

***trans*-5-Palladatricyclo[4.1.0.0^{2,4}]heptanes: Complexes with Monodentate, Weakly Coordinating Ligands, Formation of New Derivatives and Synthetic Limitations**

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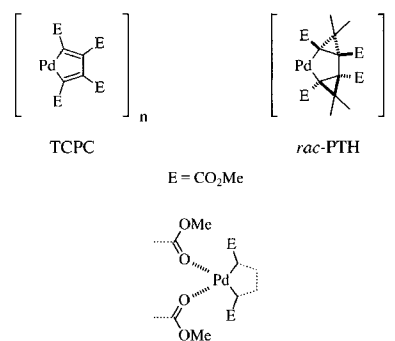
Abstract. The bis(acetone) complex of tetramethyl *rac*-3,3,7,7-tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate *rac*-**1a** was crystallized and investigated by X-ray structure analysis. Unlike in complexes with bidentate ligands in *rac*-**1a** · 2(acetone), only a small deviation from the square planar coordination of palladium was observed. Efforts to crystallize the analogous pyridine, acetonitrile and benzonitrile complexes failed; but the labile complexes *rac*-**1a** · 2([D₅]pyridine) and *rac*-**1a** · 2([D₃] acetonitrile) as well

as *rac*-**1a** · 2([D₆]acetone) could be characterized by ¹H and ¹³C NMR spectra and a fast ligand exchange was proven by nmr. Then the ability of different 1,2-disubstituted cyclopropenes to form *trans*-5-pallada-tricyclo[4.1.0.0^{2,4}] heptanes **1** was investigated. Only the diesters **5c–e** lead to PTHs, with a diester possessing sterically demanding substituents in 3-position of the cyclopropene and with other substituents in 1- respectively 2-position of the cyclopropene either the cyclopropene-formation or the PTH-formation failed.

1 Complexes with Monodentate, Weakly Coordinating Ligands

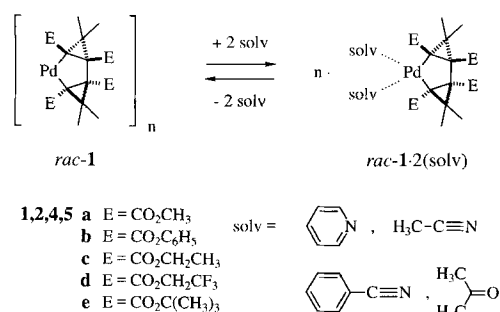
We recently reported on the synthesis and resolution of *trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptanes (PTHs) [1]. These substrates shall serve as model compounds for chiral catalysts *e.g.* for enyne metathesis and related carbocyclization reactions. So far Trost's variations [2] of Maitlis' 2,3,4,5-tetrakis(carboalkoxy)palladacyclopentadiene-(TCPC-) catalysts [3] were used as catalysts for these reactions. We assumed that solvent free PTH exists as a coordination polymer with the carbonyl-groups of neighbouring PTHs occupying the two free coordination sites at the palladium atom. Such a mode of aggregation was postulated by Maitlis for TCPC [3]. Ibers [4] was able to isolate dimers of TCPC where one of the ester carbonyls of each TCPC coordinates to the palladium of the second palladacycle in the manner postulated by Maitlis. Both, PTHs and TCPC, are soluble in solvents (solv) like acetone, benzonitrile and acetonitrile. The polymeric structure is broken up by these solvents and PTH · 2(solv) respectively TCPC · 2(solv) dissolves; we just could prove this by the characterization of the bis(acetone) complex of tetraphenyl *rac*-3,3,7,7-tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate [5]. Since such solvent-molecules are labile ligands [6], they might easily be substituted by an unsaturated organic substrate, thus allowing

catalytic reactions: PTHs and TCPC *e.g.* catalyze the cyclization/dimerization of allenyl ketones in acetone and acetonitrile [7]. Now, we wanted to prepare and characterize further complexes of monodentate ligands with *rac*-**1a**.

