Diene Complexes of *trans*-5-Palladatricyclo[4.1.0.0^{2,4}]heptanes

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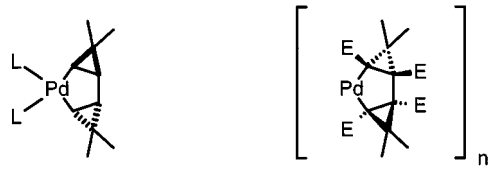
The complexes *rac*-**5** and *rac*-**6** of the *trans*-5-palladatricyclo-[4.1.0.0^{2,4}]heptane *rac*-**2a** with norbornadiene and 1,5-cyclooctadiene were prepared and investigated by X-ray structure determination. With open-chained, unsaturated substrates, e.g. **7** and **8**, no complexes could be isolated. In all cases no insertion of the olefin into the metal–carbon bond of the palladacycloalkane was observed.

trans-5-Palladatricyclo[4.1.0.0^{2,4}]heptanes (PTHs) are an interesting class of organometallic compounds in which two chiral carbon atoms are directly bound to a palladium center. The first derivatives described in the literature were Binger's racemic phosphane complexes *rac*-**1**.[1] We recently published the preparation and resolution of *rac*-PTH-tetracarboxylates **2**.[2] **2** itself is a coordination polymer,[3] monomeric complexes are for example obtained with diphosphanes[2] or acetone[3][4] as ligands. The PTHs are chiral bis-homo derivatives of the corresponding palladoles[5] − the latter being important catalysts for the enyne cyclization[6], the enyne metathesis[6][7] and related reactions.[8] That the PTHs show catalytical properties has been proven by their ability to catalyze the cycloisomerization/dimerization of allenyl ketones to furans.[9]

In reactions catalyzed by PTHs, a coordination of unsaturated substrates is the first step. Here we describe the first diolefin complexes of PTHs which may serve as model compounds for the coordination of such unsaturated substrates during catalysis reactions.

Scheme 1

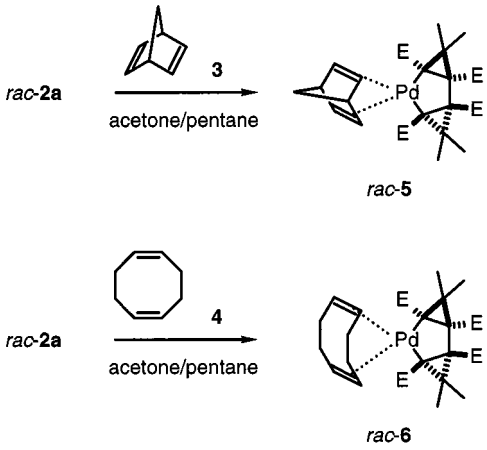


rac-**1** L = PR_3 **2** E = CO_2R, a R = Me

Synthesis of the Diene Complexes

For our investigation we used the PTH *rac*-**2a**.[2] We focused on chelating dienes, norbornadiene (NBD, **3**) and 1,5-cyclooctadiene (COD, **4**) were used. An excess of **3** or **4** was added to solutions of *rac*-**2a** in acetone. Then most of the acetone was evaporated in vacuo and pentane was added to the remaining solution. On cooling to 0°C the complexes *rac*-**5** and *rac*-**6** crystallized. Efforts with other unsaturated substrates like the diyne **7** or the enyne **8** without a rigid structure did not lead to defined products.

Scheme 2



Scheme 3

7 E = CO_2Me **8**

X-ray Structure Determination and Discussion

By the method described above, suitable crystals of *rac*-**5** and *rac*-**6** for X-ray structure determination could be obtained. The ORTEP plot of *rac*-**5** is shown in Figure 1, the one of *rac*-**6** in Figure 2. Selected crystallographic data of both compounds are listed in Table 1.[10]

rac-**5** approximately has a two-fold symmetry with the exception of the relative orientation of the methoxycarbonyl

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Figure 1. ORTEP plot of *rac*-**5**

