

Pd(I) phosphine carbonyl and hydride complexes implicated in the palladium-catalyzed oxo process

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SUPPORTING INFORMATION

Tabled S1. Hydrogen bond parameters (Å, °) for complex $[\text{Pd}(\text{bcope})(\text{H}_2\text{O})_2]^{2+}$.

Figure S1. Packing diagram of compound $[\text{Pd}(\text{bcope})(\text{H}_2\text{O})_2](\text{OTf})_2 \cdot \text{H}_2\text{O}$ showing the one-dimensional H-bonding networking along the b axis.

Table S2. Absolute Energies and Cartesian Coordinates of the Optimized Structures.

Tabled S1. Hydrogen bonding distances (Å) and angles (°) for complex
[Pd(bcope)(H₂O)₂]²⁺.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(10)#1	0.823(10)	1.859(11)	2.681(5)	177(4)
O(1)-H(1B)...O(33)#2	0.826(10)	1.97(2)	2.753(5)	159(5)
O(2)-H(2A)...O(42)#1	0.821(10)	1.786(12)	2.602(5)	173(5)
O(2)-H(2B)...O(31)#2	0.815(10)	2.001(19)	2.782(5)	161(4)
O(2)-H(2B)...O(12)	0.815(10)	2.56(4)	3.013(5)	117(3)
O(3)-H(3A)...O(21)#3	0.822(10)	1.817(11)	2.637(5)	176(5)
O(3)-H(3B)...O(12)#4	0.820(10)	2.003(18)	2.790(4)	161(4)
O(3)-H(3B)...O(31)	0.820(10)	2.56(4)	2.986(4)	114(3)
O(4)-H(4A)...O(10)	0.828(10)	1.840(13)	2.662(5)	171(5)
O(4)-H(4B)...O(11)#4	0.825(10)	1.955(18)	2.756(5)	164(5)
O(10)-H(10A)...O(43)	0.86	2.52	2.989(7)	114.9
O(10)-H(10B)...O(1)#3	0.86	2.20	2.682(5)	115.6

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z-1/2 #2 x,-y+1,z-1/2 #3 x,-y,z+1/2

#4 x,-y+1,z+1/2

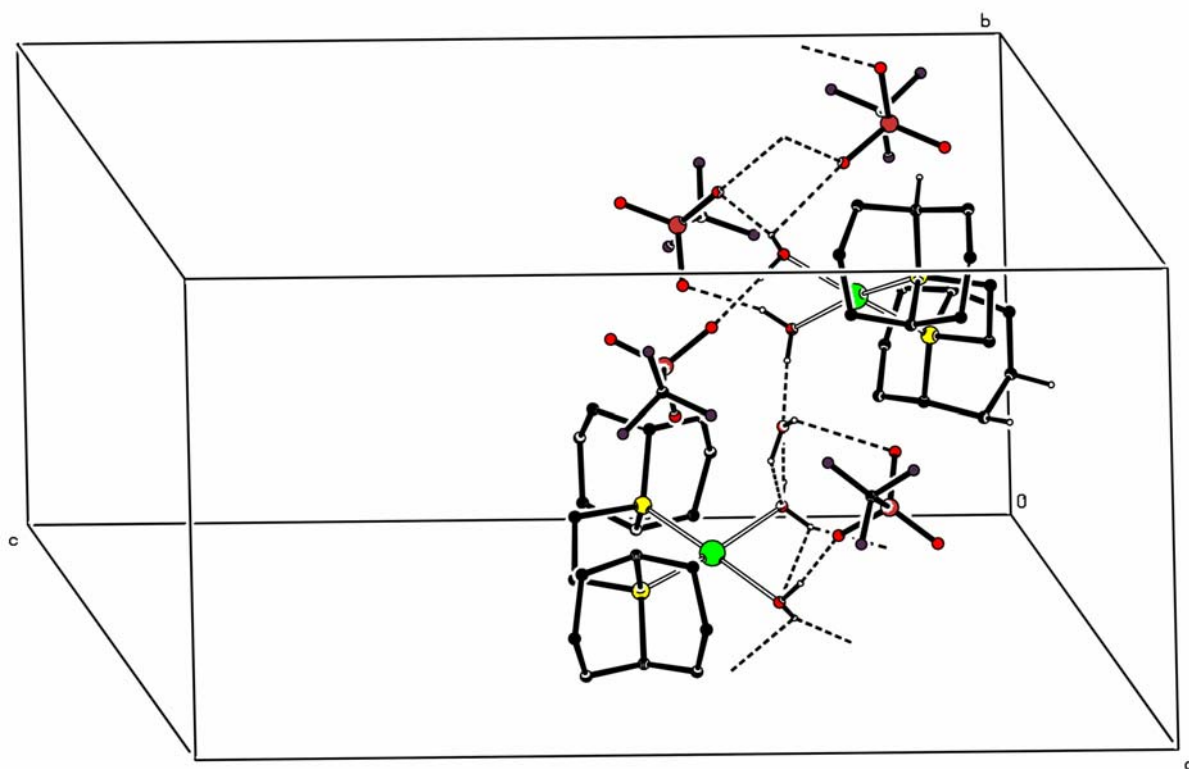


Figure S1. Packing diagram of compound $[\text{Pd}(\text{bcope})(\text{H}_2\text{O})_2](\text{OTf})_2 \cdot \text{H}_2\text{O}$ showing the one-dimensional H-bonding networking along the *b* axis.

