Supporting Information

Donor ligands based on tricoordinate boron formed by B-H-activation of bis(phosphine)boronium salts

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1. **Experimental Details**
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1. Experimental Details

Material and Methods

All experiments were carried out under an atmosphere of purified argon in a MBraun Labmaster glove box or using standard Schlenk techniques. THF and C_6D_6 were dried and distilled from Na/K alloy and stored over molecular sieves. *n*-Hexane was dried and distilled from $LiAlH_4$ and stored over molecular sieves. Toluene was dried and distilled from sodium and stored over molecular sieves. Bis(diphenylphosphino)methane (dppm) was prepared according to a previously reported procedure.[1]

^1H, ^{13}C, ^{31}P and ^{11}B NMR spectra were recorded using Bruker DRX 400, DRX 500 and Avance 500 NMR spectrometers. ^1H and $^{13}C\{^1H\}$, ^{13}C-APT (attached proton test) NMR chemical shifts are reported in ppm downfield from tetramethylsilane. The resonance of the residual protons in the deuterated solvent was used as internal standard for ^1H NMR. The solvent peak of the deuterated solvent was used as internal standard for ^{13}C NMR. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{11}B NMR chemical shifts are reported in ppm downfield from $BF_3{\cdot}Et_2O$ and referenced to an external solution of $BF_3{\cdot}Et_2O$ in $CDCl_3$. The following abbreviations are used for the description of NMR data: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), v (virtual).

FT-IR spectra were recorded by attenuated total reflection of the solid samples on a Bruker Tensor IF37 spectrometer. The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong) and br (broad).

HR-ESI mass spectra were acquired with a LTQ-FT mass spectrometer (Thermo Fisher Scientific). The resolution was set to 100.000.

Synthesis of $[H_2B(dppm)_2]Br$ (1)

dppm (880 mg, 2.2 mmol) was dissolved in CH_2Cl_2 (6 mL) and a solution of $BH_2Br{\cdot}SMe_2$ in CH_2Cl_2 (1 M, 1.1 mL, 1.1 mmoL) was added. After stirring for 10 d, reaction control via $^{31}P\{^1H\}$ NMR indicated no further conversion of *dppm*. The solvent was removed under reduced pressure and the residue was washed with Et_2O/THF (2:1, 5x 10 mL). The solvent was removed under high vacuum to obtain *$[H_2B(dppm)_2]Br$* (560 mg, 0.65 mmol, 59 %) as

colorless crystalline solid (M = 861.51 g·mol^{-1}). ^{1}H-NMR (300 MHz, THF-d_8, 27 °C) δ = 4.05 (d, 4H, $^{3}J_{HH}$ = 12.3 Hz, CH_2) 7.03-7.16 (m, 16H, phenyl-*H*), 7.19-7.27 (m, 8H, phenyl-*H*), 7.51-7.59 (m, 8H, phenyl-*H*), 7.61-7.72 (m, 8H, phenyl-*H*) ppm. Boron-bound protons were not observed. ^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2, 27 °C) δ = -34.0 (br) ppm. Only resonances that are changing upon ^{11}B-decoupling are listed in the ^{1}H{^{11}B} NMR spectrum. ^{1}H{^{11}B}NMR (300 MHz, THF-d_8, 27 °C) δ = 2.65 (t, 2H, $^{2}J_{HP}$ = 20.4 Hz, BH_2) ppm. ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2, 27 °C) δ = -25.2 (d, $^{2}J_{PP}$ = 67.1 Hz, P-CH_2-*P*), 7.5 (br, *P*-BH_2-*P*) ppm. ^{13}C{^{1}H} NMR (76 MHz, CD_2Cl_2, 27 °C) δ = 22,7 (dd, $^{1}J_{PC}$ = 39.2 Hz, $^{1}J_{PC}$ = 34.2 Hz, P-*C*H_2-P), 124.3 (dd, J_{PC} = 61.6 Hz, J_{PC} = 2.8 Hz, phenyl-*C*), 124.3 (d, J_{PC} = 70.6 Hz, phenyl-*C*), 128.9 (s, phenyl-*C*), 129.1 (s, phenyl-*C*), 129.6 (s, phenyl-*C*), 129.8 (d, J_{PC} = 1.5 Hz, phenyl-*C*), 132.8 (s, phenyl-*C*), 132.9 (s, phenyl-*C*), 133.0 (s, phenyl-*C*), 133.2 (s, phenyl-*C*), 133.3 (d, J_{PC} = 2.8 Hz, phenyl-*C*), 136.3 (d, J_{PC} = 7.3 Hz, phenyl-*C*), 136.5 (d, J_{PC} = 7.3 Hz, phenyl-*C*) ppm. FT-IR (ATR) $\tilde{\upsilon}$/cm^{-1}: 3050 (w), 3008 (w), 2983 (w), 2846 (w), 2440 (w), 2394 (w), 1586 (w), 1482 (w), 1435 (m), 1365 (w), 1314 (w), 1189 (w), 1160 (w), 1106 (m), 1070 (w), 1026 (w) 997 (w), 915 (w), 776 (m), 740 (s), 721 (m), 690 (s), 633 (m). HRMS (ESI^{+}) m/z: 781.2643 (calculated for $C_{50}H_{46}BP_4$), 781.2646 (found, Δ = 0.4 ppm).

Synthesis of [(H_2B{dppm}$_2$)Ni(CO)$_2$]Br (2)

[Ni(CO)$_4$] (24 mg, 0.14 mmol) was added to a solution of **1** (120 mg, 0.14 mmol) in 5 mL THF and the resulting solution was stirred for five hours at ambient temperature. After this period the extent of conversion was checked by ^{31}P{^{1}H} NMR spectroscopy. Addition of 10 mL *n*-hexane resulted in precipitation of **2**. The supernatant solution was decanted off and the precipitate was dried *in vacuo*. Yield: 12 mg (0.012 mmol, 8.5 %). The yield can be increased significantly by removal of all volatiles from the reaction mixture and continuous washing of the residue, but the obtained product contains inseparable byproducts according to the ^{31}P{^{1}H} NMR spectrum. ^{1}H NMR (300 MHz, CD_3CN, 27 °C) δ = 3.82 (br, 4H, CH_2), 7.05-7.14 (m, 10H, phenyl-*H*), 7.19 (dd, 4H, J_{HH} = 7.3 Hz, J_{HH} = 1.1 Hz, phenyl-*H*), 7.24-7.35 (m, 10H, phenyl-*H*), 7.40 (t br, 10H, *J* = 9.0 Hz, phenyl-*H*), 7.62-7.82 (m, 6H, phenyl-*H*) ppm. ^{11}B{^{1}H} NMR (96 MHz, C_6D_6, 27 °C) δ = -35.8 (br) ppm. Only resonances that are changing upon decoupling are listed for the ^{1}H{^{11}B} NMR spectrum. ^{1}H{^{11}B} NMR (300 MHz, C_6D_6, 27 °C) δ = 4.25 (br, 2H, BH_2) ppm. ^{31}P{^{1}H}NMR (122 MHz, $CDCl_3$, 27 °C) δ = 4.9 (br, *P*-B-*P*), 18.1 (ddd, J_{PP} = 38.4 Hz, J_{PP} = 12.0 Hz, J_{PP} = 4.0 Hz, *P*-Ni-*P*) ppm. ^{13}C-APT NMR (76 MHz, CD_3CN, 27 °C) δ = 23.8 (d, $^{1}J_{PC}$ = 36.7 Hz, P-*C*H_2-P), 129.1 (vt, J_{PC} = 4.8 Hz, phenyl-*C*), 129.8 (d, J_{PC} = 11.8 Hz, phenyl-*C*), 130.3 (s, phenyl-*C*), 130.5 (s, phenyl-*C*), 130.6 (s, phenyl-*C*), 133.0 (d, J_{PC} = 9.6 Hz, phenyl-*C*), 133.2 (d, J_{PC} = 2.8 Hz, phenyl-*C*) ppm. The

resonances for carbonyl ligands and for the quaternary carbon atoms of the phenyl rings were not observed. FT-IR (ATR) ṽ/cm^{-1}: 2963 (w) 2905 (w) 2376 (w) 2360 (w) 2349 (w) 2343 (w) 2323 (w) 2298 (w) 2002 (w, ν_{CO}) 1939 (w, ν_{CO}) 1484 (w) 1435 (w) 1413 (w) 1258 (m) 1009 (s) 864 (m) 787 (s) 687 (m) 671 (m) 664 (m) 470 (m) 417 (m). HRMS (ESI$^+$) m/z: 867.1949 (calculated for [(H_2B{dppm}$_2$)Ni(CO)]$^+$), 867.1945 (found, Δ = 0.5 ppm); 839.1993 (calculated for [(H_2B{dppm}$_2$)Ni]$^+$), 839.1999 ((found, Δ = 0.7 ppm).

Synthesis of [(HB{dppm}$_2$)PdX]X (3, X = Cl, Br)

[H_2B(dppm)$_2$]Br (**1**, 40 mg, 0.046 mmol) and [$PdCl_2$(MeCN)$_2$] (12 mg, 0.046 mmol) were dissolved in 5 mL THF and stirred at ambient temperature for 5 hours. During this period, the solution brightened up and precipitate was formed. The supernatant solution was decanted off, the residue was washed with 5 mL THF and dried *in vacuo*. Complex **3** was formed and isolated as a mixture of the two constitutional isomers, with the two cations [[(HB{dppm}$_2$)PdCl]$^+$ (**3-Cl**, ~90 %) and [[(HB{dppm}$_2$)PdBr]$^+$ (**3-Br**, ~10 %). Both isomers are very similar in their spectroscopic properties. In several attempts to grow single crystals with different solvents and under various conditions only single crystals from [**3-Br**]Br could be obtained. Yield: 34.8 mg (0.035 mmol, 76 %). ^{1}H NMR (300 MHz, DMSO-d_6, 27 °C) δ = 2.52 (partly superimposed, 4H, $^2J_{PH}$ = 4.0 Hz, CH_2), 7.10-7.20 (m, 8H, phenyl-*H*), 7.36-7.61 (m, 20H, phenyl-*H*), 7.61-7.79 (m, 10H, phenyl-*H*), 8.50 (br t, 2H, J_{HH} = 2.7 Hz, phenyl-*H*) ppm. ^{11}B{^{1}H} NMR (96 MHz, DMSO-d_6, 27 °C) δ = -24.5 (br) ppm. Only resonances that are changing upon decoupling are listed for the ^{1}H{^{11}B} NMR spectrum. ^{1}H{^{11}B} NMR(300 MHz, DMSO-d_6, 27 °C) δ = 3.57 (br t, 1H, $^2J_{HP}$ = 17.9 Hz, B*H*) ppm. ^{31}P{^{1}H} NMR (122 MHz, DMSO-d_6, 27 °C) δ = 59.3 (br, *P*-B-*P*), 81.8 (dd, $^2J_{PP}$ = 76.4 Hz, $^2J_{PP}$ = 68.1 Hz, Ph_2P-Pd-Cl), 84.4 (t, $^2J_{PP}$ = 71.9 Hz, Ph_2P-Pd-Br) ppm. ^{13}C{^{1}H} NMR (76 MHz, DMSO-d_6, 27 °C) δ = 38.5-40.5 (P-*C*H_2-P, superimposed by DMSO-d_6), 128.2-128.6 (superimposed resonances, phenyl-*C*), 128.7 (vt, J_{PC} = 5.7 Hz, phenyl-*C*), 129.3 (vt, J_{PC} = 5.7 Hz, phenyl-*C*), 130.8 (s, phenyl-*C*), 131.0 (s, phenyl-*C*), 131.3-131.8 (superimposed resonances, phenyl-*C*), 132.4 (vt, J_{PC} = 6.2 Hz, phenyl-*C*), 132.7 (s, phenyl-*C*), 132.9 (s, phenyl-*C*), 134.0 (dd, $^1J_{PC}$ = 23.7 Hz, J_{PC} = 2.9 Hz, phenyl-*C*) ppm. FT-IR (ATR) ṽ / cm^{-1}: 3053 (w), 3015 (w), 2963 (w), 2905 (w), 2586 (w), 2370 (w), 2361 (w), 2349 (w) 2343 (w), 2323 (w), 2298 (w), 1587 (w), 1572 (w), 1483 (w), 1435 (m), 1411 (w), 1307 (m), 1259 (s), 1188 (w), 1086 (s), 1013 (s), 935 (m) 865 (w), 792 (s), 737 (m), 689 (s), 665 (m), 619 (w), 604 (w), 559 (m), 533 (m), 504 (m), 485 (m), 451 (w), 406 (w). HRMS (ESI$^+$) m/z: 921.1303 (calculated for [(HB{dppm}$_2$)PdCl]$^+$), 921.1305 (found, Δ = 0.2 ppm).

