^{IV} complexes **15** as intermediates formed by *cis*-oxidative addition of H_2 to the palladacycle **14** (Scheme 9).[17]

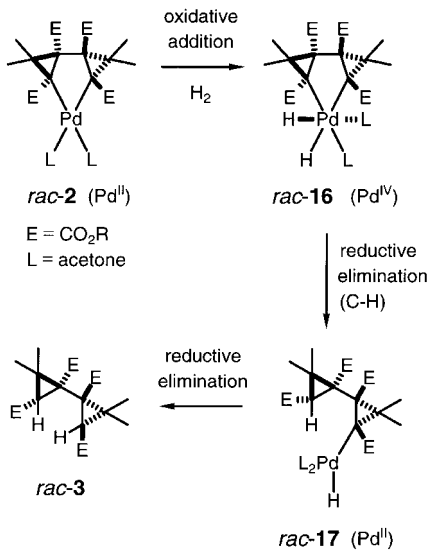


Scheme 8. Hydrogenolytic cleavage reaction of palladoles **12**.[16]



Scheme 9. Pt^{IV} and Pd^{IV} complexes **15** suggested as intermediates formed by *cis*-oxidative addition of H_2 to the palladacycle **14**.[17]

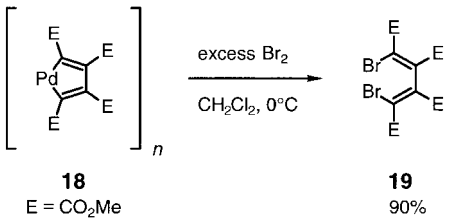
For our hydrogenations we also would like to suggest that the first step involves the oxidative addition of H_2[18, 19] to the palladium center. Thus the Pd^{II} center in the PTHs *rac*-**2** would be oxidized to Pd^{IV} in the intermediate *rac*-**16**;[20] however, the carbon ligands on palladium are not strongly electron-withdrawing. The next two steps involve subsequent and fast reductive eliminations to afford *rac*-**17** and ultimately *rac*-**3** (Scheme 10). The reductive elimination pathway explains the retention of the relative configuration of the



Scheme 10. Proposed hydrogenation mechanism.

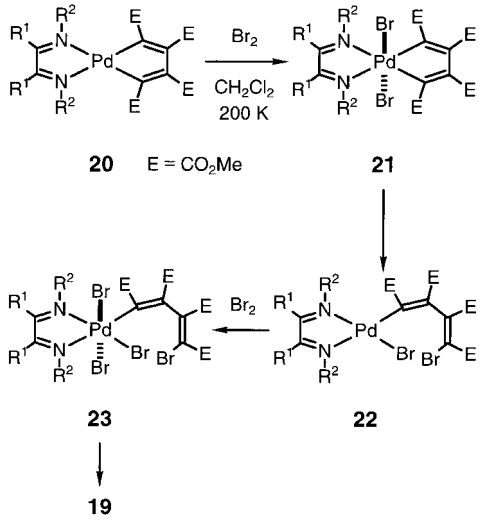
stereocenters in *rac*-**3**. On account of the mild conditions and the fact that palladium immediately precipitates, the cyclopropane rings are not even cleaved by palladium-catalyzed hydrogenation in the presence of excess hydrogen.[4]

Reactions with oxidants: Our results from the reactions of PTHs with halogens differ strongly from the known reactions of the corresponding palladoles with bromine (the PTHs could be considered as bis(homo)palladoles), where C–heteroatom bond formation was observed. Maitlis et al. obtained the dibromide **19** upon treatment of **18** with bromine (Scheme 11).[21]



Scheme 11. Treatment of **18** with bromine to give the dibromide **19**.[21]

Elsevier et al. also observed the incorporation of bromine in their products **19**; they were able to detect the intermediate **21** (*trans*-oxidative addition) at 200 K by ^1H NMR spectroscopy and to isolate the intermediate **22** (Scheme 12).[22] Structures related to **22** were also obtained much earlier by Suzuki et al.[23]



Scheme 12. Reaction of Br_2 with complex **20** to give **19** via intermediates **21**–**23**.[22]

Canty et al. observed C–O bond formation in the reactions of palladacyclopentanes with dibenzoyl peroxide.[24]