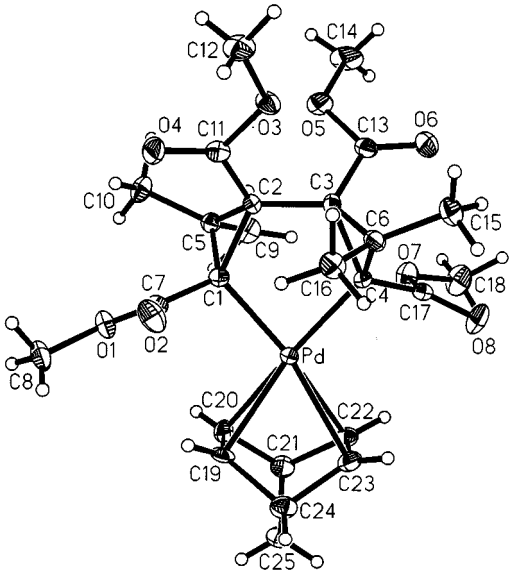
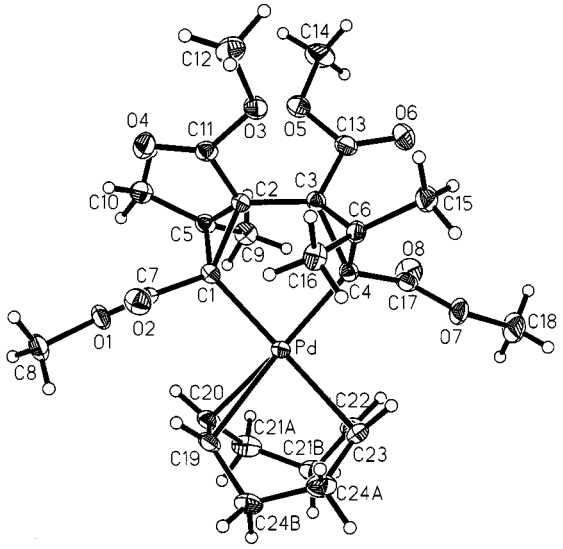


Figure 2. ORTEP plot of *rac*-**6**



groups attachted to C1 and C4. Two molecules of *rac*-**6** crystallize in the asymmetric unit, their structures show only small differences in their conformations. The Pd−C1 and Pd−C4 bond lengths are 2.05 Å in *rac*-**5** and 2.06−2.08 Å in *rac*-**6**. This is slightly longer than in the acetone complexes of PTHs (2.02 Å)[3][4] and slightly shorter than in the phosphane complexes of PTHs (2.11 and 2.13 Å, respectively)[2] and reflects the *trans* influence[11] of the different donors.

In *rac*-**5** the distances from Pd to the C atoms of the NBD group range from 2.26 to 2.31 Å. Similar distances have been found in the crystal structure of the corresponding NBD-tetrakis(methoxycarbonyl)palladole complex[12]. The hydrogen atoms at C19, C20, C22, and C23 deviate about 0.14 Å from the planes of the C−C double bonds in a direction away from the Pd atom. The molecular conformation is stabilised by a number of weak, electrostatic, intramolecular O···H contacts with distances equal to the van der Waals contact distance of 2.4 Å [O2···H16a: 2.40(3) Å; O4···H10a: 2.32(5) Å; O6···H15a: 2.34(5) Å; and O7···H9a: 2.48(4) Å]. Similar intramolecular interactions have been observed in the PTH part of *rac*-**6**. The crystal packing shows no short intermolecular contacts.

Table 1. Selected bond lengths [Å], bond angles [°], and dihedral angles [°] for *rac*-**5** and *rac*-**6**

