Tetraphenyl *rac*-3,3,7,7-Tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]-heptane-1,2,4,6-tetracarboxylate: A New PTH Derivative and the First X-ray Crystallographic Study of a Bis(acetone)palladium(II) Complex

A. Stephen K. Hashmi*, Frank Naumann, and Jan W. Bats

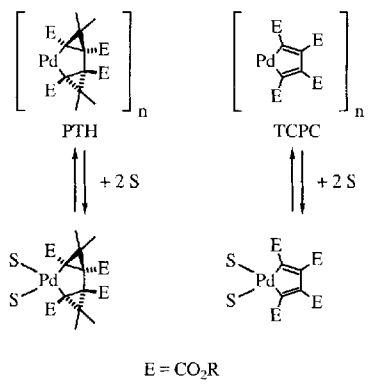
Institut für Organische Chemie der Johann Wolfgang Goethe-Universität,
Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany
Fax: (internat.) + 49(0)69/798-29464
E-mail: hashmi@chemie.uni-frankfurt.de

Received April 1, 1997

Keywords: Acetone complexes / Cyclooligomerizations / Cyclopropenes / Metallacycles / Palladium

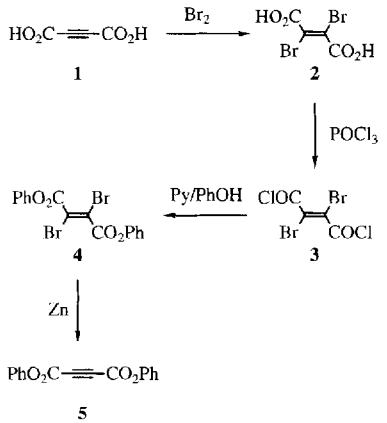
The title compound *rac*-**9** and its bis(acetone) complex *rac*-**10** were prepared, and the latter investigated by X-ray structure analysis. *rac*-**10** proves that the coordination of the weak donor acetone, an easily substitutable ligand in PTHs and related compounds, is an essential point for dissolving these coordination polymers, and thus allowing catalysis reactions in such solvents. Furthermore *rac*-**10** shows only a small deviation from the square-planar coordination expected for Pd^{II}. This indicates that the strong deviation from planarity observed in complexes with more sterically demanding, bidentate ligands is caused by steric interactions with the substituents on the PTH, rather than by electronic effects.

In connection with our efforts to synthesize chiral catalysts for enyne metathesis and related reactions, we recently reported on the synthesis and resolution of 5-palladatricyclo[4.1.0.0^{2,4}]heptanes (PTHs)[1]. Unlike Binger's PTH complexes, which needed additional stabilizing ligands[2], our organopalladium compounds were also stable in the absence of such ligands; even chromatography on silica gel was possible without decomposition. We assign this enhanced stability to the four alkoxycarbonyl substituents, and point out that a similar type of stabilization is known from the Maitlis study of TCPC[3]. We also assumed that the solvent-free PTH exists as a coordination polymer, with the carbonyl groups of neighbouring PTHs occupying the two free coordination sites at the palladium centre, as postulated by Maitlis for TCPC[3]. In coordinating solvents (**S**) like ethyl acetate, acetone, and acetonitrile, the polymeric structure is broken up and the PTH·2 **S** and TCPC·2 **S** both dissolve. Now we wish to demonstrate the existence of such PTH·2 **S** complexes of weak donor ligands such as acetone.



Synthesis of the Organopalladium Compound

We started with acetylenedicarboxylic acid (**1**) and used Charlton's[4] sequence, via dibromide **2**, dibromodiacyl dichloride **3** and dibromo diphenyl ester **4**, for the preparation of the diphenyl acetylenedicarboxylate **5**.



From **5** we generated the cyclopropene **8** by addition of 2-diazopropane (**6**) and subsequent photolysis of the resulting pyrazole **7**, in analogy to the protocol of Franck-Neumann[5]. In the final step of the sequence, the PTH *rac*-**9** was formed from $Pd_2dba_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) and **8**.