In the reactions with halogens and other oxidizing reagents, there are three conceivable pathways (Scheme 13):

a) The reaction could be initiated by an oxidative addition[19] leading to *rac*-**24**. Then the first reductive elimination would form *rac*-**25**. In contrast to *rac*-**17**, the intermediate *rac*-**25** would now possess a leaving group and a metal–carbon bond within the same molecule. This species seems to undergo a "bishomo"-1,4-elimination to **4** faster than a second reductive elimination (to **27**). During this elimination the strain[25] of two cyclopropane rings is released. If this elimination is faster than the rotation about the C–C bond that connects the two different cyclopropyl units, then (*Z*)-**4** is obtained. In this case the Walsh orbitals of both cyclopropanes are set up for a process which resembles an *anti*-

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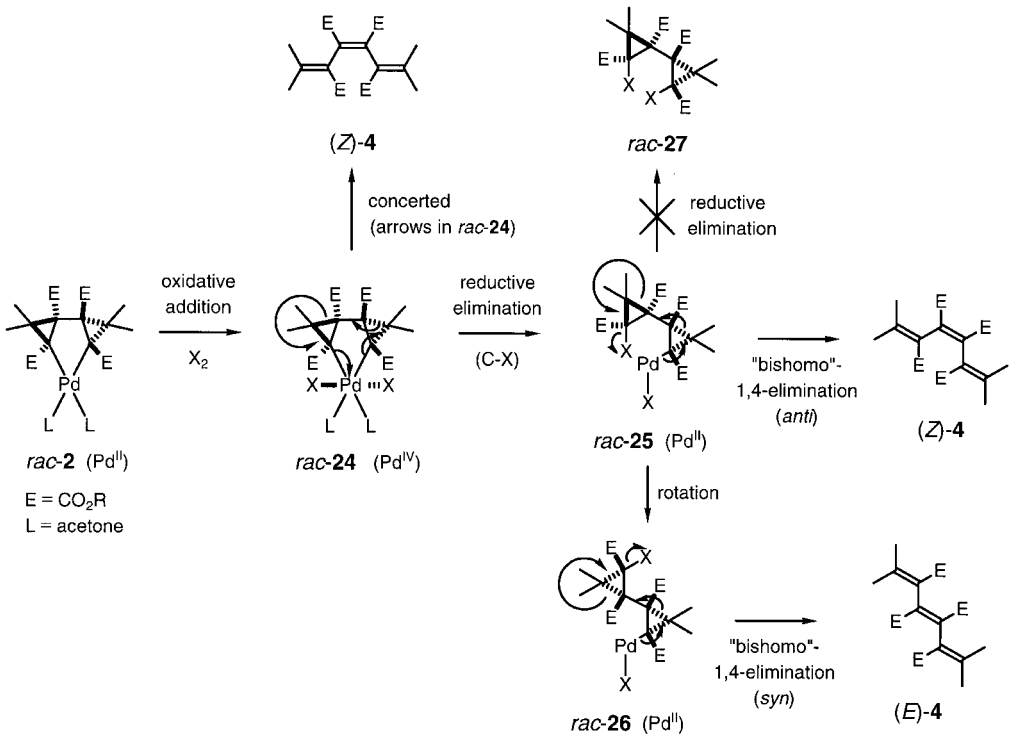


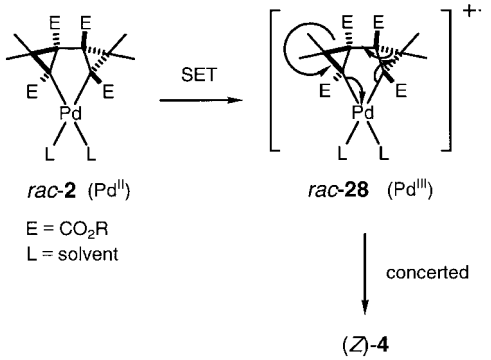
Scheme 13. Proposed pathways for oxidative addition reactions of *rac*-**2**.

elimination. If, on the other hand, the elimination is not much faster than the rotation, then some *E*-olefin is also formed via *rac*-**26** (this time by a process resembling a *syn*-elimination).

