Electronic Supplementary Information for Dalton Transactions

Synthesis, structure and coordination of the ambiphilic ligand (2-picolyl)BCy_2

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SUPPLEMENTARY INFORMATION

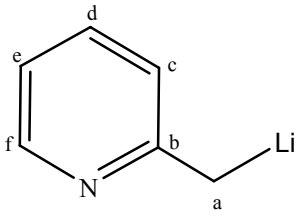
Contents

Experimental Section

General Procedures. All reactions were performed using standard Schlenk techniques under an Argon atmosphere. NMR spectra were recorded on Bruker AC 200, Avance 400, and Avance 500 spectrometers. ^{11}B, ^{1}H and ^{13}C chemical shifts are expressed with a positive sign, in parts per million, relative to external $BF_3.Et_2O$ and residual ^{1}H and ^{13}C solvent signals. Unless otherwise stated, NMR was recorded at 293 K. Mass spectra were recorded on a TSQ 7000 from ThermoQuest.

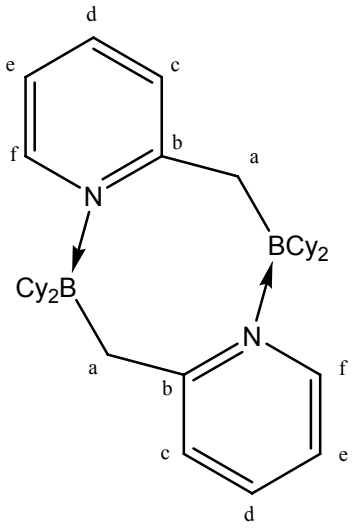
Materials and Methods. CH_2Cl_2 and pentane were dried over CaH_2 and diethylether over sodium and distilled prior to use. All organic reagents were obtained from commercial sources and used as received, except 2-picoline which was dried over CaH_2 and distilled prior to use. $RuCl_3$ was purchased from Strem and $[RuCl_2(p\text{-Cymene})]_2$ was prepared according to a literature procedure.[1]

Preparation of 2-picolyllithium: This is a procedure derived from a previously reported synthesis.[2] A solution of (3.05 mL, 31.0 mmol) of 2-picoline in diethylether (20 mL) was cooled to – 20 °C, n-butyllithium (1.6 M in hexane, 19 mL, 30.4 mmol) was then added dropwise. Before the end of the addition a yellow solid precipitates. The solution was filtered and the precipitate washed with pentane (3×10 mL) and dried in vacuo. Yield [1.47 g (48%)].

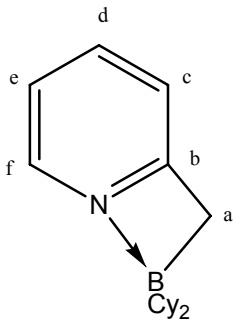


^{1}H-NMR (200.1 MHz, THF-D_8): δ = 6.74 (d, $^{3}J_{H,H}$ = 6 Hz, 1H, H_f), 5.90 (t, $^{3}J_{H,H}$ = 6 Hz, 1H, H_d), 5.51 (d, $^{3}J_{H,H}$ = 6 Hz, 1H, H_c), 4.65 (t, $^{3}J_{H,H}$ = 6 Hz, 1H, H_e), 2.52 (s, 1 H, H_a), 2.41 (s, 1 H, H_a).

Preparation of 2-picolylBCy$_2$. To a suspension of 2-picolyllithium (510 mg, 5.0 mmol) in pentane (20 mL) was added chlorodicyclohexylborane (1 M in hexane, 5.0 ml, 5.0 mmol) dropwise. During the addition a white solid precipitated. After the addition the solution was stirred for two hours after which the solid was isolated and extracted by dichloromethane. The solvent was removed under vacuum and the resulting solid was washed with pentane (3×10 mL) and dried in vacuo. Yield : 808 mg (60%). Crystals suitable for X-ray crystallography were obtained from a CH_2Cl_2 solution at 4°C.