X-ray Structure Determination and Discussion

From a solution of *rac*-**9** in acetone, suitable crystals of *rac*-**10** for an X-ray structure determination could be obtained. The ORTEP plot is shown in Figure 1, and selected crystallographic data is listed in Table 1[6].

  0009–2940/97/1010–1457 $ 17.50+.50/0

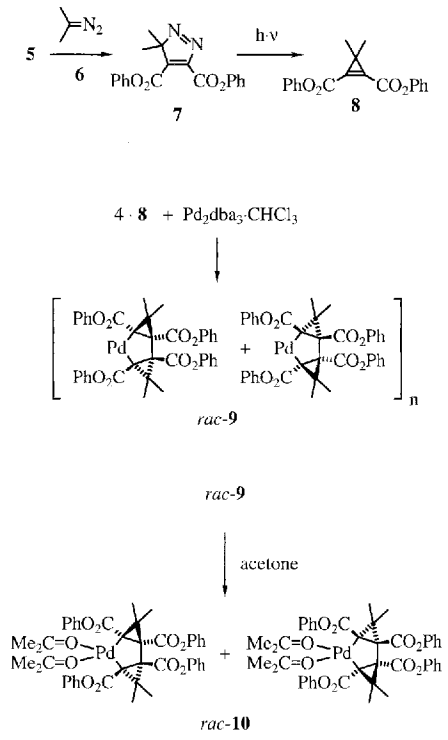


Figure 1. ORTEP plot of *rac*-**10**

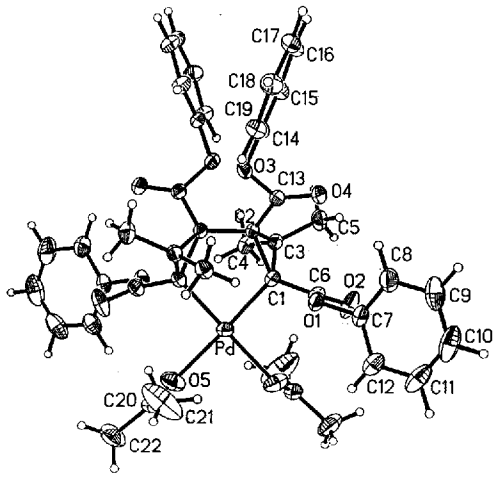


Table 1. Selected bond lengths [Å], bond angles [°], and dihedral angles [°] for *rac*-**10**

Pd–O5	2.159(2)	O5–Pd–C1	175.05(9)
Pd–C1	2.019(2)	O5–Pd–C1′	94.13(8)
O5–C20	1.206(3)	C1–Pd–C1′	84.49(8)
C1–C2	1.539(3)	Pd–C1–C2	114.5(1)
C1–C3	1.508(3)	Pd–C1–C3	123.0(2)
C1–C6	1.480(4)	Pd–C1–C6	111.2(1)
C2–C2′	1.505(3)	C2–C1–C3	61.5(1)
C2–C3	1.557(2)	C1–C2–C3	58.3(1)
C2–C13	1.482(3)	C1–C3–C2	60.2(1)
C3–C4	1.514(4)	C1–C2–C2′	113.0(2)
C3–C5	1.515(3)	Pd–O5–C20	126.5(2)
C6–O1	1.366(3)	O5–C20–C21	120.4(3)
C20–C21	1.444(6)	O5–C20–C22	122.1(3)
C20–C22	1.488(4)	C1–Pd–O5–C20	−154.8(9)
O5–Pd–O5′	87.63(8)	C1′–Pd–O5–C20	−81.1(3)

rac-**10** shows the expected C_2 symmetry, and the conformation of the molecule is stabilized by four weak, electrostatic, intramolecular O···H contacts: O1···H4a, O1′···H4a (each 2.38 Å) and O4···H5a, O4′···H5a′ (each 2.25 Å). The angle between the plane of the ester groups and the planes of the phenyl groups bound to them is 78.9° (ester group at C1) and 76.2° (ester group at C2), respectively. In the crystal packing an intermolecular distance of 2.48 Å is observed between O2 and H16 of a neighbouring molecule, which is only about 0.1 Å longer than the van der Waals distance between O and H. There are no other short intermolecular distances, the additional solvent acetone molecules serving mainly as space-fillers.