2. NMR Spectra

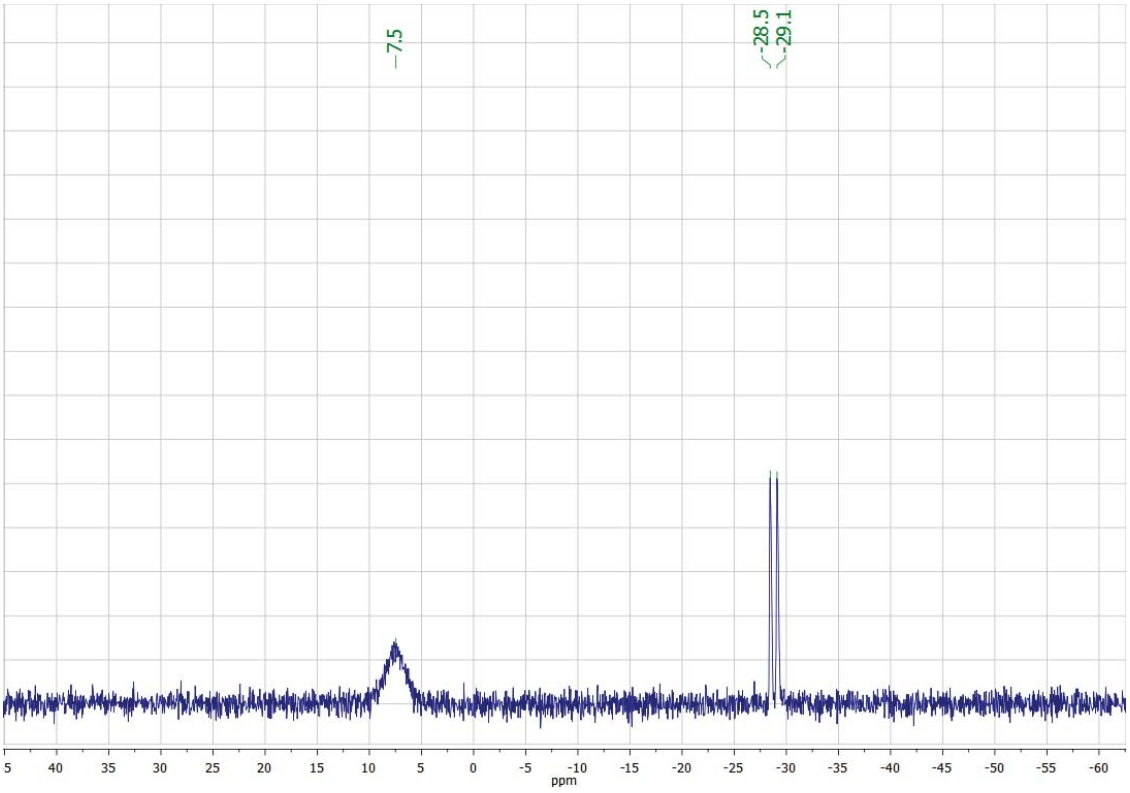


Figure 1 $^{31}P\{^{1}H\}$ NMR spectrum of compound **1** in CD_2Cl_2.

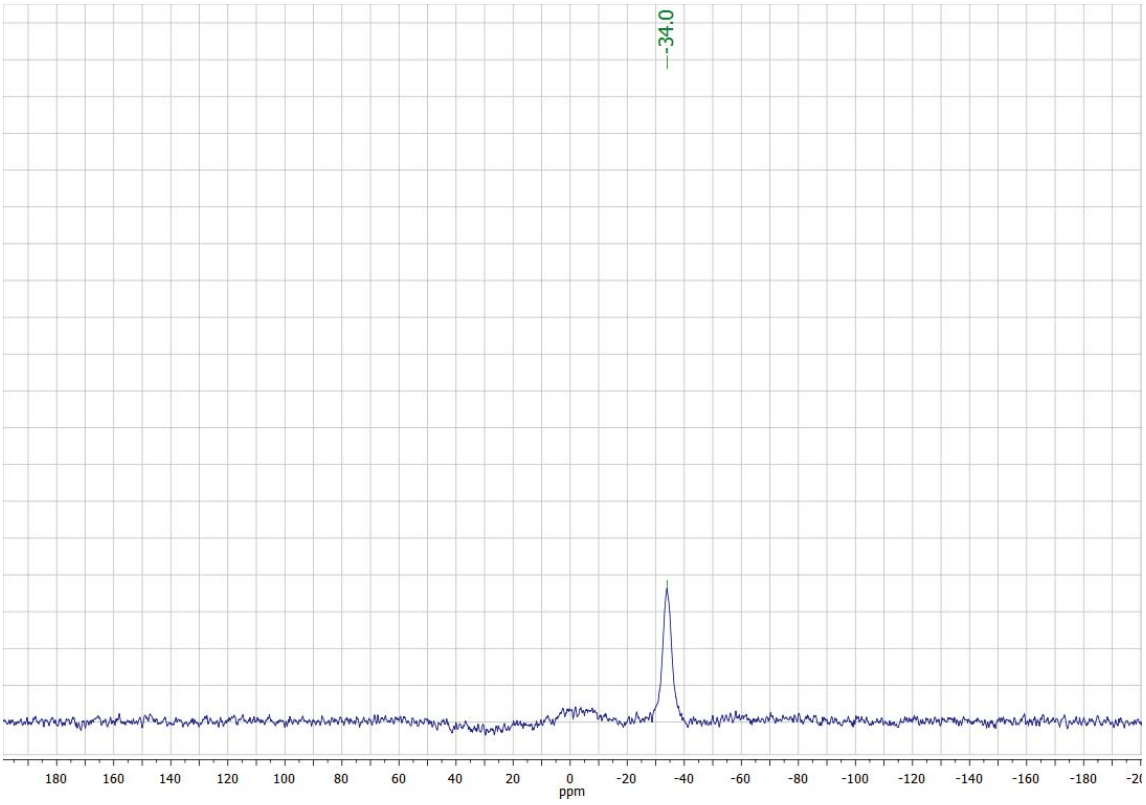


Figure 2 $^{11}B\{^{1}H\}$ NMR spectrum of compound **1** in CD_2Cl_2.

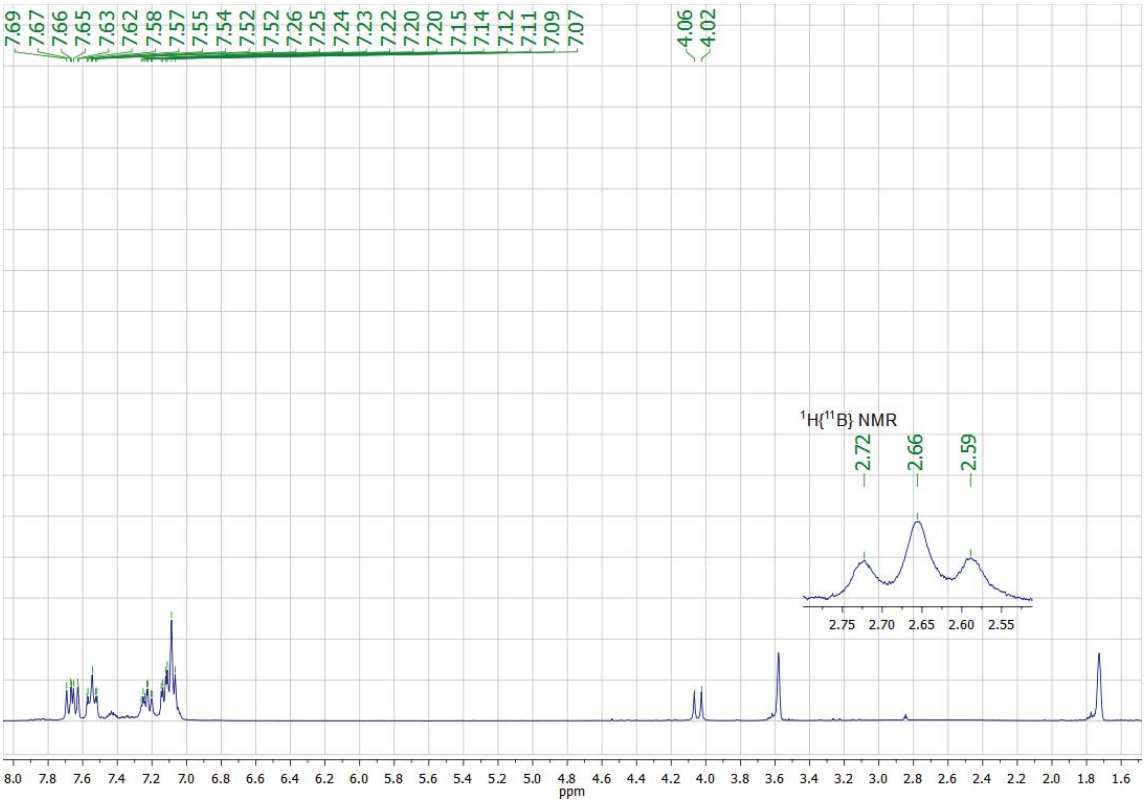


Figure 3 ^{1}H NMR spectrum of compound **1** in THF-d_8, with an inset showing the resonance of the boron-bound H-atoms in the $^{1}H\{^{11}B\}$NMR spectrum .

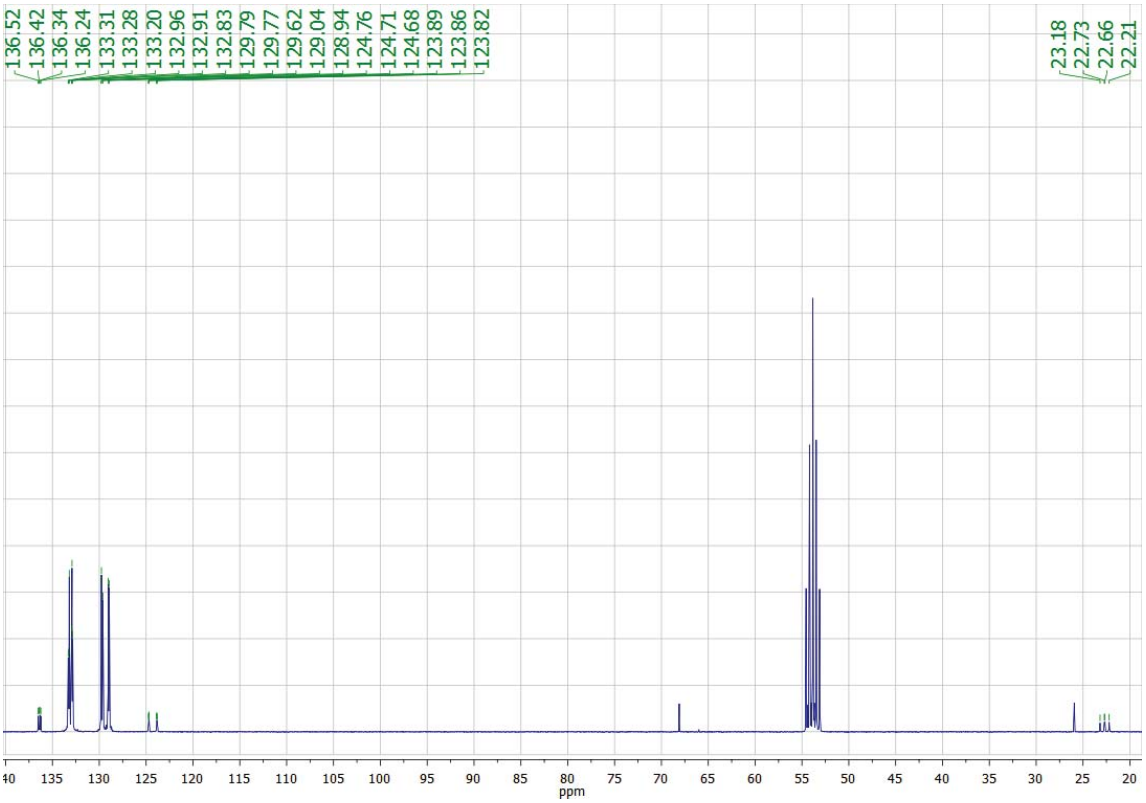


Figure 4 $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in CD_2Cl_2.

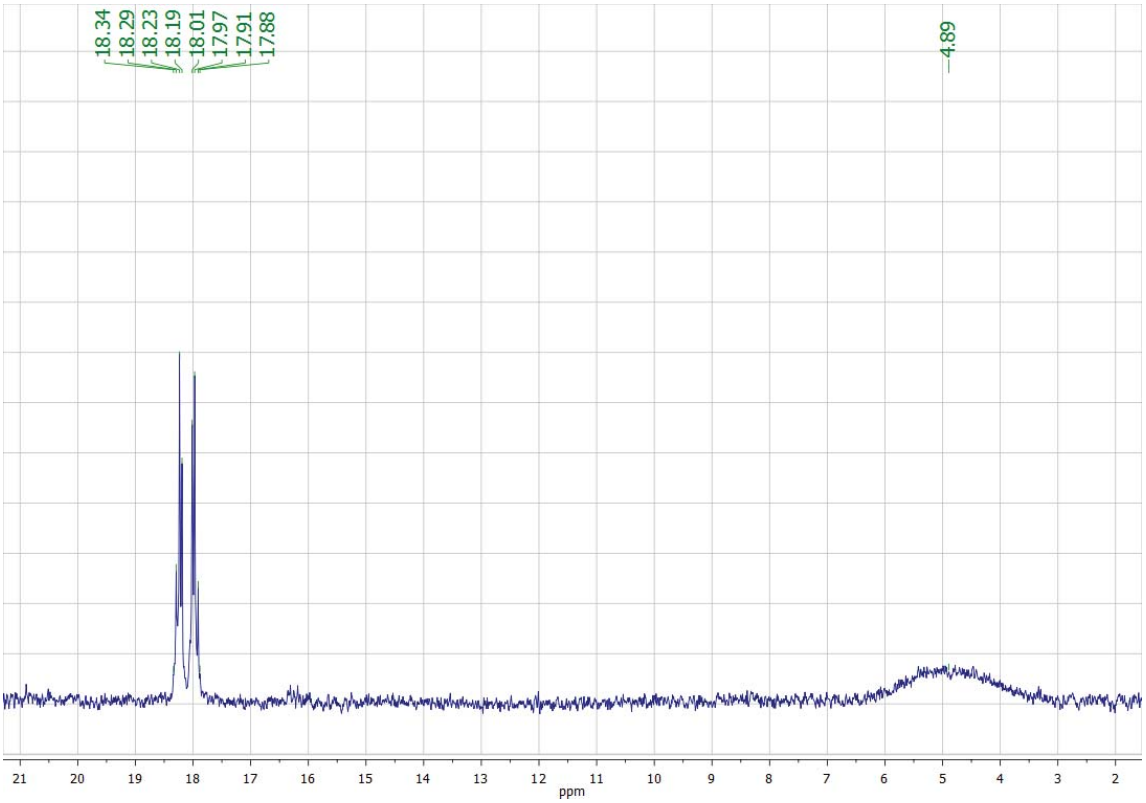


Figure 5 $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in CD_3CN.