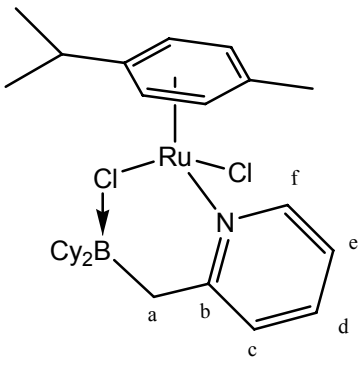
1 (dimeric head-to-tail form): ^{1}H-NMR (500.3 MHz, CD_2Cl_2) δ = 8.29 (d, $^3J_{H,H}$ = 5 Hz, 2H, H_f), 7.59 (t, $^3J_{H,H}$ = 5 Hz, 2H, H_d), 7.47 (d, $^3J_{H,H}$ = 5 Hz, 2H, H_c), 7.09 (t, $^3J_{H,H}$ = 5 Hz, 2H, H_e), 3.62 (d, $^2J_{H,H}$ = 13 Hz, 2H, H_a), 2.00 (d, $^2J_{H,H}$ = 13 Hz, 2H, H_a), 0.4-1.8 (m, 44H, H_{Cy}). ^{13}C{^{1}H}-NMR (125.8 MHz, CD_2Cl_2) δ = 172.15 (s, C_b), 145.73 (s, C_f), 136.39 (s, C_d), 129.78 (s, C_c), 118.70 (s, C_e), 37.38 (s broad, BCH$_{cy}$), 36.46 (s broad, C_a), 34.39 (s broad, BCH$_{cy}$), 31.34 (s, CH$_{2cy}$), 30.88 (s, CH$_{2cy}$), 30.05 (s, CH$_{2cy}$), 29.59 (s, CH$_{2cy}$), 29.39 (s, CH$_{2cy}$), 29.29 (s, CH$_{2cy}$), 29.07 (s, CH$_{2cy}$), 28.70 (s, CH$_{2cy}$), 27.93 (s, CH$_{2cy}$), 27.88 (s, CH$_{2cy}$). ^{11}B{^{1}H}-NMR (160.5 MHz, CD_2Cl_2) δ = 3.63.



2 (monomeric closed form): ^{1}H-NMR (500.3 MHz, CD_2Cl_2) δ = 8.11 (d, $^3J_{H,H}$ = 5 Hz, 1H, H_f), 7.81 (t, $^3J_{H,H}$ = 5 Hz, 1H, H_d), 7.27 (d, $^3J_{H,H}$ = 5 Hz, 1H, H_c), 7.26 (t, $^3J_{H,H}$ = 5 Hz, 1H, H_e), 1.76 (s, 2H, H_a), 0.4-1.8 (m, 22H, H_{Cy}). ^{13}C{^{1}H}-NMR (125.8 MHz, CD_2Cl_2) δ = 167.25 (s, C_b), 142.26 (s, C_f), 138.48, (s, C_d), 123.94 (s, C_c), 120.90 (s, C_e), 18.51 (s broad, C_a). In order to assign the signals for the cyclohexyl groups in ^{13}C NMR, it was necessary to record a spectrum at a temperature at which **2** predominated: ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6, 343K)

δ = 167.48 (s, C_b), 142.37 (s, C_f), 137.54 (s, C_d), 123.49 (s, C_c), 120.14(s, C_e), 30.01 (s, CH_{2Cy}), 28.90 (s, CH_{2Cy}), 27.95 (s, CH_{2Cy}), 19.54 (s broad, C_a). BCH_{cy} are not observed. $^{11}B\{^1H\}$-NMR (160.5 MHz, CD_2Cl_2) δ = 14.27. MS (DCI, NH_3) *m/z* (%) : 270 $[M + H]^+$.

Preparation of [$RuCl_2$(*p*-Cymene)(2-picolylBCy_2)] (3). [$RuCl_2$(*p*-Cymene)]$_2$ (300 mg, 0.49 mmol) and 2-picolylBCy_2 (236.8 mg, 0.88 mmol, 0.9 eq) were stirred in CH_2Cl_2 at RT for 50 minutes. The solution was concentrated under vacuum to approximatively 3 mL and pentane (ca 12 mL) was added until the unreacted [$RuCl_2$(*p*-Cymene)]$_2$ precipitated as a red solid. The solution was then filtered, concentrated to approximately 3 mL and pentane (ca 10 mL) was added to afford [$RuCl_2$(*p*-Cymene)(2-picolylBCy_2)] as an orange solid. The precipitate was isolated and dried in vacuo. Yield: 232 mg (46%) Crystals suitable for X-ray crystallography were obtained from a CH_2Cl_2/pentane mixture at 4°C.