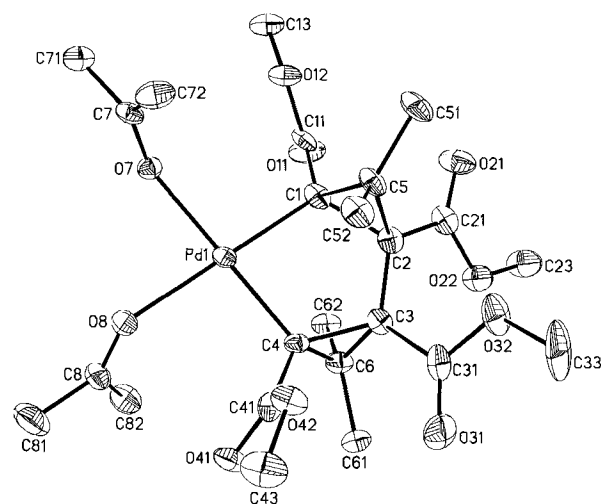
**Scheme 1**

PTH *rac*-**1a** [1] was dissolved in a minimum amount of either acetone, pyridine, acetonitrile or benzonitrile at room temperature. At –30 °C crystals separated from the benzonitrile and the acetone solution. While the crystals from the benzonitrile solution were not stable enough for a X-ray structure analysis, the X-ray structure analysis of the bis(acetone) complex was successful.

The ortep-plot is shown in figure 1. *rac*-**1a**·2 acetone approximately shows C_2 -symmetry, selected bond lengths, bond angles and dihedral angles are listed in table 1. There are two independent molecules of *rac*-**1a**·2 acetone in the asymmetric unit; in the following section the values for the second molecule are given in brackets.



Scheme 2

Fig. 1 ORTEP diagram of *rac*-**1**·2(acetone)

Different from the complexes of **1a** with bidentate ligands investigated so far, *rac*-**1a**·2(acetone) is close to the square planar coordination as one would expect for Pd(II). The angle between the C–Pd–C and the O–Pd–O plane is 9.3° (9.7°). The tilt is slightly stronger than in the tetraphenylester *rac*-**1b**·2(acetone) (6.9°, [5]). Thus the strong tilt observed in the other complexes with sterically demanding, bidentate ligands (up to 30°) [1] originates from steric interactions rather than from electronic effects. In the complexes with both the mono and the bidentate ligands these ligands are tilted away from the ester groups and towards the CMe₂ groups of the PTH.

The Pd–O bond lengths are 2.16 Å (2.16 Å) and 2.16 Å (2.14 Å). This is identical with the value observed in the X-ray structure analysis of the only (mono) acetone complex of an organopalladium compound described in the literature so far [8].

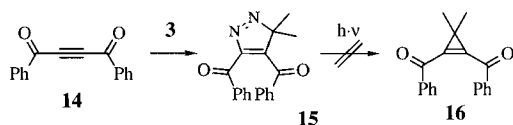
The angle between the plane through the acetone-ligands and the O–Pd–O plane is 80.3° (81.0°) for the first and 72.5° (72.2°) for the second acetone molecule. The cyclopropanes show a small distortion, two sides show C–C-bond lengths of 1.54–1.57 Å, but 1.51 Å (1.51 Å) and 1.50 Å (1.51 Å) were observed for the C1–C5 and the C4–C6 bonds, respectively. The Pd–C bond lengths correspond to known values for related compounds.

Since the efforts to grow single crystals from solutions of *rac*-**1a** in pyridine, acetonitrile and benzonitrile failed, the ¹H and ¹³C NMR spectra of *rac*-**1a** were recorded in deuterated pyridine, acetonitrile and acetone. A comparison of this data shows that the chemical shifts of the signals in both the ¹H and the ¹³C NMR are quite similar in the different solvents. Only for the carbon atom bound to palladium a significant effect is visible in the ¹³C NMR spectra. While with both N-ligands ([D₅]pyridine and [D₃]acetonitrile) the chemi-

