SUPPORTING INFROMATION

Palladium Complexes with Pd→B Dative Bonds: Analysis of the Bonding in the Palladaboratrane Compound [κ⁴–B(mim^{But})$_3$]Pd(PMe$_3$)

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EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H; 1.94 for CD_2HN).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the solvent (δ 1.32 for $\underline{C}D_3CN$).[2] ^{31}P chemical shifts are reported in ppm relative to 85% H_3PO_4 (δ = 0) and were referenced

using $P(OMe)_3$ in C_6D_6 ($\delta = 141.0$) as external standard. ^{11}B NMR spectra are reported with reference to $BF_3(OEt_2)$ ($\delta = 0.0$). Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). $[Tm^{But}]K$ was prepared by a method analogous to that used for $[Tm^{But}]Na$.[3] $Pd(OAc)_2$ was obtained from Aldrich and Janssen Chimica and used as received.

X-ray structure determinations

X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10).[4]

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 6.5 suite of *ab initio* quantum chemistry programs.[5] Geometry optimizations were performed with the B3LYP density functional[6] and the 6-31G** (C, H, N, B, P and S) and LACVP (Pd)[7] basis sets. Cartesian coordinates for geometry optimized structures are listed in Table 2. Molecular orbital analyses were performed with the aid of Jimp 2,[8] which employs Fenske-Hall calculations[9] and visualization using MOPLOT.[10]

Synthesis of $[\kappa^4\text{–}B(mim^{But})_3]Pd(PMe_3)$

A solution of $[Tm^{But}]K$ (227 mg, 0.44 mmol) in MeCN (2 mL) was treated with a suspension of $Pd(OAc)_2$ (100 mg, 0.44 mmol) in MeCN (6 mL) resulting in the formation of a yellow precipitate in a red solution. The mixture was stirred for 15 minutes and then filtered. The precipitate was suspended in benzene (15 mL) and treated with PMe_3

(*ca.* 0.1 mL, 1.5 mmol). The mixture was heated at 60˚C for 15 minutes, thereby giving an orange solution. The mixture was filtered and the volatile components were removed from the filtrate by lyophilization to give [κ^4–B(mim$^{Bu^t}$)$_3$]Pd(PMe$_3$) as an orange solid (205 mg, 71 %). Crystals of composition [κ^4–B(mim$^{Bu^t}$)$_3$]Pd(PMe$_3$)•C$_6$H$_6$ suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{24}H_{42}BN_6PPdS_3$•$(C_6H_6)_{0.8}$: C, 47.9%; H, 6.5%; N, 11.6%. Found: C, 47.6%; H, 6.7%; N, 11.7%. ^{1}H NMR (C_6D_6): 1.06 [d, $^2J_{P\text{-}H}$ = 4 Hz, 9H, P<u>Me</u>$_3$], 1.41 [s, 27H, 3 Bu^t], 6.41 [br, 3H, 3 C<u>H</u> mim$^{Bu^t}$], 8.19 [br, 3H, 3 C<u>H</u> mim$^{Bu^t}$]. ^{1}H NMR (CD_3CN): 1.17 [d, $^2J_{P\text{-}H}$ = 5 Hz, 9H, P<u>Me</u>$_3$], 1.70 [s, 27H, 3 Bu^t], 6.82 [d, $^3J_{H\text{-}H}$ = 2 Hz, 3H, 3 C<u>H</u> mim$^{Bu^t}$], 7.01 [d, $^3J_{H\text{-}H}$ = 2 Hz, 3H, 3 C<u>H</u> mim$^{Bu^t}$]. ^{13}C{^{1}H} NMR (CD_3CN): 16.6 [d, $^1J_{P\text{-}C}$ = 11 Hz, P<u>Me</u>$_3$], 28.4 [s, 3 C(<u>C</u>H$_3$)$_3$] 58.8 [s, 3 <u>C</u>(CH$_3$)$_3$], 117.7 [s, 3 <u>C</u>H mim$^{Bu^t}$], 120.3 [s, 3 <u>C</u>H mim$^{Bu^t}$], not observed [s, 3 <u>C</u>S mim$^{Bu^t}$]. ^{31}P{^{1}H} NMR (CD_3CN): -34.4 [br 1:1:1:1 q, $^2J_{B\text{-}P}$ = 116 Hz, <u>P</u>Me$_3$). ^{11}B{^{1}H} NMR (CD_3CN): 4.4 [d, $^2J_{B\text{-}P}$ = 116 Hz, <u>B</u>(mim$^{Bu^t}$)$_3$]. IR Data (KBr pellet, cm^{-1}): 3600~3100 (br), 2966 (br), 2917 (s), 2849 (m), 1379 (s), 1367 (m), 1186 (s), 1157 (s), 1097 (s, br), 1062 (s), 1024 (m), 949 (m), 762 (m), 719 (m), 685 (m), 469 (s).