^{1}H-NMR (500.3 MHz, CD_2Cl_2, 253 K): δ = 8.87 (d, $^3J_{H,H}$ = 10 Hz, 1H, H_f), 7.58 (t, $^3J_{H,H}$ = 10 Hz, 1H, H_d), 7.28 (d, $^3J_{H,H}$ = 10 Hz, 1H, H_c), 7.07 (t, $^3J_{H,H}$ = 10 Hz, 1H, H_e), 5.72 (d, $^3J_{H,H}$ = 5 Hz, 1H, $H_{p\text{-cym}}$), 5.68 (d, $^3J_{H,H}$ = 5 Hz, 1H, $H_{p\text{-cym}}$), 5.34 (d, $^3J_{H,H}$ = 5 Hz, 1H, $H_{p\text{-cym}}$), 5.16 (d, $^3J_{H,H}$ = 5 Hz, 1H, $H_{p\text{-cym}}$), 2.97 (sept, $^3J_{H,H}$ = 5 Hz, 1H, $HC_{i\text{Pr}}$), 2.54 (d, $^2J_{H,H}$ = 15 Hz, 1H, H_a), 2.40 (d, $^2J_{H,H}$ = 15 Hz, 1H, H_a), 1.75 (s, 3H, H_3C), 1.32 (d, $^3J_{H,H}$ = 5 Hz, 3H, $H_3C_{i\text{Pr}}$), 1.28 (d, $^3J_{H,H}$ = 5 Hz, 3H, $H_3C_{i\text{Pr}}$), 0.12-1.92 (m, 22H, H_{Cy}). $^{13}C\{^1H\}$-NMR (125.8 MHz, CD_2Cl_2, 253.0 K): δ = 172.40 (s, C_b), 154.58 (s, C_f), 136.93 (s, C_d), 126.88 (s, C_c), 119.98 (s, C_e), 102.38 (s, $C_{p\text{-cym}}$), 98.44 (s, $C_{p\text{-cym}}$), 86.93 (s, $CH_{p\text{-cym}}$), 84.75 (s, $CH_{p\text{-cym}}$), 81.44 (s, $CH_{p\text{-cym}}$), 79.54 (s, $CH_{p\text{-cym}}$), 38.80 (s, C_a), 33.50 (s broad, B*C*H), 30.77 (s, CH_{2Cy}), 30.70 (s broad, $HC_{i\text{Pr}}$), 30.13 (s broad, B*C*H), 28.98 (s, CH_{2Cy}), 27.69 (s, CH_{2Cy}), 22.27 (s, $H_3C_{i\text{Pr}}$), 22.12 (s, $H_3C_{i\text{Pr}}$), 17.74 (s, H_3C). $^{11}B\{^1H\}$-NMR (160.5 MHz, CD_2Cl_2): δ = 22.28.

X-ray analysis of [2-picolylBCy$_2$]$_2$ (1) and [RuCl$_2$(*p*-Cymene)(2-picolylBCy$_2$)] (3).

Data were collected at low temperature (100 and 180 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters were obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92,[3] and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97[4] included in the software package WinGX version 1.63.[5] The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography.[6] All hydrogen atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ where $P=(Fo^2+2Fc^2)/3$. For complex **3**, 36 restraints were used in the refinement on the C-C distances of the highly disordered cyclohexane rings. The DFIX command was used in SHELXL-97.

Molecular drawing was performed with the program ORTEP32[7] with 50% probability displacement ellipsoids for non-hydrogen atoms.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–635561 (**1**) and 635560 (**3**). These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Computational Details. DFT calculations were performed with the GAUSSIAN 03 series of programs[8] using two hybrid functions denoted as B3LYP[9] and B3PW91.[10] MP2 (second-order Möller-Plesset perturbation theory)[11] calculations, more accurate for B-N dative bonds, were also carried out. For ruthenium, the core electrons were represented by a relativistic small core pseudopotential using the Durand-Barthelat method.[12] The 16 electrons corresponding to the 4s, 4p, 4d and 5s atomic orbitals were described by a (7s, 6p, 6d) primitive set of Gaussian functions contracted to (5s, 5p, 3d). Standard pseudopotentials developed in Toulouse were used to describe the atomic cores of all other non-hydrogen atoms (B, C, N and Cl).[13] A double-zeta plus polarization valence basis set was employed for B, C, N and Cl (d-type function exponents were 0.60, 0.80, 0.95 and 0.65 respectively). For hydrogen, a standard primitive (4s) basis contracted to (2s) was used. A p-type polarization function (exponent 0.9) was added for the hydrogen atoms of the pyridine and CH_2 groups. The geometry of the various critical points on the potential energy surface was fully optimized with the gradient method available in GAUSSIAN 03. Calculations of harmonic vibrational frequencies were performed to determine the nature of each critical point.

For NMR calculations, the basis sets were changed to 6-311+G(d,p)[14] for all atoms. NMR chemical shifts and coupling constants were evaluated within the GIAO[15] approximation at the DFT level, using as reference the corresponding BF_3-Et_2O shielding constant calculated at the same level of theory.

B3PW91 optimised geometry for [2-picolylBCy$_2$]$_2$ (1).