Table 1 Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for *rac*-**1**·2 Acetone

	molecule 1	molecule 2		molecule 1	molecule 2
Pd1–O7	2.158(3)	2.138(3)	C1–Pd1–C4	83.7(2)	83.8(2)
Pd1–O8	2.156(3)	2.161(3)	O7–Pd1–O8	85.3(1)	84.7(1)
O7–C7	1.219(6)	1.238(6)	Pd1–O7–C7	130.3(3)	133.0(3)
O8–C8	1.219(6)	1.226(6)	Pd1–O8–C8	134.4(3)	129.9(3)
Pd1–C1	2.021(5)	2.023(4)	Pd1–C1–C2	115.3(3)	115.4(3)
Pd1–C4	2.021(5)	2.030(5)	Pd1–C4–C3	115.2(3)	114.8(3)
C1–C2	1.543(7)	1.539(6)	C1–C2–C3	112.8(4)	113.1(4)
C4–C3	1.545(6)	1.553(6)	C4–C3–C2	112.8(4)	112.6(4)
C1–C5	1.511(6)	1.507(6)	Pd1–C1–C11–O12	94.8(4)	95.5(4)
C4–C6	1.497(7)	1.509(6)	Pd1–C4–C41–O42	–85.8(4)	–82.6(4)
C2–C5	1.573(6)	1.563(6)	C2–C3–C31–O32	–0.9(6)	0.5(6)
C3–C6	1.553(6)	1.568(6)	C3–C2–C21–O22	–2.8(6)	–5.1(6)
C2–C3	1.498(7)	1.503(6)	Pd1–O7–C7–C72	–2.1(7)	–10.2(8)
C1–C11	1.499(7)	1.488(6)	Pd1–O8–C8–C82	–12.4(8)	–0.5(7)
C2–C21	1.492(7)	1.483(6)	Pd1–C1–C5–C52	–3.1(6)	–3.4(6)
C3–C31	1.491(7)	1.479(6)	Pd1–C4–C6–C62	–3.8(6)	–4.8(6)
C4–C41	1.487(7)	1.479(6)	C21–C2–C3–C31	76.5(5)	77.6(5)

Efforts to synthesize the cyclopropene **16** (such 1,2-diacylcyclopropenes are hitherto unknown) by an analogous route starting from dibenzoylacetylene **14** and proceeding through the 3,4-dibenzoylpyrazole **15** failed.



Scheme 7

In conclusion the formation of PTHs works well only with cyclopropene-1,2-dicarboxylates that don't possess sterically demanding substituents in 3-position. The other cyclopropenes investigated did not lead to PTHs.

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Experimental

General Methods and Instrumentation

All operations were carried out under N₂ and in dry solvents; transfers were effected by means of Schlenk-tube techniques. Pd₂dba₃·CHCl₃ [13], bis(2,2,2-trifluoroethyl) acetylenedicarboxylate (**2d**) [2], 2-diazopropane (**3**) [14], bis(1,1-dimethylethyl) 3,3-dimethyl-cyclopropen-1,2-dicarboxylate (**5e**) [15], 2',3'-bis(methoxy-carbonyl)fluoren-9-spiro-cyclopropen (**12**) [16] and dibenzoyl-ethyne (**14**) [17] were prepared according to literature-procedures. All other chemicals were commercially available and used as received. – IR: Perkin-Elmer 1600. – NMR: Bruker AM 250 (250 and 62.9 MHz for ¹H and ¹³C, respectively) and Bruker DRX 600 (600 MHz for ¹H). CDCl₃ as solvent δ_H/ppm = 7.25; δ_C/ppm = 77.0. The degree of substitution of the C atoms was determined by a combination of DEPT 135 and DEPT 90 spectra; if a second multiplicity is given below, it originates from ⁿJ_{C-F} coupling. – MS: VG-Instruments-Micro-Mass Tris 2000, EI 70 eV, quadrupole analyser and Finnigan CH7A (80eV). – HRMS: Finnigan MAT 711 (EI, 80 eV, 8 kV ion acceleration, resolution above 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. – Elemental analyses were performed on a elementary analyser (Perkin-Elmer 240).