This pathway cannot be true for CAN or ferrocenium hexafluorophoshate as oxidants where an oxidative addition is not possible; however, only this pathway could explain the formation of the (*E*)-**4** as side-product in the case of bromine as the oxidant. It is not yet clear why only bromine in CH_2Cl_2 led to (*E*)-**4** as a side-product. If the reactions with I_2 and Br_2 in CH_2Cl_2 are compared, it could be argued that the intermediate *rac*-**25**, which bears iodine as a better leaving group eliminates L_2PdX faster than the corresponding bromo compound. This might explain why with iodine only (*Z*)-**4** was produced, while with bromine some (*E*)-**4** was also observed. However, then even more of the *E* diastereomer should be expected in the reaction with chlorine, which was not the case. Maybe there is a second effect, the electron-donating properties of the L_2PdX fragment bonded to carbon in *rac*-**25**. On the other hand, under the same conditions the conversion of the intermediate *rac*-**25** to *rac*-**26** should become slower with increasing mass and size of the unit that rotates. This could at least explain why in the reaction of *rac*-**2a** the ratio of (*Z*)-**4a**:(*E*)-**4a** was 4.5:1.0, while in the reaction of *rac*-**2d** it increased to (*Z*)-**4d**:(*E*)-**4d** to 11:1 (both reactions with bromine).

b) Another possibility for the selective formation of the *Z* olefin would be a concerted collapse of *rac*-**24** to (*Z*)-**4** and PdX_2. A stepwise reaction would allow rotation around the C–C single bond and thus also afford (*E*)-**4**. Again this cannot apply with CAN or ferrocenium hexafluorophosphate, since the formation of (*E*)-**4** cannot be explained this way.

c) Instead of an oxidative addition, a single-electron transfer (SET) from palladium to the oxidant occurs. Thus, in *rac*-**28** Pd^{III} would be formed. Either at that stage or after a second SET leading to a Pd^{IV} fragment, the concerted collapse of the palladacycle produces (*Z*)-**4** (Scheme 14). This pathway also



Scheme 14. Proposed mechanism for the reaction of *rac*-**2** with oxidants which involves a single-electron transfer (SET) and subsequent concerted collapse to give (*Z*)-**4**.

cannot explain the observed direct formation of (*E*)-**4**; however, it is the only possible way to explain the reaction with the one-electron oxidation reagents CAN or the ferrocenium cation. While with CAN it is not quite clear whether an inner-sphere or an outer-sphere SET takes place, with the ferrocenium cation the latter should be the case.

Conclusions

The reactions of PTHs can be conducted in a highly stereoselective manner. The reactions with hydrogen are in accordance with other similar reactions described in the literature in

that the C–Pd bond is transferred into a C–H bond. No C–heteroatom bond formation is observed in the reactions with reagents that can oxidatively add to the PTHs, which is different from comparable reactions of palladoles and palladacyclopentanes recently described. The latter reagents and oxidants that are unable to undergo oxidative addition both cause a collapse of the strained organic ligand on palladium and provide persubstituted (*Z*)-1,3,5-hexatrienes as the product of a combined oxidation and isomerization of the ligand.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM250, AM270, and DRX600 spectrometers. Chemical shifts are reported downfield from $SiMe_4$ for ^{1}H and ^{13}C NMR spectroscopy. The assignments s ($C_{quart.}$), d (CH), t (CH_2), and q (CH_3) for the ^{13}C NMR signals are based on DEPT135 and DEPT90 spectra. Mass spectra (EI) were obtained on a Varian MAT711 or 112S spectrometer, for FAB(+) and FAB(−) spectrometry a DMSO/*m*-nitrobenzyl alcohol matrix and xenon bombardment was used. High-resolution mass spectra were recorded on a MAT711. Infrared spectra were measured on a Perkin Elmer 1600 spectrometer. Elemental analysis were carried out on a Foss-Heraeus CHN-O-Rapid instrument. Melting points were measured on a Kofler hot-stage instrument and are uncorrected. Column chromatography was conducted on Merck silica gel 60 with hexane/ethyl acetate or hexane/acetone as the eluent.

rac-**2a**–**c**,[2] (1*S*,2*S*,4*S*,6*S*)-**2f**,[2] **5a**,[26] **5b**,[27] 2-diazopropane,[28] and $[Pd_2(dba)_3]\cdot CHCl_3$[29] were prepared as described elsewhere.

General procedures

Reactions with hydrogen: PTH was dissolved in acetone (10 mL) in a Schlenk flask (50 mL). A vacuum was applied until the solvent started to evaporate, then hydrogen (1 atm) was added. After the precipitation of palladium was complete, the solvent was removed in vacuo and the residue purified by column chromatography.

Reactions with sodium borohydride: PTH was dissolved in methanol (5 mL) in a two-necked flask (20 mL) and cooled to 0 °C in an ice bath. Sodium borohydride was added and the reaction mixture was allowed to warm to room temperature. After 20 min the solvent was removed in vacuo and the residue was purified by column chromatography.