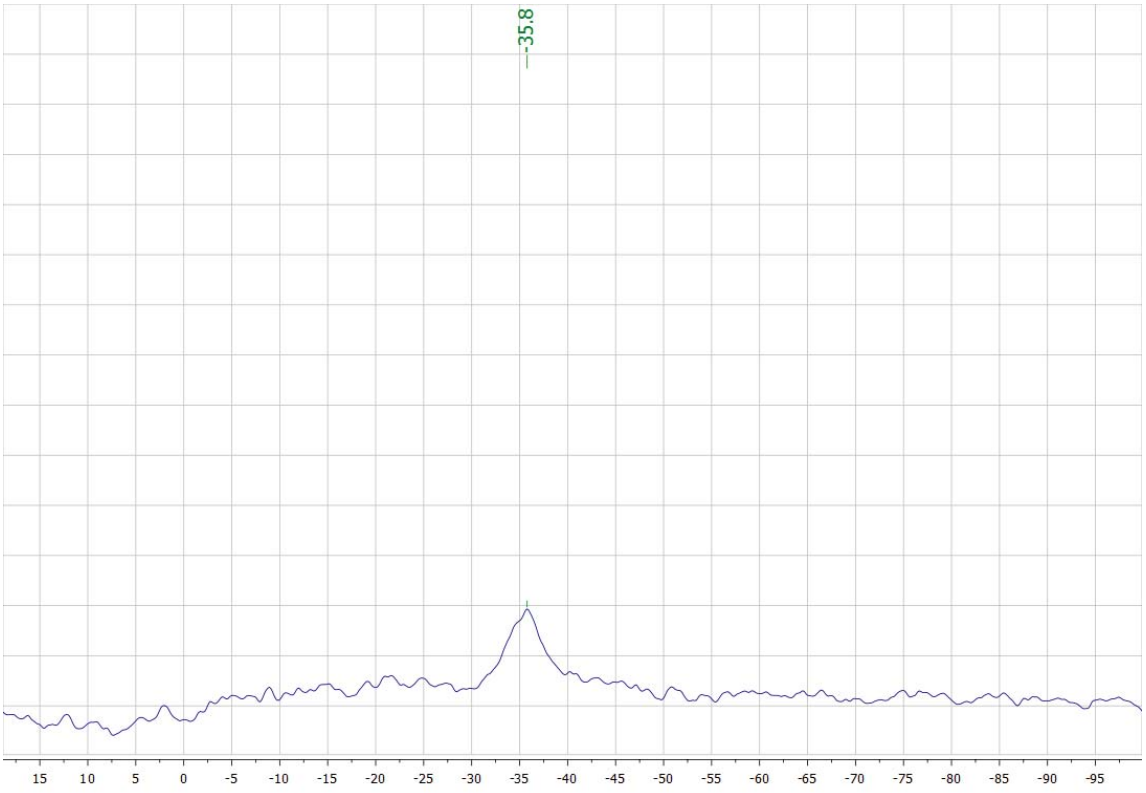


Figure 6 $^{11}B\{^{1}H\}$ NMR spectrum of complex **2** in CD_3CN.

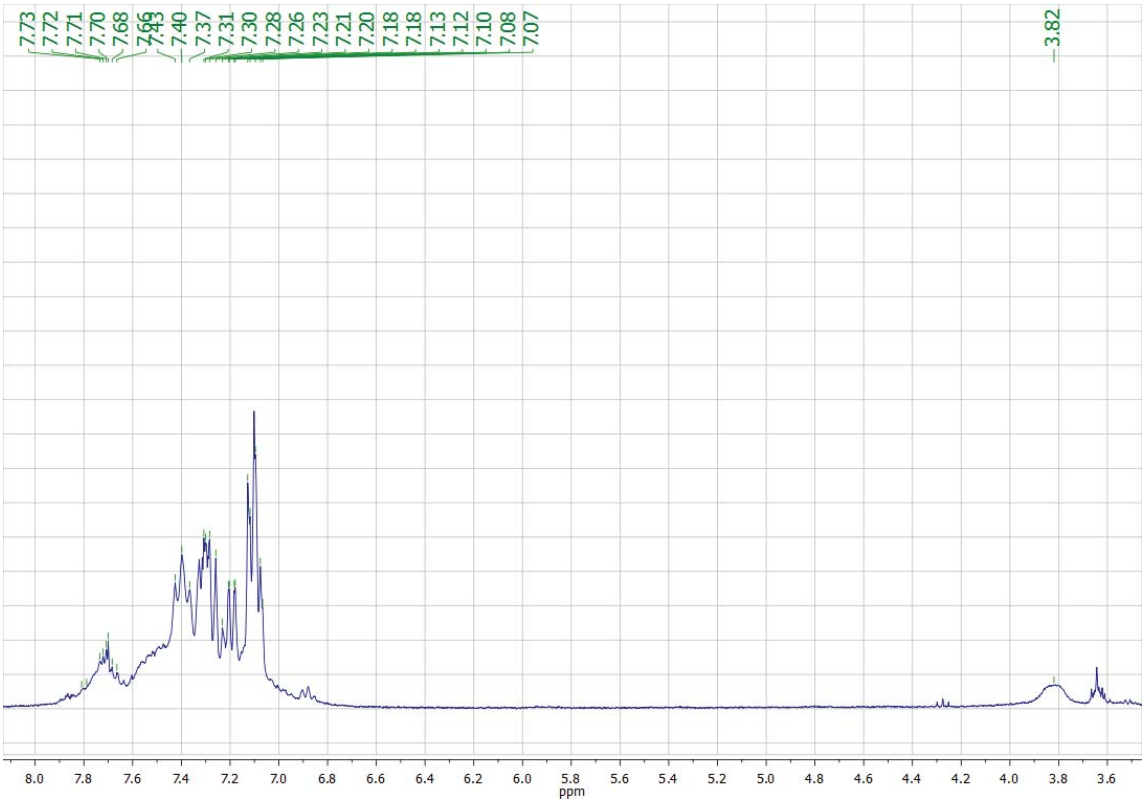


Figure 7 ^{1}H NMR spectrum of complex **2** in CD_3CN.

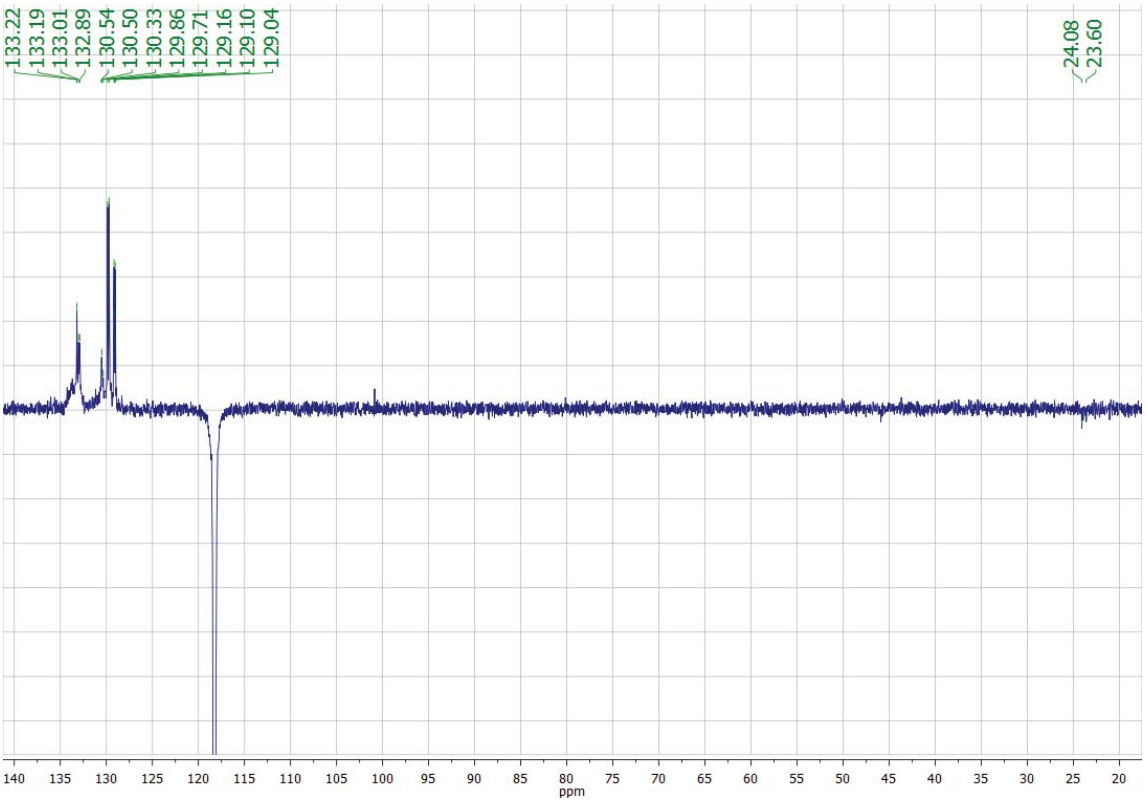


Figure 8 ^{13}C-APT NMR spectrum of complex **2** in CD_3CN.

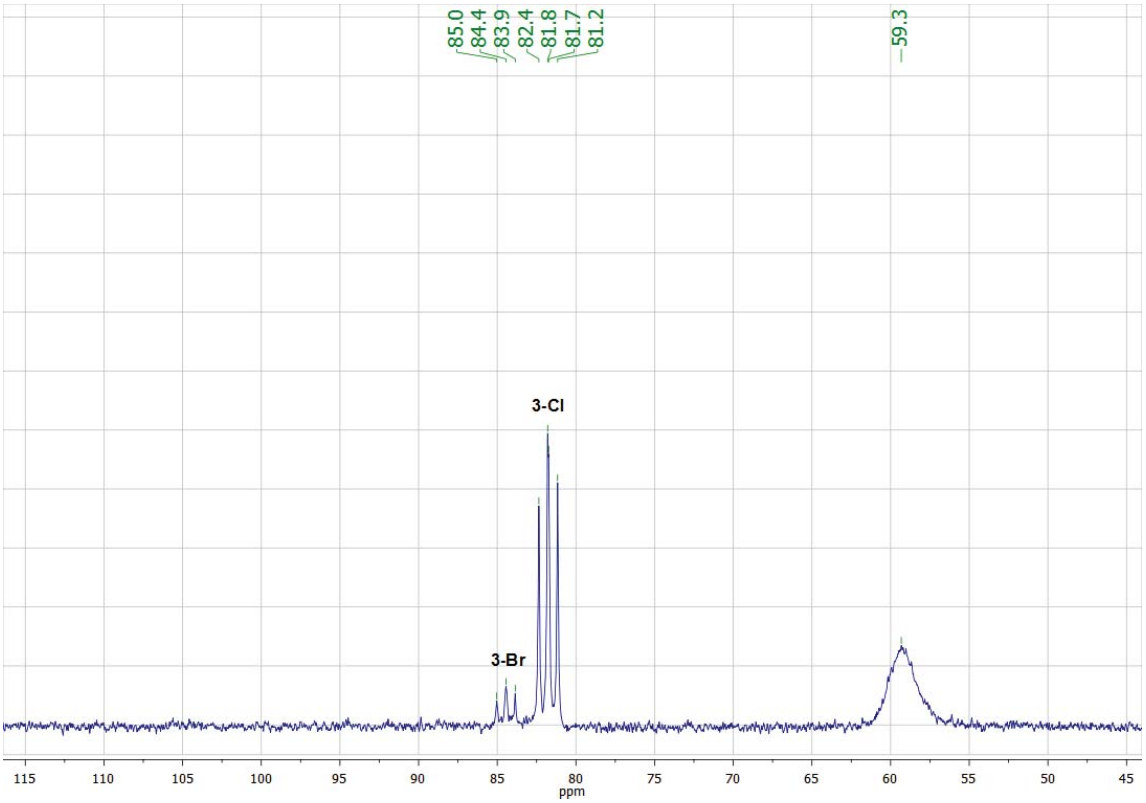


Figure 9 $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** in DMSO-*d*$_6$.

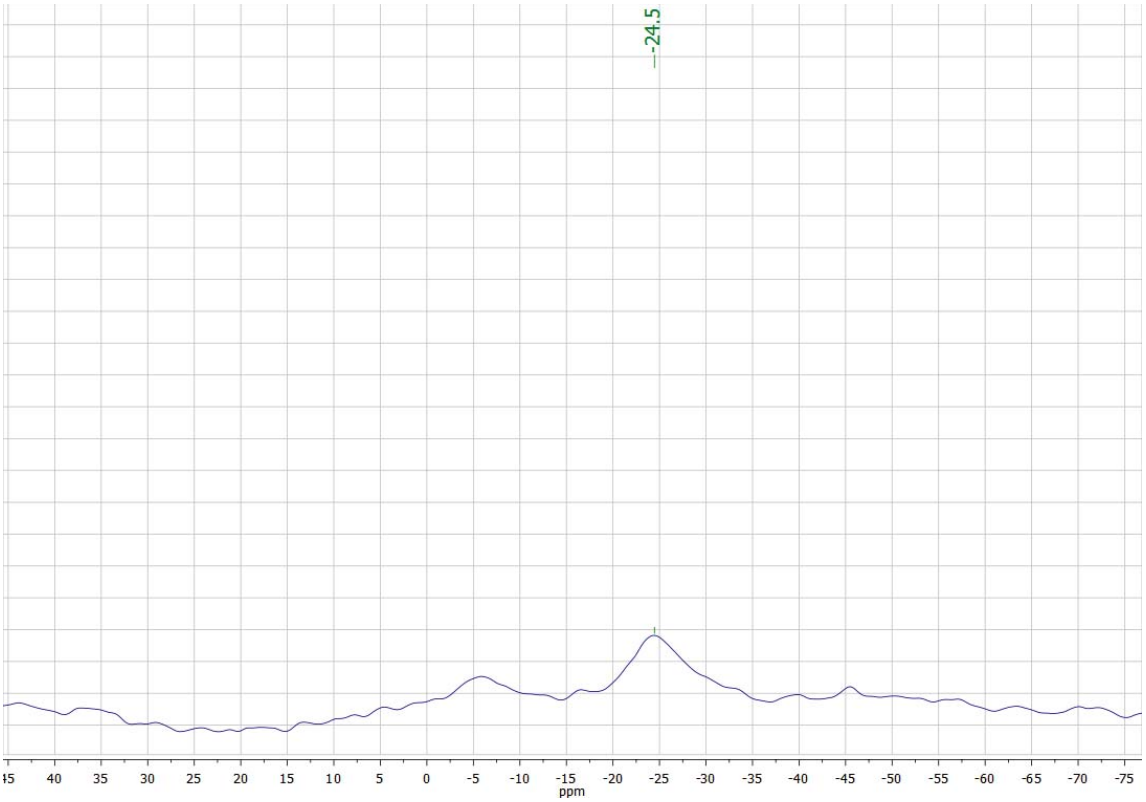


Figure 10 $^{11}B\{^{1}H\}$ NMR spectrum of complex **3** in DMSO-*d*$_6$.

