Palladium catalysed alkyne hydrogenation and oligomerisation: A Parahydrogen based NMR investigation

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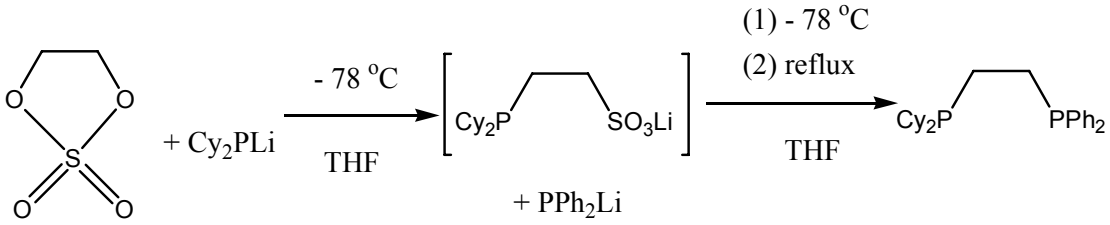
Supporting information

Ligand Synthesis

Synthesis of unsymmetrical phosphine $Ph_2PCH_2CH_2PCy_2$



Scheme S1. Synthesis of $Cy_2PCH_2CH_2PPh_2$ (cppe).

Synthesis of ethylene sulphate(1,3,2-dioxathioalane,2,2-dioxide).[1]

A 2 litre 3 necked flask equipped with a dropping funnel and a sodium hydroxide trap was charged with 12.4 g (0.20 mol) of 1,2-ethanediol in 150 mL of CCl_4. 20 mL (0.27 mol) of thionyl chloride was added to this solution dropwise over 1 h. The solution was then stirred for a further hour and the solvent evaporated under reduced pressure. The resulting yellow liquid was distilled under reduced pressure (water pump) to afford a colourless liquid of the sulphite ester (15 g 70 %). Pure by GC/MS and NMR.

10.8 g (0.1 mol) of the sulphite ester was dissolved in 100 mL of acetonitrile and cooled on an ice bath. Then 200 mg (0.76 mmol) of $RuCl_3 \cdot 3H_20$, 32 g (0.15 mol) of sodium periodate and 150 ml of cold water were added sequentially. The green mixture was stirred for 15 minutes. Then 800 mL of ethyl acetate and 80 mL of saturated sodium bicarbonate solution were added and the organic phase separated. The aqueous phase was extracted with 2 x 100 mL of ethyl acetate and the combined organic layers then washed with 50 mL of water. The organic phase was then dried over sodium sulphate, filtered and the solvent removed under reduced pressure to yield a white solid. Yield 11.2 g, 70 %. Pure by GCMS and NMR. Mp 96-97 ºC.

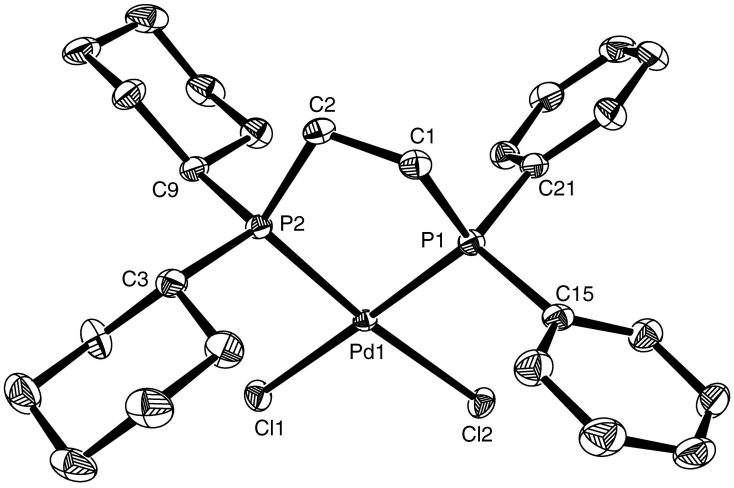
Synthesis of cppe ($Ph_2PCH_2CH_2PCy_2$).[2]

2.9 mL (4.89 mmol) of Cy_2PH was dissolved in 40 mL of dry THF. This solution was cooled to –78 ºC and 12 mL of 1.5 M BuLi were added dropwise. The solution turns from colourless to orange red. This solution was slowly allowed to warm up to room temperature and it was then stirred for a further 1 h.

2.46 mL (4.89 mmol) of Ph_2PH were dissolved in 40 mL of dry THF. The reaction mixture was cooled to –78 ºC and 12 mL of 1.5 M BuLi were added slowly. This solution was allowed to warm up to room temperature and stirred for a further 1 h.

The THF solution of Cy_2PLi was then added dropwise at –78 ºC, to a solution of 0.59 g (4.89 mmol) of ethylene sulphate in 20 ml of dry THF. This colourless solution was then allowed to warm up to room temperature and stirred for 30 minutes. This mixture was then cooled to –78 ºC and the THF solution of Ph_2PLi added dropwise. This pale red solution was allowed to warm up to room temperature over 20 min and then refluxed for 4 h. (Note: the solution goes a pale yellow and turns jelly like due to the presence of $LiSO_4$). Upon cooling to r.t., 20 mL of degassed H_20 were added; the organic phase was separated and washed with 2 x 10 mL of degassed H_20. The THF layer was dried over $MgSO_4$, filtered and dried in vacuum to leave a white gummy solid. After prolonged drying under vacuum, the gummy solid was recrystallised from hot degassed methanol to leave a white air-sensitive solid.

