Selective Reduction of a Pd Pincer PCP Complex to Well-Defined Pd(0) Species

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General procedures.

All procedures and chemical manipulations were carried out under Ar or N_2 using Schlenk or glove box techniques. Solvents were rigorously dried and degassed before use. All the commercial available reagents were used as received. NMR spectra were recorded on Bruker DRX 300 and 400 MHz spectrometers. Assignment of signals was assisted by combined monodimiensional (gated ^{13}C) and bidimensional techniques (HSQC). The ^{1}H and $^{13}C\{^{1}H\}$ resonances of the solvent were used as the internal standard but the chemical shifts are reported with respect to TMS, while ^{31}P spectra are referenced to external PPh_3 in C_6D_6 at δ −6.0 ppm. Multiplicity abbreviation is reported as: br, broad; s, singlet, d, doublet; t, triplet; m, mutiplet; v, virtual. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). (^{iPr}PCP)Pd-OH was prepared as reported previously.[1]

Synthesis and Characterization of compounds 1 and 1'

Synthesis of compound 1. (^{iPr}PCP)Pd-OH (60 mg, 0.13 mmol) was dissolved in methanol (10 mL) and allowed to stand for 48 hours at room temperature. **1** was obtained as light-green crystalline solid after decanting the methanolic solution. Yield: 70 %. Alternatively, **1** can be prepared warming up a solution of (^{iPr}PCP)Pd-OH at 50ºC for 2 hours. ^{13}C spectra was recorded in THF-d_8 since $C_{ar}H$ resonances for **1** are hidden by C_6D_6 resonances. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 9.82 (br s, 1H, ^{iPr}PC*H*P), 7.06 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, $C_{ar}H_p$), 6.90 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, $C_{ar}H_m$), 3.00 (vt, J^{*}_{HP} = 2.3 Hz, 4H, $C_{ar}CH_2$), 1.75 (m, 4H, 4 C*H*), 1.21 (dvt, $^{3}J_{HH}$ = 6.8 Hz, J^{*}_{HP} = 6.8 Hz, 12H, CH_3), 1.18 (dvt, $^{3}J_{HH}$ = 7.0 Hz, J^{*}_{HP} = 7.0 Hz, 12H, CH_3). $^{13}C\{^{1}H\}$ NMR (THF-d_8, 75 MHz, 298 K): δ 138.71 (C_{ar}), 135.20 (vt, J^{*}_{CP} = 5.0 Hz, ^{iPr}P*C*HP), 128.03 ($C_{ar}H_m$), 127.63 ($C_{ar}H_p$), 32.19 ($C_{ar}CH_2$), 26.44 (vt, J^{*}_{CP} = 6.1 Hz Hz, *C*H), 20.79 (vt, J^{*}_{CP} = 4.5 Hz,CH_3) 20.62 (CH_3). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 121 MHz, 298 K): δ 38.94. $^{13}P\{^{1}H\}$ NMR (C_6D_6, 121 MHz, 298 K): δ 41.07. Anal calcd for $C_{40}H_{72}P_4Pd_2$: C, 54.00; H, 8.16; found: C, 53.92; H, 7.84.

Synthesis of compound 1'. (^{iPr}PCP)Pd-OH (75 mg, 0.16 mmol) was dissolved in isopropanol (5mL) and the mixture was heated for seven days at 50 ºC. **1'** was obtained as off yellow crystalline solid after decanting the solution. 45 mg, 53 % yield. Anal calcd for $C_{20}H_{36}P_2Pd$: C, 54.00; H, 8.16; found: C, 53.48; H, 7.98.

Synthesis and characterization of intermediate complexes.