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C	0.012023	1.878010	0.061661
C	-0.012023	-1.878010	0.061661
N	-1.235655	1.420423	-0.264960
N	1.235655	-1.420423	-0.264960
B	-2.010968	0.027418	0.250500
B	2.010968	-0.027418	0.250500
C	-0.970320	-1.110427	0.905711
C	0.970320	1.110427	0.905711
H	-1.685316	-1.861526	1.277363
H	-0.458189	-0.740723	1.801209
H	1.685316	1.861526	1.277363
H	0.458189	0.740723	1.801209
C	-2.050224	2.221381	-1.001324
C	2.050224	-2.221381	-1.001324
C	-1.698066	3.471961	-1.477710
C	1.698066	-3.471961	-1.477710
C	-0.421386	3.955203	-1.169111
C	0.421386	-3.955203	-1.169111
C	0.409966	3.157732	-0.398911
C	-0.409966	-3.157732	-0.398911
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H	3.040368	-1.814252	-1.196311
H	-2.416673	4.048391	-2.066172
H	2.416673	-4.048391	-2.066172
H	-0.089920	4.941797	-1.509839
H	0.089920	-4.941797	-1.509839
H	1.402796	3.513269	-0.112575
H	-1.402796	-3.513269	-0.112575
C	-3.039817	0.556487	1.448296
C	3.039817	-0.556487	1.448296
C	-3.825302	-0.579137	2.155750
C	3.825302	0.579137	2.155750
C	-4.892362	-0.039864	3.135670
C	4.892362	0.039864	3.135670
C	-4.263313	0.887834	4.193719
C	4.263313	-0.887834	4.193719
C	-3.449617	2.016478	3.531414
C	3.449617	-2.016478	3.531414
C	-2.405674	1.459805	2.536854
C	2.405674	-1.459805	2.536854
H	-3.806033	1.189715	0.942025
H	3.806033	-1.189715	0.942025
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H	4.304027	1.248591	1.414959
H	3.116405	1.212689	2.731034
H	-5.662065	0.520833	2.564317
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H	5.662065	-0.520833	2.564317
H	5.418989	0.880769	3.630189
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H	5.046747	-1.310713	4.853378
H	3.592049	-0.290650	4.847028
H	-4.140674	2.694235	2.986638
H	-2.951531	2.633516	4.306084
H	4.140674	-2.694235	2.986638

H	2.951531	-2.633516	4.306084
H	-1.647639	0.879252	3.106325
H	-1.864291	2.308542	2.075099
H	1.647639	-0.879252	3.106325
H	1.864291	-2.308542	2.075099
C	-2.799259	-0.682416	-1.052679
C	2.799259	0.682416	-1.052679
C	-4.282528	-0.324145	-1.357639
C	4.282528	0.324145	-1.357639
C	-4.913137	-1.288998	-2.388670
C	4.913137	1.288998	-2.388670
C	-4.107931	-1.321551	-3.702553
C	4.107931	1.321551	-3.702553
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C	2.624022	1.645568	-3.439758
C	-2.010968	-0.691523	-2.390422
C	2.010968	0.691523	-2.390422
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H	2.852764	1.748802	-0.738328
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H	-4.370902	0.706237	-1.768282
H	4.886268	0.333242	-0.431641
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H	4.947277	2.310183	-1.953208
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H	4.545891	2.056259	-4.406981
H	4.182124	0.330485	-4.199215
H	-2.537651	-2.690745	-3.074184
H	-2.049521	-1.596590	-4.386690
H	2.537651	2.690745	-3.074184
H	2.049521	1.596590	-4.386690
H	-1.991499	0.333462	-2.820247
H	-0.951889	-0.962328	-2.219994
H	1.991499	-0.333462	-2.820247
H	0.951889	0.962328	-2.219994

B3PW91 optimised geometry for 2-picolylBCy$_2$ closed monomer (2c).

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N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.339891
C	1.213165	0.000000	2.029809
C	2.411956	-0.006084	1.299311
C	2.388064	-0.010251	-0.100136
C	1.139553	-0.007821	-0.732238
H	-0.971090	0.008986	1.844464
H	1.220458	0.003174	3.123471
H	3.370081	-0.005887	1.830627
H	3.310020	-0.013441	-0.688704
C	0.586658	0.001601	-2.122760
B	-0.938910	0.040460	-1.420595
C	-1.732630	1.469137	-1.511859
C	-1.847179	-1.314975	-1.556074
C	-2.392497	1.637178	-2.904525

H	-2.558736	1.450247	-0.765436
C	-3.196158	2.949872	-3.038709
H	-1.600077	1.615601	-3.684550
H	-3.056436	0.777062	-3.117092
C	-2.337147	4.182053	-2.693224
H	-3.606180	3.045185	-4.064288
H	-4.070030	2.911609	-2.354233
C	-1.696068	4.037156	-1.298900
H	-1.534788	4.293592	-3.453548
H	-2.947427	5.105585	-2.744475
C	-0.887797	2.725782	-1.183460
H	-1.047194	4.909875	-1.083231
H	-2.495424	4.041209	-0.527652
H	-0.020481	2.784745	-1.876411
H	-0.463596	2.646628	-0.162107
C	-3.131992	-1.310235	-0.689678
H	-2.177378	-1.326938	-2.620855
C	-4.013164	-2.562199	-0.900825
H	-2.847722	-1.251955	0.385430
H	-3.732798	-0.404504	-0.897888
C	-3.220239	-3.864731	-0.679259
H	-4.893584	-2.530125	-0.227750
H	-4.411360	-2.550879	-1.937578
C	-1.952398	-3.894358	-1.554725
H	-2.927428	-3.938561	0.390234
H	-3.857585	-4.746352	-0.890019
C	-1.078971	-2.641092	-1.325943
H	-1.367282	-4.813768	-1.350907
H	-2.248312	-3.940616	-2.624157
H	-0.692635	-2.666865	-0.282773
H	-0.191243	-2.690340	-1.986277
H	0.916308	0.882440	-2.700427
H	0.875829	-0.896763	-2.695307

B3PW91 optimised geometry for 2-picolylBCy$_2$ open monomer (2o).

