Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information for

Ligand Dynamics and Protonation Preferences of Rh- and Ir-Complexes Bearing an Almost, but Not Quite, Pendant Base

Travis J. Morrow, William E. Christman, Jacob Z. Williams, Navamoney Arulsamy, Alexander Goroncy, Elliott Hulley*

Department of Chemistry, University of Wyoming

Laramie, WY 82071, USA

*Correspondence to: ehulley@uwyo.edu

X-ray Crystallography

Crystals selected for diffraction studies were immersed in Paratone-N oil, placed on a Nylon loop (MiTiGen MicroMounts), and transferred to a precooled cold stream of N_2. A Bruker KAPPA APEX II CCD diffractometer with 0.71073 Å Mo Kα radiation was used for diffraction studies. The space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and refined using the riding model. Data collection and cell refinement, data reduction, and absorption correction were performed using Bruker's APEX2, SAINT, and SADABS programs, respectively.[1,2] Structural solutions and refinements were completed using SHELXL-13,[3] respectively, as implemented in the OLEX2 (v. 1.2.8) software package.[4]

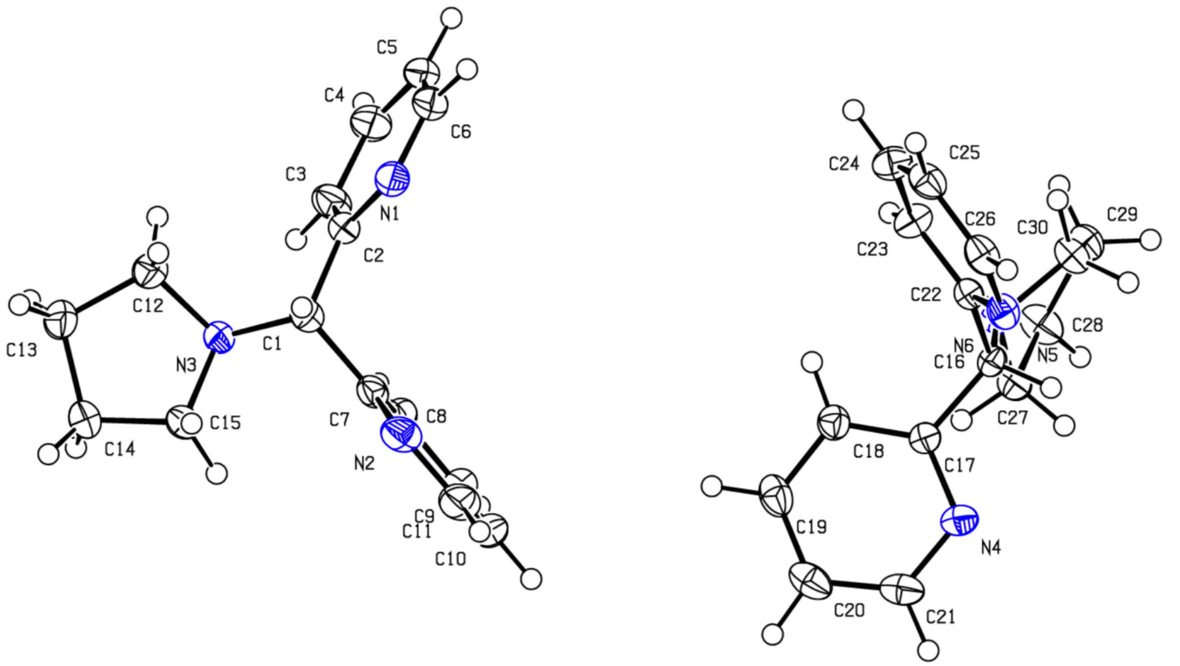
Structure of $^{H,pyr}CPy_2$. A series of narrow frames of data were collected with a scan width of 0.5° in ω or ϕ and an exposure time of 10 s per frame. The integration of the data using a triclinic unit cell yielded a total of 39882 reflections in the θ range of 2.385 to 33.139° of which 9857 were independent with $I \geq 2\sigma(I)$ (R_{int} = 0.0283). The asymmetric unit consists of two unique $CH(pyr)(py)_2$ molecules. All of the hydrogen atoms were also located in the Fourier maps and refined isotropically. Both of the molecules exhibit no disorder. The molecules share similar structural features and differ with respect to the conformation of the pyrrolidine rings. Although both rings exhibit distorted envelope conformation, the extent of distortion is unequal leading to the observed crystallographic nonequivalence. A view of one of the molecules is shown in Figure 1. The final refinement parameters are R_1 = 0.0502 and wR_2 = 0.01240 for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 21. The refinement data for all data are R_1 = 0.0716 and wR_2 = 0.1401.