Reactions with halogens or dibenzoyl peroxide: In a two-necked flask (50 mL) PTH was suspended in the given solvent (20 mL) and cooled to 0 °C. Within 5 min a solution of the halogen or dibenzoyl peroxide in CH_2Cl_2 was added. The solvent was removed in vacuo and the residue was purified by column chromatography.

Reactions with hydrogen

***rac*-3a**: Compound *rac*-**2a** (25.0 mg, 52.7 μmol) was treated with hydrogen according to the general procedure (reaction time 1 h). The crude product was purified by column chromatography (hexane/ethyl acetate 1:1) to give *rac*-**3a** (14.1 mg, 72%) as a colorless solid. M.p. 98 °C; R_f (hexane/ethyl acetate, 1:1) = 0.55; IR (film): $\tilde{\nu}$ = 2996, 2953, 1740, 1721, 1436, 1379, 1275, 1232, 1112, 1058, 1032, 956, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (s, 6H), 1.42 (s, 6H), 1.71 (s, 2H), 3.68 (s, 6H), 3.69 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.9 (q, 2C), 23.22 (q, 2C), 32.58 (s, 2C), 39.17 (d, 2C), 40.51 (s, 2C), 51.31 (q, 2C), 51.96 (q, 2C), 168.66 (s, 2C), 171.29 (s, 2C); MS (70 eV): *m*/*z* (%): 370 (64) [M^+], 339 (69) [M^+ – OMe], 247 (100); $C_{18}H_{26}O_8$ (370.4): calcd C 58.37, H 7.08; found C 58.56, H 7.18.

***rac*-3b**: Compound *rac*-**2b** (11.0 mg, 17.1 μmol) was treated with hydrogen according to the general procedure (reaction time 2 h). The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give *rac*-**3b** (8.10 mg, 88%) as a colorless oil. R_f (hexane/ethyl acetate, 4:1) = 0.55; IR (film): $\tilde{\nu}$ = 2978, 2932, 1731, 1713, 1468, 1457, 1392, 1367, 1295, 1248, 1154, 1110, 1056, 1022, 1000, 919, 851, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.35 (s, 6H), 1.40 (s, 18H), 1.46 (s, 6H), 1.47 (s, 2H), 1.49 (s, 18H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.73 (q, 2C), 23.66 (q, 2C), 27.89 (q, 6C), 28.14 (q, 6C), 31.63 (s, 2C), 39.90 (d, 2C), 40.72 (s, 2C), 80.37 (s, 2C), 80.59 (s, 2C), 167.34 (s, 2C), 169.57 (s, 2C); MS (FAB(−)): *m*/*z* (%): 481 (100) [M^+ – *t*Bu]; HRMS (80 eV): $C_{22}H_{33}O_8$ [M^+ – *t*Bu – isobutene]: calcd 425.21755; found 425.21767.

***rac*-3c**: Compound *rac*-**2c** (2.80 mg, 3.87 μmol) was treated with hydrogen according to the general procedure (reaction time 1 h). The crude product was purified by column chromatography (hexane/ethyl acetate, 1:1) to give *rac*-**3c** (1.21 mg, 51%) as a colorless oil. R_f (hexane/ethyl acetate, 1:1) = 0.55; IR (film): $\tilde{\nu}$ = 2962, 2928, 1758, 1735, 1592, 1492, 1191, 1163, 1108, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.70 (s, 6H), 1.72 (s, 6H), 2.28 (s, 2H), 7.11–7.42 (m, 20H); MS (70 eV): *m*/*z* (%): 618 (7) [M^+], 525 (100) [M^+ – OPh]; HRMS (80 eV): $C_{38}H_{34}O_8$: calcd 618.22537; found 618.22501.

***rac*-3d**: Compound *rac*-**2d** (92.6 mg, 131 μmol) was treated with hydrogen according to the general procedure(reaction time 3 h). The crude product was purified by column chromatography (hexane/ethyl acetate, 5:1) to give *rac*-**3d** (70.0 mg, 89%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2956, 1751, 1458, 1438, 1382, 1292, 1206, 1173, 1112, 1081, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.42 (s, 6H), 1.48 (s, 6H), 1.95 (s, 2H), 3.72 (s, 6H), 3.75 (s, 6H), 4.53 (d, J = 15.9 Hz, 2H), 4.54 (d, J = 15.8 Hz, 2H), 4.70 (d, J = 15.8 Hz, 2H), 4.74 (d, J = 15.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.78 (q, 2C), 23.19 (q, 2C), 33.74 (s, 2C), 38.94 (d, 2C), 39.95 (s, 2C), 51.84 (q, 2C), 52.00 (q, 2C), 60.77 (t, 2C), 61.11 (t, 2C), 166.99 (s, 2C), 167.51 (s, 2C), 167.98 (s, 2C), 170.02 (s, 2C); MS (70 eV): *m*/*z* (%): 602 (52) [M^+], 571 (25), 513 (35), 439 (42), 332 (55), 305 (68), 215 (96), 187 (100).