	rac-**5**	*rac*-**6** (molecule 1)	*rac*-**6** (molecule 2)
Pd−C1	2.047(3)	2.075(2)	2.058(2)
Pd−C4	2.049(2)	2.071(2)	2.083(2)
Pd−C19	2.273(3)	2.336(2)	2.318(2)
Pd−C20	2.257(3)	2.282(2)	2.283(2)
Pd−C22	2.290(3)	2.326(2)	2.306(2)
Pd−C23	2.309(3)	2.287(2)	2.284(2)
C19−C20	1.359(5)	1.358(3)	1.363(3)
C22−C23	1.367(6)	1.360(3)	1.358(3)
C1−Pd−C4	83.8(1)	83.0(1)	83.3(1)
C1−Pd−C19	103.1(1)	99.1(1)	98.5(1)
C4−Pd−C22	104.4(1)	98.5(1)	100.0(1)
C1−Pd−C20	100.9(1)	94.2(1)	90.7(1)
C4−Pd−C23	105.6(1)	94.1(1)	95.3(1)
C1−Pd−C22	158.2(1)	163.2(1)	158.3(1)
C4−Pd−C20	160.7(1)	162.3(1)	162.4(1)
C1−Pd−C23	162.4(1)	162.6(1)	167.3(1)
C4−Pd−C19	162.2(1)	163.5(1)	163.0(1)
C4−Pd−C1−C2	1.9(3)	−3.2(1)	2.5(1)
C1−Pd−C4−C3	−5.0(3)	0.1(1)	−4.9(1)
C1−C2−C3−C4	−5.7(5)	−5.8(2)	−4.2(2)

The COD ligand in *rac*-**6** occupies a twist-boat conformation as known from most of the other (COD)Pd^{II} complexes.[13] The bond lengths of Pd to the olefinic carbon atoms of the COD range from 2.28 to 2.34 Å, such values were also reported for the known (COD)Pd^{II} complexes.[8] Different from the NBD ligand in *rac*-**5**, one hydrogen atom of each double bond of the COD ligand in *rac*-**6** shows weak intramolecular O···H contacts with distances equal to the van der Waals contact distance (2.46 and 2.41 Å, respectively) to the ether oxygen atom of the ester group at C1 and C4 of the PTH framework.

The angle between the plane through C1−Pd−C4 and the plane through Pd and the midpoints of the C19−C20 and C22−C23 double bonds is 2.6° in *rac*-**5** and 0.4° for molecule 1 and 4.5° for molecule 2 in *rac*-**6**! Essentially this is, like in the bis(acetone) complexes (6.9 and 9.3°, respectively),[3][4] the square planar coordination as one would expect for Pd^{II}. On the other hand in complexes with sterically demanding bidentate phosphanes a tilt of up to 30° was observed.[2]

Ittel's and Ibers's[14] structural parameters α and β characterize the hybridization changes at the coordinated olefinic carbon atoms. α is defined as the angle between the normals of the two planes defined by the three atoms of each $R_2C=$ unit of the olefin, so α would be 0° for a planar alkene. β and β′ are the angles between the olefinic C=C bond and the normals mentioned before, so the β angles decrease from 90° with increasing distortion. For *rac*-**5** and *rac*-**6** these parameters are listed in Table 2. Clearly, the ole-

fins are non-planar, but the values correspond to those of other related complexes,[13] so the coordinated olefin does not experience any unusual distortion.

Table 2. Structural parameters for *rac*-**5** and *rac*-**6**

	rac-**5**	*rac*-**6** (molecule 1)	*rac*-**6** (molecule 2)
	C19−C20, C22−C23	C19−C20, C22−C23	C19−C20, C22−C23
α	19°, 23°	18°, 15°	18°,16°
β	85°, 75°	82°, 80°	81°, 81°
β′	77°, 82°	81°, 85°	82°, 84°

PTHs are the first palladacycloalkanes without stabilizing ligands at the palladium center, the coordination sphere is saturated by easily substitutable solvent molecules.[4][9] Since it is part of a cyclopropyl ring, the carbon atom attached to the palladium center has a hybridization close to sp^2.[15] The fact that only coordination but no insertion of the olefins was observed, proves the stability of the Pd−C bonds in these exceptional palladacycloalkanes. This is in agreement with the formation of the PTHs: even when the Pd^0 precursor was subjected to an excess of cyclopropene, only the PTH was formed and the remaining cyclopropene remained untouched. This is in contrast to Binger's results. He also observed the formation of seven-membered metallacycles[16] and nine-membered[17] palladacycles or products of a reductive elimination from such insertion products, i.e. cyclic trimers[18] or tetramers[17][18] of the cyclopropene. For catalysis reactions this suggests that the PTH framework is also not destroyed readily by insertion (maybe followed by reductive elimination) reactions.

^{1}H- and ^{13}C-NMR Spectra

The chemical shifts of the coordinated and uncoordinated diene ligand are listed in Tables 3 and 4.

