Reaction of Pentaarylboroles with Carbon Monoxide: An Isolable Organoboron Carbonyl Complex.

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Electronic Supplementary Information

Experimental Details.

General Procedures. All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene and hexanes were dried and purified by passing through activated alumina, and vacuum distilled from Na/benzophenone. CH_2Cl_2, were dried over and distilled from CaH_2 twice. 4-DMAP was obtained from Alfa Aesar and dried under vacuum prior to use. CO was obtained from Aldrich and passed through a 30cm drying column containing Drierite prior to admittance to the reaction vessels. ^{13}CO was obtained from Cambridge Isotopes. Perfluoropentaphenylborole[i] and pentaphenylborole[ii] were prepared as previous reported. All ^1H, ^{11}B, and ^{19}F NMR spectra were recorded on a Brucker 400 MHz spectrometer (operating at 400 MHz (^1H), 128 MHz (^{11}B), and 376 MHz (^{19}F)) at 25°C or as indicated. Chemical shifts reported were relative to $SiMe_4$ (^1H), or BF_3•OEt_2 (^{11}B and ^{19}F) standards; all chemical shifts are in units of ppm. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a Nonius Kappa CCD diffractometer in a cold (150 or 173K) N_2 stream.

Synthesis of 1•CO. Perfluoropentaphenylborole (30 mg, 0.03 mmol) was suspended in CD_2Cl_2 (0.5 mL) in a J. Young NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The tube was warmed to room temperature and one atmosphere CO of was admitted into the tube. The tube was shaken to obtain a light yellow solution, and the solution held at room temperature overnight to give colorless crystals of **1•CO**. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): -16.6 (br). $^{19}F\{^1H\}$ NMR (CD_2Cl_2):-131.0 (m, 2F, *o*-C_6F_5), -140.0 (br, 4F, *o*-C_6F_5), -140.7 (m, 4F, *o*-C_6F_5), -151.2 (t, 2F, *p*-C_6F_5), -152.9 (t, 1F, *p*-C_6F_5), -153.1 (t, 2F, *p*-C_6F_5), -160.5 (br, 4F, *m*-C_6F_5), -160.8 (m, 4F, *m*-C_6F_5), -160.1 (m, 2F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 166.4 (br, B*C*O). IR (ν, KBr pellet) 2199 cm^{-1}.

Synthesis of 1•DMAP. A solution of 4-DMAP (0.012 g, 0.11 mmol; CH_2Cl_2 2 mL) was added to a deep purple solution of **1** (0.100 g, 0.11 mmol; CH_2Cl_2 2 mL) resulting in the immediate production of a yellow solution. N-hexane (10 mL) was added resulting in the precipitation of a light yellow solid. The solution was decanted, the solids washed with hexanes (3 x 5 mL) and then dried *in vacuo* giving **1•DMAP** as a yellow powder. Yield 0.098 g, 88 %. ^1H NMR (CD_2Cl_2) 7.95 (d, $^3J_{H\text{-}H}$ 7 Hz, 2H), 6.56 (d, $^3J_{H\text{-}H}$ 7 Hz, 2H), 3.13 (s, 6H); $^{19}F\{^1H\}$ NMR (CD_2Cl_2) -128.2 (br, 2F, *o*-C_6F_5), -140.0 (br, 4F, *o*-C_6F_5), -140.7 (d, 4F, *o*-C_6F_5), -154.5 (t, 2F, *p*-C_6F_5), -156.6 (t, 2F, *p*-C_6F_5), -158.1 (t, 1F, *p*-C_6F_5), -162.0 (m, 4F, *m*-C_6F_5), -162.4 (m, 4F, *m*-C_6F_5), -163.3 (m, 2F, *m*-C_6F_5).

Generation of 2•CO. A quartz J. Young tube was charged with a solution of **2** (10 mg, 0.023 mmol) in CD_2Cl_2 (*ca.* 0.5 mL). The deep purple solution was subjected to three freeze-pump-thaw cycles, cooled to -78˚C in a dry ice/acetone bath and placed under *ca.* 1 atm. of ^{13}CO (*ca.* 1 atm). Upon inverting the J. Young tube, the solution immediately became clear yellow and was quickly placed in a dry ice/acetone bath until it could be transferred to a pre-cooled (-83ºC) NMR probe. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -80˚C): 172.2 (br, B*C*O). The sample was then gradually warmed to room temperature and the ^{13}C NMR spectrum recorded. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, RT): 184.8 (*C*O); 145.9 (quaternary carbon); 124-135 ppm (C-H aromatic carbons); 92.3, 86.7 ppm (quaternary carbons). See Figure S1 below.