$^{31}P\{1H\}$ NMR (161.9 MHz, C_6D_6): δ –12.28 (d, J_{PP} = 30 Hz, PPh_2); 0.93 (d, J_{PP} = 30 Hz, PCy_2). The NMR data agrees with that reported in the literature.



Cl(1)-Pd(1)	2.3662(6)	P(1)-Pd(1)	2.2297(6)
Cl(2)-Pd(1)	2.3767(5)	P(2)-Pd(1)	2.2486(6)
P(1)-Pd(1)-P(2)	86.30(2)	P(1)-Pd(1)-Cl(2)	88.69(2)
P(1)-Pd(1)-Cl(1)	179.03(2)	P(2)-Pd(1)-Cl(2)	174.39(2)
P(2)-Pd(1)-Cl(1)	92.75(2)	Cl(1)-Pd(1)-Cl(2)	92.25(2)

Fig S1. Molecular structure of $[Pd(Ph_2PCH_2CH_2PCy_2)(Cl)_2]\cdot 2CH_2Cl_2$, ortep view showing 50 % probability ellipsoids, and selected bond lengths (Å) and angles (º). Hydrogen atoms and crystallization CH_2Cl_2 molecules have been omitted for clarity.

Synthesis of [Pd(dppm)(OTf)$_2$]

To a suspension of $[Pd(dppm)(Cl)_2]$ (250 mg, 0.44 mmol) in dry, degassed dichloromethane (20 mL) was added AgOTf (178 mg, 0.67 mmol). The new suspension was stirred overnight (14 h) in the absence of light, after which time it was filtered off. The yellow solution was concentrated to ca. 2 mL under reduced pressure and diethyl ether was then added (10 mL). The resulting solid was collected by filtration, washed with diethyl ether (3 x 3 mL) and dried under vacuum for 1 h to yield a bright yellow fine powder. Yield: 285 mg, 85 % for $C_{27}H_{22}F_6O_6P_2PdS_2$. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ -52.44 (s, PPh_2). The spectroscopic data matches that reported in the literature.[4]

Synthesis of [Pd(dppe)(OTf)$_2$]

To a solution of [Pd(dppe)(Cl)$_2$] (200 mg, 0.30 mmol) in dry, degassed dichloromethane (20 mL) was added AgOTf (247 mg, 0.90 mmol). The resulting suspension was stirred for 72 h with the exclusion of light, after which time it was filtered off. The yellow solution was concentrated to dryness under reduced pressure and n-pentane was then added (10 mL). The resulting solid was collected by filtration, washed with n-pentane (3 x 3 mL) and dried in vacuo for 1 h to yield a white powder. Yield: 180 mg, 68 % for $C_{28}H_{24}F_6O_6P_2PdS_2$. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ 74.24 in methanol (s, PPh_2). The spectroscopic data matches that reported in the literature.[8]

Synthesis of [Pd(dppp)(OTf)$_2$]

A solution of [Pd(dppp)(Cl)$_2$] (250 mg, 0.42 mmol) in dry, degassed dichloromethane (10 mL) was added AgOTf (325 mg, 1.26 mmol) and the resulting suspension stirred overnight (16 h) in the absence of light. The resulting suspension was filtered off, the solution concentrated to ca. 5 mL and n-pentane (10 mL) added to precipitate a solid which was washed with n-pentane (2 x 2 mL) and dried under vacuum to give the title compound as a pale yellow solid. Yield 170 mg, 64 % for $C_{29}H_{26}F_6O_6P_2PdS_2$. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 17.4 (s, PPh_2). The spectroscopic data matches that reported in the literature.[4]

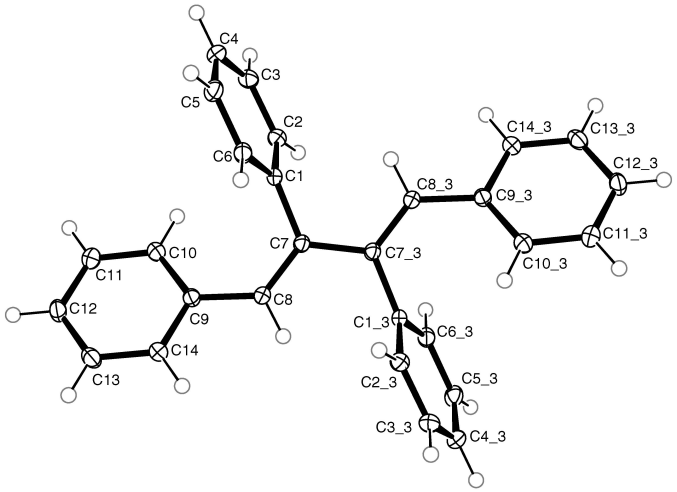


Fig S2 . Molecular structure of *cis*,*cis*-1,2,3,4-tetraphenyl-1,3-butadiene, ortep view showing 50 % probability ellipsoids. Selected bond lengths (Å) and angles (º): C(7)-C(7)_3 = 1.483(2), C(8)-C(7) = 1.3534(15), C(8)-C(7)-C(7)_3 = 120.76(12). The atoms with labels ending by _3 where generated using symmetry operations.