Table 3. NMR data of free NBD and *rac*-**5** in $CDCl_3$ at 298 K[a]

	free NBD	*rac*-**5**	Δδ
^{1}H NMR	1.95	1.98	0.03
	3.53	3.96	0.43
	6.66	5.71	−0.95
		6.23	−0.43
^{13}C NMR	50.4	50.4	0.0
	75.2	73.4	−1.8
	143.2	107.6	−35.6
		113.8	−29.4

[a] Chemical shifts in ppm (δ).

In the coordinated dienes the symmetry is reduced, thus some NMR signals of the free diene split into several new signals of the corresponding nuclei in the coordinated diene. As one can see, only the chemical shift of the olefinic hydrogen and carbon atoms experience a relevant change.

While in the coordinated COD the signals of the olefinic hydrogen atoms are both shifted to lower and higher field by the same amount, in the NBD they are both shifted to lower field. The signals of the olefinic carbon atoms are all shifted downfield by coordination to *rac*-**2a**, but again the effect is stronger in the NBD ligand. The C_2 symmetry of the PTHe leads to a chemical shift difference between the signals of the two non-equivalent carbon atoms of the coordinated olefin of about 5 ppm in both *rac*-**5** and *rac*-**6**, but the signals of the two non-equivalent hydrogen atoms differ by 0.52 ppm in *rac*-**5** and 1.13 in *rac*-**6**.

Table 4. NMR data of free COD and *rac*-**6** in $CDCl_3$ at 298 K[a]

	free COD	*rac*-**6**	Δδ
^{1}H NMR	2.25	2.08−2.21	−0.10
		2.36−2.52	0.19
		2.69−2.78	0.49
	5.50	4.86−4.96	−0.56
		6.03−6.10	0.57
^{13}C NMR	27.9	26.4	−1.5
		32.2	4.3
	128.3	113.9	−14.4
		117.7	−10.6

[a] Chemical shifts in ppm (δ).

Conclusion

PTHs readily form complexes with chelating, rigid dienes. In these complexes, where Pd is surrounded by six carbon atoms, only a small deviation from a perfect square planar coordination (considering the midpoints of the double bonds) was observed. Like the related bis(acetone) complexes of PTHs, this demonstrates that the strong deviation from a square-planar coordination geometry observed with diphosphanes originates from intramolecular sterical repulsion of the latter ligands and substituents on the PTH framework. No insertion of the olefins into the Pd−C bond of the PTH was observed. This suggests that the PTHs remain intact during catalysis reactions or at least show a low tendency for insertion of unsaturated substrates.

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Experimental Section

General: All operations were carried out under N_2 and in dry solvents. *rac*-**2a**[2][4] was prepared according to literature procedures. − IR: Perkin-Elmer 1600. − NMR: Bruker AM 250 (250 and 62.9 MHz for ^{1}H and ^{13}C, respectively). $CDCl_3$ as solvent δ_H = 7.25; δ_C = 77.0. The degree of substitution of the C atoms was determined by a combination of DEPT-135 and DEPT-90. − MS: VG-Instruments-Micro-Mass Tris 2000, EI 70 eV, quadrupol analysator and Finnigan CH7A (80 eV). − Melting points (uncorrected): Kofler hot-stage.

rac-**5**: To 50 mg (10.5 μmol) of *rac*-**2a** in 5 ml of acetone 2 equiv. of norbornadiene (**3**, 19.3 mg, 21.0 μmol) were added. After 30 min at room temparatue, the solution was concentrated to about 0.5 ml in a rotary evaporator and 0.5 ml of pentane was added. Then the soution was placed in a refrigerator (0°C), over night 38.8 mg (65%) of *rac*-**5** precipitated as yellow crystals. − M.p. 197°C. − IR (neat, NaCl): $\tilde{\nu}$ = 2947 cm^{-1}, 1715, 1691, 1432, 1369, 1310, 1221,

1172, 1106, 1067, 1000, 920, 733. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.38 (s, 6 H, Me), 1.67 (s, 6 H, Me), 1.98 (m, 2 H), 3.61 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.96 (m, 2 H, CH_2), 5.71 (m, 2 H, CH), 6.23 (m, 2 H, CH). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.39 (q, 2 C), 25.69 (q, 2 C), 37.29 (s, 2 C), 49.57 (s, 2 C), 50.42 (d, 2 C), 51.14 (q, 2 C), 51.27 (q, 2 C), 57.95 (s, 2 C), 73.36 (t), 107.61 (d, 2 C), 113.82 (d, 2 C), 172.24 (s, 2 C), 172.46 (s, 2 C). – MS (70 eV); *m/z* (%): 566 (1) [(^{106}Pd) M^+], 474 (46) [M^+ – NBD], 415 (8). – $C_{25}H_{32}O_8Pd$ (566.9): calcd. C 52.96, H 5.69; found C 53.23, H 5.89.