Syntehsis of (^{iPr}PCP)Pd-OCH_3. A solution of (^{iPr}PCP)Pd-Cl (1.59 g, 3.3 mmol)[2] in THF (60 mL) was transferred to a flask charged with $NaNH_2$ (1.29 g, 33.2 mmol), and the resulting suspension was sonicated for 2 h. The initially colorless solution turned red. The excess of $NaNH_2$ was eliminated by centrifugation, and methanol (0.20 mL, 5.0 mmol) was added at room temperature. After 10 min of stirring, the solvent was evaporated under reduced pressure, and the residue extracted with hexane (20 mL). The solution was layered with hexamethyldisiloxane (ca. 2 mL). The complex (PCP)PdOCH$_3$ was obtained as a yellow crystalline solid after cooling to −30 ºC, and its crystal structure has been determined (see below). Yield: 58%. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ 7.06 (t, $^3J_{HH}$ = 7. 4 Hz, 1H, C$_{ar}$*H*$_p$), 6.97 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C$_{ar}$*H*$_m$), 4.44 (s, 3H, OC*H*$_3$), 2.76 (vt, J^*_{HP} = 4.1 Hz, 4H, C*H*$_2$), 2.02-1.95 (m, 4H, C*H*), 1.35 (dvt, $^3J_{HH}$ = 7.9 Hz, J^*_{HP} = 7.9 Hz, 12H, C*H*$_3$), 0.91 (dvt, $^3J_{HH}$ = 7.0 Hz, J^*_{HP} = 7.0 Hz, 12H, C*H*$_3$).^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 283 K): δ 159.29 (s, C$_{ar–i}$), 150.90 (vt, J^*_{CP} = 10.8 Hz, C$_{ar–o}$), 124.55 (*C*$_{ar}$H$_p$), 122.55 (vt, J^*_{CP} = 10.1 Hz, C$_{ar}$H$_m$), 62.43 (O*C*H$_3$) 33.22 (vt, J^*_{CP} = 11.5 Hz, *C*H$_2$), 24.33 (vt, J^*_{CP} = 10.5 Hz, *C*H), 18.89 (vt, J^*_{CP} = 3.3 Hz, C*H*$_3$) 18.4 (s, 4 C*H*$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 298 K): δ 56.13. IR (nujol mull). ν$_{max}$ (cm^{-1}): 1078 (ν C-O), 434 (ν Pd-O). X-ray diffraction analysis confirmed the proposed structure (see Figure **S3**).

Synthesis of (^{iPr}PCP)Pd-O^{i}Pr. A solution of (^{iPr}PCP)Pd-Cl (0.96 g, 0.2 mmol)[2] in THF (5 mL) was transferred to a flask charged with NaNH$_2$ (0.78 g, 2.0 mmol), and the resulting suspension was sonicated for 2 h. The excess of NaNH$_2$ was eliminated by centrifugation. Isopropanol (23 µL, 0.3 mmol) was added at room temperature. Due to its extreme hydrolytic sensitivity this product could not be isolated in pure state. The ^{31}P{^{1}H} NMR spectrum of the THF solution displayed a singlet at δ 54.90 ppm, which shifted to δ 55.63 ppm when the solution was taken to dryness and re-dissolved in neat isopropanol.