Table S1. Crystallographic Data for ^{H,pyr}**CPy$_2$**, **[(^{Me,pyr}CPy$_2$)Rh(COD)][B(C$_6$F$_5$)$_4$]**, and **[(^{H,pyr}CPy$_2$)Ir(COD)]Cl·1½ H$_2$O.**

compound	**^{H,pyr}CPy$_2$**	**[(^{Me,pyr}CPy$_2$)Rh(COD)][B(C$_6$F$_5$)$_4$]**	**[(^{H,pyr}CPy$_2$)Ir(COD)]Cl**·1½ H$_2$O
color	colorless	yellow	yellow
chemical formula	$C_{15}H_{17}N_3$	$C_{48}H_{31}BF_{20}N_3Rh$	$C_{23}H_{29}ClIrN_3O_{1.5}$
f. wt., g/mol	239.31	1143.48	599.14
T, K	150(2)	150(2)	150(2)
λ, Å	0.71073	0.71073	0.71073
space group	*P-1*	*P-1*	*P-1*
a, Å	8.7964(1)	10.2339(1)	9.5235(2)
b, Å	9.1641(1)	13.4237(2)	15.9622(4)
c, Å	21.090(2)	16.5737(2)	16.7580(4)
α, °	95.602(1)	100.030(2)	114.387(2)
β, °	98.361(1)	101.556(2)	97.829(1)
γ, °	109.356(1)	96.792(2)	99.861(1)
V, Å^3	1298.40(3)	2168.74(5)	2224.30(9)
Z	4	2	4
D_{calc}, Mg m^{-3}	1.224	1.751	1.789
GoF on F^2	1.022	1.038	1.059
μ, mm^{-1}	0.075	0.522	6.145
$R1[I > 2\sigma(I)]$[a]	0.0502	0.0289	0.0382
$wR2[I > 2\sigma(I)]$[b]	0.1240	0.0757	0.0886