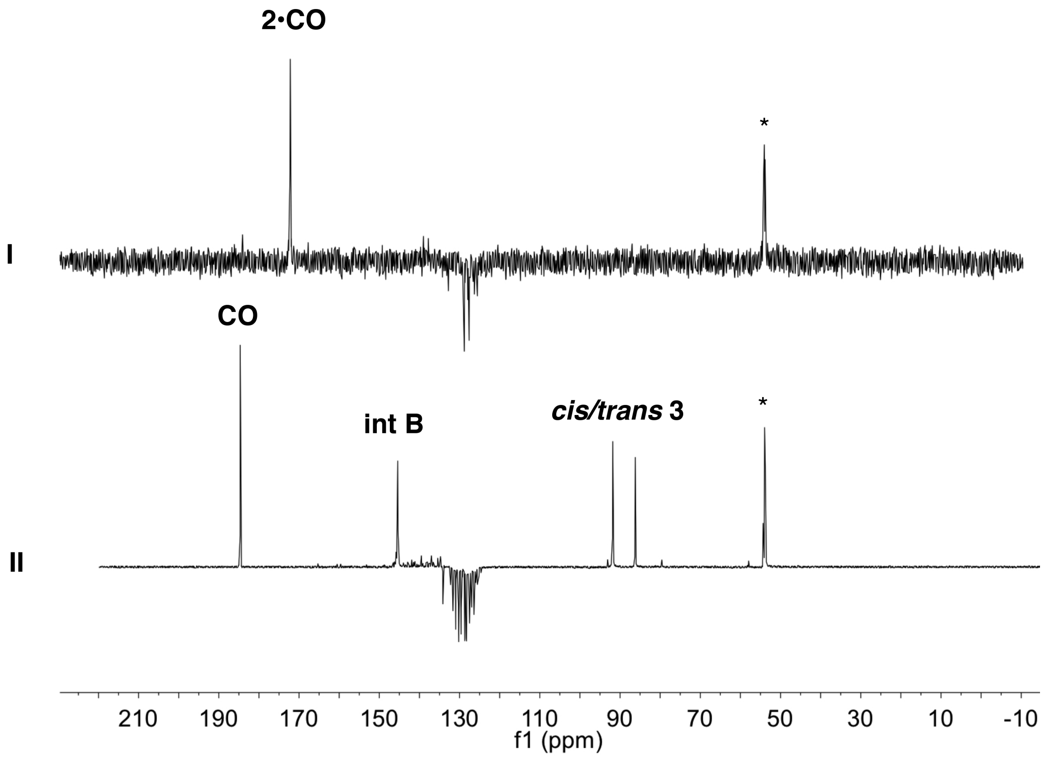


Figure S1. ^{13}C NMR spectra of I) the reaction of **2** with ^{13}CO at -80˚C and II) the same reaction after warming to room temperature and allowing the reaction to go to completion. The peak marked with the "*" is due to CD_2Cl_2 solvent; other peaks are assigned to the species depicted in Scheme 2 of the paper.

Computational Methods. Geometry optimizations and frequency calculations of **1•CO**, **2•CO**, and free CO were performed at the B3LYP level of theory with the 6-311G(d,p) basis set, implemented in the Gaussian 03 program.[iii] All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0 for minima). Natural bond orbital (NBO) analyses[iv,v] of **1•CO** and **2•CO** were performed using the B3LYP theory and 6-311G(d,p) basis set as implemented in the Gaussian 03 program. The optimized geometries were used as initial geometries.

Table S1. Cartesian Coordinates (Å) of the Optimized Geometry for **1•CO**[a]