Synthesis of (^{iPr}PCP)Pd-H. A solution of (^{iPr}PCP)Pd-OMe in THF (20 mL) was directly generated from (^{iPr}PCP)Pd-Cl (479 mg, 1 mmol) NaNH$_2$ (390 mg, 10 mmol), and methanol (0.20 mL, 5.0 mmol) as described above. The THF solvent was eliminated under reduced pressure and replaced with a similar amount of hexane. The hexane solution was cooled to 0 ºC, and HSi(OEt)$_3$ (0.9 mL, 5 mmol) was then added. After 5 min stirring at room temperature, the solvent and the volatiles residues were removed under reduce pressure, leaving the title compound as a pure yellow solid. Yield: 90%. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 7. 28 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C$_{ar}$*H*), 7.23 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C$_{ar}$*H*), 3.24 (vt, J^*_{HP} = 4.1 Hz, 4H, C*H*$_2$), 1.93-1.82 (m, 4H, C*H*), 1.17 (dvt, $^3J_{HH}$ = 7.8 Hz, J^*_{HP} = 7.8 Hz, 12H, C*H*$_3$), 0.91 (dvt, $^3J_{HH}$ = 7.2 Hz, J^*_{HP} = 7.2 Hz, 12H, C*H*$_3$), −3.77 (t, 1H, $^2J_{HP}$ = 17.0 Hz, Pd−H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz, 298 K): δ 179.7 (t, $^2J_{CP}$ = 3.8 Hz, C$_{ar–i}$), 150.3 (vt, J^*_{CP} = 10.7 Hz, C$_{ar–o}$), 125.0 (C$_{ar}$H$_p$), 121.4 (tv, J^*_{CP} = 9.6 Hz, C$_{ar}$H$_m$), 39.8 (tv, J^*_{CP} = 11.7 Hz, *C*H$_2$), 25.3 (vt, J^*_{CP} = 11.6 Hz, *C*H), 20.1 (vt, J^*_{CP} = 3.4 Hz, *C*H$_3$) 18.7 (*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 125 MHz): = δ 71.7; IR (Nujol mull) $\overline{\nu}$= 1721 and 1763 cm^{-1} (ν Pd-H); IR (C$_6$D$_6$ solution) ν$_{max}$ (cm^{-1}): 1721 (Pd-H); Anal calcd for C$_{20}$H$_{36}$P$_2$Pd: C, 54.00; H, 8.16; found: C, 53.49; H, 8.24.

DFT Modelization of the structure of palladium of monomer, dimer and trimer Pd(0) complexes 1”, 1and 1’.

All DFT calculations were carried out with with the B3LYP functional using the Spartan 08 package,[3] using the “BIGGRID” keyword to increase the accuracy of the density grid. The Pd atom was described with the LACVP* effective core potential and basis set, and the 6-31G* basis set was used for all lighter atoms. Optimized structures were subjected to vibrational frequency calculations to ensure the absence of imaginary frequencies.

Guess initial structures for the dimer and polymer complexes were obtained replacing the isopropyl by methyl grops in the crystal structures of **1** and **1’** (Figure S1). A model for the monomer (**1”**) was built from scratch and fully optimized. The polymer model consisted in four palladium atoms bridged by three PCHP ligand units and the two terminal fragments were capped with PMe_3 ligands. The structures were then subjected to full geometry optimization without restrictions. The structure minimization did not alter the general configuration of the molecules and only causes minor changes in bond lengths and atoms. In order to determine the energy of the monomer unit in the polymer, the main polymer section was subdivided in Fragments 1 – 3, and their energies were computed individually by single-point calculations. Table S1 collects the final energy values and relevant metric parameters for the optimized molecules and fragments. As can be seen, the geometry optimization preserves the overall shape of the dimer and polymer molecules is largely preserved after only introduces minor changes in the bond lengths and angles. Atomic coordinates for molecules **A**, **B** and **C** are collected on tables S2 – S4.

The repeating monomeric unit can be considered to correspond to a fragment containing one PCHP ligand and one palladium atom, plus the contribution corresponding to an additional Pd-P bond. This energy was calculated as the difference between those of Fragment 2 and Fragment 1. In turn, the difference between the energy of the monomeric unit and Fragment 2 provides the energy of the Pd-P bond interaction in the polymer.