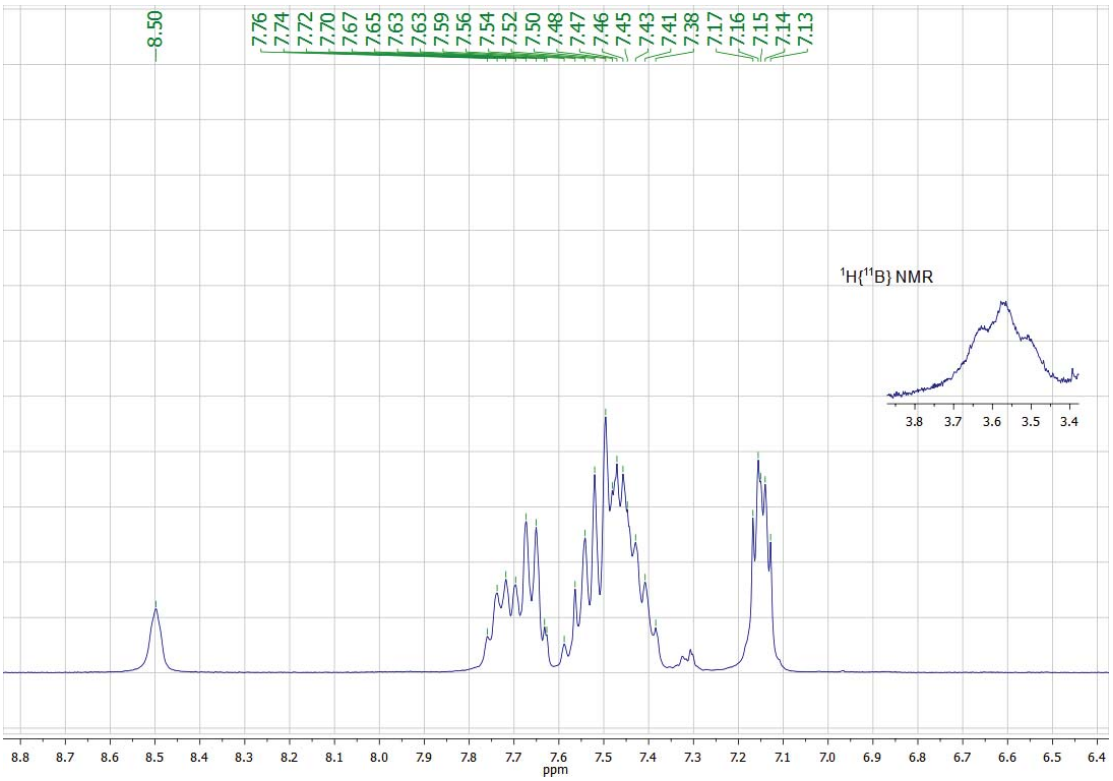


Figure 11 ^{1}H NMR spectrum of complex **3** in DMSO-d_6, with an inset showing the resonance of the boron-bound H-atom in the $^{1}H\{^{11}B\}$NMR spectrum.

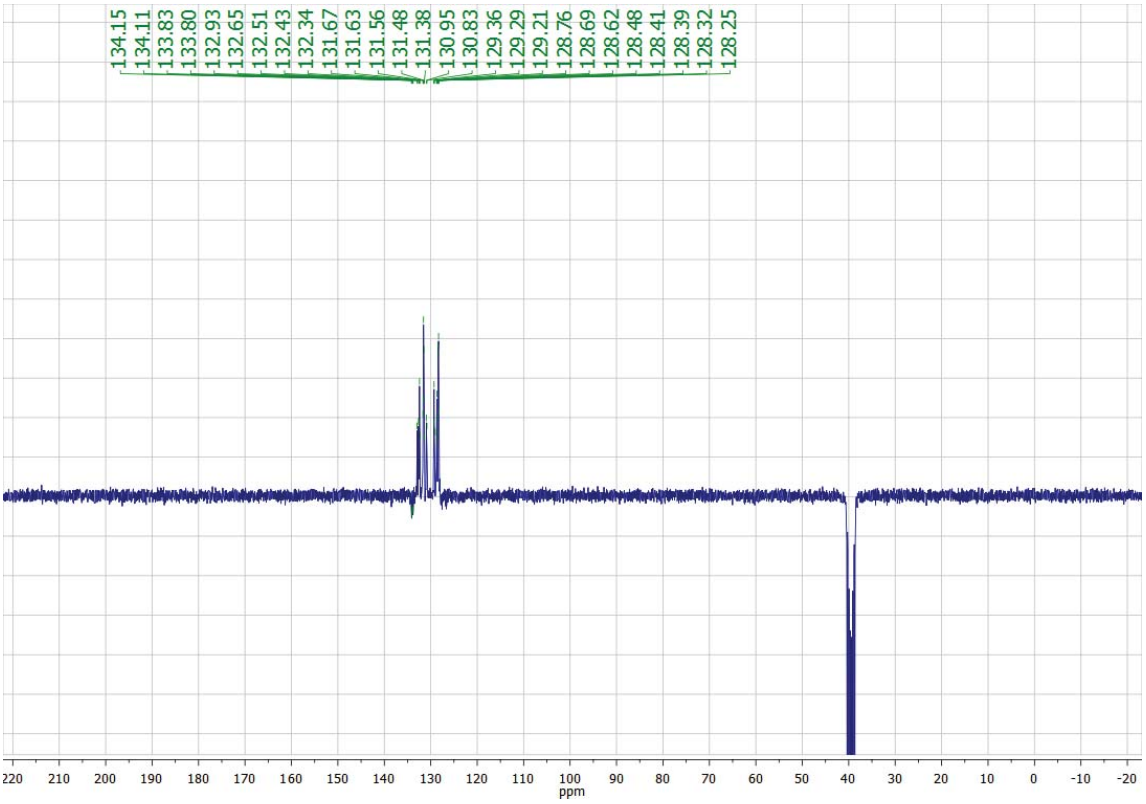


Figure 12 ^{13}C-APT NMR spectrum of complex **3** in DMSO-d_6.

X-Ray Crystallography

The single crystal X-ray diffraction data for the structural analysis of **1** has been collected using graphite-monochromated Mo-K_α-radiation ($\lambda_{MoK\alpha}$ = 0.71073) on the image plate system IPDSII, **2·1^1/$_2$THF** and **[3-Br]Br·1^1/$_4$THF** have been collected using graphite-monochromated Mo-K_α-radiation ($\lambda_{MoK\alpha}$ = 0.71073) on the pixel detector system BRUKER D8-QUEST. The structures were solved by direct methods with SHELXS-97 and refined against F^2 by full-matrix-least-square techniques using SHELXL-97.[2] Based on the crystal descriptions, numerical absorption corrections were applied.[3, 4] Crystallographic data for **1**, **2·1^1/$_2$THF** and **[3-Br]Br·1^1/$_4$THF** have been deposited at Cambridge Crystallographic Data Centre (CCDC 1540277-1540279) and can be obtained free of charge via www.ccdc.cam.ac.uk/. Details of the data collection and the refinement can be found in Table 1. Figure 13 shows the molecular structure of **1** in the solid state.

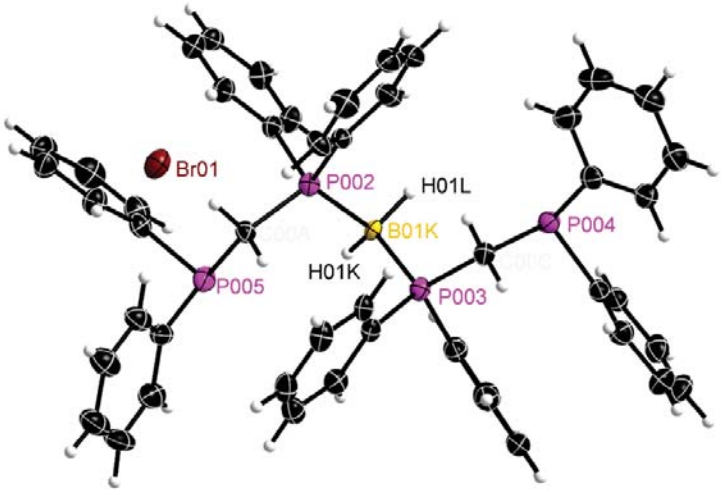


Figure 13 Molecular structure of **1** in the solid state (ellipsoids are drawn at 30 % probability, carbon-bound hydrogen atoms are omitted).

Table 1 Crystallographic data for **1-3**.

Compound	**1**	**2·1^1/$_2$THF**	**[3-Br]Br·1^1/$_4$THF**
Empirical formula	$C_{50}H_{46}BBrP_4$	$C_{52}H_{46}BBrNiO_2P_4 \cdot 1^1/_2C_4H_8O$	$C_{50}H_{45}BBr_2P_4Pd \cdot 1^1/_2C_4H_8O$
Fw/g·mol^{-1}	861.47	1084.35	1136.90
T/K	100(2)	100(2)	110(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a/Å	10.306(2)	16.5199(6)	9.6936(3)
b/Å	13.535(3)	13.4032(6)	24.8956(9)
c/Å	30.934(6)	25.3996(11)	23.1874(10)
α/°	90	90	90
β/°	90	96.7900(10)	91.2630(10)
γ/°	90	90	90
V/Å^3	4315.0(15)	5584.5(4)	5594.4(4)
Z	4	4	4
ρ_{calc}/g·cm^{-3}	1.326	1.290	1.350
$\mu(MoK_\alpha)$/mm^{-1}	1.136	1.220	1.910
F(000)	1784	2248	2304
2θ range/°	2.63-53.44	4.43-53.46	4.51-54.20
Reflections measured	25668	70947	48722
Independent reflections	9087 (R_{Int} = 0.0483)	11812 (R_{Int} = 0.0549)	12151 (R_{Int} = 0.0419)
Ind. reflections (I>2σ(I))	8270	9409	8920
Parameters/Restraints	513/0	624/0	568/39
R_1 *(I>2σ(I))*	0.0350	0.0479	0.0733
wR_2 *(all data)*	0.0840	0.1487	0.2245
GooF (all data)	0.999	0.978	1.047
Max. peak/hole/e·Å^{-3}	0.753/-0.535	2.314/-0.604	1.601/-2.354
CCDC	1540277	1540278	1540279

3. DFT Calculations

DFT calculations were performed with Gaussian 09, Revision C.01.[5] Natural Bond Orbital Analysis was done with NBO 5.9.[6] Grimmes general-gradient approximated and dispersion including B97D functional was used.[7] All geometries were first optimized with the def2-SVP basis set and then reoptimized using the def2-TZVPP basis set.[8, 9] Minima were confirmed with frequency calculations (0 imaginary frequencies). Visualization of molecular orbitals was done with ChemCraft.[10] QTAIM Analysis was performed with AIMAll[11] and pictures were created with Multiwfn.[12] The simplified methyl-substituted complexes **3^{Me}-Br, B^{Me}** and **A^{Me}** were derived by replacing phenyl with methyl groups and subsequent geometry optimization. Bond lengths and selected angles, as well as NBO charges are given in tables 2 and 3.

Table 2 Comparison of experimentally derived bond length and angles of **3-Br** with the results of DFT calculations.