Synthesis of {[μ–κ^1,κ^3–B(mim$^{Bu^t}$)$_3$]Pd}$_2$

A solution of [Tm$^{Bu^t}$]K (227 mg, 0.44 mmol) in MeCN (3 mL) was treated with a solution of Pd(OAc)$_2$ (100 mg, 0.44 mmol) in MeCN (9 mL) resulting in the formation of a yellow precipitate in a red solution. The mixture was stirred for 15 minutes and then filtered. The precipitate was washed with MeOH/H$_2$O (10 mL of a 1:1 mixture), THF (2 × 5mL), Et$_2$O (2 × 5mL) and dried *in vacuo* to give {[μ–κ^1,κ^3–B(mim$^{Bu^t}$)$_3$]Pd}$_2$ as a yellow solid (119 mg, 46 %). Crystals suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution. Anal. calcd. for $C_{42}H_{66}B_2N_{12}Pd_2S_6$: C, 43.3%; H, 5.7%; N, 14.4%. Found: C, 42.3%; H, 5.7%; N, 13.9%. ^{1}H NMR (CD_3CN, 300K): 1.70 [s, 27H, 3 Bu^t], 6.94 [s, br, 3C<u>H</u> mim$^{Bu^t}$], not observed [3C<u>H</u> mim$^{Bu^t}$]. ^{1}H NMR (CD_3CN, 228K): 1.59 [br, 9H, 1Bu^t], 1.66 [br, 9 H, 1Bu^t], 1.72 [br, 9H, 1Bu^t], 5.25 [br, 1H, 1C<u>H</u> mim$^{Bu^t}$], 6.32 [br, 1 H, 1C<u>H</u> mim$^{Bu^t}$], 6.62 [br, 1 H, 1C<u>H</u> mim$^{Bu^t}$], 6.76 [br, 1H, 1C<u>H</u> mim$^{Bu^t}$], 6.98 [br, 1H, 1C<u>H</u>

mim^{Bu^t}], 7.07 [br, 1H, C<u>H</u> mim^{Bu^t}]. IR Data (KBr pellet, cm^{-1}): 3600~3200 (br), 2975 (w), 2920 (w), 1398 (m), 1383 (s), 1365 (m), 1348 (s), 1264 (w), 1190 (s), 1158 (s), 1061 (m), 821 (w), 794 (w), 770 (w), 746 (w), 714 (w), 669 (w), 472 (w). Mass spectrum: m/z = 1166.4 $\{M\}^+$.

Synthesis of $[\kappa^2$–AcOB$(mim^{Bu^t})_3]_2$Pd

A solution of $[Tm^{Bu^t}]K$ (23 mg, 0.04 mmol) in MeCN (0.5 mL) was treated with a solution of $Pd(OAc)_2$ (10 mg, 0.04 mmol) in MeCN (1 mL) resulting in the formation of a yellow precipitate in a red solution. The mixture was stirred for 15 minutes and then filtered. The precipitate was suspended in MeCN (0.5 mL) and treated with a solution of I_2 (11 mg, 0.04 mmol) in MeCN (0.5 mL). The resulting dark red solution was filtered and allowed to crystallize at ambient temperature. Red crystals formed over a period of two days (3 mg, 13%). Anal. calcd. for $C_{46}H_{72}B_2N_{12}O_4PdS_6 \bullet CH_3CN$: C, 47.3 %; H, 6.2 %; N, 14.9 %. Found: C, 46.8 %; H, 5.8 %; N, 15.2 %. IR Data (KBr pellet, cm^{-1}): 3188 (w), 3156 (w), 3110 (w), 2979 (m), 2926 (m), 1712 (m), 1562 (w), 1407 (m), 1358 (s), 1335 (m), 1266 (s), 1197 (m), 1167 (m), 1079 (m), 1036 (m), 825 (m), 809 (m), 792 (m), 747 (w), 664 (m).