atom	*x*	*y*	*z*
B	0.294145	1.372291	0.595957
C	0.159703	1.419103	2.173612
C	1.296127	0.100654	0.408352
C	0.536601	-0.998596	0.165264
C	-0.910545	-0.670280	0.110613
C	-1.145433	0.652474	0.294873
C	2.766015	0.154842	0.398684
C	3.486486	0.776661	1.422681
C	4.868657	0.881170	1.417932
C	5.587290	0.358712	0.349035
C	4.910273	-0.252238	-0.699111
C	3.524478	-0.343835	-0.668991
C	1.045334	-2.375779	-0.027870
C	1.779811	-3.021316	0.968677
C	2.260774	-4.313462	0.805145
C	2.009161	-4.993743	-0.380666
C	1.281681	-4.377833	-1.393051
C	0.813021	-3.085112	-1.207067
C	-1.955794	-1.696629	-0.117313
C	-2.134051	-2.749335	0.781068
C	-3.110699	-3.717721	0.597674
C	-3.945587	-3.642382	-0.511698
C	-3.796040	-2.603899	-1.423734
C	-2.808934	-1.648033	-1.220534
C	-2.480121	1.276911	0.366663
C	-3.399236	0.943080	1.365850
C	-4.651558	1.536284	1.449658
C	-5.016638	2.496321	0.513103
C	-4.128297	2.853041	-0.495185
C	-2.880637	2.246798	-0.556752
C	0.678622	2.785987	-0.055781
C	1.193673	2.857016	-1.348309
C	1.512888	4.060630	-1.963178
C	1.312713	5.252886	-1.276217
C	0.794236	5.228064	0.012484
C	0.489634	4.002836	0.589269
F	2.826327	1.299708	2.475762
F	5.508357	1.472438	2.429129
F	6.915901	0.449249	0.327293
F	5.594520	-0.739327	-1.736444
F	2.921531	-0.908144	-1.722511
F	2.029581	-2.399639	2.129115
F	2.954802	-4.906768	1.779008
F	2.465455	-6.233597	-0.547665
F	1.048787	-5.027600	-2.535454
F	0.137099	-2.505091	-2.207765
F	-1.353207	-2.829850	1.869367
F	-3.259393	-4.709463	1.478621
F	-4.889361	-4.563115	-0.698749
F	-4.596514	-2.534664	-2.489362
F	-2.684224	-0.668526	-2.123429
F	-3.068198	0.033280	2.297479
F	-5.500735	1.196846	2.422513
F	-6.215057	3.073418	0.581633
F	-4.482815	3.768110	-1.399617
F	-2.057488	2.599583	-1.551941
F	1.389398	1.729920	-2.053492
F	2.006732	4.084347	-3.203588
F	1.614403	6.415824	-1.853108
F	0.595950	6.369252	0.677891
F	-0.022054	4.015929	1.843932
O	-0.006315	1.304974	3.281448

[a] Calculated at the B3LYP/6-311G(d,p) level.

Table S2. Cartesian Coordinates (Å) of the Optimized Geometry for **2•CO**[a]

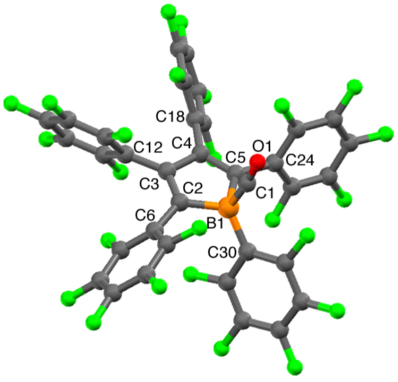
atom	*x*	*y*	*z*
B	-0.330938	-1.317897	0.413897
C	-0.247019	-1.441880	1.963029
C	-1.293065	0.001603	0.313246
C	-0.486155	1.085466	0.099327
C	0.953386	0.709299	0.034938
C	1.146123	-0.633599	0.201924
C	-2.766546	-0.038364	0.338318
C	-3.450817	-0.892539	1.220173
C	-4.839940	-0.966190	1.229197
C	-5.588962	-0.198356	0.341323
C	-4.929795	0.638924	-0.557068
C	-3.541973	0.718899	-0.559493
C	-0.945417	2.490090	-0.070995
C	-1.706670	3.112352	0.927843
C	-2.145142	4.424448	0.776481
C	-1.837307	5.136764	-0.380971
C	-1.081376	4.529583	-1.381822
C	-0.632769	3.221266	-1.225317
C	2.031704	1.703082	-0.213327
C	2.183193	2.828753	0.608857
C	3.209646	3.741447	0.384404
C	4.095799	3.554917	-0.674635
C	3.949651	2.445957	-1.505409
C	2.929714	1.527348	-1.275076
C	2.441152	-1.336744	0.311520
C	3.459741	-0.873724	1.162693
C	4.662886	-1.561286	1.280955
C	4.881405	-2.727151	0.548708
C	3.881995	-3.201399	-0.297910
C	2.673080	-2.519917	-0.410254
C	-0.749775	-2.665674	-0.348780
C	-1.199147	-2.578422	-1.676002
C	-1.535020	-3.716116	-2.404819
C	-1.439484	-4.977770	-1.819412
C	-1.003491	-5.088502	-0.502133
C	-0.662073	-3.945047	0.219065
O	-0.149726	-1.409852	3.093013
H	5.431898	-1.185596	1.947105
H	5.820619	-3.261318	0.639485
H	-0.313111	-4.064457	1.241222
H	4.040890	-4.107100	-0.872963
H	1.901790	-2.898196	-1.068978
H	3.300885	0.031309	1.736686
H	3.314001	4.602112	1.035733
H	1.495801	2.987829	1.431350
H	4.632089	2.293372	-2.334204
H	2.823529	0.663574	-1.920622
H	4.891791	4.269294	-0.852515
H	-0.927414	-6.064200	-0.034091
H	-1.706022	-5.864497	-2.383897
H	-1.877972	-3.617832	-3.429326
H	-1.289829	-1.604348	-2.145111
H	-0.039650	2.759816	-2.006007
H	-0.835394	5.076777	-2.285076
H	-2.181236	6.157984	-0.500932
H	-1.955960	2.558470	1.825440
H	-2.730328	4.889501	1.562074
H	-2.893260	-1.508592	1.916367
H	-5.336379	-1.630045	1.928348
H	-6.671381	-0.258228	0.342827
H	-5.499076	1.231369	-1.265034
H	-3.048979	1.366207	-1.272923