	3-Br (X-Ray)	**3^{Me}-Br** (DFT)	**3^{Me}-Cl** (DFT)
Pd-B	2.129(11)	2.17566	2.17221
Pd-P	2.3031(15)	2.28473	2.28753
Pd-P	2.3041(15)	2.30044	2.29873
P-B	2.005(12)	1.93269	1.92982
P-B	1.929(12)	1.91929	1.91930
P-M-P	170.98(5)	170.37	170.31

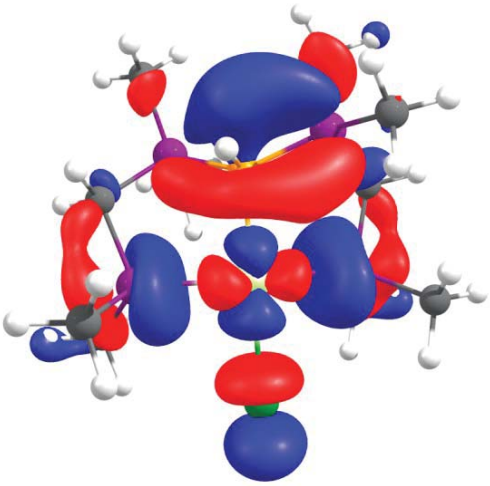
Table 3 Charges from Natural Population Analysis for the complexes $\mathbf{3^{Me}}$**-Br**, $\mathbf{B^{Me}}$ and $\mathbf{A^{Me}}$

	$\mathbf{3^{Me}}$**-Cl**	$\mathbf{B^{Me}}$	$\mathbf{A^{Me}}$
Pd	0.116	0.056	0.296
B	-0.848	0.434	0.902
P(Pd)	1.044	1.022	1.15
P(Pd)	1.049	1.01	1.136
P(B)	1.328		
P(B)	1.330		
C(B)		-0.302	-0.368
C(B)		-0.279	-0.367
H(B)	0.051		
N(B)		-0.428	
C(B)			-0.469

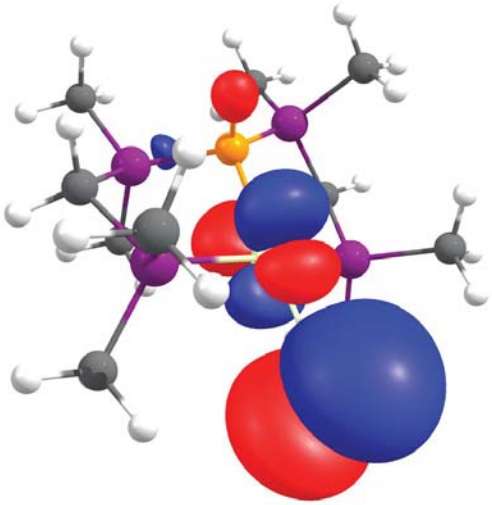
Molecular Orbitals (Molecular Orbitals are shown with isocontour values at 0.03; Pd: pale green, P: violet, Cl: green, Br: dark red, C: grey, B: orange)

Complex **3^{Me}-Cl**

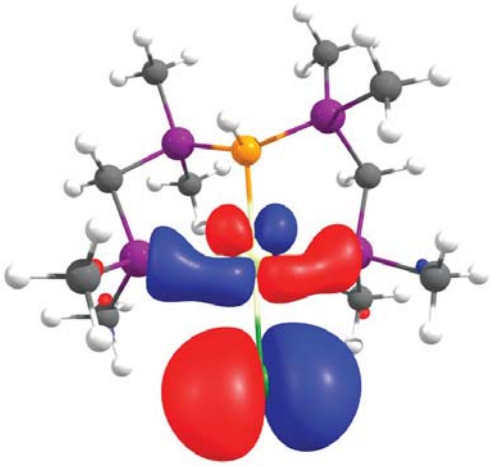
LUMO



HOMO



HOMO-1



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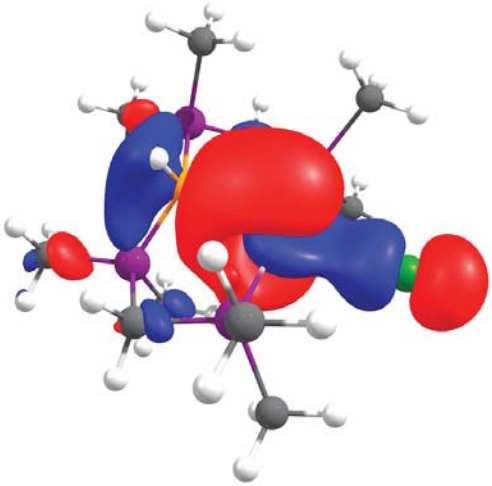
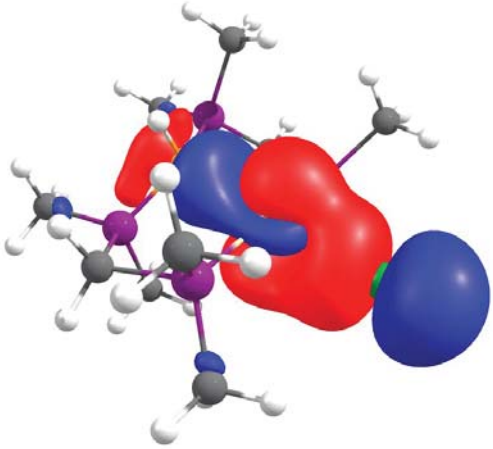


HOMO-3



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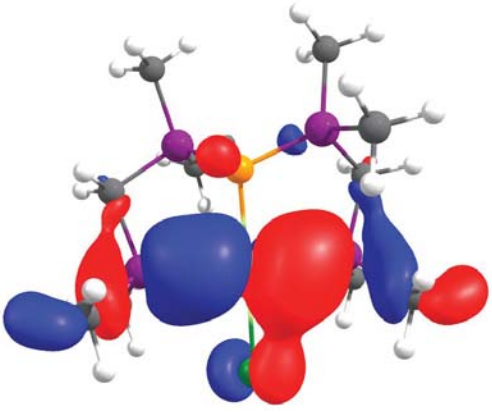

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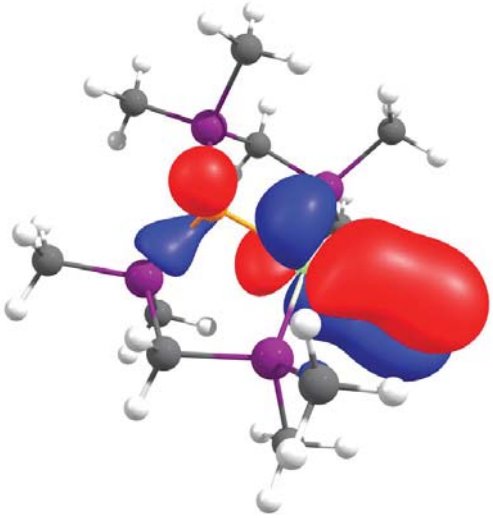

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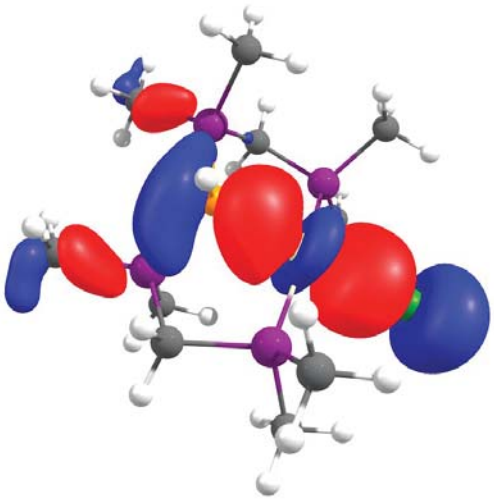

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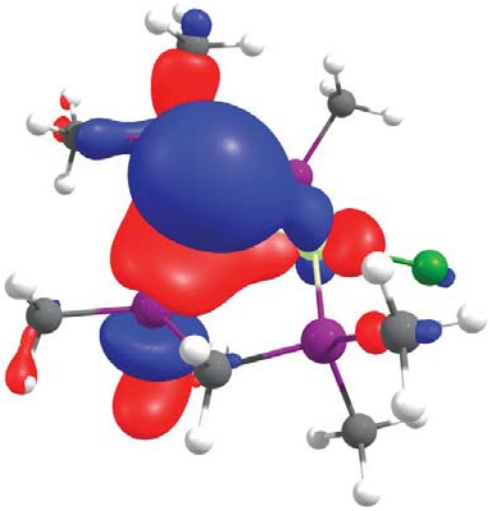

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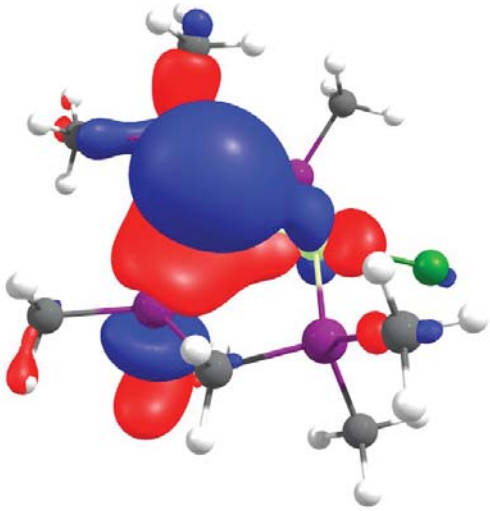
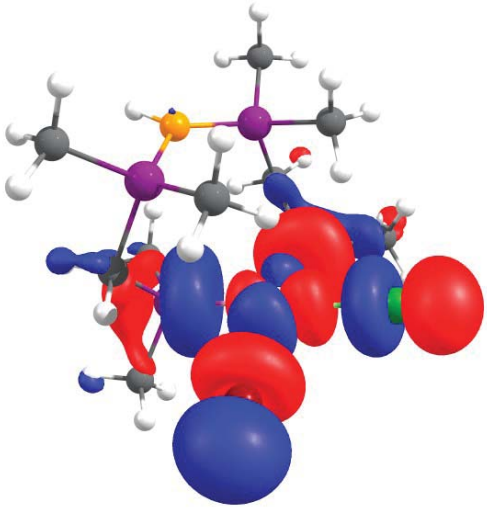


Complex **4^{Me}-Cl/Br**

LUMO



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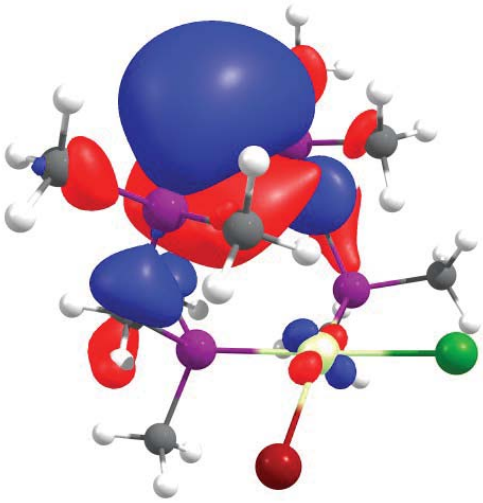

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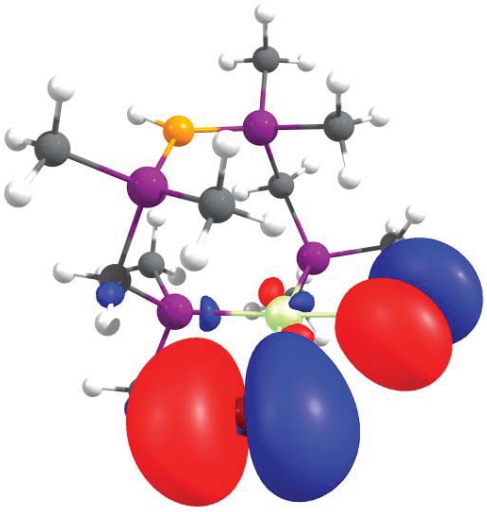

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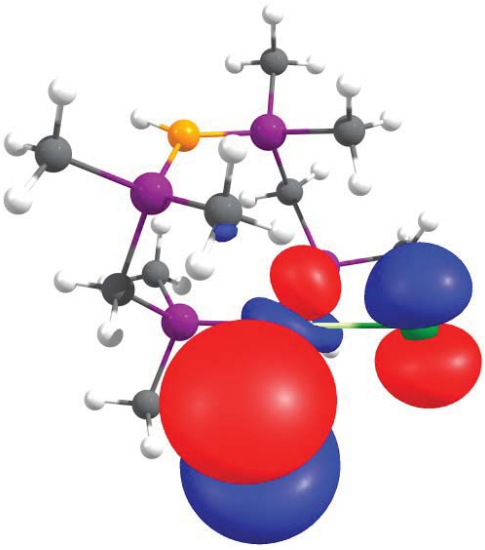

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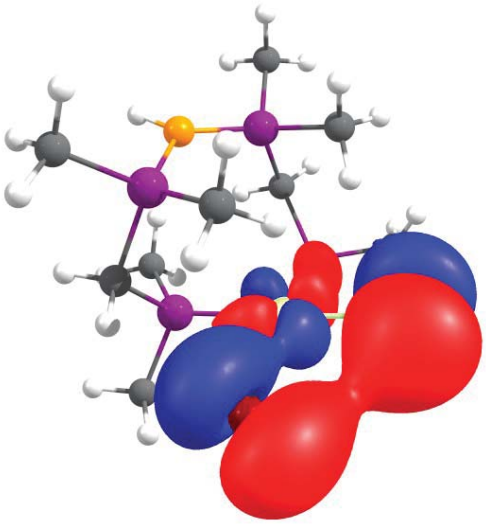

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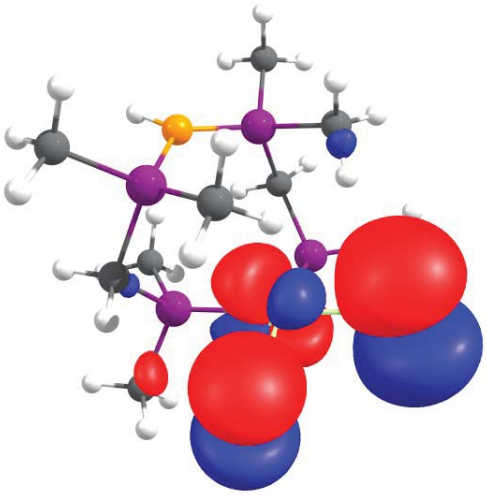

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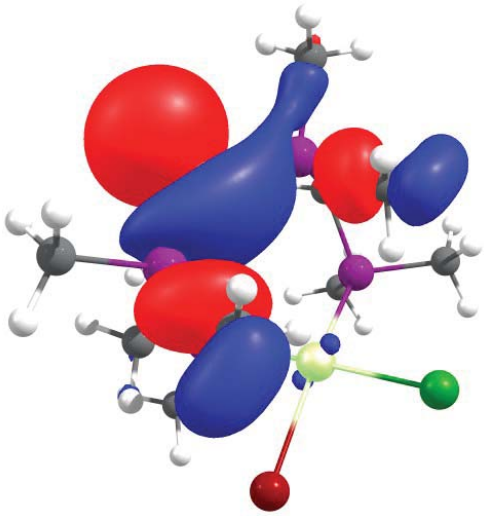