Relative signal intensity of species 2 and 4 vs. T

Table S1 Relative signal intensity (CHD_2 resonance of the deuterated methanol used as solvent = 1) for the indicated alkyl resonances of species **2** and **4** vs. T. (The integrals were measured from spectra processed in magnitude calculation).

		δ	295 K	323 K
dcpe	**2a**	4.38	1.75	4.28
dppe	**2b**	4.24	0.05	0.14
	3b	3.70	0.1	0.03
	4b	5.10	0.18	0.01
dppm	**2c**	4.96	-	0.01
dppp	**2d**	3.71	1.37	2.53
	4d	4.87	-	0.02
cppe	**2e**	4.49	0.45	13.27
	2e'	3.70	0.60	2.53
	4e	5.42	0.06	0.31

The NMR data shows a good qualitative agreement with the conversion rates and even with the organic product speciation seen by GC/MS. It should be said however, that a higher signal intensity does not necessarily infers a higher conversion into the final product as has been shown for the cases of **2e** and **2e'**.

Note Cis,cis-1,2,3,4-tetraphenyl-1,3-butadiene appears in the CSD 4 times under the reference codes TEPBUT, TEPBUT01, TEPBUT02 & TEPBUT03.

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Crystal data and structure refinement for $[Pd(Ph_2PCH_2CH_2PCy_2)Cl_2]\cdot 2CH_2Cl_2$.

Empirical formula	C28 H40 Cl6 P2 Pd	
Formula weight	757.64	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.0021(10) Å	α= 90°.
	b = 17.4753(15) Å	β= 109.045(2)°.
	c = 16.5180(14) Å	γ = 90°.
Volume	3274.9(5) $Å^3$	
Z	4	
Density (calculated)	1.537 Mg/m^3	
Absorption coefficient	1.172 mm^{-1}	
F(000)	1544	
Crystal size	0.30 x 0.07 x 0.07 mm^3	
Theta range for data collection	1.75 to 28.31°.	
Index ranges	-15<=h<=13, -23<=k<=23, -22<=l<=22	
Reflections collected	32946	
Independent reflections	8132 [R(int) = 0.0478]	
Completeness to theta = 28.31°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8132 / 0 / 372	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0759	
R indices (all data)	R1 = 0.0436, wR2 = 0.0795	
Largest diff. peak and hole	0.749 and -0.677 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6330(2)	2869(1)	8173(1)	17(1)
C(2)	5921(2)	2096(1)	8403(1)	18(1)
C(3)	6041(2)	938(1)	7131(1)	19(1)
C(4)	6788(2)	1411(1)	6722(2)	26(1)
C(5)	7639(2)	915(2)	6427(2)	31(1)
C(6)	6971(2)	284(2)	5828(2)	32(1)
C(7)	6277(2)	-202(2)	6253(2)	32(1)
C(8)	5403(2)	280(1)	6540(2)	26(1)
C(9)	4044(2)	958(1)	7818(1)	18(1)
C(10)	3093(2)	1433(1)	8021(2)	22(1)
C(11)	2281(2)	921(2)	8330(2)	30(1)
C(12)	2992(2)	439(2)	9101(2)	34(1)
C(13)	3907(2)	-43(2)	8888(2)	31(1)
C(14)	4745(2)	453(1)	8584(2)	25(1)
C(15)	5787(2)	4000(1)	6803(1)	17(1)
C(16)	5283(2)	4716(1)	6557(2)	23(1)
C(17)	5776(2)	5215(2)	6104(2)	30(1)
C(18)	6751(2)	4998(2)	5892(2)	32(1)
C(19)	7241(2)	4283(2)	6124(2)	33(1)
C(20)	6759(2)	3781(2)	6573(2)	26(1)
C(21)	4281(2)	3849(1)	7879(1)	17(1)
C(22)	3144(2)	3620(1)	7818(1)	20(1)
C(23)	2538(2)	4003(1)	8290(2)	26(1)
C(24)	3059(3)	4617(2)	8803(2)	31(1)
C(25)	4178(3)	4855(1)	8858(2)	31(1)
C(26)	4802(2)	4468(1)	8408(2)	25(1)
Cl(1)	2912(1)	1459(1)	5538(1)	22(1)
Cl(2)	3039(1)	3413(1)	5504(1)	20(1)
P(1)	5112(1)	3316(1)	7324(1)	14(1)
P(2)	5020(1)	1570(1)	7446(1)	14(1)
Pd(1)	4040(1)	2423(1)	6448(1)	12(1)
C(27A)	5524(3)	2497(2)	802(2)	53(1)
Cl(3A)	4484(3)	3006(2)	-33(2)	30(1)

Cl(4A)	5111(6)	2200(6)	1640(4)	74(2)
C(27B)	5524(3)	2497(2)	802(2)	53(1)
Cl(3B)	4389(10)	2923(7)	25(7)	73(3)
Cl(4B)	4829(6)	1933(4)	1349(8)	51(2)
C(28A)	-9(3)	2490(2)	9478(2)	49(1)
Cl(5A)	-636(2)	2311(2)	8409(1)	52(1)
Cl(6A)	1574(2)	2587(1)	9757(1)	42(1)
C(28B)	-9(3)	2490(2)	9478(2)	49(1)
Cl(5B)	-542(4)	2730(8)	8238(3)	69(2)
Cl(6B)	1248(14)	2336(9)	9806(4)	123(5)

Table S3. Bond lengths [Å] and angles [°].

