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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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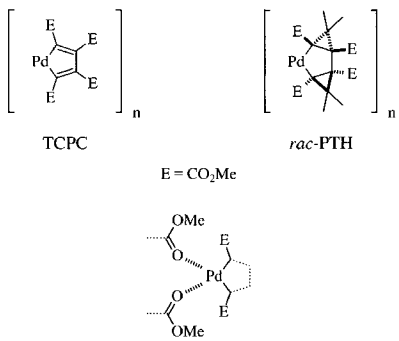
Abstract. The bis(acetone) complex of tetramethyl *rac*-3,3,7,7-tetramethyl-*trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate *rac*-**1a** was crystallized and investigated by X-ray structure analysis. Unlike in complexes with bidendate ligands in *rac*-**1a** · 2(acetone), only 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([D$_5$]pyridine) and *rac*-**1a** · 2([D$_3$] acetonitrile) as well as *rac*-**1a** · 2([D$_6$]acetone) could be characterized by ^{1}H and ^{13}C 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

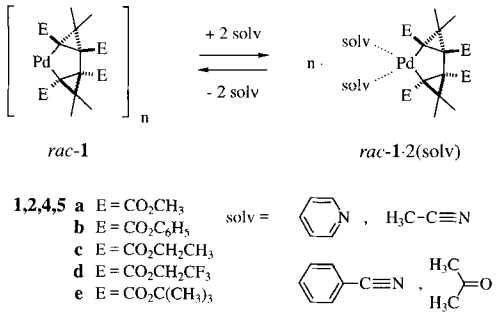
We recently reported on the synthesis and resolution of *trans*-5-palladatricyclo[4.1.0.0^{2,4}]heptanes (PTHs) [1]. These substrates shall serve as model compounds for chiral catalysts *e.g.* for enyne metathesis and related carbocyclization reactions. So far Trost's variations [2] of Maitlis' 2,3,4,5-tetrakis(carboalkoxy)palladacyclopentadiene-(TCPC-) 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-palladatricyclco[4.1.0.0^{2,4}]heptane-1,2,4,6-tetracarboxylate [5]. Since such solvent-mol-ecules are labile ligands [6], they might easily be substituted by an unsaturated organic substrate, thus allowing catalytic reactions: PTHes 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

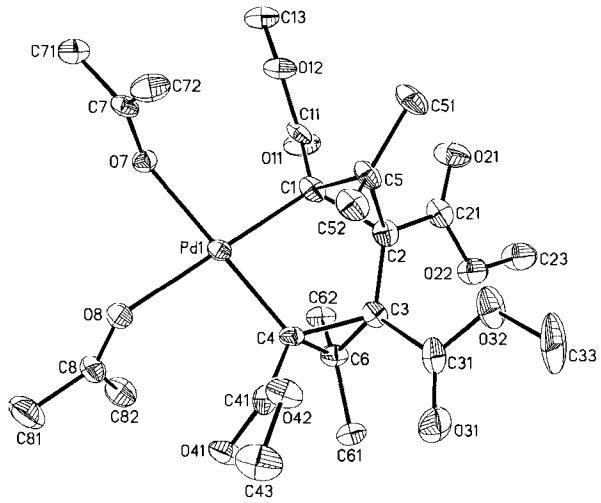


Fig. 1 ORTEP diagram of *rac*-**1**·2(acetone)

Different from the complexes of **1a** with bidendate 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 sterical 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 CMe_2 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 ^{13}C 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 ^{13}C NMR are quite similar in the different solvents. Only for the carbon atom bound to palladium a significant effect is visible in the ^{13}C NMR spectra. While with both N-ligands ([D_5]pyridine and [D_3]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)

cal shift of this carbon atom is about 44 ppm, with the O-coordinated acetone it is 39.5 ppm. This is not unexpected because the *trans*-bound ligand, which is the solvent for each Pd-bound carbon in *rac*-**1a**·2(solv), has the strongest influence [9].

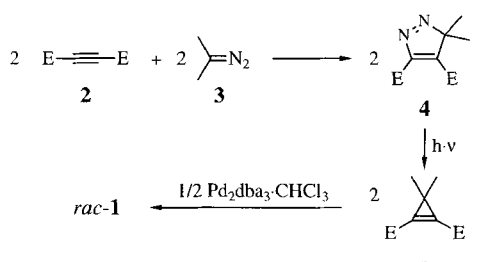
The coordinated solvents exchanged easily. When *e.g.* *rac*-**1a**·2 acetonitrile was dissolved in [D_6]acetone, only free acetonitrile could be detected in the nmr spectra taken immediately.