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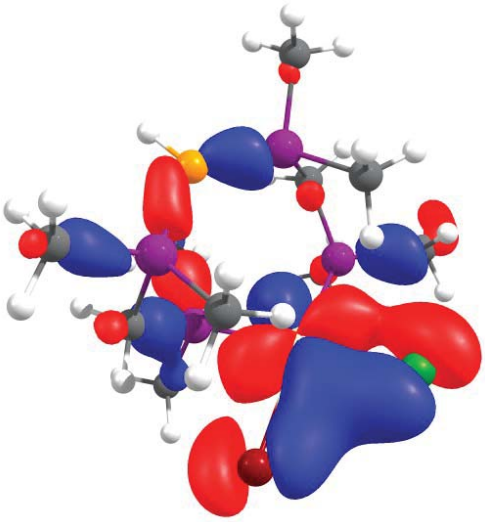

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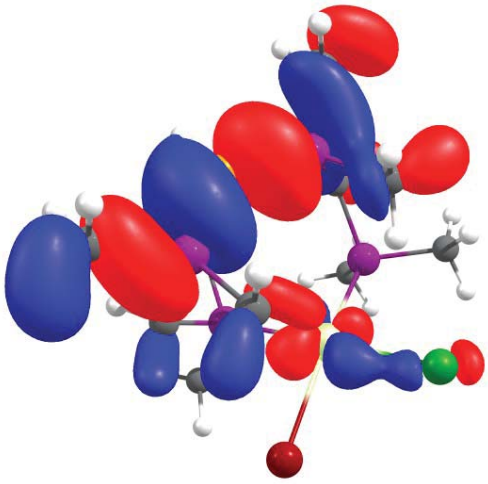
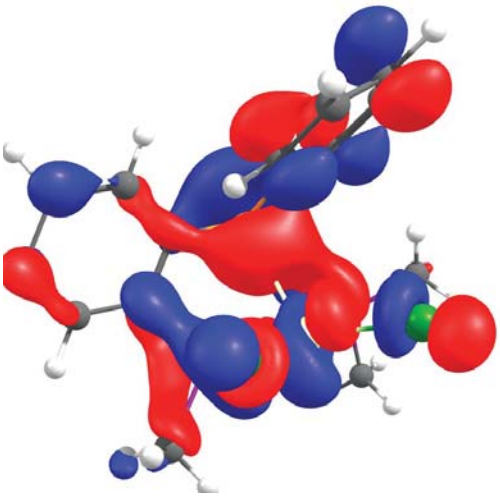


Complex $\mathbf{A}^{\mathbf{Me}}$

LUMO



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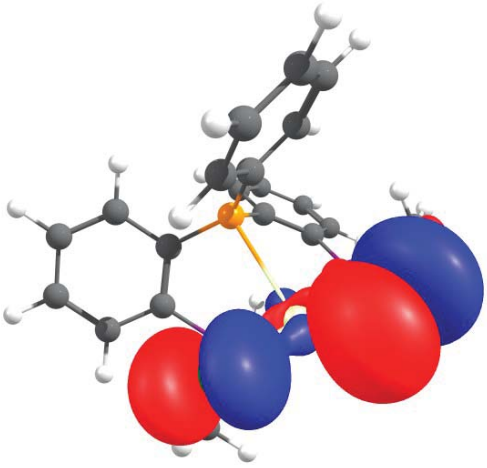

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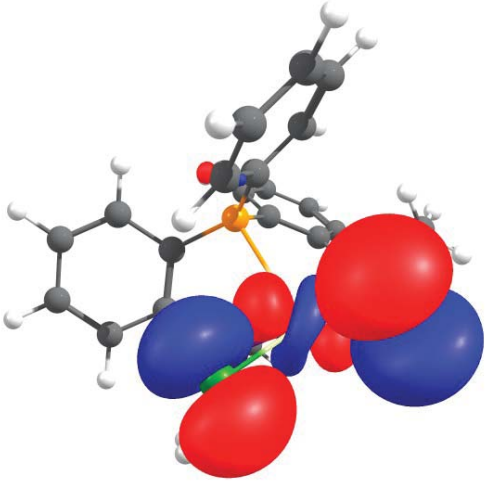

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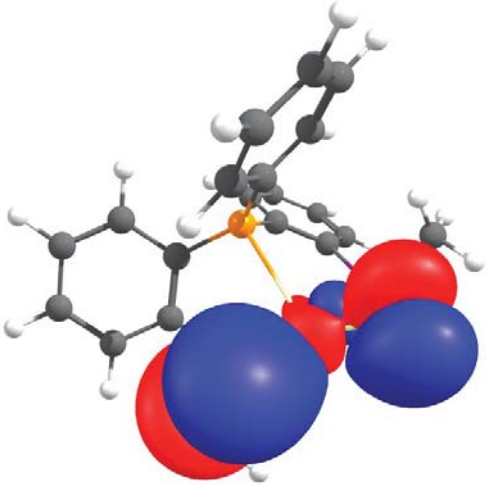

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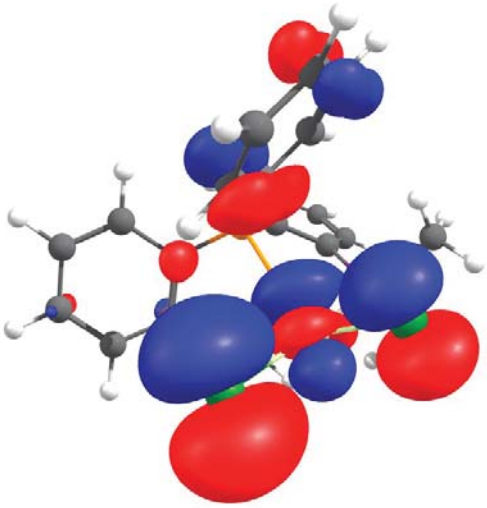

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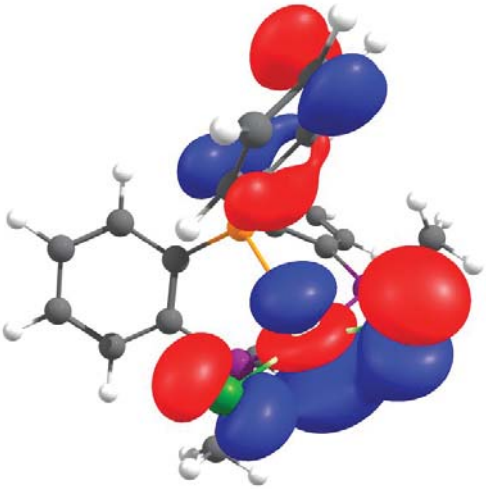

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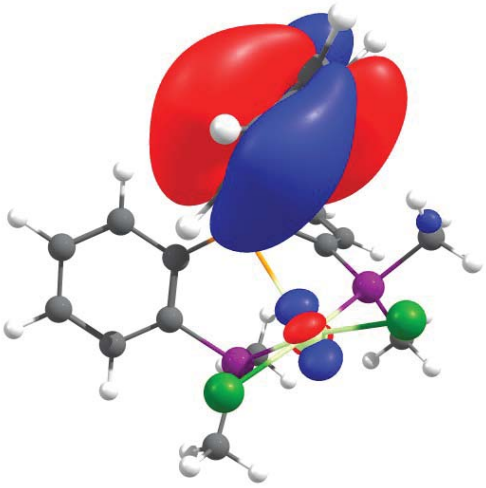

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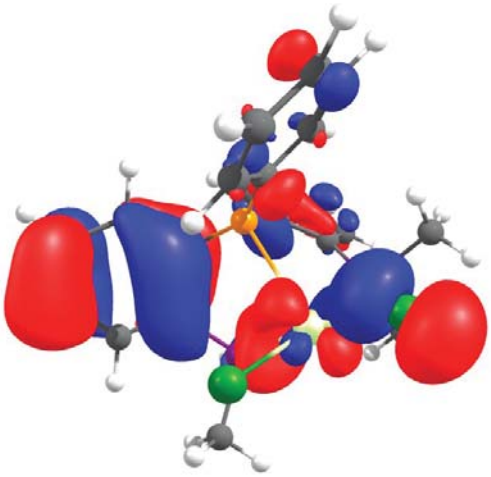

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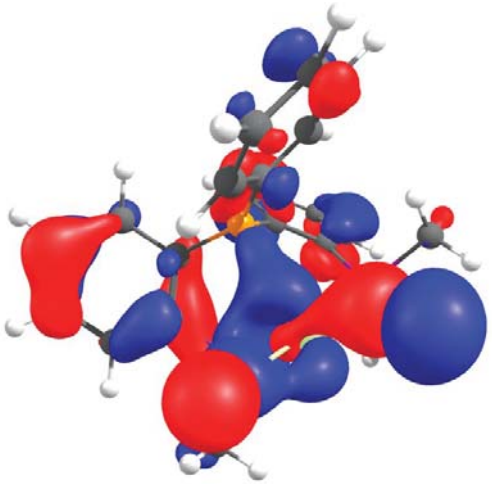
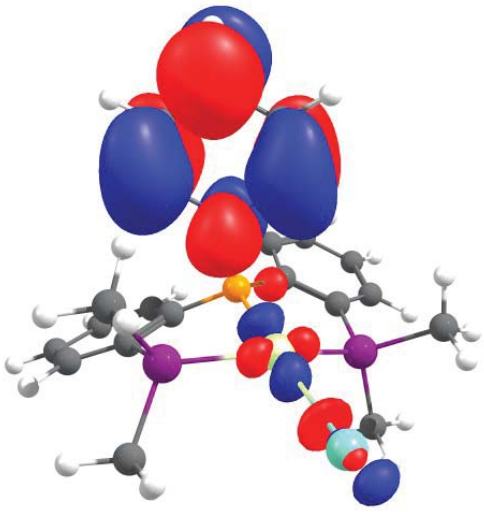


Complex $\mathbf{B^{Me}}$

LUMO



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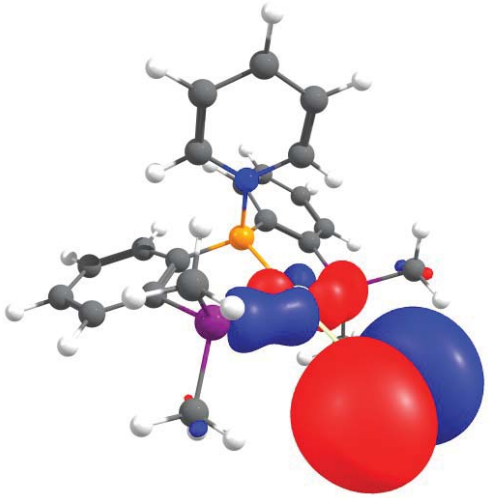

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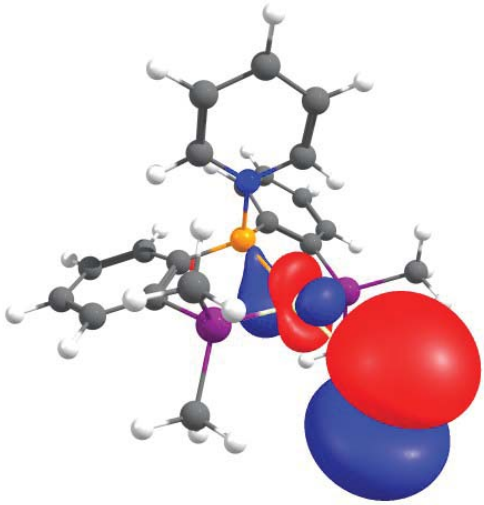

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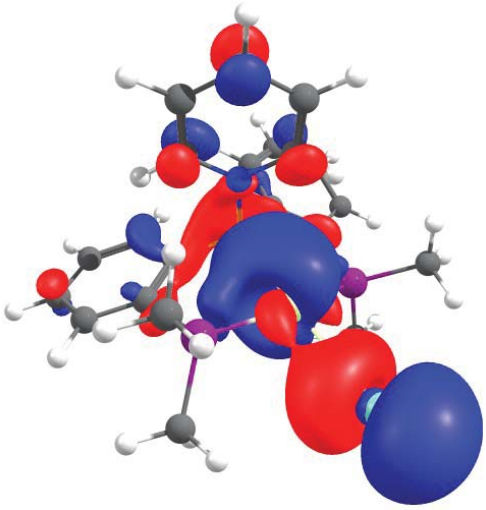

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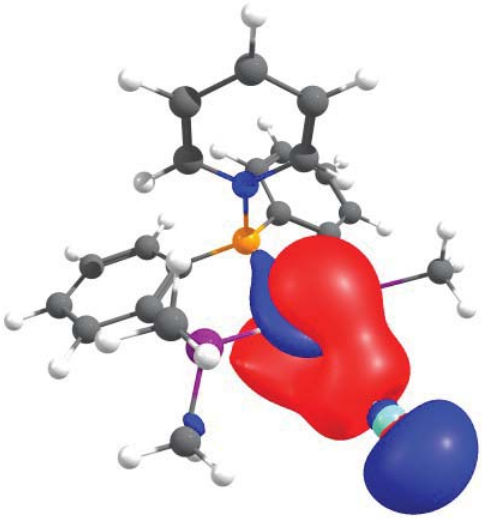