C(1)-C(2)	1.528(3)
C(1)-P(1)	1.838(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-P(2)	1.844(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.530(3)
C(3)-C(8)	1.540(3)
C(3)-P(2)	1.846(2)
C(3)-H(3)	1.0000
C(4)-C(5)	1.535(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.524(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.513(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.535(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.533(3)
C(9)-C(14)	1.546(3)
C(9)-P(2)	1.834(2)
C(9)-H(9)	1.0000
C(10)-C(11)	1.528(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.532(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.514(4)

C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.531(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.393(3)
C(15)-C(20)	1.394(3)
C(15)-P(1)	1.810(2)
C(16)-C(17)	1.399(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.380(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.381(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.391(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.394(3)
C(21)-C(26)	1.403(3)
C(21)-P(1)	1.815(2)
C(22)-C(23)	1.398(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.383(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.381(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.390(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
Cl(1)-Pd(1)	2.3662(6)
Cl(2)-Pd(1)	2.3767(5)
P(1)-Pd(1)	2.2297(6)
P(2)-Pd(1)	2.2486(6)
C(27A)-Cl(4A)	1.697(4)
C(27A)-Cl(3A)	1.770(5)
C(27A)-H(27A)	0.9900

C(27A)-H(27B)	0.9900
C(28A)-Cl(5A)	1.708(4)
C(28A)-Cl(6A)	1.811(4)
C(28A)-H(28A)	0.9900
C(28A)-H(28B)	0.9900

C(2)-C(1)-P(1)	109.01(14)
C(2)-C(1)-H(1A)	109.9
P(1)-C(1)-H(1A)	109.9
C(2)-C(1)-H(1B)	109.9
P(1)-C(1)-H(1B)	109.9
H(1A)-C(1)-H(1B)	108.3
C(1)-C(2)-P(2)	111.96(14)
C(1)-C(2)-H(2A)	109.2
P(2)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2B)	109.2
P(2)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
C(4)-C(3)-C(8)	111.41(19)
C(4)-C(3)-P(2)	109.87(16)
C(8)-C(3)-P(2)	112.77(16)
C(4)-C(3)-H(3)	107.5
C(8)-C(3)-H(3)	107.5
P(2)-C(3)-H(3)	107.5
C(3)-C(4)-C(5)	112.4(2)
C(3)-C(4)-H(4A)	109.1
C(5)-C(4)-H(4A)	109.1
C(3)-C(4)-H(4B)	109.1
C(5)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.9
C(6)-C(5)-C(4)	110.6(2)
C(6)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.1
C(7)-C(6)-C(5)	110.9(2)
C(7)-C(6)-H(6A)	109.5

C(5)-C(6)-H(6A)	109.5
C(7)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.0
C(6)-C(7)-C(8)	111.8(2)
C(6)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7A)	109.3
C(6)-C(7)-H(7B)	109.3
C(8)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
C(7)-C(8)-C(3)	110.9(2)
C(7)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.0
C(10)-C(9)-C(14)	112.02(18)
C(10)-C(9)-P(2)	111.08(15)
C(14)-C(9)-P(2)	111.70(16)
C(10)-C(9)-H(9)	107.2
C(14)-C(9)-H(9)	107.2
P(2)-C(9)-H(9)	107.2
C(11)-C(10)-C(9)	110.9(2)
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.0
C(10)-C(11)-C(12)	110.8(2)
C(10)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
C(12)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(13)-C(12)-C(11)	111.2(2)
C(13)-C(12)-H(12A)	109.4
C(11)-C(12)-H(12A)	109.4
C(13)-C(12)-H(12B)	109.4

C(11)-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	108.0
C(12)-C(13)-C(14)	111.4(2)
C(12)-C(13)-H(13A)	109.3
C(14)-C(13)-H(13A)	109.3
C(12)-C(13)-H(13B)	109.3
C(14)-C(13)-H(13B)	109.3
H(13A)-C(13)-H(13B)	108.0
C(13)-C(14)-C(9)	110.5(2)
C(13)-C(14)-H(14A)	109.5
C(9)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(9)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(16)-C(15)-C(20)	119.3(2)
C(16)-C(15)-P(1)	120.88(18)
C(20)-C(15)-P(1)	119.55(18)
C(15)-C(16)-C(17)	119.8(2)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(18)-C(17)-C(16)	120.4(2)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(17)-C(18)-C(19)	119.9(2)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	120.4(3)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
C(19)-C(20)-C(15)	120.2(2)
C(19)-C(20)-H(20)	119.9
C(15)-C(20)-H(20)	119.9
C(22)-C(21)-C(26)	119.5(2)
C(22)-C(21)-P(1)	120.17(17)
C(26)-C(21)-P(1)	120.25(18)
C(21)-C(22)-C(23)	119.8(2)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1