Crystal Structure Analysis of rac-**5**:[10] Siemens Smart diffractometer, Mo-K_α radiation, –100°C, empirical absorption correction, structure determination by direct methods (SIR92); the positions of the hydrogen atoms were determined by a difference Fourier synthesis, refinement of the hydrogen atoms with isotropic thermal parameters. $C_{25}H_{32}O_8Pd$, triclinic, space group $P(-1)$; a = 9.064(2), b = 8.484(2), c = 17.685(4) Å, α = 95.20(2), β = 78.84(1), γ = 66.82(1)°; V = 1205.4(5) Å^3; Z = 2; $\rho_{calcd.}$ = 1.562 g cm^{-1}; μ = 8.2 cm^{-1}; sphere up to 2θ = 59°; 6062 independent reflections with $I > 0$; 436 parameters refined, R = 0.038; R_w = 0.065; residual density between –0.26 and +1.16 e Å^{-3}.

rac-**6**: To 50 mg (10.5 μmol) of *rac*-**2a** in 5 ml of acetone 2 equiv. of 1,5-cyclooctadiene (**4**, 22.7 mg, 21 μmol) were added. After 30 min at room temparatue, the solution was concentrated to about 0.5 ml in a rotary evaporator and 0.5 ml of pentane was added. Then the soution was placed in a refrigerator (0°C), over night 61.4 mg (75%) of *rac*-**6** precipitated as yellow crystals. – M.p. 191°. – IR (neat, NaCl): $\tilde{\nu}$ = 2946 cm^{-1}, 1714, 1690, 1430, 1368, 1304, 1215, 1105, 1066, 1006. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.43 (s, 6 H), 1.79 (s, 6 H), 2.08–2.21 (m, 2 H), 2.36–2.52 (m, 2 H), 2.69–2.78 (m, 4 H), 3.57 (s, 6 H), 3.60 (s, 6 H), 4.86–4.96 (m, 2 H), 6.03–6.10 (m, 2 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.61 (q, 2 C), 26.37 (q, 2 C), 26.37 (t, 2 C), 32.23 (t, 2 C), 37.11 (s, 2 C), 50.09 (s, 2 C), 50.54 (q, 2 C), 51.30 (q, 2 C), 55.16 (s, 2 C), 113.88 (d, 2 C), 117.73 (d, 2 C), 172.98 (s, 2 C), 173.77 (s, 2 C); the two different signals at δ = 26.37 are nicely separated in C_6D_6 as solvent. – MS (70 eV); *m/z* (%): 582 (17) [(^{106}Pd) M^+], 474 (100) [M^+ – COD], 415 (19). – $C_{26}H_{36}O_8Pd$ (583.0): calcd. C 53.57, H 6.22; found C 53.36, H 6.30.

Crystal Structure Analysis of rac-**6**:[10] Siemens Smart diffractometer, Mo-K_α radiation, –123°C, empirical absorption correction, structure determination by direct methods (SHELXS); the positions of the hydrogen atoms were determined by a difference Fourier synthesis, refinement of the hydrogen atoms with isotropic thermal parameters. $C_{26}H_{36}O_8Pd$, monoclinic, space group $P2_1/c$; a = 28.536(3), b = 9.742(1), c = 18.845(2) Å, β = 104.36(1)°; V = 5075.2(9) Å^3; Z = 8; $\rho_{calcd.}$ = 1.526 g cm^{-1}; μ = 7.8 cm^{-1}; θ = 1.47–25.79°; 8815 reflections with $I > 0$; 920 parameters refined, R = 0.029; R_w = 0.051; residual density between –0.69 and +0.36 e Å^{-3}.

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