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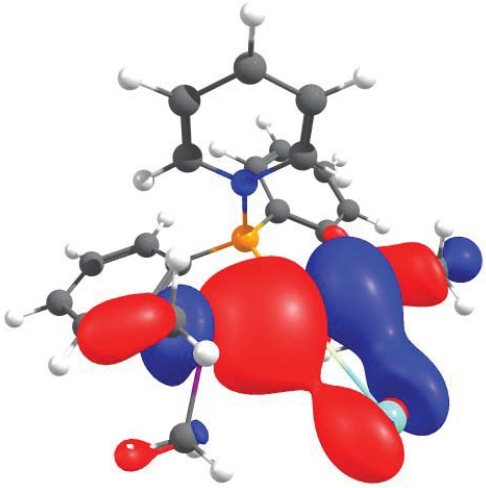

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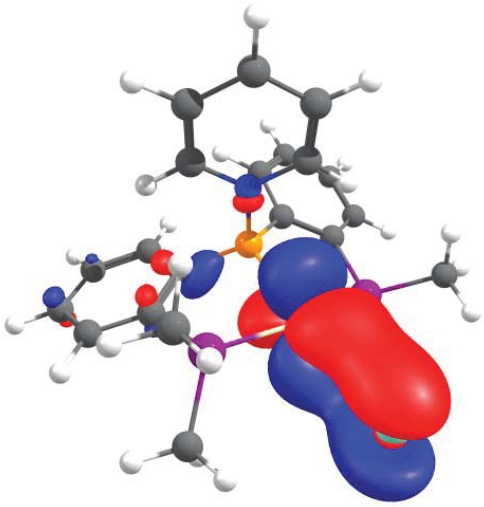

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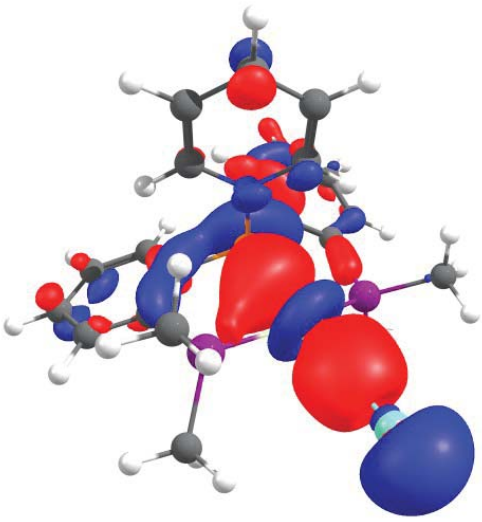

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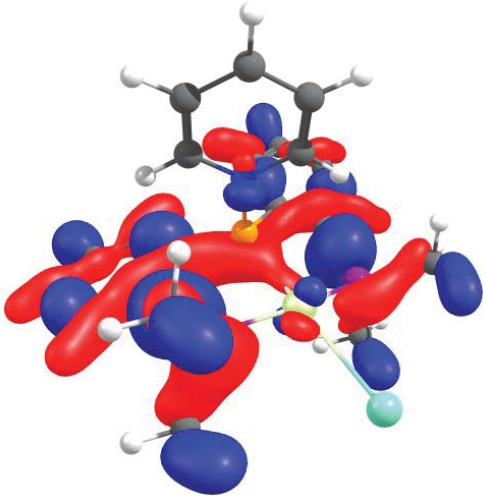
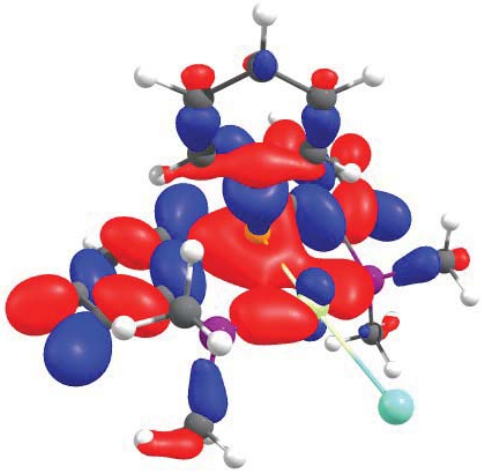


HOMO-17



Quantum Theory of Atoms and Molecules (QTAIM)

Table 4 Comparison of bond critical point data in atomic units of the Pd-B-bond in **3^{Me}-Br**, **3^{Me}-Cl**, **A^{Me}** and **B^{Me}**.

	ρ	$\nabla^2\rho$	$\in$	K_{bcp}	V_{bcp}	H_{bcp}
3^{Me}-Br	0.090626	-0.007863	0.063472	0.038974	-0.075977	-0.037003
3^{Me}-Cl	0.091572	-0.008755	0.069699	0.039596	-0.076998	-0.037402
A^{Me}	0.020004	0.029088	0.606243	0.001389	-0.01005	-0.008661
B^{Me}	0.085673	-0.037487	0.026577	0.038215	-0.067059	-0.028844

Table 5 Bond critical point data in atomic units for **3^{Me}-Cl**.

Bond	ρ	$\nabla^2\rho$	∈	K_{bcp}	V_{bcp}	H_{bcp}
Pd1 - Cl2	0.066421	0.187503	0.04863	0.01266	-0.07217	-0.05951
Pd1 - P3	0.103726	0.138338	0.015354	0.040441	-0.115394	-0.074953
Pd1 - B5	0.091572	-0.008755	0.069699	0.039596	-0.076998	-0.037402
Pd1 - P4	0.101723	0.136356	0.025098	0.038802	-0.111626	-0.072824
B5 - P8	0.129748	-0.214093	0.173496	0.120813	-0.188103	-0.06729
B5 - P9	0.128225	-0.217616	0.119375	0.118576	-0.182748	-0.064172
B5 - H14	0.165223	-0.186382	0.012748	0.176202	-0.305809	-0.129607

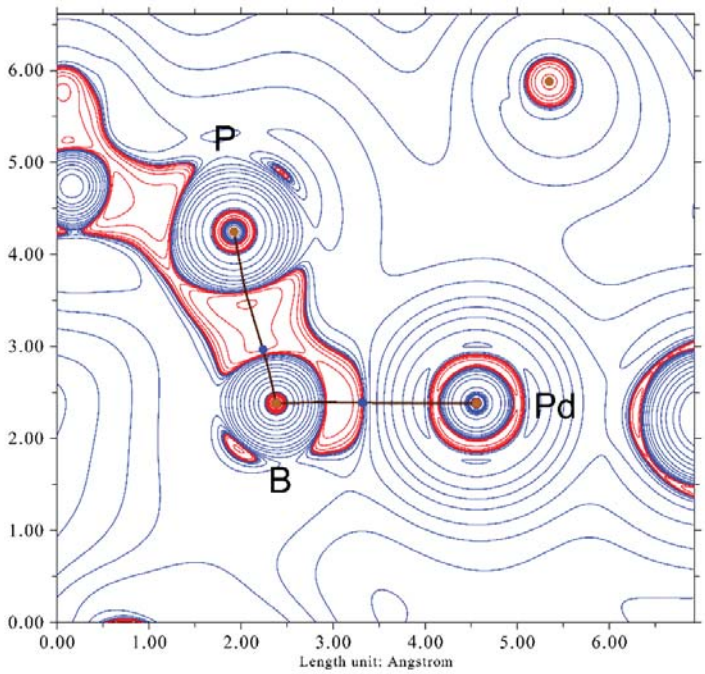


Figure 14 Molecular graph for complex **3^{Me}-Cl** derived from QTAIM analysis with a contour plot of the Laplacian in the P-B-Pd plane. Bond critical points are indicated as blue dots. Positive values of the Laplacian (charge depletion) are depicted as solid blue lines, and negative values (charge accumulation) as red lines.

Table 6 Bond critical point data in atomic units for **3^{Me}-Br**.

Bond	ρ	$\nabla^2\rho$	$\in$	K_{bcp}	V_{bcp}	H_{bcp}
Pd1 - Br2	0.058248	0.137973	0.057183	0.009988	-0.054462	-0.044474
Pd1 - P3	0.103841	0.138583	0.021378	0.04055	-0.115674	-0.075124
Pd1 - P4	0.10133	0.136374	0.027284	0.038493	-0.111015	-0.072522
Pd1 - B5	0.090626	-0.007863	0.063472	0.038974	-0.075977	-0.037003
B5 - P8	0.129942	-0.21554	0.167124	0.121051	-0.188216	-0.067165
B5 - P9	0.127743	-0.217593	0.111006	0.117738	-0.181078	-0.06334
B5 - H14	0.165415	-0.189149	0.016006	0.176547	-0.305807	-0.12926

Table 7 Bond critical point data in atomic units for $\mathbf{A^{Me}}$.

Bond	ρ	$\nabla^2\rho$	∈	K_{bcp}	V_{bcp}	H_{bcp}
Pd1 - Cl2	0.076242	0.19468	0.042741	0.017069	-0.082808	-0.065739
Pd1 - B6	0.020004	0.029088	0.606243	0.001389	-0.01005	-0.008661
Pd1 - Cl3	0.072847	0.190121	0.046568	0.015519	-0.078568	-0.063049
Pd1 - P4	0.111596	0.097202	0.022069	0.048259	-0.120818	-0.072559
Pd1 - P5	0.107013	0.097435	0.029939	0.044407	-0.113174	-0.068767
B6 - C14	0.190579	-0.22681	0.126211	0.211937	-0.367172	-0.155235
B6 - C15	0.180126	-0.225792	0.239159	0.196062	-0.335677	-0.139615

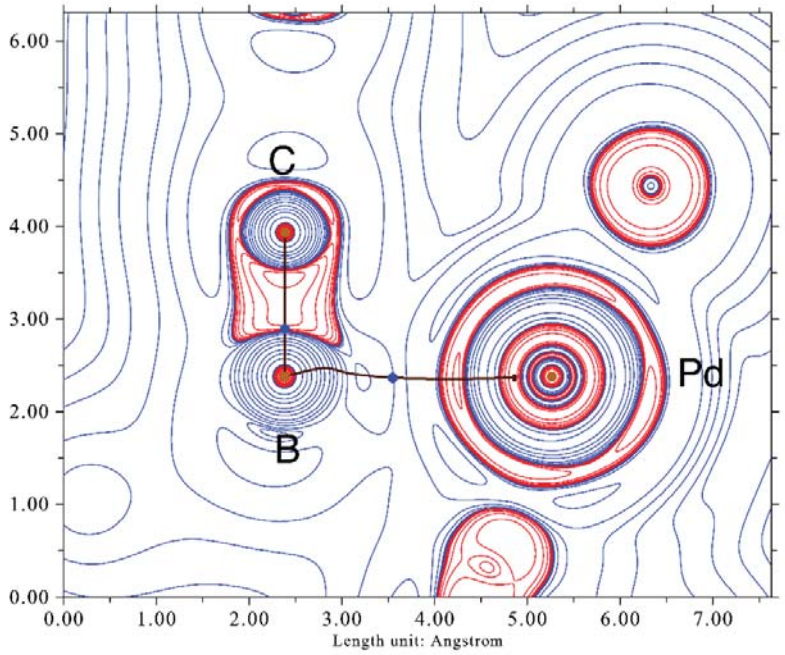


Figure 15 Molecular graph for complex $\mathbf{A^{Me}}$ derived from QTAIM analysis with a contour plot of the Laplacian in the C-B-Pd plane. Bond critical points are indicated as blue dots. Positive values of the Laplacian (charge depletion) are depicted as solid blue lines, and negative values (charge accumulation) as red lines.

Table 8 Bond critical point data in atomic units for $\mathbf{B^{Me}}$.

Bond	ρ	$\nabla^2\rho$	$\in$	K_{bcp}	V_{bcp}	H_{bcp}
Pd1 - B5	0.085673	-0.037487	0.026577	0.038215	-0.067059	-0.028844
Pd1 - P2	0.108143	0.139611	0.020959	0.044832	-0.124568	-0.079736
Pd1 - P3	0.10403	0.144808	0.025885	0.041348	-0.118898	-0.07755
Pd1 - I4	0.045642	0.087695	0.061059	0.007382	-0.036688	-0.029306
B5 - C12	0.164056	-0.188483	0.08083	0.172342	-0.297562	-0.12522
B5 - C14	0.165549	-0.19283	0.073636	0.174529	-0.300851	-0.126322
B5 - N13	0.116784	0.290182	0.059865	0.089818	-0.252181	-0.162363

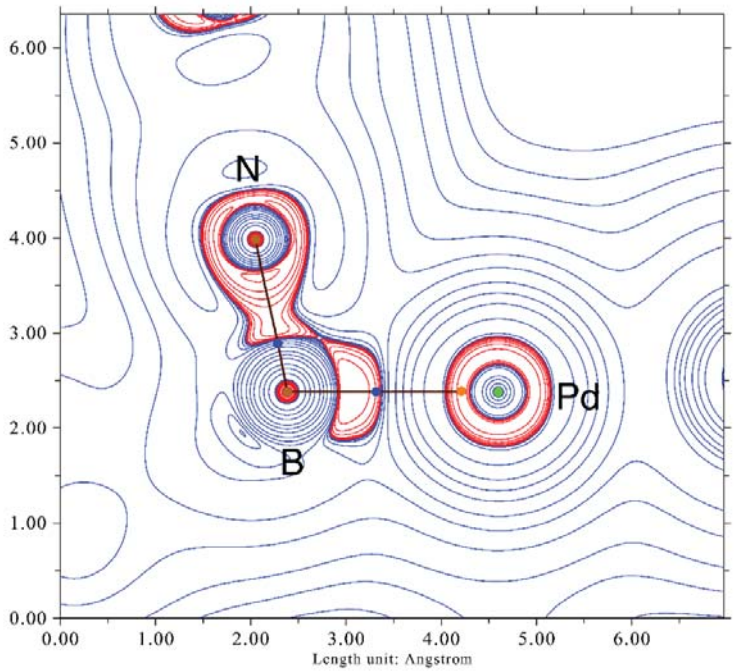


Figure 16 Molecular graph for complex $\mathbf{B^{Me}}$ derived from QTAIM analysis with a contour plot of the Laplacian in the C-B-Pd plane. Bond critical points are indicated as blue dots. Positive values of the Laplacian (charge depletion) are depicted as solid blue lines, and negative values (charge accumulation) as red lines.