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N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.340470
C	1.164939	0.000000	2.112460
C	2.394839	0.008411	1.444531
C	2.406935	0.024098	0.048891
C	1.183964	0.026572	-0.648021
H	-0.986801	-0.015063	1.821393
H	1.107630	-0.008012	3.205464
H	3.335140	0.004269	2.007299
H	3.351485	0.034780	-0.504725
C	1.075646	0.073535	-2.150235
B	-0.300996	-0.635262	-2.578090
C	-1.455185	0.218895	-3.274616
C	-0.461552	-2.224491	-2.514282
C	-0.984747	0.565234	-4.721185
H	-2.364764	-0.410197	-3.384041
C	-2.052550	1.365702	-5.499887
H	-0.050453	1.165223	-4.674144
H	-0.736622	-0.360505	-5.278615
C	-2.471984	2.640311	-4.740116
H	-1.669116	1.627667	-6.506106

H	-2.943332	0.722836	-5.659159
C	-2.941150	2.309929	-3.308829
H	-1.607421	3.335849	-4.689385
H	-3.269330	3.172108	-5.295531
C	-1.873969	1.511075	-2.530300
H	-3.191634	3.242158	-2.764775
H	-3.877488	1.715089	-3.359675
H	-0.982568	2.154670	-2.372147
H	-2.247038	1.254750	-1.521600
C	-1.659496	-2.673698	-1.628771
H	-0.743797	-2.490401	-3.563437
C	-1.904598	-4.196430	-1.706883
H	-1.450282	-2.388620	-0.577627
H	-2.577829	-2.129847	-1.921362
C	-0.634764	-4.995873	-1.353562
H	-2.735587	-4.481009	-1.031070
H	-2.230231	-4.461768	-2.735079
C	0.555503	-4.569059	-2.235538
H	-0.379376	-4.823123	-0.286569
H	-0.822045	-6.082622	-1.458938
C	0.800191	-3.046111	-2.160383
H	1.470038	-5.118974	-1.936811
H	0.349031	-4.853120	-3.289454
H	1.131133	-2.783420	-1.133199
H	1.635477	-2.773791	-2.835923
H	1.111182	1.133348	-2.466680
H	1.954577	-0.416952	-2.606489

B3PW91 optimised geometry for [$RuCl_2$(*p*-Cymene)(2-picolylBCy_2)] (3).

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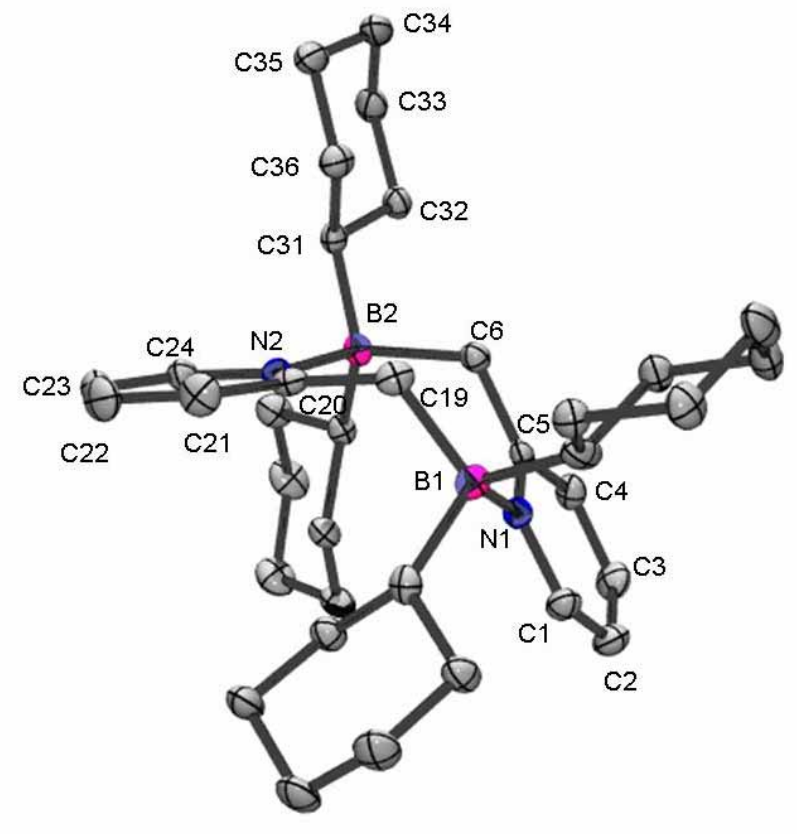
C	-3.745788	0.187586	0.640592
C	-3.014726	1.346075	0.289977
C	-2.333199	1.327336	-0.983254
C	-2.425439	0.228670	-1.867594
C	-3.164781	-0.947564	-1.492763
C	-3.817069	-0.952667	-0.231049
C	-2.882983	2.562989	1.190411
C	-3.820667	3.676598	0.684505
C	-3.233934	-2.133622	-2.415890
C	-3.106839	2.265576	2.676674
Cl	0.236663	0.742169	0.966431
Ru	-1.714700	-0.465858	0.121124
Cl	-1.685537	-1.642693	2.207996
B	1.898389	0.473816	-0.326932
C	2.342098	1.989246	-0.787163
C	2.918402	2.868641	0.345056
C	3.454203	4.222633	-0.146170
C	2.399308	5.004994	-0.934880
C	1.838764	4.157517	-2.082112
C	1.299362	2.809307	-1.577555
C	1.203375	-0.336939	-1.590555
C	0.728361	-1.729554	-1.367186
N	-0.375911	-1.973250	-0.605532
C	-0.730559	-3.254525	-0.341926
C	-0.056763	-4.356046	-0.853607
C	1.047159	-4.129928	-1.683285
C	1.433061	-2.818633	-1.928546