C(24)-C(23)-C(22)	120.0(2)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.6(2)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(24)-C(25)-C(26)	120.0(2)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(21)	120.0(2)
C(25)-C(26)-H(26)	120.0
C(21)-C(26)-H(26)	120.0
C(15)-P(1)-C(21)	107.83(10)
C(15)-P(1)-C(1)	105.98(10)
C(21)-P(1)-C(1)	105.29(10)
C(15)-P(1)-Pd(1)	113.97(7)
C(21)-P(1)-Pd(1)	113.00(8)
C(1)-P(1)-Pd(1)	110.17(7)
C(9)-P(2)-C(2)	105.28(10)
C(9)-P(2)-C(3)	107.50(10)
C(2)-P(2)-C(3)	106.40(10)
C(9)-P(2)-Pd(1)	113.18(7)
C(2)-P(2)-Pd(1)	108.58(7)
C(3)-P(2)-Pd(1)	115.25(7)
P(1)-Pd(1)-P(2)	86.30(2)
P(1)-Pd(1)-Cl(1)	179.03(2)
P(2)-Pd(1)-Cl(1)	92.75(2)
P(1)-Pd(1)-Cl(2)	88.69(2)
P(2)-Pd(1)-Cl(2)	174.39(2)
Cl(1)-Pd(1)-Cl(2)	92.25(2)
Cl(4A)-C(27A)-Cl(3A)	118.1(3)
Cl(4A)-C(27A)-H(27A)	107.8
Cl(3A)-C(27A)-H(27A)	107.8
Cl(4A)-C(27A)-H(27B)	107.8
Cl(3A)-C(27A)-H(27B)	107.8
H(27A)-C(27A)-H(27B)	107.1
Cl(5A)-C(28A)-Cl(6A)	110.63(19)
Cl(5A)-C(28A)-H(28A)	109.5

Cl(6A)-C(28A)-H(28A)	109.5
Cl(5A)-C(28A)-H(28B)	109.5
Cl(6A)-C(28A)-H(28B)	109.5
H(28A)-C(28A)-H(28B)	108.1

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	21(1)	15(1)	-1(1)	2(1)	-1(1)
C(2)	19(1)	22(1)	13(1)	3(1)	3(1)	1(1)
C(3)	18(1)	22(1)	15(1)	2(1)	3(1)	6(1)
C(4)	23(1)	29(1)	29(1)	0(1)	14(1)	2(1)
C(5)	23(1)	43(2)	30(1)	0(1)	14(1)	9(1)
C(6)	28(1)	47(2)	20(1)	-2(1)	7(1)	20(1)
C(7)	33(2)	30(1)	32(1)	-5(1)	9(1)	11(1)
C(8)	25(1)	21(1)	33(1)	-7(1)	10(1)	3(1)
C(9)	20(1)	19(1)	14(1)	2(1)	5(1)	-1(1)
C(10)	21(1)	25(1)	24(1)	-1(1)	11(1)	-3(1)
C(11)	28(1)	38(2)	29(1)	-7(1)	17(1)	-11(1)
C(12)	43(2)	41(2)	22(1)	-3(1)	17(1)	-21(1)
C(13)	43(2)	29(1)	17(1)	4(1)	6(1)	-14(1)
C(14)	29(1)	24(1)	20(1)	6(1)	6(1)	-2(1)
C(15)	16(1)	21(1)	12(1)	-1(1)	1(1)	-6(1)
C(16)	22(1)	24(1)	21(1)	2(1)	4(1)	-2(1)
C(17)	43(2)	23(1)	22(1)	5(1)	5(1)	-7(1)
C(18)	40(2)	37(2)	19(1)	-1(1)	10(1)	-20(1)
C(19)	33(2)	40(2)	32(1)	-1(1)	19(1)	-6(1)
C(20)	27(1)	28(1)	27(1)	2(1)	14(1)	-1(1)
C(21)	20(1)	18(1)	14(1)	1(1)	6(1)	2(1)
C(22)	21(1)	21(1)	19(1)	0(1)	7(1)	3(1)
C(23)	28(1)	29(1)	25(1)	6(1)	13(1)	11(1)
C(24)	44(2)	31(1)	19(1)	4(1)	15(1)	17(1)
C(25)	49(2)	22(1)	19(1)	-5(1)	8(1)	3(1)
C(26)	28(1)	23(1)	21(1)	-4(1)	5(1)	-2(1)
Cl(1)	25(1)	17(1)	19(1)	-2(1)	-1(1)	-2(1)
Cl(2)	21(1)	18(1)	18(1)	4(1)	0(1)	0(1)
P(1)	13(1)	15(1)	14(1)	0(1)	3(1)	-2(1)
P(2)	15(1)	16(1)	12(1)	1(1)	4(1)	1(1)
Pd(1)	11(1)	13(1)	10(1)	0(1)	2(1)	0(1)
C(27A)	26(2)	80(3)	54(2)	31(2)	14(1)	14(2)
Cl(3A)	26(1)	43(1)	20(1)	6(1)	6(1)	10(1)