***rac*-3e**: Compound *rac*-**2e** (75.2 mg, 85.9 μmol) and sodium borohydride (13.5 mg, 357 μmol) were treated according to the general procedure. The crude product was purified by column chromatography (hexane/ethyl acetate, 1:1) to give *rac*-**3e** (44.1 mg, 67%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2954, 1736, 1475, 1435, 1388, 1308, 1226, 1191, 1153, 1109, 1053, 1015, 870, 809, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.17 (s, 6H), 1.18 (s, 6H), 1.20 (s, 12H), 1.24 (s, 6H), 1.38 (s, 6H), 1.61 (s, 2H), 3.65 (s, 6H), 3.67 (s, 6H), 4.02–4.22 (m, 8H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.14 (q, 2C), 22.17 (q, 4C), 22.67 (q, 2C), 22.78 (q, 2C), 23.29 (q, 2C), 32.53 (s, 2C), 38.95 (d, 2C), 40.41 (s, 2C), 42.15 (s, 4C), 51.84 (q, 2C), 51.89 (q, 2C), 70.54 (t, 2C), 71.02 (t, 2C), 167.50 (s, 2C), 170.11 (s, 2C), 175.62 (s, 2C), 175.72 (s, 2C); MS (70 eV): *m*/*z* (%): 770 (86) [M^+], 739 (19), 638 (58), 506 (53), 374 (100), 115 (94); $C_{38}H_{58}O_{16}$ (770.9): calcd C 59.21, H 7.58; found C 58.70, H 7.76.

(1*R*,2*R*,1′*R*,2′*R*)-**3f**: Compound (1*S*,2*S*,4*S*,6*S*)-**2f** (8.09 mg, 9.90 μmol) was treated with hydrogen according to the general procedure (reaction time 16 h). The crude product was purified by column chromatography (hexane/ethyl acetate, 1:1) to give (1*R*,2*R*,1′*R*,2′*R*)-**3f** (7.01 mg, 99%) as a colorless oil. R_f (hexane/ethyl acetate, 1:1) = 0.50; IR (film): $\tilde{\nu}$ = 2987, 2939, 1746, 1732, 1450, 1380, 1268, 1199, 1095, 1132, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (t, J = 7.1 Hz, 6H), 1.28 (t, J = 7.1 Hz, 6H), 1.39 (d, J = 7.1 Hz, 6H), 1.45 (d, J = 7.1 Hz, 6H), 1.48 (s, 6H), 1.50 (s, 6H), 1.92 (s, 2H), 4.14–4.24 (m, 8H), 4.94–5.06 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.36 (q, 2C), 14.40 (q, 2C), 16.91 (q, 2C), 17.03 (q, 2C), 17.59 (q, 2C), 23.54 (q, 2C), 33.95 (s, 2C), 39.37 (d, 2C), 40.12 (s, 2C), 61.50 (t, 2C), 61.54 (t, 2C), 69.22 (d, 2C), 70.17 (d, 2C), 167.19 (s, 2C), 170.47 (s, 2C), 170.57 (s, 2C), 171.18 (s, 2C); MS (70 eV): *m*/*z* (%): 714 (3) [M^+], 669 (8) [M^+ – OEt].