Tetramethyl *rac*-3,3,7,7-tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate (*rac*-**1a**)

rac-**1a** was synthesized according to the literature. Addition of **3** to dimethyl acetylenedicarboxylate provided **4a** [11, 18]. Irradiation with a mercury-vapor lamp in a normal glass apparatus provided **5a** [18c, 19]. When less than 2 g of the pyrazole in 100 ml of ether were irradiated, we observed the fast and clean formation of the cyclopropene. It is also possible to use more concentrated solutions, but then relevant amounts of dimethyl 1-diazo-3-methyl-but-2-en-1,2-dicarboxylate form. Still this causes no problem since on prolonged irradiation the diazo-compound is completely converted into the

cyclopropene; this is probably the best way for the large-scale preparation of the cyclopropene: we did the reaction with 16.0 g of the pyrazole in 100 ml of ether and obtained the analytically pure cyclopropene after 14 h of irradiation (the reaction can easily be followed by TLC, *R_f*-values are given below) and simple removal of the solvent *in vacuo*. Then *rac*-**1** is prepared from the cyclopropene and Pd₂dba₃·CHCl₃ as reported previously [1].

Since the ¹³C data of the pyrazole and the cyclopropene and the spectroscopic data of the diazo-compound have not been reported in the literature yet, this data is given below.

Dimethyl 5,5-Dimethyl-5H-pyrazol-3,4-dicarboxylate (**4a**)

R_f (H/EA, 2:1) = 0.36. – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm 19.8 (q, 2 C), 52.6 (q), 52.7 (q), 97.1 (s), 144.4 (s), 153.2 (s), 160.5 (s), 162.6 (s).

Dimethyl 1-Diazo-3-methyl-but-2-en-1,2-dicarboxylate

Yellow oil, slowly decomposes at room temperature. – *R_f* (H/EA, 2:1) = 0.48. – IR (neat, NaCl): ν/cm⁻¹ = 2953, 2850, 2092 (C=N=N), 1836, 1622, 1438, 1347, 1230, 1148, 1089, 1025, 744. – ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 1.91 (s, 3H), 2.19 (s, 3H), 3.72 (s, 3H), 3.74 (s, 3H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 22.7 (q), 24.4 (q), 51.6 (q, 2C), 51.8 (s), 113.9 (s), 155.4 (s), 166.0 (s, 2C).

C₉H₁₂O₄ calcd.: C 50.94 H 5.70 (212.2) found: C 50.83 H 5.73.

Dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate (**5a**)

R_f (H/EA, 2:1) = 0.60. – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 25.3 (q, 2C), 31.0 (s), 52.3 (q, 2C), 131.9 (s, 2C), 160.2 (s, 2C).

Crystal Structure Determination of *rac*-**1**·**2** (acetone)

X-ray crystal data for C₂₄H₃₆O₁₀Pd: orthorhombic, Pca2₁, a = 29.1553 (3) Å, b = 9.0888 (1) Å, c = 25.5762 (2) Å, V = 6777.35 (12) Å³, Z = 8, D_{calc} = 1.329 g cm⁻³, MoKα radiation (λ = 0.71073 Å), μ = 0.60 mm⁻¹, T = 133 K. 73973 reflections were collected on a SIEMENS CCD three-circle diffractometer for 2° < 2θ < 53°. The data were corrected for absorption effects using the program SADABS (G. Sheldrick, University of Goettingen, 1996). The structure was solved by direct methods and refined by full-matrix least-square against F² to R1 = 0.0432 (wR2 = 0.1025) and S = 1.163 for 13816 (R_{int} = 0.0351) unique reflections. There are two independent molecules of the title compound in the asymmetric unit. In addition five acetone molecules were found. Only two of the acetone positions are fully occupied, while the site occupation of the remaining three are 0.309(3), 0.246(5) and 0.445(4). Similarity restraints were applied for refinement of these acetone molecules. The crystals appeared to be a racemic twin, and the ratio of the two twin components refined to 0.62(2). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101-071. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223)336-033; e-mail: deposit@chemcrs.cam.ac.uk).

NMR Spectra of the Complexes

Since the ligands exchange quickly, only the solvent signals but no special set of signals for the coordinated solvent could be detected.

rac-**1**•2([D₆]acetone). – ¹H NMR ([D₆]acetone, 250 MHz, 23 °C): δ/ppm = 1.30 (s, 6H), 1.87 (s, 6H), 3.35 (s, 6H), 3.49 (s, 6H). – ¹³C NMR ([D₆]acetone, 62.9 MHz, 23 °C): δ/ppm = 20.30 (q, 2C), 27.31 (q, 2C), 35.84 (s, 2C), 39.50 (s, 2C), 47.76 (s, 2C), 50.37 (q, 2C), 50.93 (q, 2C), 173.42 (s, 2C), 173.90 (s, 2C).