There are two geometrical features of major interest. (1) The palladium centre is in an almost square-planar environment (the angle between the C–Pd–C and O–Pd–O planes is 6.9°), the coordination geometry expected for Pd^{II}. This indicates that the strong tilt observed in complexes with sterically demanding bidendate ligands (up to 30°[11]) originates from the steric interactions rather than from electronic effects. (2) The Pd–O bond length is 2.16 Å, which is identical to the value reported for the only mono(acetone) complex of an organometallic compound for which an X-ray structure is published[7]. In the literature there is described one other X-ray structure analysis of an organometallic compound, and five of inorganic complexes where a weak interaction of (also only one) acetone molecule with Pd has been observed[8]. While in two of these cases the acetone molecule still shows a loose contact with Pd (an identical Pd–O distance of 3.06 Å)[8b][8e], in the remaining four the acetone molecule is distant from Pd (values of 3.61–4.00 Å)[8a][8c][8d][8f].

Overall there is only one X-ray structure analysis of an organometallic compound of palladium with one acetone molecule as a true ligand described in the literature[7]; and organometallic compounds with two or more acetone molecules coordinated to palladium are unknown. Inorganic complexes of Pd with two or more acetone ligands are known[9], but no crystallographic data is available on these systems. This demonstrates the uniqueness of *rac*-**10**.

Conclusion

With *rac*-**10**, the bis(acetone) complex of the new PTH *rac*-**9**, the coordination of the weak donor ligand acetone was proven. This is of relevance for reactions catalyzed by **9** because the acetone ligand is not only capable of breaking the polymeric structure of **9** (so that the catalyst is brought into solution) but also labile enough to be replaced by an organic substrate.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. Furthermore we are grateful to the *Degussa AG* for the donation of palladium salts.

Experimental Section

General: All operations were carried out under N_2 and in dry solvents; transfers were effected by means of Schlenk-tube techniques. 2-Diazopropane (**6**[10]), dibromofumaroyl dichloride (**3**[5]), and $Pd_2dba_3 \cdot CHCl_3$[11] were prepared according to literature pro-

cedures. – IR: Perkin-Elmer 1600. – NMR: Bruker AM 250 (250 and 62.9 MHz for ^1H and ^{13}C, respectively). $CDCl_3$ as solvent $\delta_H = 7.25$; $\delta_C = 77.0$. 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, quadrupole analyser and Finnigan CH7A (80 eV). – HRMS: Finnigan MAT 711 (EI, 80 eV, 8 kV ion acceleration, resolution above $R = 20000$, peak match). – M.p. (uncorrected): Kofler hot-stage. – Column chromatography: Merck Kieselgel 60 using hexane/ethyl acetate (H/EA) or hexane/acetone (H/A) as eluent.

Diphenyl Dibromofumarate (**4**): The procedure for the preperation of **4** was analagous to that in ref.[4]: 5.00 g (16.1 mmol) of **3**, 2.30 g (29.1 mmol) of pyridine, and 2.74 g (29.1 mmol) of phenol in 100 ml of CCl_4. The crude product was washed with EA, thus 5.54 g (81%) of **4** were obtained as a colourless solid. – M.p. 107°C. – R_f (H/EA, 5:1) = 0.45. – IR (neat, NaCl): $\tilde{\nu}$ = 1736 cm^{-1}, 1587, 1482, 1240, 1216, 1180, 962, 807. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.21–7.49 (m, 10 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 113.26 (s, 2 C), 120.89 (d, 4 C), 126.74 (d, 2 C), 129.63 (d, 4 C), 149.88 (s, 2 C), 160.43 (s, 2 C). – MS (70 eV); *m/z* (%): 426 (0.1) [M$^+$], 347 (1) [M$^+$ – Br], 80 (16), 77 (100). – $C_{16}H_{10}Br_2O_4$ (426.1): calcd. C 45.11, H 2.37; found C 44.84, H 2.38.