Cl(4A)	53(2)	127(4)	48(2)	42(2)	25(2)	36(2)
C(27B)	26(2)	80(3)	54(2)	31(2)	14(1)	14(2)
Cl(3B)	65(4)	118(6)	40(3)	21(3)	23(3)	33(4)
Cl(4B)	46(2)	55(3)	50(3)	24(2)	12(2)	-4(2)
C(28A)	59(2)	55(2)	49(2)	-13(2)	37(2)	-15(2)
Cl(5A)	33(1)	80(2)	38(1)	0(1)	3(1)	16(1)
Cl(6A)	35(1)	57(1)	36(1)	-14(1)	16(1)	-15(1)
C(28B)	59(2)	55(2)	49(2)	-13(2)	37(2)	-15(2)
Cl(5B)	31(2)	122(7)	47(2)	17(3)	4(2)	2(2)
Cl(6B)	165(8)	129(8)	38(2)	-18(3)	-18(4)	117(7)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3).

	x	y	z	U(eq)
H(1A)	7016	2797	7973	21
H(1B)	6574	3204	8685	21
H(2A)	5454	2177	8791	22
H(2B)	6619	1784	8713	22
H(3)	6587	703	7665	22
H(4A)	7246	1793	7141	31
H(4B)	6261	1692	6223	31
H(5A)	8058	1239	6128	37
H(5B)	8234	684	6933	37
H(6A)	6427	515	5300	39
H(6B)	7537	-44	5665	39
H(7A)	6829	-463	6758	38
H(7B)	5839	-600	5847	38
H(8A)	5003	-50	6847	32
H(8B)	4795	494	6030	32
H(9)	3631	606	7336	21
H(10A)	3474	1814	8469	27
H(10B)	2622	1713	7501	27
H(11A)	1834	578	7858	36
H(11B)	1708	1242	8492	36
H(12A)	3388	782	9587	41
H(12B)	2451	101	9278	41
H(13A)	3506	-414	8434	37
H(13B)	4367	-335	9402	37
H(14A)	5296	121	8410	29
H(14B)	5215	783	9060	29
H(16)	4607	4867	6697	28
H(17)	5437	5706	5942	36
H(18)	7084	5339	5586	38
H(19)	7911	4133	5976	40
H(20)	7094	3287	6723	32
H(22)	2782	3204	7457	24
H(23)	1769	3842	8258	31

H(24)	2643	4876	9122	37
H(25)	4522	5283	9202	37
H(26)	5580	4623	8458	30
H(27A)	5768	2040	548	64
H(27B)	6230	2824	1032	64
H(27C)	6034	2884	1186	64
H(27D)	6010	2182	547	64
H(28A)	-192	2065	9811	59
H(28B)	-342	2966	9628	59
H(28C)	-194	2926	9795	59
H(28D)	-443	2037	9577	59

Table S6. Torsion angles [°].

P(1)-C(1)-C(2)-P(2)	40.89(19)
C(8)-C(3)-C(4)-C(5)	-53.1(3)
P(2)-C(3)-C(4)-C(5)	-178.78(17)
C(3)-C(4)-C(5)-C(6)	54.8(3)
C(4)-C(5)-C(6)-C(7)	-56.7(3)
C(5)-C(6)-C(7)-C(8)	57.8(3)
C(6)-C(7)-C(8)-C(3)	-55.5(3)
C(4)-C(3)-C(8)-C(7)	52.6(3)
P(2)-C(3)-C(8)-C(7)	176.73(17)
C(14)-C(9)-C(10)-C(11)	-54.4(3)
P(2)-C(9)-C(10)-C(11)	179.93(16)
C(9)-C(10)-C(11)-C(12)	55.5(3)
C(10)-C(11)-C(12)-C(13)	-57.3(3)
C(11)-C(12)-C(13)-C(14)	57.4(3)
C(12)-C(13)-C(14)-C(9)	-55.2(3)
C(10)-C(9)-C(14)-C(13)	53.9(3)
P(2)-C(9)-C(14)-C(13)	179.21(16)
C(20)-C(15)-C(16)-C(17)	-1.7(3)
P(1)-C(15)-C(16)-C(17)	-175.69(18)
C(15)-C(16)-C(17)-C(18)	0.7(4)
C(16)-C(17)-C(18)-C(19)	0.3(4)
C(17)-C(18)-C(19)-C(20)	-0.1(4)
C(18)-C(19)-C(20)-C(15)	-0.9(4)
C(16)-C(15)-C(20)-C(19)	1.8(4)
P(1)-C(15)-C(20)-C(19)	175.9(2)
C(26)-C(21)-C(22)-C(23)	-0.6(3)
P(1)-C(21)-C(22)-C(23)	175.96(17)
C(21)-C(22)-C(23)-C(24)	1.2(3)
C(22)-C(23)-C(24)-C(25)	-0.2(4)
C(23)-C(24)-C(25)-C(26)	-1.3(4)
C(24)-C(25)-C(26)-C(21)	1.9(4)
C(22)-C(21)-C(26)-C(25)	-0.9(3)
P(1)-C(21)-C(26)-C(25)	-177.45(18)
C(16)-C(15)-P(1)-C(21)	-26.9(2)
C(20)-C(15)-P(1)-C(21)	159.14(18)
C(16)-C(15)-P(1)-C(1)	-139.24(18)