Reactions with halogens or dibenzoyl peroxide

(*Z*)-4a and (*E*)-4a: Compound *rac*-**2a** (148 mg, 312 μmol) in CH_2Cl_2 (20 mL) was treated with bromine (500 mg, 3.12 mmol, 10 equiv) according to the general procedure. Column chromatography of the crude product (hexane/ethyl acetate, 1:1) afforded a 4.5:1 mixture of (*Z*)-**4a** and (*E*)-**4a**, which were separated by semipreparative HPLC (hexane/ethyl acetate, 20:11) to give (*E*)-**4a** (18.4 mg, 16%) and (*Z*)-**4a** (80.4 mg, 70%) as colorless oils. (*Z*)-**4a**: R_f (hexane/ethyl acetate, 1:1) = 0.35; IR (film): $\tilde{\nu}$ = 2999, 2952, 2844, 1725, 1627, 1434, 1372, 1286, 1223, 1179, 1090, 1038, 1007, 898, 840, 798 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.72 (s, 6H), 2.06 (s, 6H), 3.55 (s, 6H), 3.70 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.51 (q, 2C), 23.96 (q, 2C), 51.21 (q, 2C), 52.29 (q, 2C), 122.26 (s, 2C), 137.45 (s, 2C), 154.53 (s, 2C), 165.60 (s, 2C), 167.37 (s, 2C); MS (70 eV): *m*/*z* (%): 368 (100) [M^+], 337 (34) [M^+ – OMe]; $C_{18}H_{24}O_8$ (368.4): calcd C 58.69, H 6.57; found C 58.55, H 6.46; HRMS (80 eV): $C_{18}H_{24}O_8$: calcd 368.14712; found 368.14736; (*E*)-**4a**: R_f (hexane/ethyl acetate, 1:1) = 0.35; IR (film): $\tilde{\nu}$ = 2994, 2953, 2845, 1726, 1635, 1431, 1370, 1288, 1222, 1173, 1087, 1021, 898, 797, 782 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.86 (s, 6H), 2.25 (s, 6H), 3.66 (s, 6H), 3.69 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.34 (q, 2C), 24.01 (q, 2C), 51.17 (q, 2C), 52.04 (q, 2C), 123.05 (s, 2C), 137.90 (s, 2C),

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152.73 (s, 2C), 164.45 (s, 2C), 167.20 (s, 2C); MS (70 eV): *m/z* (%): 368 (82) [M^+], 337 (100) [$M^+ - OMe$]; $C_{18}H_{24}O_8$ (368.4): calcd C 58.69, H 6.57; found C 58.45, H 6.75; HRMS (80 eV): $C_{18}H_{24}O_8$: calcd 368.14712; found 368.14699.

(*Z*)-4b: Compound *rac*-**2b** (100 mg, 155 μmol) was treated with iodine (39.3 mg, 155 μmol) according to the general procedure. Column chromatography of the crude product (hexane/ethyl acetate, 3:1) gave (*Z*)-**4b** (70.1 mg, 84%) as a colorless oil. R_f (hexane/ethyl acetate, 3:1) = 0.55; IR (film): $\tilde{\nu}$ = 3004, 2980, 2933, 1715, 1626, 1478, 1455, 1392, 1368, 1252, 1237, 1159, 1089, 1020, 848, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.36 (s, 18H), 1.41 (s, 18H), 1.75 (s, 6H), 1.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.04 (q, 2C), 24.71 (q, 2C), 27.84 (q, 6C), 28.07 (q, 6C), 80.53 (s, 2C), 80.63 (s, 2C), 124.46 (s, 2C), 137.77 (s, 2C), 150.61 (s, 2C), 164.83 (s, 2C), 165.89 (s, 2C); MS (70 eV): *m/z* (%): 536 (0.1) [M^+], 480 (1), 276 (100); $C_{30}H_{48}O_8$ (536.7): calcd C 67.14, H 9.01; found C 66.71, H 8.77; HRMS (80 eV): $C_{30}H_{48}O_8$: calcd 536.33492; found 536.33457.

(*Z*)-4d: Compound *rac*-**2d** (70.4 mg, 99.6 μmol) and iodine (25.3 mg, 99.7 μmol) were treated according to the general procedure. The crude product was purified by column chromatography (hexane/ethyl acetate, 1:1) to give (*Z*)-**4d** (58.2 mg, 97%) as a pale-yellow oil. R_f (hexane/ethyl acetate, 1:3) = 0.58; IR (film): $\tilde{\nu}$ = 3006, 2956, 2853, 1765, 1731, 1621, 1438, 1382, 1291, 1200, 1144, 1102, 1073, 1022, 975, 900, 849 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.86 (s, 6H), 2.13 (s, 6H), 3.66 (s, 6H), 3.67 (s, 6H), 4.54 (s, 4H), 4.62 (s, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.91 (q, 2C), 24.83 (q, 2C), 51.89 (q, 4C), 60.57 (t, 2C), 61.40 (t, 2C), 121.03 (s, 2C), 137.50 (s, 2C), 158.13 (s, 2C), 164.24 (s, 2C), 165.80 (s, 2C), 167.59 (s, 2C), 167.90 (s, 2C); MS (70 eV): *m/z* (%): 600 (32) [M^+], 569 (28), 527 (43), 482 (54), 303 (55), 275 (49), 240 (100); $C_{26}H_{32}O_{16}$ (600.5): calcd C 52.00, H 5.37; found C 51.65, H 5.51; UV: λ_{max} = 210 nm (hexane, lg ε: 4.467).