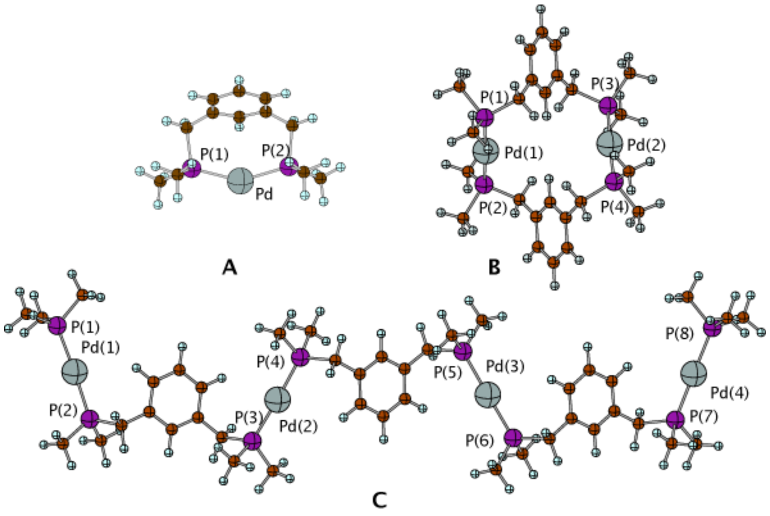
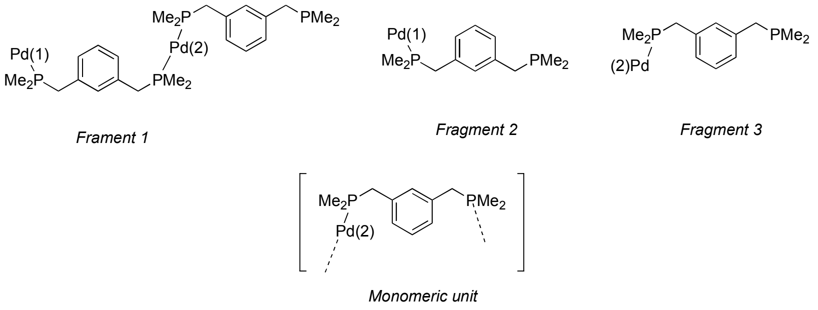


Figure S1. Optimized model structures for compound **1”** (**A**, monomer), **1** (**B**, dimer) and **1’** (**C**, polymer). In the latter, the palladium end groups have been terminated wit PMe_3 ligands.



Frament 1 Fragment 2 Fragment 3

Monomeric unit

Figure S2. Partition of the polymer model **C** in fragments 1, 2 and 3 used to calculate the energy for monomeric unit.

Table S1 Energies and selected metric parameters for the model structures.

Molecule	d(Pd-P) (Å)	P-Pd-P (º)	d(Pd-Pd) (Å)	Energy (Kcal/mol)	Rel. Energy /Pd atom (Kcal/mol)
Monomer (**A**)	Pd-P1, 2,352	146.4		-802489,71	+13.8
	Pd-P2, 2,351				
	Ave. 2.352				
Dimer (**B**)	Pd1-P1, 2.321	176.7	5.742	-1605007,05	0.00
	Pd1-P2, 2.319				
	Ave. 2.320				
Polymer (**C**)	Pd1-P1, 2.315	P1-Pd1-P2, 177.0	Pd1-Pd2, 9.58	-12827230.90	
	Pd1-P2, 2.317	P3-Pd2-P4, 178.9	Pd2-Pd3, 9.74		
	Pd2-P3, 2.317	*Ave. 178.0*			
	Pd2-P4, 3.317				
	Ave. 2.316				
Fragment 1				-1604973,86	
Fragment 2				-802470,44	
Fragment 3				-802470,43	
Monomer Unit (Frg.1- Frg. 2)				-802503,42	+0.11

Table S2. Atomic coordinates for molecular model **A** (monomer)

	x	*y*	*z*		*x*	*y*	*z*
H	-0.196447	0.000588	1.880938	Pd	-1.735100	0.000528	-0.277621
C	0.742315	0.000041	1.333706	C	-2.115257	-3.706165	0.367172
C	3.132564	-0.001332	-0.052369	H	-2.939441	-3.826529	-0.343658
C	1.285013	-1.224503	0.931783	H	-2.548613	-3.513325	1.353825
C	1.285746	1.223875	0.930575	H	-1.541718	-4.640510	0.404871
C	2.507878	1.213780	0.247569	C	-0.322781	-2.917395	-1.714881
C	2.507171	-1.215779	0.248776	H	-1.083866	-2.937625	-2.501153