Table 1. Crystal, intensity collection and refinement data.

	{[μ–κ^1,κ^3–B(mim^{But})$_3$]Pd}$_2$ 2CH$_3$CN	**[κ^4–B(mim^{But})$_3$]Pd(PMe$_3$) C$_6$H$_6$**
Lattice	Monoclinic	Monoclinic
Formula	$C_{46}H_{72}B_2N_{14}Pd_2S_6$	$C_{30}H_{48}BN_6PPdS_3$
formula weight	1247.96	737.10
space group	$P2_1/c$	$P2_1/n$
a/Å	12.6473(6)	13.5495(14)
b/Å	18.2555(9)	13.3193(13)
c/Å	12.4059(6)	21.005(2)
α/°	90	90
β/°	101.6250(10)	108.513(2)
γ/°	90	90
V/Å^3	2805.6(2)	3594.6(6)
Z	2	4
temperature (K)	243	243
Radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.477	1.362
μ (Mo Kα), mm^{-1}	0.911	0.764
θ max, deg.	28.35	28.30
no. of data	6611	8406
no. of parameters	317	379
R_1	0.0425	0.0667
wR_2	0.0870	0.1434
GOF	1.005	1.012

	$[\kappa^2$–AcOB(mim$^{Bu^t}$)$_3]_2$Pd 2CH_3CN	$[\kappa^2$–AcOB(mim$^{Bu^t}$)$_3]_2$Pd 2CH_3CN
Lattice	Monoclinic	Triclinic
Formula	$C_{50}H_{78}B_2N_{14}O_4PdS_6$	$C_{50}H_{78}B_2N_{14}O_4PdS_6$
formula weight	1259.64	1259.64
space group	$P2_1/c$	$P\text{-}1$
a/Å	10.7707(5)	10.8342(4)
b/Å	16.3500(8)	11.2770(5)
c/Å	18.0972(9)	13.6177(6)
α/°	90	93.8670(10)
β/°	99.8880(10)	92.8400(10)
γ/°	90	106.2340(10)
V/Å^3	3139.6(3)	1589.73(12)
Z	2	1
temperature (K)	243	243
Radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.332	1.316
μ (Mo Kα), mm^{-1}	0.547	0.541
θ max, deg.	28.30	28.32
no. of data	7407	7200
no. of parameters	351	350
R_1	0.0420	0.0354
wR_2	0.1108	0.0852
GOF	1.030	1.011

Table 2. Cartesian Coordinated for Geometry Optimized Structures

$[\kappa^4$–B(mim$^{Bu^t}$)$_3$]Pd(PMe$_3$) (C3v)
-2956.61709126372 Hartrees

atom	x	y	z
Pd1	0.0000000000	0.0000000000	1.2728178788
P2	0.0000000000	0.0000000000	3.7695635605
S3	-1.2628261129	2.1872789886	1.0931464958
S4	-1.2628261129	-2.1872789886	1.0931464958
S5	2.5256522258	0.0000000000	1.0931464958
N6	-1.8535235850	3.2103970222	-1.4503939609
N7	-0.7434741892	-1.2877350699	-1.4007624440
N8	-1.8535235850	-3.2103970222	-1.4503939609
N9	1.4869483785	0.0000000000	-1.4007624440
N10	3.7070471700	0.0000000000	-1.4503939609
N11	-0.7434741892	1.2877350699	-1.4007624440
B12	0.0000000000	0.0000000000	-0.8258810580
C13	-1.3027032231	2.2563481696	-0.6144240704
C14	-0.9491179755	1.6439205560	-2.7284754575
C15	-1.6230879727	2.8112708338	-2.7664041160
C16	-2.5937123673	4.4924416004	-1.1898646062
C17	-2.7759123883	4.8080212940	0.3005423718
C18	-1.7888562311	5.6394330228	-1.8374571077
C19	-3.9894641451	4.3689114512	-1.8374571077
C20	-1.3027032231	-2.2563481696	-0.6144240704