[a] Calculated at the B3LYP/6-311G(d,p) level.

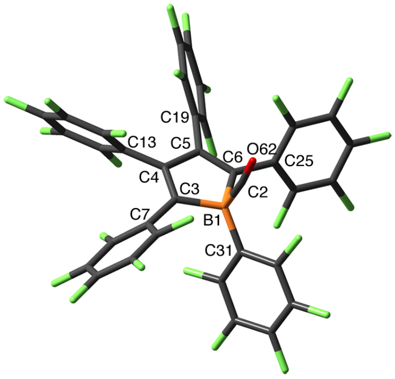
Table S3. Cartesian Coordinates (Å) of the Optimized Geometry for Free CO[a]

atom	*x*	*y*	*z*
C	0.000000	0.000000	-0.643977
O	0.000000	0.000000	0.482982

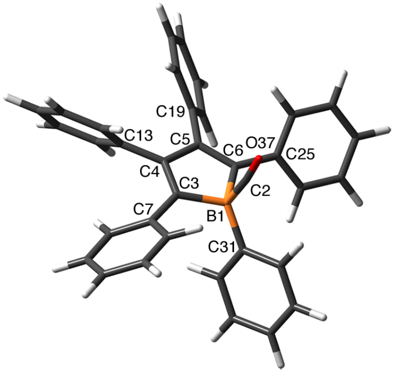
Table S4. Comparison of Structural Parameters between Crystal Structure of **1•CO** and Optimized geometries for **1•CO** and **2•CO.**



1·CO
(X-ray)



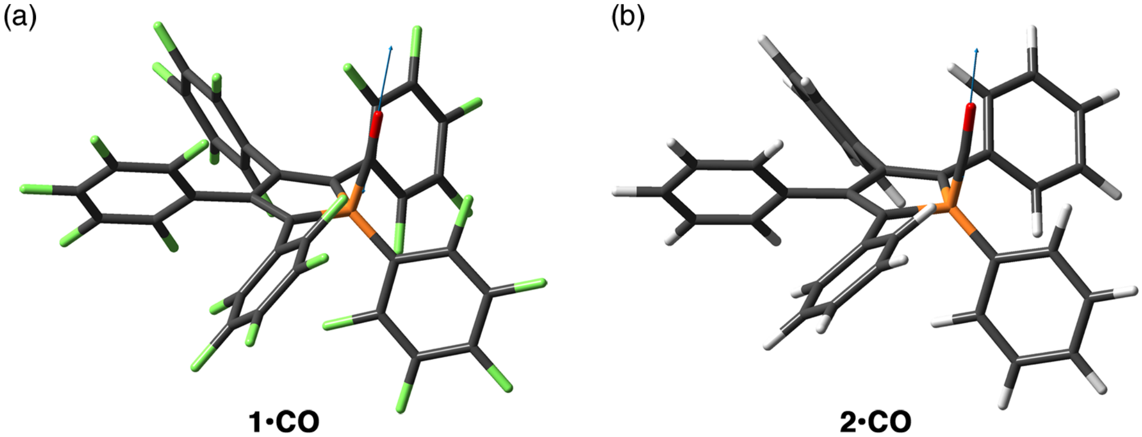
1·CO
(calculated)