H	2.961455	2.150295	-0.070118	H	0.080875	-3.928754	-1.581139
H	2.960215	-2.152880	-0.067983	H	0.481188	-2.250063	-2.038939
H	4.089159	-0.001873	-0.568743	C	-0.324377	2.919947	-1.715773
C	0.397673	-2.438491	1.048567	H	-1.086408	2.940990	-2.501263
H	-0.035104	-2.521246	2.053358	H	0.479570	2.253628	-2.041843
H	0.929886	-3.373383	0.834822	H	0.078836	3.931326	-1.580800
C	0.399215	2.438538	1.046529	C	-2.115012	3.704949	0.368749
H	0.931965	3.372917	0.831680	H	-2.939805	3.825782	-0.341319
H	-0.033030	2.522559	2.051506	H	-1.541959	4.639494	0.407375
P	-1.071859	2.252322	-0.150280	H	-2.547540	3.510497	1.355371
P	-1.072407	-2.252203	-0.149289				

Table S3. Atomic coordinates for molecular model **B** (dimer)

	x	*y*	*z*		*x*	*y*	*z*
C	0.368607	3.277276	1.084452	H	3.993618	0.744797	-3.973119
C	-0.369305	-3.277925	1.085624	H	-2.847123	2.977495	4.051351
C	0.806779	4.608556	1.068968	H	2.847464	-2.976200	4.051789
C	-0.807199	-4.609326	1.069218	H	-2.340377	4.607218	0.459246
C	-0.520719	2.768969	2.194406	H	2.340185	-4.606779	0.460371
C	0.519922	-2.770152	2.195918	H	-0.512200	3.467399	3.041165
C	1.621828	5.072787	0.036595	H	0.512196	-3.469487	3.042020
C	-1.621779	-5.073089	0.036240	H	-0.159645	1.801206	2.562754
C	2.006906	4.214733	-0.993394	H	0.158318	-1.802927	2.565404
C	-2.006544	-4.214486	-0.993476	H	-2.392404	-2.506439	-2.961808
C	-1.578346	-2.879912	-1.002262	H	2.394710	2.507445	-2.961911
C	1.578485	2.880284	-1.003098	H	-1.130479	-1.368759	-2.469695
C	-0.763317	-2.428325	0.043652	H	1.131562	1.370197	-2.471977
C	0.762815	2.428278	0.042142	P	-3.278270	-0.666846	-1.589392
C	-1.993867	-1.940839	-2.109618	P	3.277853	0.666665	-1.588992
C	1.994808	1.941621	-2.110511	P	-2.306617	2.484574	1.671862
C	-4.747751	-1.754895	-1.269921	P	2.305315	-2.483998	1.672548
C	4.747823	1.753740	-1.267975	Pd	-2.732280	0.887378	0.043347
C	-3.718536	0.035038	-3.253444	Pd	2.729028	-0.886451	0.043516
C	3.719295	-0.035791	-3.252627	H	-2.718906	1.224976	3.733471
C	-3.077856	2.179171	3.334997	H	-4.163619	2.105358	3.218900
C	3.077130	-2.177759	3.335186	H	-3.936524	4.220030	1.124044
C	-2.863647	4.222983	1.339201	H	-2.670174	4.887921	2.190063
C	2.863987	-4.221834	1.339557	H	-4.965238	-2.412761	-2.120633
H	0.513372	5.281042	1.871981	H	-4.559307	-2.367387	-0.383948
H	-0.513879	-5.282307	1.871919	H	-4.559432	0.726148	-3.139761
H	1.957849	6.106560	0.034697	H	-2.869510	0.603776	-3.645478
H	-1.957567	-6.106973	0.033595	H	2.672233	-4.886741	2.190753
H	2.638593	4.583143	-1.798669	H	3.936599	-4.217834	1.123147
H	-2.637719	-4.582598	-1.799295	H	4.162789	-2.103050	3.218437
H	-0.427197	-1.394671	0.044935	H	2.717537	-1.223791	3.733728
H	0.426594	1.394690	0.042754	H	4.558164	2.367357	-0.382752
H	-5.620946	-1.126487	-1.070791	H	4.967241	2.410556	-2.119100
H	5.620424	1.124817	-1.066582	H	4.559694	-0.727447	-3.138029
H	-3.991649	-0.745874	-3.974019	H	2.870204	-0.604042	-3.645397