In conclusion, solvents like acetonitrile and acetone are able to break the polymeric structure and dissolve **1**. Still, these ligands can easily be exchanged by other ligands like substrates for catalytical reactions. Thus these complexes of our 1,2,4,6-tetra(carbomethoxy)-PTH behave different from Binger's complexes of at 1-, 2-,4- and 6-position unsubstituted PTHs [10] where bidentate ligands, which are necessary for the stabilization of his PTHs, block the coordination sites and prevent catalytical reactions.

2 New Derivatives and Synthetic Limitations

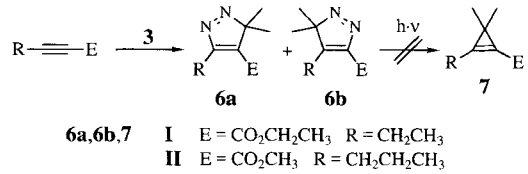
Up till now we focused on tetramethyl *trans*-5-palladatricyclo[4.1.0.$0^{2,4}$]heptane-1,2,4,6-tetracarboxylate **1a** [1]. The only other *trans*-5-palladatricyclo[4.1.0.$0^{2,4}$] heptane (PTH) derivative without additional stabilizing ligands we synthesized so far was the analogous tetraphenyl ester **1b** [5]. Now, we were interested in the scope and the limitation of our synthetic approach to these substrates. We did not investigate in 1- and 2-position unsubstituted cyclopropenes, since Binger has already shown that with these substrates mixtures of different palladacycles are obtained [10b] and that additional bidentate ligands are necessary to obtain stable compounds.

First we tried the preparation of the tetraethyl ester **1c**, the tetrakis(2,2,2-trifluoroethyl) ester **1d** and the tetrakis-*tert*-butyl ester **1e**. The sequence started with a cycloaddition of the 1,3-dipole diazopropane **3** to the alkynes **2c–e**. The pyrazoles **4c–e** formed that way were converted to the cyclopropenes **5c–e** by irradiating with a mercury-vapor lamp. Finally the PTHs **1c–e** formed in the reaction of Pd_2dba_3·$CHCl_3$ with four equivalents of **5c–e**.



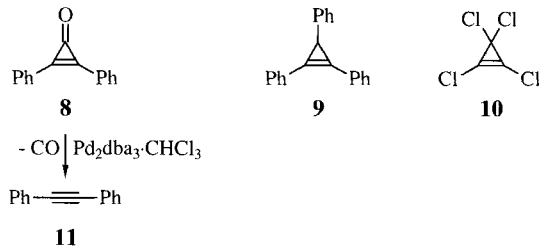
Scheme 3

Efforts to obtain the cyclopropenemonocarboxylates **7I** respectively **7II** from the pyrazols **6aI** and **6bI** respectively **6aII** and **6bII** failed. This observation is in accordance with similar substrates described in the literature [11].



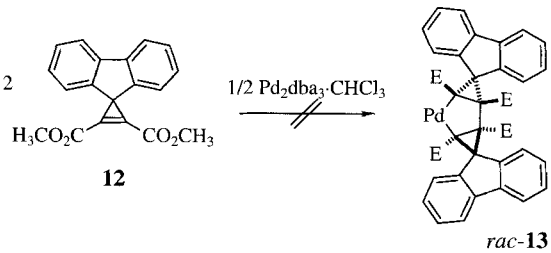
Scheme 4

In the reactions of the commercially available cyclopropenes **8**, **9** and **10** with Pd_2dba_3·$CHCl_3$, no PTHs were formed. **8** was decarbonylated to **11** by Pd_2dba_3·$CHCl_3$ [12]. With **9** and **10** no defined product could be isolated at all.



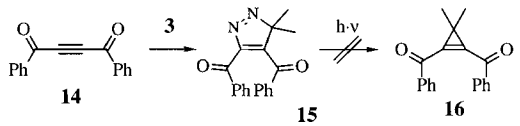
Scheme 5

The known cyclopropene-1,2-dicarboxylate **12** also did not form any PTHs in the reaction with Pd_2dba_3·$CHCl_3$. If one constructs a model of the PTH **13** that would form from **12**, one can see that there is a strong steric interaction between the *peri*-hydrogens of the fluorenyliden group and the carbon-atom bound to palladium. Probably, this is the reason for the failure of the formation of **13**.



Scheme 6

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 leed to PTHs.

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

Experimental

General Methods and Instrumentation

All operations were carried out unter N_2 and in dry solvents; transfers were effected by means of Schlenk-tube techniques. $Pd_2dba_3 \cdot CHCl_3$ [13], bis(2,2,2-trifluoroethyl) acetylendicarboxylate (**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 ^{13}C, respectively) and Bruker DRX 600 (600 MHz for ^1H). $CDCl_3$ 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, quadropole 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 $Pd_2dba_3 \cdot CHCl_3$ as reported previously [1].