rac-**1**•2([D₅]pyridine). – ¹H NMR ([D₅]pyridine, 250 MHz, 23 °C): δ/ppm = 1.95 (s, 6H), 2.59 (s, 6H), 3.14 (s, 6H), 3.75 (s, 6H). – ¹³C NMR ([D₅]pyridine, 62.9 MHz, 23 °C): δ/ppm = 21.05 (q, 2C), 27.82 (q, 2C), 36.27 (s, 2C), 44.04 (s, 2C), 49.24 (s, 2C), 49.66 (q, 2C), 51.15 (q, 2C), 174.27 (s, 2C), 174.81 (s, 2C).

rac-**1**•2([D₃]acetonitrile). – ¹H NMR ([D₃]acetonitrile, 250 MHz, 23 °C): δ/ppm = 1.29 (s, 6H), 1.71 (s, 6H), 3.44 (s, 6H), 3.48 (s, 6H). – ¹³C NMR ([D₃]acetonitrile, 62.9 MHz, 23 °C): δ/ppm = 20.28 (q, 2C), 27.09 (q, 2C), 35.95 (s, 2C), 43.67 (s, 2C), 49.11 (s, 2C), 50.57 (q, 2C), 51.26 (q, 2C), 174.04 (s, 2C), 174.92 (s, 2C).

Bis(2,2,2-trifluoroethyl) Acetylenedicarboxylate (**2d**)

The spectroscopic data of **2d** has not been reported yet. **2d**: ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 4.59 (q, ³J_{C-F} = 7.1 Hz, 4H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 61.8 (t, q, ²J_{C-F} = 37.8 Hz, 2C), 74.9 (s, 2C), 122.2 (s, q, ¹J_{C-F} = 277.1 Hz, 2C), 149.7 (s, 2C).

Diethyl 5,5-Dimethyl-5H-pyrazol-3,4-dicarboxylate (**4c**)

4c was prepared in analogy to Franck-Neumann's procedure [11] from a solution of 8.00 g (47.0 mmol) diethyl acetylenedicarboxylate **2c** in 100 ml dichloromethane (DCM) and 60.0 ml (790 mM, 47.4 mmol) of a solution of **3** in ether at –30 °C. Column chromatography of the crude product (H/EA, 4:1) provided 7.41 g (66%) **4c** as a yellow oil. – *R*_f (H/EA, 3:1) = 0.35. – IR (neat, NaCl): ν/cm^{–1} = 2985, 2939, 1729, 1637, 1451, 1372, 1324, 1260, 1176, 1104, 1050, 860, 774. – ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 1.28 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.50 (s, 6H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 13.80 (q), 13.88 (q), 19.88 (q, 2C), 61.98 (t, 2C), 97.01 (s), 144.61 (s), 153.02 (s), 160.27 (s), 162.36 (s). – MS (70 eV); *m/z* (%): 241 (9) [M⁺ + 1], 195 (25), 111 (64), 67 (100).

C₁₁H₁₆N₂O₄ calcd.: C 54.99 H 6.71 N 11.66 (240.26) found: C 54.79 H 6.66 N 11.59.

Bis(2,2,2-trifluoroethyl) 5,5-Dimethyl-5H-pyrazol-3,4-dicarboxylate (**4d**)

4d was prepared in analogy to Franck-Neumann's procedure [11] from a solution of 1.04 g (3.74 mmol) **2d** in 50 ml DCM and 5.00 ml (756 mM, 3.78 mmol) of a solution of **3** in ether at –30 °C. Column chromatography of the crude product (H/EA, 7:1) provided 474 mg (36%) **4d** as a yellow oil. – *R*_f (H/EA, 3:1) = 0.45. – IR (neat, NaCl): ν/cm^{–1} = 2988, 2913, 1757, 1638, 1454, 1414, 1336, 1286, 1233, 1169, 1116, 1071, 984, 962, 889, 842, 790. – ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 1.62 (s, 6H), 4.67 (q, ³J_{H-F} = 8.2 Hz, 2H), 4.75 (q, ³J_{H-F} = 8.2

Hz, 2H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 19.81 (q, 2C), 61.14 (t, q, ²J_{C-F} = 37.3 Hz), 61.34 (t, q, ²J_{C-F} = 37.3 Hz), 98.43 (s), 120.22 (s, q, ¹J_{C-F} = 277.5 Hz), 122.34 (s, q, ¹J_{C-F} = 277.5 Hz), 143.36 (s), 152.78 (s), 158.16 (s), 160.45 (s). – MS (70 eV); *m/z* (%): 348 (24) [M⁺], 320 (8) [M⁺ – N₂], 243 (100).