C	2.988145	-0.298239	0.615362
C	4.324867	-0.528578	-0.134056
C	5.429376	-1.079441	0.783382
C	4.989759	-2.352910	1.515922
C	3.663890	-2.137636	2.255879
C	2.570872	-1.611744	1.312770
H	3.220314	0.405672	1.443207
H	1.631514	-1.467237	1.874662
H	2.366216	-2.397010	0.558962
H	3.817845	-1.408945	3.077963
H	3.335099	-3.081026	2.733382
H	5.780138	-2.684274	2.217205
H	4.864186	-3.172358	0.777855
H	5.688117	-0.303280	1.532187
H	6.351827	-1.270673	0.200427
H	4.681801	0.408130	-0.601823
H	4.161614	-1.244627	-0.967832
H	3.180892	1.804120	-1.499060
H	0.922597	2.232937	-2.444446
H	0.425906	3.002746	-0.920640
H	2.643038	3.971344	-2.823281
H	1.043463	4.712801	-2.617760
H	2.824112	5.950848	-1.323065
H	1.570360	5.289077	-0.254097
H	4.336277	4.049939	-0.796808
H	3.813702	4.823337	0.711813
H	3.730108	2.337319	0.872726
H	2.126498	3.045981	1.101871
H	1.950514	-0.355503	-2.403894
H	0.362934	0.276678	-1.952339
H	2.304755	-2.600866	-2.551798
H	1.603839	-4.965228	-2.121747
H	-0.397945	-5.363406	-0.599973
H	-1.581963	-3.373235	0.332230
H	-1.673671	2.160516	-1.243280
H	-1.865454	0.240043	-2.807217
H	-4.318748	-1.858785	0.119718
H	-4.171978	0.096661	1.641677
H	-3.439531	-3.064447	-1.862874
H	-4.052878	-1.980644	-3.144458
H	-2.295908	-2.259983	-2.981203
H	-1.840948	2.914367	1.074774
H	-3.676204	4.595377	1.281320
H	-3.627363	3.927801	-0.374412
H	-4.880506	3.373517	0.774725
H	-2.858919	3.161124	3.273529
H	-4.161865	2.011912	2.891533
H	-2.466232	1.434743	3.021249