Table S4. Fractional coordinates for molecular model **C** (polymer).

	x	*y*	*z*		*x*	*y*	*z*
C	9.777236	-1.991706	-0.041100	H	14.067976	-3.684433	-1.917811
C	-0.055197	1.357100	0.853690	H	14.603294	5.100376	-0.341834
C	-9.775224	-1.991601	-0.284791	H	-5.734813	-4.758273	-1.074025
C	8.728444	-1.489864	0.741029	H	-4.227528	3.348883	2.630268
C	0.997564	0.805841	0.111478	H	16.319891	4.179872	1.505120
C	-10.811210	-1.186440	0.207417	H	11.645143	-2.790352	-1.692416
C	8.629653	-0.102783	0.916109	H	-1.912248	2.200396	2.522014
C	1.023238	-0.582052	-0.081944	H	-7.843636	-3.346793	-1.461876
C	-10.619483	0.201781	0.241475	H	15.152637	3.041241	2.232686
C	9.558970	0.747747	0.317770	H	11.893479	-1.215791	-2.456014
C	0.012957	-1.383847	0.449525	H	-2.434364	0.601627	3.069494
C	-9.420913	0.756206	-0.206778	H	-7.001493	-1.945821	-2.136823

C	10.594975	0.234215	-0.462307	H	8.090912	-3.456584	1.349952
C	-1.031305	-0.819719	1.182742	H	1.746320	2.737894	-0.472579
C	-8.397118	-0.058571	-0.689622	H	-11.982098	-2.886609	0.827525
C	10.717136	-1.149695	-0.650399	H	-16.807737	4.371122	-0.321813
C	-1.074190	0.564543	1.397667	H	7.530819	-2.154713	2.407120
C	-8.563093	-1.449447	-0.732945	H	2.324312	1.404343	-1.479319
C	7.716649	-2.424645	1.360428	H	-12.399869	-1.378577	1.651099
C	2.082977	1.693153	-0.449400	H	-17.333383	2.667551	-0.234711
C	-12.104599	-1.804767	0.684435	P	3.706840	1.611394	0.502190
C	-16.485687	3.346183	-0.097662	P	6.035250	-2.391467	0.511858
C	4.592484	3.050291	-0.275535	P	-15.081845	2.798879	-1.184409
C	5.234488	-3.848985	1.344685	P	-13.565212	-1.517067	-0.468809
C	-15.778929	3.170371	-2.865401	P	13.544631	-1.564590	-0.719991
C	-14.813310	-2.654654	0.307740	P	15.256873	2.705670	-0.191180
C	3.202490	2.342577	2.131712	P	-6.040985	-2.539315	0.010101
C	6.458277	-3.115232	-1.144352	P	-3.813876	1.334737	1.222233
C	-13.903184	4.220186	-0.977471	Pd	4.855536	-0.398608	0.522080
C	-13.050524	-2.514770	-1.947082	Pd	-14.267057	0.660631	-0.832842
C	15.937844	3.151758	1.478415	Pd	14.390437	0.574094	-0.436021
C	11.833670	-1.728359	-1.487998	Pd	-4.877858	-0.621250	0.588679
C	-2.199760	1.197884	2.179772	H	-16.176918	3.289292	0.950778
C	-7.452833	-2.349155	-1.222504	H	16.748209	2.462176	1.735275
C	16.680666	3.177331	-1.286822	H	-14.389295	5.186655	-1.160071