C(20)-C(15)-P(1)-C(1)	46.8(2)
C(16)-C(15)-P(1)-Pd(1)	99.44(18)
C(20)-C(15)-P(1)-Pd(1)	-74.54(19)
C(22)-C(21)-P(1)-C(15)	134.87(18)
C(26)-C(21)-P(1)-C(15)	-48.6(2)
C(22)-C(21)-P(1)-C(1)	-112.31(19)
C(26)-C(21)-P(1)-C(1)	64.2(2)
C(22)-C(21)-P(1)-Pd(1)	8.0(2)
C(26)-C(21)-P(1)-Pd(1)	-175.47(16)
C(2)-C(1)-P(1)-C(15)	-157.86(15)
C(2)-C(1)-P(1)-C(21)	88.03(17)
C(2)-C(1)-P(1)-Pd(1)	-34.12(16)
C(10)-C(9)-P(2)-C(2)	71.76(17)
C(14)-C(9)-P(2)-C(2)	-54.10(18)
C(10)-C(9)-P(2)-C(3)	-175.10(15)
C(14)-C(9)-P(2)-C(3)	59.04(18)
C(10)-C(9)-P(2)-Pd(1)	-46.67(17)
C(14)-C(9)-P(2)-Pd(1)	-172.54(13)
C(1)-C(2)-P(2)-C(9)	-152.40(16)
C(1)-C(2)-P(2)-C(3)	93.69(17)
C(1)-C(2)-P(2)-Pd(1)	-30.92(17)
C(4)-C(3)-P(2)-C(9)	173.77(15)
C(8)-C(3)-P(2)-C(9)	48.84(19)
C(4)-C(3)-P(2)-C(2)	-73.85(17)
C(8)-C(3)-P(2)-C(2)	161.22(16)
C(4)-C(3)-P(2)-Pd(1)	46.55(18)
C(8)-C(3)-P(2)-Pd(1)	-78.38(17)
C(15)-P(1)-Pd(1)-P(2)	131.46(8)
C(21)-P(1)-Pd(1)-P(2)	-104.97(8)
C(1)-P(1)-Pd(1)-P(2)	12.49(8)
C(15)-P(1)-Pd(1)-Cl(2)	-51.05(8)
C(21)-P(1)-Pd(1)-Cl(2)	72.51(8)
C(1)-P(1)-Pd(1)-Cl(2)	-170.02(8)
C(9)-P(2)-Pd(1)-P(1)	123.99(8)
C(2)-P(2)-Pd(1)-P(1)	7.49(8)
C(3)-P(2)-Pd(1)-P(1)	-111.71(8)
C(9)-P(2)-Pd(1)-Cl(1)	-55.80(8)
C(2)-P(2)-Pd(1)-Cl(1)	-172.30(8)

C(3)-P(2)-Pd(1)-Cl(1)	68.50(8)

Symmetry transformations used to generate equivalent atoms:

Crystal data and structure refinement for *cis*,*cis*-1,2,3,4-tetraphenyl-1,3-butadiene.

Empirical formula	C40 H36	
Formula weight	516.69	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 5.7583(6) Å	α= 90°.
	b = 21.214(2) Å	β= 96.165(2)°.
	c = 7.8566(8) Å	γ = 90°.
Volume	954.20(17) $Å^3$	
Z	1	
Density (calculated)	0.899 Mg/m^3	
Absorption coefficient	0.051 mm^{-1}	
F(000)	276	
Crystal size	0.26 x 0.11 x 0.04 mm^3	
Theta range for data collection	1.92 to 30.01°.	
Index ranges	-7<=h<=7, -29<=k<=29, -11<=l<=11	
Reflections collected	10569	
Independent reflections	2728 [R(int) = 0.0317]	
Completeness to theta = 30.01°	98.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2728 / 0 / 127	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1145	
R indices (all data)	R1 = 0.0652, wR2 = 0.1243	
Largest diff. peak and hole	0.486 and -0.208 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5365(2)	4083(1)	-196(1)	14(1)
C(6)	7027(2)	3793(1)	-1097(2)	17(1)
C(8)	7425(2)	4884(1)	1708(2)	15(1)
C(7)	5735(2)	4747(1)	428(2)	14(1)
C(2)	3414(2)	3735(1)	161(2)	17(1)
C(14)	11179(2)	4673(1)	3442(2)	17(1)
C(11)	9858(2)	3470(1)	4280(2)	22(1)
C(3)	3180(2)	3107(1)	-327(2)	20(1)
C(9)	8983(2)	4451(1)	2762(1)	15(1)
C(5)	6769(2)	3166(1)	-1605(2)	20(1)
C(13)	12705(2)	4297(1)	4484(2)	19(1)
C(4)	4857(2)	2820(1)	-1214(2)	21(1)
C(10)	8345(2)	3841(1)	3209(2)	18(1)
C(12)	12050(2)	3694(1)	4915(2)	21(1)

Table S3. Bond lengths [Å] and angles [°].