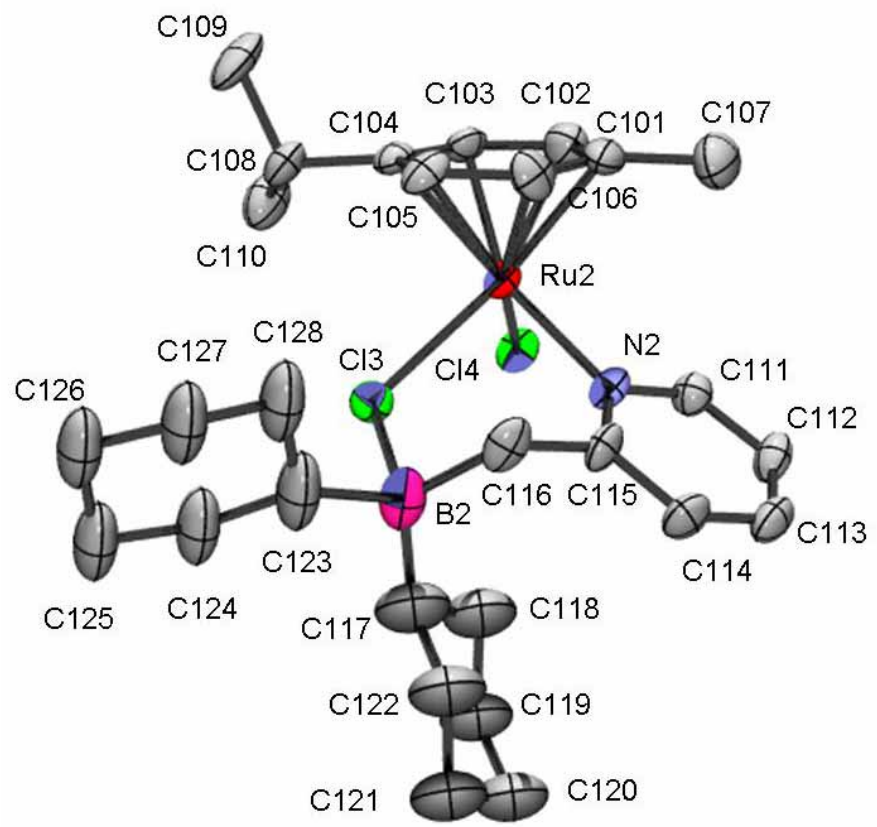
Selected bond lengths and angles for [2-picolylBCy$_2$]$_2$ (1).



Bond	x-ray structure (Å)	B3PW91 optimised structure (Å)
B2C6	1.661(3)	1.675
C5C6	1.487(3)	1.490
C5N1	1.361(3)	1.368
N1B1	1.659(3)	1.675

Angle	x-ray structure	B3PW91 optimised structure
C6B2N2	113.69(16)	113.42
B2C6C5	119.91(17)	121.86
C6C5N1	123.33(18)	123.32
C5N1B1	128.73(17)	128.79

Selected bond lengths and angles for [$RuCl_2$(*p*-Cymene)(2-picolylBCy_2)] (3).



Bond	x-ray structure (Å)	B3PW91 optimised structure (Å)
B2C116	1.621(13)	1.654
C116C115	1.484(10)	1.488
C115N2	1.352(8)	1.363
N2Ru2	2.128(5)	2.143
Cl4Ru2	2.3990(18)	2.396
Cl3Ru2	2.4190(19)	2.446
Cl3B2	2.103(9)	2.123
B2N2	3.330	3.352

Angle	x-ray structure	B3PW91 optimised structure
C115C116B2	119.9(7)	118.56
N2C115C116	118.7(6)	120.64
C115N2Ru2	125.5(5)	124.73
N2Ru2Cl3	88.69(17)	88.06
N2Ru2Cl4	87.12(16)	86.69
Cl4Ru2Cl3	85.74(7)	86.09
B2Cl3Ru2	110.0(3)	110.58
ΣB2α	346.0	344.4

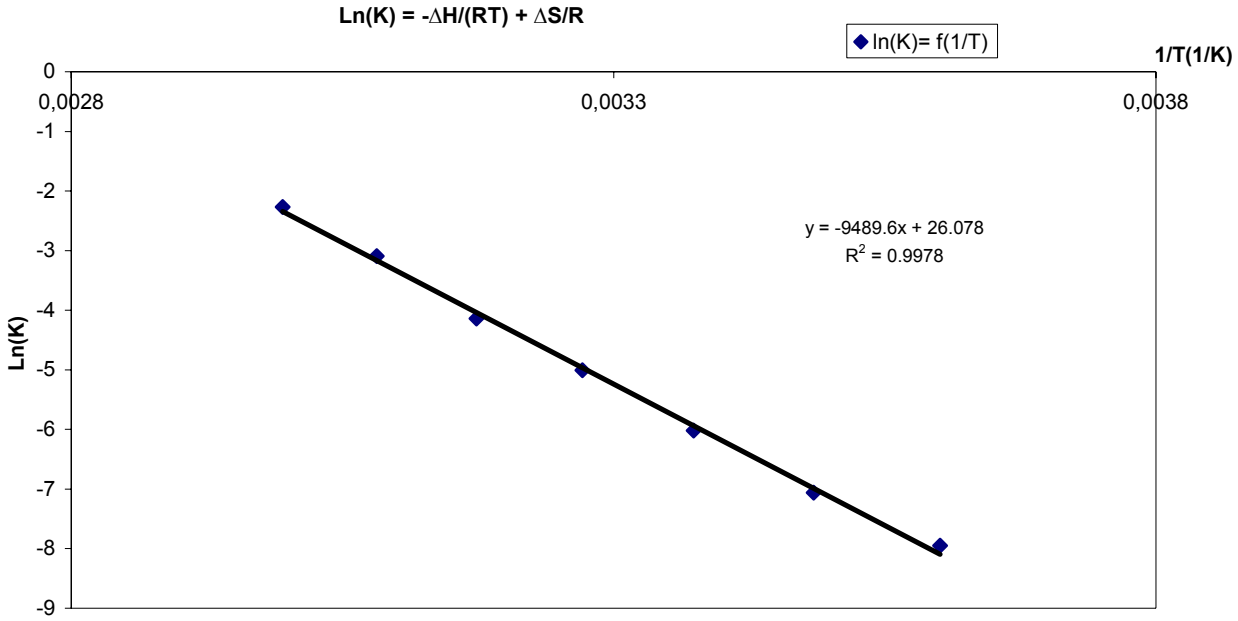
^{11}B NMR chemical shift for 1, 2c and 2o.