C	13.371713	-2.638115	0.785090	H	-13.494864	4.212108	0.038067
C	-3.349002	2.546621	-0.106749	H	-16.597293	2.475567	-3.078438
C	-6.885854	-3.467619	1.378686	H	-15.004476	3.017882	-3.623536
C	14.507417	-2.681393	-1.851237	H	-12.806988	-3.550504	-1.679373
C	14.105138	4.133591	-0.487104	H	-12.174327	-2.050183	-2.408397
C	-5.089830	-3.911699	-0.808382	H	-15.126217	-2.245993	1.273564
C	-4.773922	2.431552	2.376808	H	-15.697191	-2.708852	-0.335261
H	9.861328	-3.068188	-0.183303	H	-4.304663	-4.262611	-0.131090
H	-0.082417	2.434049	1.012327	H	-7.382899	-4.377598	1.019606
H	-9.914071	-3.071323	-0.314483	H	-4.605517	-3.532272	-1.713536
H	7.814311	0.304947	1.508493	H	-6.144934	-3.740912	2.136424
H	1.843202	-1.029196	-0.638385	H	-5.726332	2.701086	1.909861
H	-11.414360	0.844682	0.610901	H	-4.998230	1.884518	3.297894
H	9.473937	1.822395	0.458969	H	-4.242966	2.807369	-0.681768
H	0.039850	-2.459001	0.290797	H	-2.908486	3.464720	0.302580
H	-9.282565	1.834137	-0.176728	H	4.267384	-4.049557	0.873279
H	11.321056	0.902717	-0.918222	H	5.050425	-3.610134	2.396874
H	-1.825634	-1.446654	1.580256	H	7.100065	-2.415485	-1.687180
H	-7.457437	0.378527	-1.016778	H	6.973728	-4.079868	-1.056829
H	3.985679	3.964241	-0.263905	H	2.730855	3.326166	2.015443
H	5.855766	-4.751278	1.285434	H	2.500036	1.665228	2.625499
H	-16.153784	4.199011	-2.936740	H	5.527440	3.236433	0.262014
H	-14.417821	-3.667012	0.457292	H	4.846333	2.803543	-1.311214
H	4.085731	2.442824	2.769820	H	14.542565	-2.238182	-2.851387
H	5.539133	-3.252993	-1.721995	H	15.535361	-2.764511	-1.485327
H	-13.068435	4.102189	-1.675573	H	13.000293	-3.640363	0.538178
H	-13.862886	-2.515429	-2.680116	H	14.345525	-2.728143	1.275883
H	17.514521	2.489961	-1.113412	H	13.716241	4.082448	-1.509057
H	12.679124	-2.163138	1.485643	H	13.254961	4.064146	0.198958
H	-2.630213	2.079619	-0.785547	H	16.378998	3.080800	-2.334398
H	-7.629813	-2.817115	1.847043	H	17.019801	4.204779	-1.104135

Crystal structures of compounds 1, 1’ and (^{iPr}PCP)Pd-OMe.

The main parameters for the title structures are collected in Table S5. An ORTEP view of the crystal structure of (iPrPCP)Pd-OMe is shown in Figure S3. The latter contains two crystallographically different molecules, both of them showing a disordered methoxy ligand.