(*Z*)-4e: Compound *rac*-**2e** (99.1 mg, 113 μmol) and iodine (28.7 mg, 113 μmol) were treated according to the general procedure. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give (*Z*)-**4e** (83.4 mg, 96%) as a colorless solid. M.p. 64 °C; R_f (hexane/ethyl acetate, 1:1) = 0.43; IR (film): $\tilde{\nu}$ = 2953, 1731, 1624, 1438, 1368, 1306, 1244, 1152, 1086, 1039 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.12 (s, 24H), 1.67 (s, 6H), 1.99 (s, 6H), 3.57 (s, 6H), 3.60 (s, 6H), 3.98 (s, 4H), 4.08 (s, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.07 (q, 4C), 22.13 (q, 4C), 22.26 (q, 2C), 23.92 (q, 2C), 42.16 (s, 2C), 42.26 (s, 2C), 51.75 (q, 2C), 51.87 (q, 2C), 70.28 (t, 2C), 70.84 (t, 2C), 121.99 (s, 2C), 137.80 (s, 2C), 153.50 (s, 2C), 164.84 (s, 2C), 165.34 (s, 2C), 175.68 (s, 4C); MS (70 eV): *m/z* (%): 768 (14) [M^+], 737 (63), 637 (5), 608 (9), 276 (13), 115 (100); $C_{38}H_{56}O_{16}$ (768.9): calcd C 59.36, H 7.34; found C 59.13, H 7.25; UV: λ_{max} = 215 nm (hexane, lg ε: 4.595).

***rac*-6**: From **5a** (275 mg, 1.49 mmol), **5b** (400 mg, 1.49 mmol), and $[Pd_2(dba)_3] \cdot CHCl_3$ (617 mg, 596 μmol) in analogy to the literature[2] after column chromatography (hexane/ethyl acetate, 1:1; then hexane/acetone, 2:3) gave *rac*-**6** (280 mg, 42%), *rac*-**2a**[2] (119 mg, 21%), and *rac*-**2b**[2] (161 mg, 21%) as yellow solids. *rac*-**6**: R_f (hexane/acetone, 2:3) = 0.35; IR (film): $\tilde{\nu}$ = 2974, 2945, 1702, 1674, 1613, 1438, 1366, 1306, 1232, 1166, 1108, 1073, 1000, 957, 907, 866, 818, 779 cm^{-1}; ^1H NMR ([D$_6$]acetone, 250 MHz): δ = 1.31 (s, 3H), 1.32 (s, 9H), 1.34 (s, 3H), 1.40 (s, 9H), 1.87 (s, 3H), 2.01 (s, 3H), 3.34 (s, 3H), 3.53 (s, 3H); ^{13}C NMR ([D$_6$]acetone, 62.9 MHz): δ = 20.05 (q), 20.71 (q), 27.63 (q), 27.86 (q), 28.48 (q, 6C), 35.45 (s), 35.52 (s), 39.07 (s), 39.80 (s), 48.24 (s), 50.24 (q), 50.60 (q), 55.41 (s), 78.24 (s, 2C), 171.83 (s), 173.07 (s), 173.57 (s), 173.99 (s); MS (FAB(+)): *m/z* (%): 558 (3) [(^{106}Pd)M^+], 57 (100) [*t*Bu].

(*Z*)-7: Compound *rac*-**6** (110 mg, 197 μmol) and iodine (50.1 mg, 197 μmol) were treated according to the general procedure. Column chromatography of the crude product (hexane/ethyl acetate, 3:1) gave (*Z*)-**7** (73.2 mg, 82%) as a colorless oil. R_f (hexane/ethyl acetate, 3:1) = 0.50; IR (film): $\tilde{\nu}$ = 2980, 2950, 1723, 1716, 1628, 1454, 1434, 1368, 1280, 1252, 1225, 1161, 1091, 1044, 1031, 985, 919, 848, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.41 (s, 9H), 1.46 (s, 9H), 1.72 (s, 3H), 1.83 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 3.60 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.11 (q), 22.40 (q), 24.03 (q), 24.42 (q), 27.70 (q, 3C), 27.98 (q, 3C), 51.09 (q), 51.97 (q), 80.78 (s), 81.22 (s), 122.59 (s), 124.06 (s), 135.44 (s), 139.73 (s), 151.73 (s), 153.37 (s), 164.45 (s), 165.74 (s), 165.88 (s), 167.68 (s); MS (70 eV): *m/z* (%): 395 (15) [$M^+ - C_4H_9$], 308 (100), 276 (92); HRMS (80 eV): $C_{20}H_{27}O_8$ [$M^+ - C_4H_9$]: calcd 395.17060, found 395.17048.