	1	**2c**	**2o**
Theoretical calculations GIAO	3.1	9.2	83.1
Experience (CD_2Cl_2)	3.6	14.3	

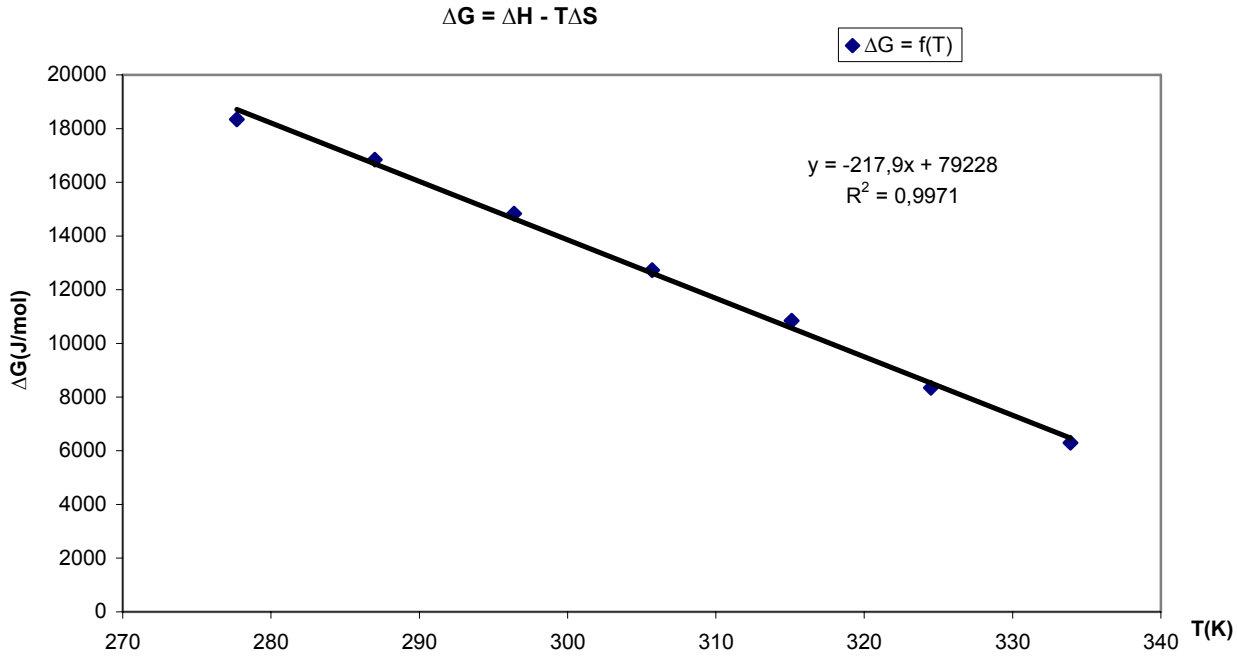
Energy gap (kJ.mol^{-1}) between 2c and 2o.

	2c	**2o**
B3PW91	0.0	15.9
B3LYP	0.0	2.1
MP2	0.0	31.3

lnK = f(1/T) and ΔG = f(T) plots for the monomer / dimer equilibrium with $[1]_0$ = 0.053 mol.L^{-1} in C_7D_8.



$-\Delta H/R = -9487 \pm 145$ J.mol^{-1} (90% confidence factor)
$-\Delta H/R = -9487 \pm 277$ J.mol^{-1} (99% confidence factor)



$\Delta H = 79.2 \pm 1.2$ kJ.mol^{-1} (90% confidence factor)
$\Delta H = 79.2 \pm 2.3$ kJ.mol^{-1} (99% confidence factor)

$\Delta S = 218 \pm 71$ J.K^{-1}.mol^{-1} (90% confidence factor)
$\Delta S = 218 \pm 137$ J.K^{-1}.mol^{-1} (99% confidence factor)

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