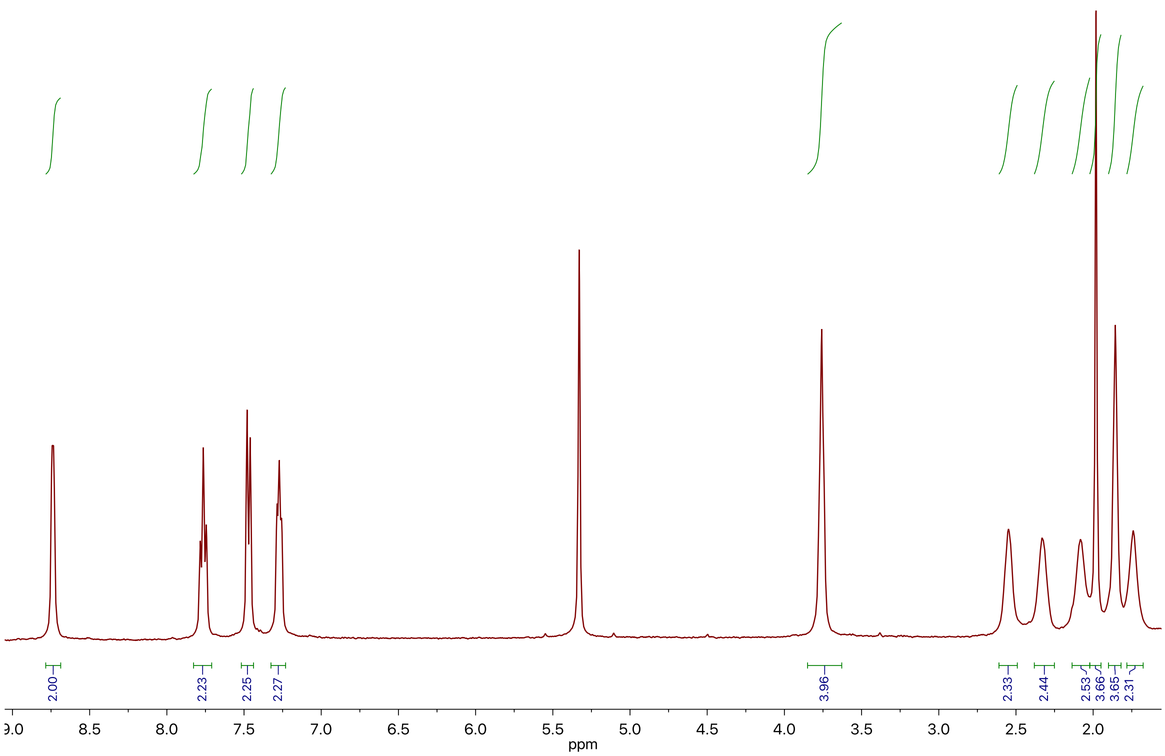
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$

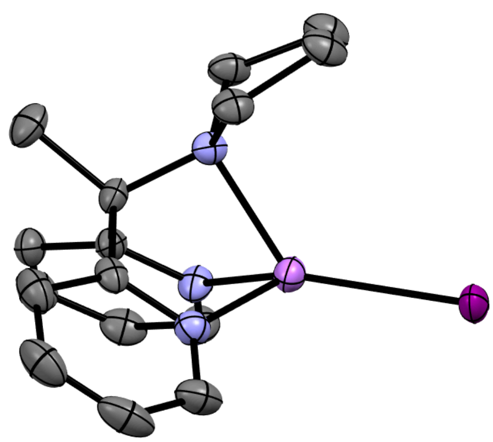
Figure S1. Solid-state Structure of $^{H,Pyr}CPy_2$.



A colorless rectangular prism of $^{H,pyr}CPy_2$ ($0.48 \times 0.34 \times 0.22$ mm^3) was glued to a glass fiber using Paratone N oil. The integration of the data using a triclinic unit cell yielded a total of 39882 reflections in the θ range of 2.385 to 33.139° of which 9857 were independent with $I \geq 2\sigma(I)$ (R_{int} = 0.0283). The data were corrected for absorption effects by the multi-scan method (SADABS). Crystallographic data collection parameters and refinement data are collected below in Table 1. The asymmetric unit consists of two unique $^{H,pyr}CPy_2$ molecules. All of the hydrogen atoms were also located in the Fourier maps and refined isotropically. Both of the molecules exhibit no disorder. The molecules share similar structural features and differ with respect to the conformation of the pyrrolidine rings. Although both rings exhibit a distorted envelope conformation, the extent of distortion is unequal leading to the observed crystallographic nonequivalence. A view of one of the molecules is shown in Figure 1. The final refinement parameters are $R_1 = 0.0502$ and $wR_2 = 0.01240$ for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 21. The refinement data for all data are $R_1 = 0.0716$ and $wR_2 = 0.1401$.