Table S2. Absolute Energies and Cartesian Coordinates of the Optimized Structures.

Pd ₂ – planar (bridging CO)				O	0.249998	1.294558	-3.148154
E: -2007.177380				C	-3.590239	-2.064847	0.666649
Pd	0.517716	1.168975	0.612826	H	-3.881987	-2.909096	1.300102
Pd	-0.517762	-1.168876	-0.612862	H	-4.183629	-1.199168	0.983295
P	2.635236	1.982879	1.460164	C	-3.828010	-2.383367	-0.817436
C	2.452427	3.805846	1.792480	H	-4.899508	-2.472575	-1.023663
H	3.234657	4.138804	2.482201	H	-3.362488	-3.335907	-1.095529
H	2.618001	4.321370	0.839438	H	4.539904	0.869618	0.997134
C	1.058059	4.126127	2.359659	H	3.514755	0.332839	2.837424
H	0.902114	5.208518	2.410336	H	-0.862550	2.464426	1.716616
H	0.946825	3.733424	3.376950	H	0.327824	3.287318	0.099216
P	-0.278550	3.341379	1.327844	H	-1.150870	-2.873290	1.151281
P	0.269180	-3.356292	-1.291525	H	-1.772992	-1.139557	2.299156
P	-2.625869	-1.966932	-1.497922	H	-4.063979	-0.076426	-2.028134
C	1.410728	-0.665806	0.079539	H	-3.081603	-1.616665	-3.206086
O	2.455054	-1.159638	0.138431	Pd ₂ - TS			
C	-1.410531	0.666332	-0.080486	E: -2007.173723			
O	-2.454659	1.160455	-0.140448	Pd	-1.406501	0.155112	-0.141728
C	-1.219699	-4.388194	-1.722148	Pd	1.406364	-0.155332	-0.141584
H	-0.918129	-5.233529	-2.348981	P	-3.443103	1.439768	-0.210787
H	-1.603683	-4.800941	-0.782113	C	-4.860598	0.273056	0.106974
C	-2.290668	-3.541842	-2.432973	H	-5.740972	0.839497	0.427743
H	-3.218481	-4.111512	-2.547425	H	-5.106540	-0.196313	-0.852500
H	-1.960999	-3.251803	-3.437295	C	-4.480525	-0.782460	1.159062
H	3.810779	1.840187	0.699481	H	-5.257254	-1.550459	1.232038
H	3.029081	1.408025	2.684761	H	-4.377158	-0.329286	2.151737
H	-1.466487	3.456327	2.073833	P	-2.844837	-1.575842	0.749496
H	-0.527728	4.242809	0.274023	P	2.844613	1.575843	0.749339
H	1.077566	-3.349937	-2.445501	P	3.442986	-1.439988	-0.210187
H	1.046508	-4.137895	-0.416451	C	-0.166558	1.593659	-0.697655
H	-3.578806	-2.300408	-0.515123	O	0.125229	2.616763	-1.131618
H	-3.390836	-1.157034	-2.358032	C	0.166468	-1.594017	-0.697264
Pd ₂ – twisted (terminal CO)				O	-0.125288	-2.617223	-1.131006
E: -2007.183369				C	4.480265	0.782569	1.159243
Pd	1.256476	0.241903	0.441046	H	5.256984	1.550588	1.232115
Pd	-1.001008	-0.366668	-0.840515	H	4.376805	0.329624	2.152012
P	3.271583	0.963283	1.600539	C	4.860444	-0.273191	0.107436
C	3.049972	2.769330	2.006771	H	5.740793	-0.839550	0.428420
H	3.721231	3.055324	2.822965	H	5.106472	0.195957	-0.852124
H	3.356428	3.335808	1.119926	H	-3.783700	2.157299	-1.372638
C	1.590227	3.072788	2.379117	H	-3.546925	2.442062	0.773781
H	1.420396	4.152211	2.449162	H	-2.491685	-2.313979	1.895414
H	1.334287	2.638363	3.352556	H	-3.147916	-2.611460	-0.156724
P	0.411252	2.335226	1.133616	H	3.147765	2.611241	-0.157110
P	-1.801643	-1.635707	0.982964	H	2.491355	2.314259	1.895045
P	-3.073592	-1.072056	-1.908015	H	3.546740	-2.442070	0.774605
C	1.835612	-1.508360	-0.255738	H	3.783686	-2.157766	-1.371856
O	2.215241	-2.508152	-0.639488				
C	-0.180681	0.691529	-2.286731				