C21	-0.9491179755	-1.6439205560	-2.7284754575
C22	-1.6230879727	-2.8112708338	-2.7664041160
C23	-2.5937123673	-4.4924416004	-1.1898646062
C24	-2.7759123883	-4.8080212940	0.3005423718
C25	-3.9894641451	-4.3689114512	-1.8374571077
C26	-1.7888562311	-5.6394330228	-1.8374571077
C27	2.6054064462	0.0000000000	-0.6144240704
C28	1.8982359510	0.0000000000	-2.7284754575
C29	3.2461759453	0.0000000000	-2.7664041160
C30	5.1874247346	0.0000000000	-1.1898646062
C31	5.5518247767	0.0000000000	0.3005423718
C32	5.7783203762	-1.2705215716	-1.8374571077
C33	5.7783203762	1.2705215716	-1.8374571077
C34	0.8294841478	1.4367086880	4.5959223664
C35	-1.6589682956	0.0000000000	4.5959223664
C36	0.8294841478	-1.4367086880	4.5959223664
H37	-0.6070282086	1.0514036989	-3.5574429747
H38	-1.9560115710	3.3879114212	-3.6127109970
H39	-0.6070282086	-1.0514036989	-3.5574429747
H40	-1.9560115710	-3.3879114212	-3.6127109970
H41	1.2140564172	0.0000000000	-3.5574429747
H42	3.9120231421	0.0000000000	-3.6127109970
H43	0.3435704950	2.3619977327	4.2729902371

H44	0.7915950452	1.3710828373	5.6894430487
H45	1.8737647927	1.4785396430	4.2729902371
H46	-2.2173352877	0.8834580897	4.2729902371
H47	-2.2173352877	-0.8834580897	4.2729902371
H48	-1.5831900904	0.0000000000	5.6894430487
H49	0.3435704950	-2.3619977327	4.2729902371
H50	1.8737647927	-1.4785396430	4.2729902371
H51	0.7915950452	-1.3710828373	5.6894430487
H52	-1.8220414810	4.9194334100	0.8165585667
H53	-3.3227738069	5.7552130557	0.3680056880
H54	-3.3493335648	4.0376509143	0.8165585667
H55	-1.6739924445	5.5114581269	-2.9176788981
H56	-2.3024137452	6.5910105407	-1.6681342881
H57	-0.7911616657	5.7035523712	-1.3931371116
H58	-3.9360665275	4.2054490461	-2.9176788981
H59	-4.5438404124	3.5369422866	-1.3931371116
H60	-4.5567756923	5.2894540637	-1.6681342881
H61	-1.8220414810	-4.9194334100	0.8165585667
H62	-3.3493335648	-4.0376509143	0.8165585667
H63	-3.3227738069	-5.7552130557	0.3680056880
H64	-3.9360665275	-4.2054490461	-2.9176788981
H65	-4.5567756923	-5.2894540637	-1.6681342881
H66	-4.5438404124	-3.5369422866	-1.3931371116

H67	-1.6739924445	-5.5114581269	-2.9176788981
H68	-0.7911616657	-5.7035523712	-1.3931371116
H69	-2.3024137452	-6.5910105407	-1.6681342881
H70	5.1713750458	0.8817824957	0.8165585667
H71	5.1713750458	-0.8817824957	0.8165585667
H72	6.6455476139	0.0000000000	0.3680056880
H73	5.6100589720	-1.3060090808	-2.9176788981
H74	6.8591894375	-1.3015564770	-1.6681342881
H75	5.3350020781	-2.1666100846	-1.3931371116
H76	5.6100589720	1.3060090808	-2.9176788981
H77	5.3350020781	2.1666100846	-1.3931371116
H78	6.8591894375	1.3015564770	-1.6681342881

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