C₁₁H₁₀F₆N₂O₄ calcd.: C 37.94 H 2.89 N 8.05 (348.20) found: C 38.09 H 2.85 N 8.14.

Diethyl 3,3-Dimethyl-1-cyclopropen-1,2-dicarboxylate (**5c**)

Irradiation of 1.30 g (5.41 mmol) **4c** in 100 ml of oxygen-free ether (normal glass apparatus) and purification of the crude product by column chromatography (H/EA, 12:1) provided 868 mg (76%) of **5c** as a colourless oil. – *R*_f (H/EA, 3:1) = 0.55. – IR (neat, NaCl): ν/cm^{–1} = 2981, 2870, 1834, 1718, 1461, 1448, 1369, 1245, 1097, 1056. – ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 1.34 (t, *J* = 7.3 Hz, 6H), 1.40 (s, 6H), 4.31 (q, *J* = 7.3 Hz, 4H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 13.92 (q, 2C), 25.29 (q, 2C), 31.05 (s), 61.51 (t, 2C), 131.90 (s, 2C), 159.99 (s, 2C). – MS (70 eV); *m/z* (%): 212 (5) [M⁺], 197 (8), 111 (22), 79 (46), 67 (100).

C₁₁H₁₆O₄ calcd.: C 62.25 H 7.60 (212.25) found: C 62.42 H 7.64.

Bis(2,2,2-trifluoroethyl) 3,3-Dimethyl-1-cyclopropen-1,2-dicarboxylate (**5d**)

Irradiation of 450 mg (1.29 mmol) **4d** in 100 ml of oxygen-free ether (normal glass apparatus) and purification of the crude product by column chromatography (H/EA, 12:1) provided 225 mg (54%) of **5d** as a colourless oil. – *R*_f (H/EA, 5:1) = 0.33. – IR (neat, NaCl): ν/cm^{–1} = 2979, 2931, 1838, 1738, 1453, 1413, 1376, 1287, 1229, 1170, 1078, 980. – ¹H NMR (CDCl₃, 250 MHz): δ/ppm = 1.45 (s, 6H), 4.62 (q, ³J_{H-F} = 8.2 Hz, 4H). – ¹³C NMR (CDCl₃, 62.9 MHz): δ/ppm = 25.15 (q, 2C), 32.70 (s), 60.96 (t, q, ²J_{C-F} = 37.1 Hz, 2C), 122.37 (s, q, ¹J_{C-F} = 277.5 Hz, 2C), 133.36 (s, 2C), 157.66 (s, 2C). – MS (70 eV); *m/z* (%): 321 (4) [M⁺ + 1], 83 (100).

Tetraethyl *rac*-3,3,7,7-Tetramethyl-trans-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate (*rac*-**1c**)

The crude product obtained from 400 mg (1.88 mmol) **5c** and 390 mg (377 μmol) Pd₂dba₃ CHCl₃ was purified by column chromatography (H/A, 2:3). 352 mg (88%) of *rac*-**1c** were isolated as yellow solid. – *R*_f (H/A, 2:3) = 0.40. – IR (neat, NaCl): ν/cm^{–1} = 2980, 2939, 2903, 2870, 1711, 1601, 1466, 1444, 1371, 1301, 1228, 1208, 1186, 1105, 1026. – ¹H NMR ([D₆]acetone, 600 MHz): δ/ppm = 1.11 (t, *J* = 7.2 Hz, 6H), 1.17 (t, *J* = 7.2 Hz, 6H), 1.35 (s, 6H), 1.95 (s, 6H), 3.69–3.74 (m, 2H), 3.87–3.92 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 4H). – ¹³C NMR ([D₆]acetone, 62.9 MHz): δ/ppm = 14.55 (q, 2C), 14.66 (q, 2C), 20.38 (q, 2C), 27.55 (q, 2C), 35.61 (s, 2C), 39.13 (s, 2C), 47.89 (s, 2C), 58.91 (t, 2C), 59.44 (t, 2C), 172.85 (s, 2C), 173.24 (s, 2C). – MS (FAB); *m/z* (%): 530 (25) [(¹⁰⁶Pd) M⁺].