C(1)-C(6)	1.3935(16)
C(1)-C(2)	1.3979(16)
C(1)-C(7)	1.4987(15)
C(6)-C(5)	1.3913(16)
C(8)-C(7)	1.3534(15)
C(8)-C(9)	1.4748(15)
C(7)-C(7)#1	1.483(2)
C(2)-C(3)	1.3898(16)
C(14)-C(13)	1.3883(16)
C(14)-C(9)	1.4010(16)
C(11)-C(10)	1.3878(16)
C(11)-C(12)	1.3902(17)
C(3)-C(4)	1.3897(18)
C(9)-C(10)	1.4001(16)
C(5)-C(4)	1.3845(18)
C(13)-C(12)	1.3848(18)

C(6)-C(1)-C(2)	118.64(10)
C(6)-C(1)-C(7)	120.01(10)
C(2)-C(1)-C(7)	121.30(10)
C(5)-C(6)-C(1)	120.65(11)
C(7)-C(8)-C(9)	128.99(10)
C(8)-C(7)-C(7)#1	120.76(12)
C(8)-C(7)-C(1)	120.68(10)
C(7)#1-C(7)-C(1)	118.52(12)
C(3)-C(2)-C(1)	120.48(11)
C(13)-C(14)-C(9)	121.27(11)
C(10)-C(11)-C(12)	120.74(11)
C(4)-C(3)-C(2)	120.39(11)
C(10)-C(9)-C(14)	117.80(10)
C(10)-C(9)-C(8)	123.81(10)
C(14)-C(9)-C(8)	118.27(10)
C(4)-C(5)-C(6)	120.38(11)
C(12)-C(13)-C(14)	120.24(11)
C(5)-C(4)-C(3)	119.43(11)
C(11)-C(10)-C(9)	120.70(11)

C(13)-C(12)-C(11)	119.21(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	12(1)	15(1)	1(1)	-2(1)	1(1)
C(6)	16(1)	16(1)	18(1)	2(1)	0(1)	1(1)
C(8)	15(1)	12(1)	17(1)	0(1)	-1(1)	1(1)
C(7)	12(1)	12(1)	16(1)	0(1)	1(1)	1(1)
C(2)	15(1)	16(1)	19(1)	-1(1)	0(1)	0(1)
C(14)	17(1)	17(1)	17(1)	0(1)	-1(1)	0(1)
C(11)	24(1)	16(1)	23(1)	4(1)	-2(1)	1(1)
C(3)	19(1)	17(1)	23(1)	1(1)	-3(1)	-4(1)
C(9)	15(1)	15(1)	14(1)	-1(1)	0(1)	2(1)
C(5)	23(1)	18(1)	20(1)	-2(1)	1(1)	6(1)
C(13)	15(1)	24(1)	18(1)	-3(1)	-2(1)	2(1)
C(4)	28(1)	13(1)	22(1)	-2(1)	-5(1)	2(1)
C(10)	16(1)	17(1)	20(1)	1(1)	-2(1)	0(1)
C(12)	21(1)	21(1)	19(1)	1(1)	-4(1)	6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(6)	8350	4025	-1366	20
H(8)	7637	5319	1962	18
H(2)	2239	3929	743	20
H(14)	11632	5090	3185	20
H(11)	9391	3059	4582	26
H(3)	1867	2871	-53	24
H(5)	7910	2975	-2225	24
H(13)	14205	4453	4902	23
H(4)	4694	2391	-1549	26
H(10)	6861	3678	2775	22
H(12)	13086	3437	5637	25

Table S6. Torsion angles [°].

C(2)-C(1)-C(6)-C(5)	-1.00(17)
C(7)-C(1)-C(6)-C(5)	176.55(11)
C(9)-C(8)-C(7)-C(7)#1	176.97(13)
C(9)-C(8)-C(7)-C(1)	-5.23(19)
C(6)-C(1)-C(7)-C(8)	-69.42(15)
C(2)-C(1)-C(7)-C(8)	108.06(13)
C(6)-C(1)-C(7)-C(7)#1	108.42(15)
C(2)-C(1)-C(7)-C(7)#1	-74.10(17)
C(6)-C(1)-C(2)-C(3)	1.94(17)
C(7)-C(1)-C(2)-C(3)	-175.57(11)
C(1)-C(2)-C(3)-C(4)	-1.52(18)
C(13)-C(14)-C(9)-C(10)	1.86(18)
C(13)-C(14)-C(9)-C(8)	178.20(11)
C(7)-C(8)-C(9)-C(10)	-31.8(2)
C(7)-C(8)-C(9)-C(14)	152.10(12)
C(1)-C(6)-C(5)-C(4)	-0.38(18)
C(9)-C(14)-C(13)-C(12)	-1.93(19)
C(6)-C(5)-C(4)-C(3)	0.83(18)
C(2)-C(3)-C(4)-C(5)	0.12(18)
C(12)-C(11)-C(10)-C(9)	-0.8(2)
C(14)-C(9)-C(10)-C(11)	-0.51(18)
C(8)-C(9)-C(10)-C(11)	-176.63(12)
C(14)-C(13)-C(12)-C(11)	0.61(19)
C(10)-C(11)-C(12)-C(13)	0.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z