Cartesian coordinates of all DFT-optimized geometries

3^{Me}-Br

Pd	0.606577000	-0.127272000	-0.175605000
Br	3.086058000	-0.798753000	0.047385000
P	-0.046345000	-2.240651000	0.396519000
P	1.168859000	2.093162000	-0.388985000
B	-1.441454000	0.455605000	-0.622043000
C	-1.895456000	-2.280717000	0.697725000
C	-0.371783000	3.155193000	-0.255182000
P	-1.693477000	2.061824000	0.397873000
P	-2.648573000	-1.039921000	-0.418159000
H	-2.348010000	-3.274654000	0.589772000
H	-2.056626000	-1.939091000	1.728753000
H	-0.226026000	4.046534000	0.366053000
H	-0.682543000	3.474237000	-1.257445000
H	-1.517254000	0.806530000	-1.784258000
C	-2.835489000	-1.852045000	-2.040536000
H	-3.410594000	-1.194402000	-2.700899000
H	-1.844185000	-2.000275000	-2.478984000
H	-3.348363000	-2.814644000	-1.940037000
C	0.659322000	-2.861447000	1.966244000
H	0.278394000	-3.861494000	2.207505000
H	1.747645000	-2.884845000	1.845028000
H	0.417081000	-2.163789000	2.774716000
C	-1.388791000	1.871740000	2.187529000
H	-2.185112000	1.264108000	2.633189000
H	-0.434076000	1.351181000	2.316409000
H	-1.365072000	2.845164000	2.690415000
C	1.992139000	2.626791000	-1.931771000
H	2.216088000	3.700391000	-1.919975000
H	2.922395000	2.053491000	-2.015065000
H	1.354220000	2.386132000	-2.788550000
C	-4.349663000	-0.734839000	0.191345000
H	-4.924529000	-1.666681000	0.236525000
H	-4.305034000	-0.294282000	1.193499000
H	-4.854163000	-0.035342000	-0.484447000
C	0.286984000	-3.581026000	-0.806275000
H	-0.170847000	-3.352531000	-1.773290000
H	1.373714000	-3.620934000	-0.942315000
H	-0.077481000	-4.549153000	-0.441473000
C	2.244721000	2.706554000	0.959011000
H	1.749991000	2.559551000	1.924791000
H	3.160984000	2.106870000	0.947388000
H	2.479864000	3.769346000	0.822526000
C	-3.271399000	2.984456000	0.251873000
H	-3.216932000	3.947292000	0.772884000
H	-3.486720000	3.157529000	-0.808211000
H	-4.084576000	2.392429000	0.686548000

3^{Me}-Cl

Pd	0.388539000	-0.788850000	-0.184373000
Cl	1.341268000	-3.013909000	0.119741000
P	-1.662582000	-1.591416000	0.426654000
P	2.468770000	0.157512000	-0.431724000
B	-0.419138000	1.180722000	-0.616717000
C	-2.856289000	-0.168537000	0.680799000
C	2.346000000	2.014940000	-0.190745000
P	0.662226000	2.334616000	0.470893000
P	-2.343327000	1.159796000	-0.470844000
H	-3.913975000	-0.438283000	0.566890000
H	-2.702869000	0.199617000	1.703872000
H	3.130697000	2.411167000	0.463826000
H	2.415643000	2.517337000	-1.162943000
H	-0.167323000	1.505325000	-1.761797000
C	-3.015636000	0.704114000	-2.103328000
H	-2.848094000	1.531959000	-2.800278000
H	-2.474166000	-0.172763000	-2.470833000
H	-4.086966000	0.485150000	-2.039562000
C	-1.669615000	-2.469112000	2.031439000
H	-2.674844000	-2.824876000	2.288882000
H	-0.976486000	-3.312126000	1.937582000
H	-1.297396000	-1.801214000	2.815402000
C	0.699097000	1.886029000	2.240219000
H	-0.286439000	2.067778000	2.684606000
H	0.927153000	0.817641000	2.316025000
H	1.446344000	2.477433000	2.781464000
C	3.333725000	-0.066751000	-2.027493000
H	4.311050000	0.430999000	-2.032751000
H	3.467067000	-1.144200000	-2.176869000
H	2.710169000	0.324526000	-2.838020000
C	-3.226730000	2.684731000	0.033028000
H	-4.312382000	2.536247000	0.014354000
H	-2.924344000	2.967649000	1.047510000
H	-2.963470000	3.494218000	-0.657003000
C	-2.498877000	-2.747896000	-0.719840000
H	-2.659418000	-2.276157000	-1.693557000
H	-1.823890000	-3.600422000	-0.856086000
H	-3.456847000	-3.093730000	-0.312796000
C	3.660762000	-0.387768000	0.843109000
H	3.273232000	-0.139017000	1.836598000
H	3.737192000	-1.477964000	0.771742000
H	4.642470000	0.079954000	0.699377000
C	0.400031000	4.149053000	0.421928000
H	1.185306000	4.676085000	0.976058000
H	0.403971000	4.485919000	-0.620405000
H	-0.571137000	4.391253000	0.868486000

4^{Me}-Cl/Br

Pd	0.675871000	-0.921726000	-0.036269000
Cl	0.604954000	-2.262611000	-2.012409000
P	0.853076000	0.632122000	1.612686000
P	-1.280841000	-1.841928000	0.656085000
B	-1.962320000	2.320745000	-0.034006000
C	1.102115000	2.298809000	0.872801000
C	-2.726349000	-0.729565000	0.818654000
P	-2.809064000	0.768882000	-0.414525000
P	-0.220171000	2.696047000	-0.421839000
H	1.026577000	3.049381000	1.672974000
H	2.103547000	2.329823000	0.429112000
H	-3.631784000	-1.345397000	0.728790000
H	-2.719783000	-0.271779000	1.812800000
H	-2.473430000	2.976457000	0.842929000
C	0.065467000	4.511010000	-0.548927000
H	-0.477167000	4.892707000	-1.419465000
H	-0.332884000	4.991696000	0.351603000
H	1.134903000	4.736337000	-0.642423000
C	2.291809000	0.361591000	2.721759000
H	2.374500000	1.192284000	3.434188000
H	2.139403000	-0.573688000	3.273415000
H	3.198038000	0.276392000	2.117591000
C	-2.483812000	-0.054966000	-2.017938000
H	-2.613934000	0.678061000	-2.819240000
H	-1.468921000	-0.464959000	-2.058131000
H	-3.195357000	-0.877985000	-2.156423000
C	-1.062895000	-2.663564000	2.291194000
H	-2.017263000	-3.055829000	2.664046000
H	-0.359067000	-3.492645000	2.154025000
H	-0.639571000	-1.971727000	3.022768000
C	0.437144000	2.004467000	-1.979208000
H	1.516254000	2.173057000	-2.047114000
H	0.269268000	0.926540000	-2.028904000
H	-0.084463000	2.496899000	-2.806640000
C	-0.485835000	0.963360000	2.833651000
H	-1.343518000	1.382934000	2.298472000
H	-0.776261000	0.057721000	3.373443000
H	-0.111794000	1.697598000	3.559430000
C	-1.945039000	-3.220470000	-0.353308000
H	-2.201773000	-2.857991000	-1.350579000
H	-1.172036000	-3.984160000	-0.469517000
H	-2.829662000	-3.633429000	0.148787000
C	-4.635064000	1.010474000	-0.356348000
H	-5.168140000	0.057755000	-0.462741000
H	-4.898313000	1.472113000	0.601895000
H	-4.921680000	1.693396000	-1.161867000
Br	3.046325000	-0.171578000	-0.691255000

A^{Me}

Pd	4.182481000	8.338374000	0.845033000
Cl	2.385814000	8.531725000	-0.701789000
Cl	5.738825000	8.059590000	-0.958232000
P	2.709098000	8.753549000	2.501525000
P	5.978686000	7.785185000	2.131550000
B	5.165659000	10.792192000	1.996207000
C	2.136971000	7.229050000	3.350611000
C	1.144803000	9.595265000	2.061638000
C	3.431865000	9.831544000	3.791681000
C	7.209870000	9.120893000	1.999776000
C	6.778407000	6.220611000	1.611457000
C	5.798030000	7.476812000	3.942346000
C	4.534096000	10.646038000	3.453267000
C	4.413259000	11.598482000	0.900334000
C	6.703529000	10.431547000	1.854789000
H	1.691445000	6.581540000	2.587770000
H	2.985548000	6.713139000	3.807386000
H	1.386117000	7.452406000	4.117566000
H	1.381935000	10.487788000	1.477909000
H	0.537176000	8.928868000	1.444716000
H	0.621091000	9.869540000	2.986459000
C	2.923696000	9.816494000	5.099550000
C	8.583604000	8.865165000	1.953631000
H	6.030422000	5.422232000	1.668889000
H	7.117965000	6.317060000	0.578828000
H	7.610907000	5.982272000	2.284486000
H	5.350093000	8.331860000	4.449756000
H	5.175181000	6.588802000	4.099928000
H	6.794045000	7.287511000	4.360343000
C	5.109834000	11.419748000	4.479503000
C	4.853003000	11.572189000	-0.442445000
C	3.252902000	12.346325000	1.202191000
C	7.630074000	11.469176000	1.656952000
H	2.082214000	9.175654000	5.352356000
C	3.502686000	10.606244000	6.094147000
C	9.485967000	9.918639000	1.776919000
H	8.956381000	7.846717000	2.027756000
C	4.602175000	11.410193000	5.780253000
H	5.978093000	12.035601000	4.252221000
H	5.719698000	10.971128000	-0.701142000
C	4.149436000	12.240053000	-1.441079000
C	2.556670000	13.032374000	0.208692000
H	2.902308000	12.386116000	2.231468000
H	7.264828000	12.483845000	1.511721000
C	9.006780000	11.220883000	1.625963000
H	3.106827000	10.584041000	7.106554000
H	10.553570000	9.717196000	1.734154000
H	5.070391000	12.019151000	6.550316000
H	4.481407000	12.176291000	-2.474265000
C	3.000525000	12.970814000	-1.117620000

H	1.666413000	13.605508000	0.458867000
H	9.701972000	12.041505000	1.463440000
H	2.446633000	13.486474000	-1.899131000

B^{Me}

Pd	6.662778000	5.352965000	-0.045676000
P	5.513447000	3.426855000	0.224020000
P	7.163134000	7.432768000	-0.825825000
I	6.977295000	5.859125000	2.700391000
B	6.520176000	4.887162000	-2.209419000
C	3.851203000	3.686796000	0.968211000
C	6.197977000	2.061929000	1.254347000
C	5.228709000	2.706600000	-1.431268000
C	6.364567000	7.484413000	-2.479143000
C	6.407047000	8.814289000	0.119704000
C	8.898721000	8.015358000	-1.056569000
C	5.772160000	3.466350000	-2.487268000
N	8.092024000	4.640614000	-2.598706000
C	5.986470000	6.213729000	-2.982267000
H	3.995220000	4.097811000	1.973730000
H	3.303341000	4.415098000	0.362049000
H	3.285616000	2.747512000	1.019802000
H	7.153088000	1.728188000	0.834327000
H	6.379921000	2.467131000	2.256565000
H	5.509660000	1.209322000	1.312103000
C	4.587252000	1.479666000	-1.659537000
C	6.043030000	8.667895000	-3.152436000
H	5.329133000	8.640235000	0.193920000
H	6.827924000	8.793998000	1.131241000
H	6.595725000	9.786173000	-0.353807000
H	9.365403000	8.087544000	-0.067193000
H	9.454955000	7.285603000	-1.653733000
H	8.932864000	8.994449000	-1.551802000
C	5.684302000	2.914462000	-3.781662000
C	8.760852000	3.635508000	-1.972806000
C	8.767500000	5.395432000	-3.498235000
C	5.223730000	6.200128000	-4.163768000
C	4.490384000	0.973404000	-2.955951000
H	4.173752000	0.913905000	-0.826229000
H	6.343776000	9.630694000	-2.742777000
C	5.294754000	8.620119000	-4.333308000
H	6.131331000	3.446109000	-4.620162000
C	5.052293000	1.691555000	-4.018721000
H	8.172604000	3.069916000	-1.260637000
C	10.098820000	3.378339000	-2.205298000
C	10.118140000	5.195703000	-3.768714000
H	8.192022000	6.171735000	-3.986684000
C	4.871766000	7.382629000	-4.825931000
H	4.882714000	5.250926000	-4.568386000
H	3.995050000	0.022195000	-3.137648000
H	5.023079000	9.539473000	-4.847257000

H	5.000206000	1.292440000	-5.029903000
H	10.581570000	2.567591000	-1.668892000
C	10.806672000	4.176744000	-3.114771000
H	10.610031000	5.839038000	-4.492053000
H	4.263866000	7.337637000	-5.727563000
H	11.862349000	4.004241000	-3.303802000

Literature

1. K. Sommer, *Z. Anorg. Allg. Chem.*, 1970, **376**, 37-43.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.
3. X.-R. 1.01, *Data Reduction Program, Stoe & Cie GmbH, Darmstadt, Germany, 2001*.
4. X.-S. 1.06, *Crystal Optimization for Numerical Absorption Correction Program, Stoe & Cie GmbH, Darmstadt, 1999*.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision C.01, Gaussian Inc. Wallingford CT 2009*.
6. E. D. Glendening, J.K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, *(Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2012)*, NBO 5.9, **www.chem.wisc.edu/~nbo5**.
7. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
8. A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
9. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
10. *Chemcraft version 1.8*, **www.chemcraftprog.com**.
11. Todd A. Keith and O. P. K. TK Gristmill Software, USA, *AIMAll (Version 17.01.25)*, 2017, **www.aim.tkgristmill.com**.
12. Tian Lu and F. Chen, *J. Comp. Chem.*, 2012, **33**, 580-592.