Diphenyl 5,5-Dimethyl-5H-pyrazol-3,4-dicarboxylate (**7**): Compound **7** was prepared from a solution of 1.05 g (3.94 mmol) of **5** in 50 ml of CH_2Cl_2 and 7.00 ml (570 mM, 3.99 mmol) of a solution of **6** in ether at –10°C in a procedure analagous to that described in ref.[5] Column chromatography of the crude product (H/EA, 3:1) provided 875 mg (66%) of **7** as a yellow solid. – M.p. 68°C. – R_f (H/EA, 3:1) = 0.2. – IR (neat, NaCl): $\tilde{\nu}$ = 2989 cm^{-1}, 1747, 1633, 1589, 1484, 1187. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.74 (s, 6 H), 7.14–7.20 (m, 2 H), 7.22–7.34 (m, 4 H), 7.37–7.48 (m, 4 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.11 (q, 2 C), 98.04 (s), 121.10 (d, 2 C), 121.24 (d, 2 C), 126.55 (d), 126.67 (d), 129.60 (d, 2 C), 129.63 (d, 2 C), 144.64 (s), 149.52 (s), 149.86 (s), 153.64 (s), 158.71 (s), 160.93 (s). – MS (70 eV); *m/z* (%): 336 (10) [M$^+$], 84 (100). – $C_{19}H_{16}N_2O_4$ (336.4): calcd. C 67.85, H 4.80, N 8.33; found C 67.93, H 5.00, N 8.05.

Diphenyl 3,3-Dimethylcyclopropene-1,2-dicarboxylate (**8**): Irradiation of 500 mg (1.49 mmol) of **7** in 100 ml of oxygen-free ether (normal glass apparatus) and purification of the crude product by column chromatography (H/EA, 10:1) provided 73.7 mg (16%) of **8** as a colourless solid. – M.p. 92°C. – R_f (H/EA, 3:1) = 0.6. – IR (neat, NaCl): $\tilde{\nu}$ = 2922 cm^{-1}, 2854, 1723, 1591, 1201, 1184, 1030. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.56 (s, 6 H), 7.19–7.31 (m, 6 H), 7.38–7.47 (m, 4 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.49 (q, 2 C), 32.74 (s), 121.21 (d, 4 C), 126.25 (d, 2 C), 129.44 (d, 4 C), 133.56 (s, 2 C), 150.02 (s, 2 C), 158.21 (s, 2 C). – MS (70 eV); *m/z* (%): 308 (0.3) [M$^+$], 279 (2), 233 (2), 215 (54), 187 (100). – $C_{19}H_{16}O_4$: calcd. 308.10487; found 308.10486 (MS).

Tetraphenyl rac-3,3,7,7-Tetramethyl-trans-5-palladatricyclo-[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate (*rac*-**9**): 70.0 mg (227 µmol, 1.25 eq.) of **8** and 47.0 mg (45.4 µmol) of $Pd_2dba_3 \cdot CHCl_3$ in 30 ml of acetone were treated according to ref.[1] Column chromatography of the crude product (H/A, 1:1) gave 46.6 mg (71%) of *rac*-**9** as an orange solid. – R_f (H/A, 1:1) = 0.2. – IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1}, 2930, 2870, 1728, 1675, 1624, 1493, 1188, 1160. – ^1H NMR ([D$_6$]acetone, 250 MHz): δ = 1.57 (s, 6 H), 2.35 (s, 6 H), 7.03–7.42 (m, 20 H). – ^{13}C NMR ([D$_6$]acetone, 62.9 MHz): δ = 20.21 (q, 2 C), 27.52 (q, 2 C), 37.61 (s, 2 C), 39.58 (s, 2 C), 48.33 (s, 2 C), 122.5 (d, 4 C), 123.05 (d, 4 C), 125.52 (d, 2 C), 125.82 (d, 2 C), 129.66 (d, 4 C), 130.08 (d, 4 C), 152.77 (s, 2 C), 152.88 (s, 2 C), 171.51 (s, 2 C), 171.60 (s, 2 C). – MS (70 eV); *m/z* (%): 723 (12) [M$^+$], 647 (100).

[1] A. S. K. Hashmi, F. Naumann, R. Probst, J. W. Bats, *Angew. Chem.* **1997**, *109*, 127–130; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 104–106.