2·CO
(calculated)

1•CO (X-ray)[a]		**1•CO** (calc)[b]		**2•CO** (calc)[b]	
bond	length (Å)	bond	length (Å)	bond	length (Å)
B1–C1	1.609(3)	B1–C2	1.5841	B1–C2	1.5563
C1–O1	1.115(3)	C2–O62	1.126	C2–O37	1.1346
B1–C2	1.623(3)	B1–C3	1.6298	B1–C3	1.6361
C2–C3	1.348(3)	C3–C4	1.3581	C3–C4	1.3681
C3–C4	1.491(3)	C4–C5	1.4849	C4–C5	1.4893
C4–C5	1.345(4)	C5–C6	1.356	C5–C6	1.3669
C5–B1	1.619(3)	C6–B1	1.6374	C6–B1	1.6416
C2–C6	1.473(3)	C3–C7	1.4709	C3–C7	1.4742
C3–C12	1.485(4)	C4–C13	1.4808	C4–C13	1.4876
C4–C18	1.481(4)	C5–C19	1.4825	C5–C19	1.4873
C5–C24	1.472(3)	C6–C25	1.4753	C6–C25	1.4777
B1–C30	1.591(4)	B1–C31	1.6035	B1–C31	1.6042

[a] Selected parameters from crystal structure. [b] Calculated at the B3LYP/6-311G(d,p) level.



1•CO
2230.95 cm^{-1}
(IR intensity: 326.0241 KM•mol^{-1})

2•CO
2161.58 cm^{-1}
(IR intensity: 491.1381 KM•mol^{-1})

Figure S2. Displacement vectors of the C–O stretching vibrations for (a) **1•CO** and (b) **2•CO** calculated at the B3LYP/6-311G(d,p) level (gray, carbon; orange, boron; red, oxygen; white, hydrogen; green, fluorine).

Table S5. Crystal data and structure refinement for **1•CO**.

Identification code	**1•CO**
Empirical formula	$C_{35.50}$ D_1 B_1 Cl_1 F_{25} O_1
Formula weight	972.62
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 28.3510(12) Å alpha = 90 deg.
	b = 13.1576(6) Å beta = 112.633(2) deg.
	c = 19.6080(7) Å gamma = 90 deg.
Volume	6751.1(5) Å^3
Z, Calculated density	8, 1.914 Mg/m^3
Absorption coefficient	2.634 mm^-1
F(000)	3752
Crystal size	0.26 x 0.19 x 0.13 mm
Theta range for data collection	3.38 to 68.03 deg.
Limiting indices	-34<=h<=33, -15<=k<=15, -22<=l<=23
Reflections collected / unique	21967 / 6101 [R(int) = 0.0327]
Completeness to theta = 68.03	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7258 and 0.5475
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6101 / 0 / 559
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1236
R indices (all data)	R1 = 0.0560, wR2 = 0.1309
Largest diff. peak and hole	0.398 and -0.209 e. Å ^-3

Table S6. Crystal data and structure refinement for **1•DMAP•0.5 CH_2Cl_2.**

Identification code	**1•DMAP• 0.5 CH_2Cl_2**
Empirical formula	$C_{41.25} H_{10.5} B_1 Cl_{0.25} F_{25} N_2$
Formula weight	1028.19
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.003(2) A alpha = 76.77(3) deg.
	b = 19.158(4) Å beta = 85.03(3) deg.
	c = 20.004(4) Å gamma = 73.96(3) deg.
Volume	3944.0(14) A^3
Z, Calculated density	4, 1.732 Mg/m^3
Absorption coefficient	0.201 mm^-1
F(000)	2023
Crystal size	0.35 x 0.25 x 0.18 mm
Theta range for data collection	2.16 to 25.02 deg.
Limiting indices	-13<=h<=13, -22<=k<=22, -23<=l<=23
Reflections collected / unique	25050 / 13686 [R(int) = 0.0363]
Completeness to theta = 25.02	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9647 and 0.9329
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13686 / 1 / 1261
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1758
R indices (all data)	R1 = 0.0857, wR2 = 0.1963
Largest diff. peak and hole	0.786 and -0.448 e. Å ^-3

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