Tetrakis(2,2,2-trifluoroethyl)*rac*-3,3,7,7-Tetramethyl-trans-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate (*rac*-**1d**)

The crude product obtained from 220 mg (687 μmol) **5d** and

142 mg (137 μ mol) $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ was purified by column chromatography (H/A, 1:1). 166 mg (81%) of *rac*-**1d** were isolated as a yellow solid. – R_f (H/A, 1:1) = 0.35. – IR (neat, NaCl): ν/cm^{-1} = 2966, 2937, 1706, 1624, 1448, 1413, 1373, 1282, 1161, 1105, 1084, 1034, 977. – ^1H NMR ($[\text{D}_6]$ acetone, 250 MHz): δ/ppm = 1.33 (s, 6H), 1.97 (s, 6H), 4.01–4.18 (m, 2H), 4.25–4.65 (m, 6H). – ^{13}C NMR ($[\text{D}_6]$ acetone, 62.9 MHz): δ/ppm = 19.46 (q, 2C), 26.50 (q, 2C), 38.99 (s, 2C), 47.28 (s, 2C), 55.34 (s, 2C), 60.19 (t, q, $^2J_{\text{C-F}}$ = 35.5 Hz, 2C), 60.50 (t, q, $^2J_{\text{C-F}}$ = 35.5 Hz, 2C), 124.63 (s, q, $^1J_{\text{C-F}}$ = 276.5 Hz, 2C), 124.72 (s, q, $^1J_{\text{C-F}}$ = 276.5 Hz, 2C), 170.92 (s, 2C), 171.10 (s, 2C). – MS (FAB); m/z (%): 769 (1) [^{106}Pd] M^+ + Na], 746 (7) [^{106}Pd] M^+].

Tetrakis(1,1-dimethylethyl) *rac*-3,3,7,7-Tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate (*rac*-**1e**)

The crude product obtained from 700 mg (2.61 mmol) **5e** and 540 mg (522 μ mol) $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ was purified by column chromatography (H/A, 4:1). 604 mg (90%) of *rac*-**1e** were isolated as a yellow solid. – R_f (H/A, 4:1) = 0.20. – IR (neat, NaCl): ν/cm^{-1} = 2975, 2931, 2869, 1710, 1677, 1659, 1614, 1453, 1391, 1366, 1308, 1246, 1224, 1159, 1106, 1033. – ^1H NMR ($[\text{D}_6]$ acetone, 250 MHz): δ/ppm = 1.29 (s, 18H), 1.33 (s, 6H), 1.43 (s, 18H), 1.95 (s, 6H). – ^{13}C NMR ($[\text{D}_6]$ acetone, 62.9 MHz): δ/ppm = 20.44 (q, 2C), 28.32 (q, 2C), 28.50 (q, 6C), 28.62 (q, 6C), 35.06 (s, 2C), 40.14 (s, 2C), 48.53 (s, 2C), 77.87 (s, 2C), 78.29 (s, 2C), 172.18 (s, 2C), 173.07 (s, 2C). – MS (FAB); m/z (%): 642 (2) [^{106}Pd] M^+].

Ethyl 4-Ethyl-5,5-dimethyl-5H-pyrazole-3-carboxylate (**6aI**)