Since the ^{13}C 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. – ^{13}C NMR ($CDCl_3$, 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 ($CDCl_3$, 250 MHz): δ/ppm = 1.91 (s, 3H), 2.19 (s, 3H), 3.72 (s, 3H), 3.74 (s, 3H). – ^{13}C NMR ($CDCl_3$, 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).

$C_9H_{12}O_4$	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. – ^{13}C NMR ($CDCl_3$, 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 $C_{24}H_{36}O_{10}Pd$: orthorhombic, $Pca2_1$, a = 29.1553 (3) Å, b = 9.0888 (1) Å, c = 25.5762 (2) Å, V = 6777.35 (12) Å^3, Z = 8, D_{calc} = 1.329 g cm^{-3}, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), μ = 0.60 mm^{-1}, T = 133K. 73973 reflections were collected on a SIEMENS CCD three-circle diffractometer for 2° < 2 Θ< 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 F^2 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@chemcrys.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([D_6]acetone). – ^{1}H NMR ([D_6]acetone, 250 MHz, 23°C): δ/ppm = 1.30 (s, 6H), 1.87 (s, 6H), 3.35 (s, 6H), 3.49 (s, 6H). – ^{13}C NMR ([D_6]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([D_5]pyridine). – ^{1}H NMR ([D_5]pyridine, 250 MHz, 23 °C): δ/ppm = 1.95 (s, 6H), 2.59 (s, 6H), 3.14 (s, 6H), 3.75 (s, 6H). – ^{13}C NMR ([D_5]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([D_3]acetonitrile). – ^{1}H NMR ([D_3]acetonitrile, 250 MHz, 23 °C): δ/ppm = 1.29 (s, 6H), 1.71 (s, 6H), 3.44 (s, 6H), 3.48 (s, 6H). – ^{13}C NMR ([D_3]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) Acetylendicarboxylate (**2d**)

The spectroscopic data of **2d** has not been reported yet. **2d**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 4.59 (q, $^3J_{C-F}$ = 7.1 Hz, 4H). – ^{13}C NMR ($CDCl_3$, 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 acetylendicarboxylate **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. – ^{1}H NMR ($CDCl_3$, 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). – ^{13}C NMR ($CDCl_3$, 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).

$C_{11}H_{16}N_2O_4$	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. – ^{1}H NMR ($CDCl_3$, 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). – ^{13}C NMR ($CDCl_3$, 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$^+$ – N_2], 243 (100)

$C_{11}H_{10}F_6N_2O_4$	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. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.34 (t, J = 7.3 Hz, 6H), 1.40 (s, 6H), 4.31 (q, J = 7.3 Hz, 4H). – ^{13}C NMR ($CDCl_3$, 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).

$C_{11}H_{16}O_4$	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. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.45 (s, 6H), 4.62 (q, $^3J_{H-F}$ = 8.2 Hz, 4H). – ^{13}C NMR ($CDCl_3$, 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) Pd_2dba_3 $CHCl_3$ 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. – ^{1}H NMR ([D_6]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). – ^{13}C NMR ([D_6]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) [(^{106}Pd) 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 μmol) $Pd_2dba_3 \cdot CHCl_3$ 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. – ^{1}H NMR ([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 ([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, $^2J_{C-F}$ = 35.5 Hz, 2C), 60.50 (t, q, $^2J_{C-F}$ = 35.5 Hz, 2C), 124.63 (s, q, $^1J_{C-F}$ = 276.5 Hz, 2C), 124.72 (s, q, $^1J_{C-F}$ = 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 μmol) $Pd_2dba_3 \cdot CHCl_3$ 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. – ^{1}H NMR ([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 ([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. – ^{1}H 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).

$C_{10}H_{16}N_2O_2$	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. – ^{1}H 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).

$C_{10}H_{16}N_2O_2$	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. – ^{1}H 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) [$C_6H_5^+$].

$C_{19}H_{16}N_2O_2$	calcd.:	C 74.98	H 5.30	N 9.21
(304.35)	found:	C 74.75	H 5.39	N 9.08.

References

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

[2] B. M. Trost, M. K. Trost, J. Am. Chem. Soc. **1991**, *113*, 1850

[3] a) K. Moseley, P. M. Maitlis, J. Chem. Soc., Chem. Commun. **1971**, 1604. b) P. M. Maitlis, P. Espinet, M. J. H. Russel in Comprehensive Organometallic Chemistry, Vol. 6 (Eds. G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, 1982, p. 455. c) A. Segnitz in Houben Weyl, Vol. 13/9b (Ed. A. Segnitz), Thieme Verlag, Stuttgart, 1984, p. 808

[4] L. D. Brown, K. Itoh, H. Suzuki, K. Hirai, J. A. Ibers, J. Am. Chem. Soc. **1978**, *100*, 8232

[5] A. S. K. Hashmi, F. Naumann, J. W. Bats, Chem. Ber./Recueil **1997**, *130*, 1457