[2] P. Binger, H. M. Büch, R. Benn, R. Mynott, *Angew. Chem.* **1982**, *94*, 66–66; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 62–63.

[3] [3a] K. Moseley, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.* **1971**, 1604–1605. – [3b] P. M. Maitlis, P. Espinet, M. J. H. Russel in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford **1982**, vol. 6, pp. 465–469.

[4] [4a] J. L. Charlton, G. Chee, *Tetrahedron Lett.* **1994**, *35*, 6243–6246. – [4b] J. L. Charlton, G. Chee, H. McColeman, *Can. J. Chem.* **1995**, *73*, 1454–1462.

[5] [5a] C. Dietrich-Buchecker, M. Franck-Neumann, *Tetrahedron* **1977**, *33*, 745–749, 751–755. – [5b] T. Ohta, H. Takaya in *Comprehensive Organic Synthesis*, vol. 5 (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon, Oxford **1991**, pp. 1185–1205.

[6] Crystal structure analysis of *rac*-**10**: Siemens Smart diffractometer, Mo-K_α radiation, –140°C, empirical absorption correction, structure determination by direct methods (SIR92); hydrogen atoms of the acetone groups from difference Fourier synthesis, the remaining hydrogen atoms were placed at calculated positions. $C_{44}H_{44}O_{10}Pd \cdot 2$ (C_3H_6O), monoclinic, space group *C2/c*; a = 16.446(1), b = 17.977(1), c = 17.715(1) Å, β = 115.82(1)°; V = 4715(1) Å^3, Z = 4; $\rho_{calcd.}$ = 1.346 g cm^{-1}; μ = 4.5 cm^{-1}; sphere up to 2θ = 61°; 6066 reflections with $I > 0$; 285 parameters refined, R = 0.049; R_w = 0.066; residual density less than 0.71 e Å^{-1}. Crystallographic data (excluding structure factors) for *rac*-**10** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-100285. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].

[7] L. R. Falvello, J. Forniés, R. Navarro, V. Sicilia, M. Tomás, *J. Chem. Soc., Dalton Trans.* **1994**, 3143–3148.

[8] [8a] C. P. Brock, J. L. Huckaby, T. G. Attig, *Acta Crystallogr., Sect. B: Struct. Sci.* **1984**, 40, 595–606. – [8b] G. Reid, A. J. Blake, T. I. Hyde, M. Schröder, *J. Chem. Soc., Chem. Commun.* **1988**, 1397–1399. – [8c] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **1989**, *111*, 6301–6311. – [8d] V. P. Zagorodnikov, S. B. Katser, M. N. Vargaftik, M. A. Porai-Koshits, I. I. Moiseev, *Koord. Khim.* **1989**, *15*, 1540–1544 (*Chem. Abstr.* **1990**, *112*, 198760v). – [8e] A. J. Blake, G. Reid, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1990**, 3363–3373. – [8f] J. H. Yamamoto, G. P. A. Yap, C. M. Jensen, *J. Am. Chem. Soc.* **1991**, *113*, 5060–5061.

[9] For inorganic complexes of Pd with two acetone ligands (no X-ray structure analysis), see: [9a] J. A. Davies, F. R. Hartley, S. G. Murray, *J. Chem. Soc., Dalton Trans.* **1980**, 2246–2254. – [9b] F. R. Hartley, S. G. Murray, A. Wilkinson, *Inorg. Chem.* **1989**, *28*, 549–554. – [9c] Even a tetrakis(acetone) complex was reported, but not fully characterized: M. Crocker, R. H. M. Herold, J. G. Buglass, P. Companje, *J. Catal.* **1993**, *141*, 700–712. – [9d] For a review covering complexes of the platinum metals with, among others, acetone, see: J. A. Davies, F. R. Hartley, *Chem. Rev.* **1981**, *81*, 79–90.

[10] [19a] A. C. Day, P. Raymond, R. M. Southam, M. C. Whiting, *J. Chem. Soc. C* **1966**, 467–469. – [10b] S. D. Andrews, A. C. Day, P. Raymond, M. C. Whiting, *Org. Synth.* **1971**, *50*, 27–30.

[11] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253–266.

[97075]