6aI was prepared in analogy to Franck-Neumann's procedure [11] from a solution of 5.00 g (39.6 mmol) ethyl 2-pentynoate in 150 ml DCM and 70.2 ml (570 mM, 40.0 mmol) of a solution of **3** in ether at -30°C . Column chromatography of the crude product (H/EA, 8:1) provided 3.30 g (42%) of **6aI/6bI** (mixture of constitutional isomers) as a yellow oil. From this mixture of isomers small amounts of pure **6aI** could be separated. – **6aI**: R_f (H/EA, 8:1) = 0.25. – IR (neat, NaCl): ν/cm^{-1} = 2980, 2938, 2878, 1712, 1637, 1459, 1395, 1378, 1371, 1343, 1251, 1186, 1095, 1070, 1016, 793. – ^1H NMR (CDCl_3 , 250 MHz): δ/ppm = 1.25–1.32 (m, 6H), 1.44 (s, 6H), 3.03 (q, J = 6.5 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H). – ^{13}C NMR (CDCl_3 , 62.9 MHz): δ/ppm = 12.25 (q), 13.90 (q), 20.50 (q, 2C), 20.83 (t), 60.62 (t), 95.43 (s), 139.57 (s), 162.37 (s, 2C). – MS (70 eV); m/z (%): 197 (20) [M^+ + 1], 183 (8), 81 (100). $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2$ calcd.: C 61.20 H 8.22 N 14.27 (196.25) found: C 61.37 H 8.16 N 12.74.

Methyl 5,5-Dimethyl-4-propyl-5H-pyrazole-3-carboxylate (**6aII**)

6aII was prepared in analogy to Franck-Neumann's procedure [11] from a solution of 5.00 g (39.6 mmol) methyl 2-hexynoate in 150 ml DCM and 70.2 ml (570 mM, 40.0 mmol) of a solution of **3** in ether at -30°C . Column chromatography of the crude product (H/EA, 8:1) provided 3.42 g (44%) of **6aII/6bII** (mixture of constitutional isomers) as a yellow oil. From this mixture of isomers small amounts of pure **6aII** could be separated. – **6aII**: R_f (H/EA, 8:1) = 0.20. – IR (neat, NaCl):

ν/cm^{-1} = 2962, 2935, 2874, 1715, 1638, 1457, 1437, 1360, 1332, 1256, 1196, 1177, 1155, 1099, 1078, 1066, 968, 792. – ^1H NMR (CDCl_3 , 250 MHz): δ/ppm = 0.89 (t, J = 7.4 Hz, 3H), 1.43 (s, 6H), 1.66 (m, 2H), 2.98 (t, J = 7.4 Hz, 2H), 3.76 (s, 3H). – ^{13}C NMR (CDCl_3 , 62.9 MHz): δ/ppm = 13.56 (q), 20.55 (q, 2C), 21.14 (t), 29.08 (t), 51.60 (q), 95.45 (s), 140.05 (s), 161.26, 162.89 (s). – MS (70 eV); m/z (%): 197 (20) [M^+ + 1], 95 (100).

$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2$ calcd.: C 61.20 H 8.22 N 14.27 (196.25) found: C 61.44 H 8.24 N 13.60.

3,4-Dibenzoyl-5,5-dimethyl-5H-pyrazole (**15**)

7a was prepared in analogy to Franck-Neumann's procedure [11] from a solution of 1.11 g (4.74 mmol) **12** in 100 ml DCM and 8.40 ml (570 mM, 4.79 mmol) of a solution of **3** in ether at -30°C . The crude product is rinsed with cold ether, 730 mg (51%) of **13** remain as a yellow solid. – R_f (H/EA, 3:1) = 0.33. – *m.p.* 113°C . – IR (neat, NaCl): ν/cm^{-1} = 3063, 2984, 2934, 1661, 1597, 1579, 1449, 1325, 1262, 1173, 1138, 1067, 1024, 912, 890, 722, 694. – ^1H NMR (CDCl_3 , 250 MHz): δ/ppm = 1.65 (s, 6H), 7.36–7.68 (m, 8H), 8.11–8.15 (m, 2H). – ^{13}C NMR (CDCl_3 , 62.9 MHz): δ/ppm = 20.73 (q, 2 C), 97.22 (s), 128.59 (d, 2C), 128.64 (d, 2C), 128.88 (d, 2C), 130.31 (d, 2C), 133.98 (d), 134.30 (d), 135.85 (s), 136.20 (s), 151.03 (s), 162.88 (s), 186.47 (s), 192.42 (s). – MS (70 eV); m/z (%): 304 (2) [M^+], 276 (7) [M^+ – N_2], 77 (100) [C_6H_5^+]. $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2$ calcd.: C 74.98 H 5.30 N 9.21 (304.35) found: C 74.75 H 5.39 N 9.08.

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