[6] J. A. Davies, F. R. Hartley, Chem. Rev. **1981**, *81*, 79

[7] a) A. S. K. Hashmi, L. Schwarz, Chem. Ber./Recueil **1997**, *130*, 1449. b) A. S. K. Hashmi, Angew. Chem. **1995**, *107*, 1749; Angew. Chem. Int. Ed. Engl. **1995**, *34*, 1581

[8] a) L. R. Falvello, J. Forniés, R. Navarro, V. Sicilia, M. Tomás, J. Chem. Soc., Dalton Trans. **1994**, 3143. In the literature X-ray structure analyses of one other organometallic compound and of five inorganic complexes with acetone as ligand have been reported. But they show only a loose contact between acetone and Pd (Pd–O distances from 3.06 to 4.00 Å); b) C. P. Brock, J. L.

Huckaby, T. G. Attig, Acta Crystallogr., Sect. B **1984**, *40*, 595; c) G. Reid, A. J. Blake, T. I. Hyde, M. Schröder, J. Chem. Soc., Chem. Commun. **1988**, 1397; d) T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, J. Am. Chem. Soc. **1989**, *111*, 6301; e) V. P. Zagorodnikov, S. B. Katser, M. N. Vargaftik, M. A. Porai-Koshits, I. I. Moiseev, Koord. Khim. **1989**, *15*, 1540; f) A. J. Blake, G. Reid, M. Schröder, J. Chem. Soc., Dalton Trans. **1990**, 3363; g) J. H. Yamamoto, G. P. A. Yap, C. M. Jensen, J. Am. Chem. Soc. **1991**, *113*, 5060. Inorganic complexes of Pd with two or more acetone ligands are also described in the literature, but no crystallographic data is available; h) J. A. Davies, F. R. Hartley, S. G. Murray, J. Chem. Soc., Dalton Trans. **1980**, 2246; i) F. R. Hartley, S. G. Murray, A. Wilkinson, Inorg. Chem. **1989**, *28*, 549; j) M. Crocker, R. H. M. Herold, J. G. Buglass, P. Companje, J. Catal. **1993**, *141*, 700

[9] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987, p. 242

[10] a) P. Binger, H. M. Büch, R. Benn, R. Mynott, Angew. Chem. **1982**, *94*, 66; Angew. Chem. Int. Ed. Engl. **1982**, *21*, 62; b) P. Binger, H. M. Büch, Top. Curr. Chem. **1987**, *135*, 77

[11] C. Dietrich-Buchecker, M. Franck-Neumann, Tetrahedron **1977**, *33*, 745

[12] We assume that this decarbonylation proceeds through an insertion of Pd(0) into the C1–C3 bond of the cyclopropenone [as known for Pt(0): a) W. Wong, S. J. Singer, W. D. Pitts, S. F. Watkins, W. H. Baddley, J. Chem. Soc., Chem. Commun. **1972**, 672 and b) J. P. Visser, J. E. Ramakers-Blom, J. Organomet. Chem. **1972**, *44*, C63] followed by the loss of CO [as known for Rhodacyclobutenones; c) L. Song, A. M. Arif, P. J. Stang, Organometallics **1990**, *9*, 2792]

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

[14] a) A. C. Day, P. Raymond, R. M. Southam, M. C. Whiting, J. Chem. Soc. C **1966**, 467; b) S. D. Andrews, A. C. Day, P. Raymond, M. C. Whiting, Org. Synth. **1971**, *50*, 27

[15] C. G. Sims, D. Wege, Aust. J. Chem. **1995**, *48*, 469

[16] a) G. Ege, Tetrahedron Lett. **1963**, 1667; b) H. Dürr, L. Schrader, H. Seidl, Chem. Ber. **1971**, *104*, 391

[17] I. Iwai, K. Tomita, Chem. Pharm. Bull. **1963**, *11*, 524

[18] a) M. Franck-Neumann, Angew. Chem. **1967**, *79*, 98; Angew. Chem. Int. Ed. Engl. **1967**, *6*, 79; b) M. Franck-Neumann, M. Miesch, Tetrahedron **1983**, *39*, 1247; c) M. W. Majchrzak, M. Békhazi, I. Tse-Sheepy, J. Warkentin, J. Org. Chem. **1989**, *54*, 1842; d) Y. Nakano, M. Hamaguchi, T. Nagai, J. Org. Chem. **1989**, *54*, 5912

[19] a) M. Franck-Neumann, C. Buchecker, Tetrahedron Lett. **1969**, 15; b) H. Duerr, B. Ruge, T. Ehrhardt, Liebigs Ann. Chem. **1973**, 214; c) C. Dietrich-Buchecker, M. Franck-Neumann, Tetrahedron **1977**, *33*, 751; d) N. Galloway, B. Halton, Aust. J. Chem. **1979**, *32*, 1743

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