(*Z*)-**9**: Compound *rac*-**8** (86.5 mg, 146 μmol) and iodine (37.1 mg, 146 μmol) were treated according to the general procedure and purified by column chromatography (hexane/ethyl acetate, 1:1) to give (*Z*)-**9** (69.3 mg, 98%) as a colorless oil. R_f (hexane/ethyl acetate, 1:1) = 0.45; IR (film): $\tilde{\nu}$ = 3003, 2954, 2850, 1746, 1724, 1624, 1437, 1381, 1283, 1221, 1198, 1143, 1097, 1059, 998, 898, 849, 797 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.77 (s, 3H), 1.79 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 3.56 (s, 3H), 3.67 (s, 3H), 3.68 (s, 3H), 3.70 (s, 3H), 4.50 (s, 2H), 4.61(s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.56 (q), 22.81 (q), 24.32 (q), 24.35 (q), 51.26 (q), 51.96 (q, 2C), 52.46 (q), 60.44 (t), 61.28 (t), 121.36 (s), 121.77 (s), 136.99 (s), 138.06 (s), 155.54 (s), 156.76 (s), 164.28 (s), 165.03 (s), 166.07 (s), 166.80 (s), 167.49 (s), 167.71 (s); MS (70 eV): *m/z* (%): 484 (28) [M^+], 469 (7), 453 (21), 424 (21), 411 (100), 366 (34), 240 (60); $C_{22}H_{28}O_{12}$ (484.5): calcd C 54.54, H 5.83; found C 54.27, H 6.14; UV: λ_{max} = 214 nm (hexane, lg ε = 4.510).

(*Z*)-4d from *rac*-2d and dibenzoyl peroxide: Compound *rac*-**2d** (30.0 mg, 42.4 μmol) was suspended in CH_2Cl_2 (10 mL) and cooled to 0 °C. Dibenzoyl peroxide (10.6 mg, 43.8 μmol) was added in small portions. After 5 min the reaction was worked-up as described above for the reaction of *rac*-**2d** with iodine to give (*Z*)-**4d** (24.2 mg, 98%).

Reactions with oxidants unable to undergo oxidative addition

Reaction with CAN: Compound *rac*-**2d** (25.0 mg, 35.4 μmol) was dissolved in acetonitrile (5 mL) and cooled to 0 °C and CAN (40.4 mg, 73.6 mmol) was slowly added. After 45 min (*Z*)-**4d** (21.0 mg, 99%) was isolated as described above.

Reaction with ferrocenium tetrafluoroborate: Compound *rac*-**2a** (20.0 mg, 42.1 μmol) was dissolved in acetonitrile (5 mL) and cooled to 0 °C and ferrocenium tetrafluoroborate (24.1 mg, 88.4 mmol) was slowly added. After 45 min (*Z*)-**4a** (12.7 mg, 82%) was isolated as described above.

Crystal structure analysis of 3a: Siemens CCD three-circle diffractometer, $Mo_{K\alpha}$ radiation, 0.71073 Å, ω scans, Lorentz and polarization correction, empirical absorption correction with SADABS.[30] The structure was solved by direct methods and refined with SHELXL-97,[31] by full-matrix least-square methods against F^2. Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters by means of a riding model. $C_{18}H_{26}O_8$: 0.35 × 0.30 × 0.20 mm; monoclinic, space group *C*2/*c*; a = 16.954(1), b = 11.136(1), c = 10.219(1) Å, β = 99.12(1)°; V = 1905.0(3) Å^3, Z = 4; ρ_{calcd} = 1.291 gcm^{-1}; μ = 0.101 mm^{-1}, T_{min}/T_{max} = 0.9800/0.9654; $2\theta_{max}$ = 56.5°; T = 173 K, 18782 measured reflections, 2371 independent reflections; 121 parameters refined; $R1$ = 0.0409, $wR2$ = 0.0954; max. residual electron density 0.338 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-113 319 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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