Crystals coated with dry perfluoropolyether were mounted on a glass fiber and fixed in a cold nitrogen stream and the Intensity data were collected on a Bruker-Nonius X8kappa APEX II

CCD area detector diffractometer equipped with a Mo $K_{\alpha 1}$ radiation (λ = 0.71073 Å) source and graphite monochromator. The data were reduced (SAINT, Bruker Apex 2 software package)[4] and corrected for Lorentz polarisation and absorption effects by multi-scan method (SADABS, Bruker Apex 2 software package).[5] The structures were solved by direct methods (Bruker Apex 2 software package)[6] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.14)[7] minimizing $w[Fo^2-Fc^2]^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached carbon atoms with the isotropic temperature factors (*U*iso values) fixed at 1.2 times (1.5 times for methyl groups) those *U*eq values of the corresponding carbon atoms. CCDC-774541 CCDC-774542, and CCDC-774543 contain the supplementary crystallographic data for compounds **1**, **1'** and **(^{iPr}PCP)Pd-OCH$_3$**, contained in this paper. The crystal structure of the latter compound is represented in Figure S3.These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Crystal and Refinement Data for 1, 1' and (^{iPr}PCP)Pd-OCH$_3$

Compound	**1**	**1'**	**(^{iPr}PCP)Pd-OCH$_3$**
Formula	$C_{40}H_{72}P_4Pd_2$	$C_{20}H_{36}P_2Pd$	$C_{21}H_{38}OP_2Pd$
Fw	889.66	444.83	474.85
Temperature	173(2)	298(2)	173(2)
Crystal size (mm)	0.42 x 0.34 x 0.21	0.21 x 0.21 x 0.14	0.52 x 0.41 x 0.34
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/c	$P2_1/c$	$P2_1/n$
a, Å	27.2916(11)	12.984(4)	11.3085(8)
b, Å	11.1607(4)	11.268(3)	14.3116(10)
c, Å	16.0500(7)	15.661(5)	28.797(2)
α, deg	90	90	90
β, deg	114.9890(10)	99.864(8)	98.271(2)
γ, deg	90	90	90
V, $Å^3$	4431.1(3)	2257.3(13)	4612.1(6)
Z	4	4	8
D_{calc}, Mg/m^3	1.334	1.309	1.368
μ (mm^{-1})	0.981	0.963	0.950
θ range, deg	2.00 - 30.55	1.59 - 27.62	1.86 - 30.65
n° reflections collected	26363	31164	60067
n° reflections used	6703	5154	13900
R_{int}	0.0298	0.0567	0.0456
n° of parameters	216	211	487
R_1 [I > 2σ(I)]	0.0289	0.0639	0.0745
wR2 (all data)	0.0714	0.2374	0.1741

GOF	1.015	1.090	1.187

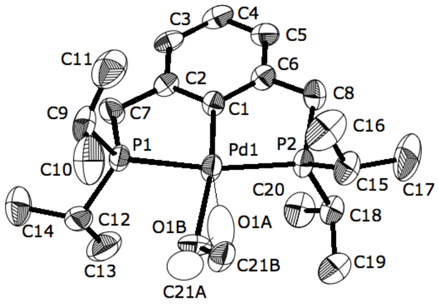


Figure S3. ORTEP view of (^{iPr}PCP)Pd-OMe (one of two molecules in the unit cell). The methoxide group is disordered in both molecules, occupying two alternative positions. White ellipsoids represent one of the two positions of the disordered methoxide. Selected bond distances (Å) and angles (°): Pd-O1A, 2.088(9); Pd1-O1B, 2.074(15); Pd-P1, 2.2829(16); Pd-P2, 2.660(16); Pd-C1, 2.020(5); O1A-C21A, 1.297(16); O1B-C21B, 1.289(17); C1-Pd-O1A 170.1((3); C1-Pd-O1B, 160.8(5); Pd1-O1A-C21A, 125.8(9); Pd1-O1B-C21B, 113.9(8). Angles between mean coordination plane (defined by Pd, P1, P2 and C1) and methoxide unit A (Pd-O1A-C21A), 23.82°; methoxide unit B (Pd-O1B-C21B), 48.29°.

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