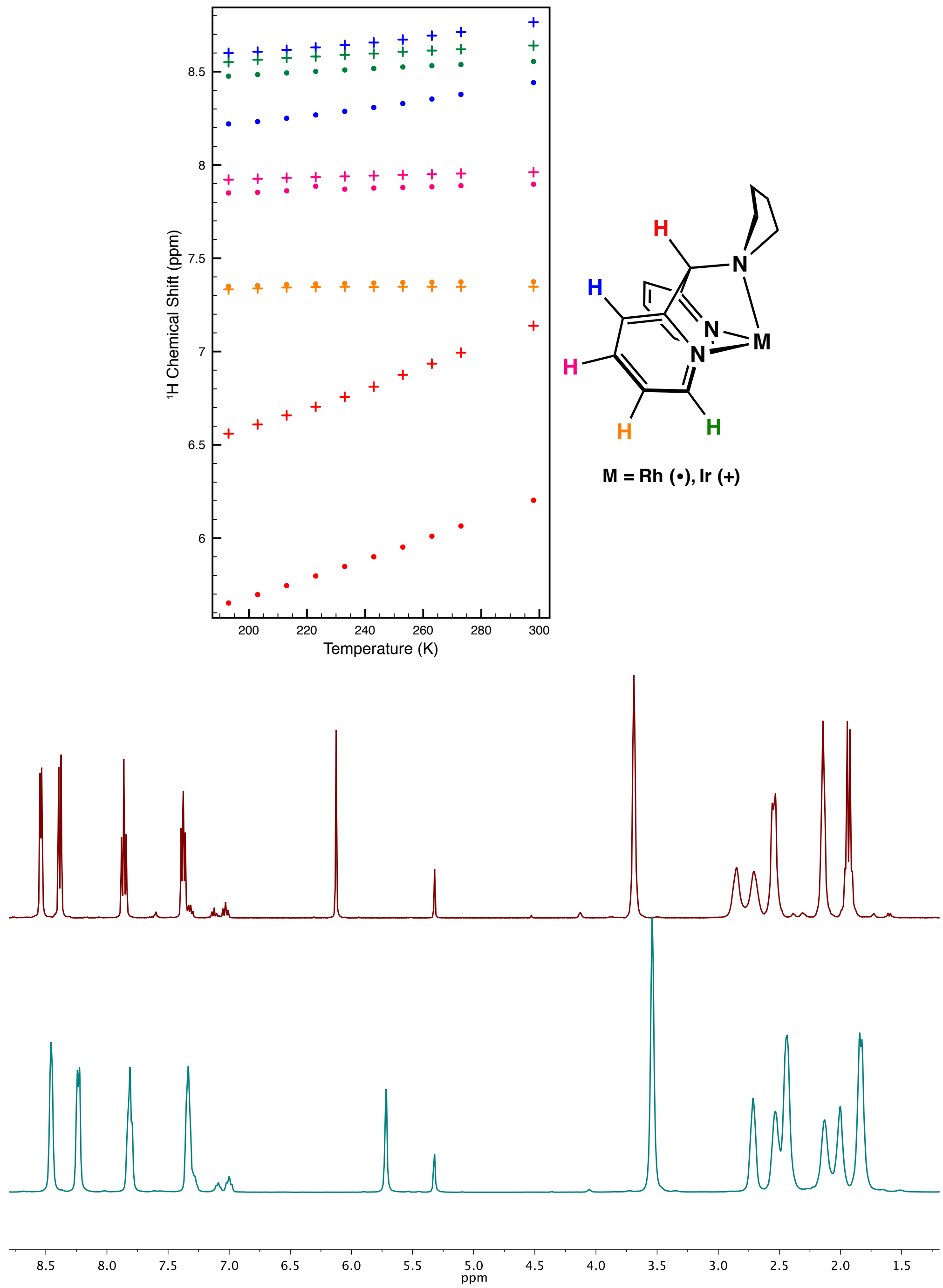
Figure S2. ^{1}H NMR Spectrum and Solid-state Structure of (^{Me,Pyr}CPy$_2$)LiI.





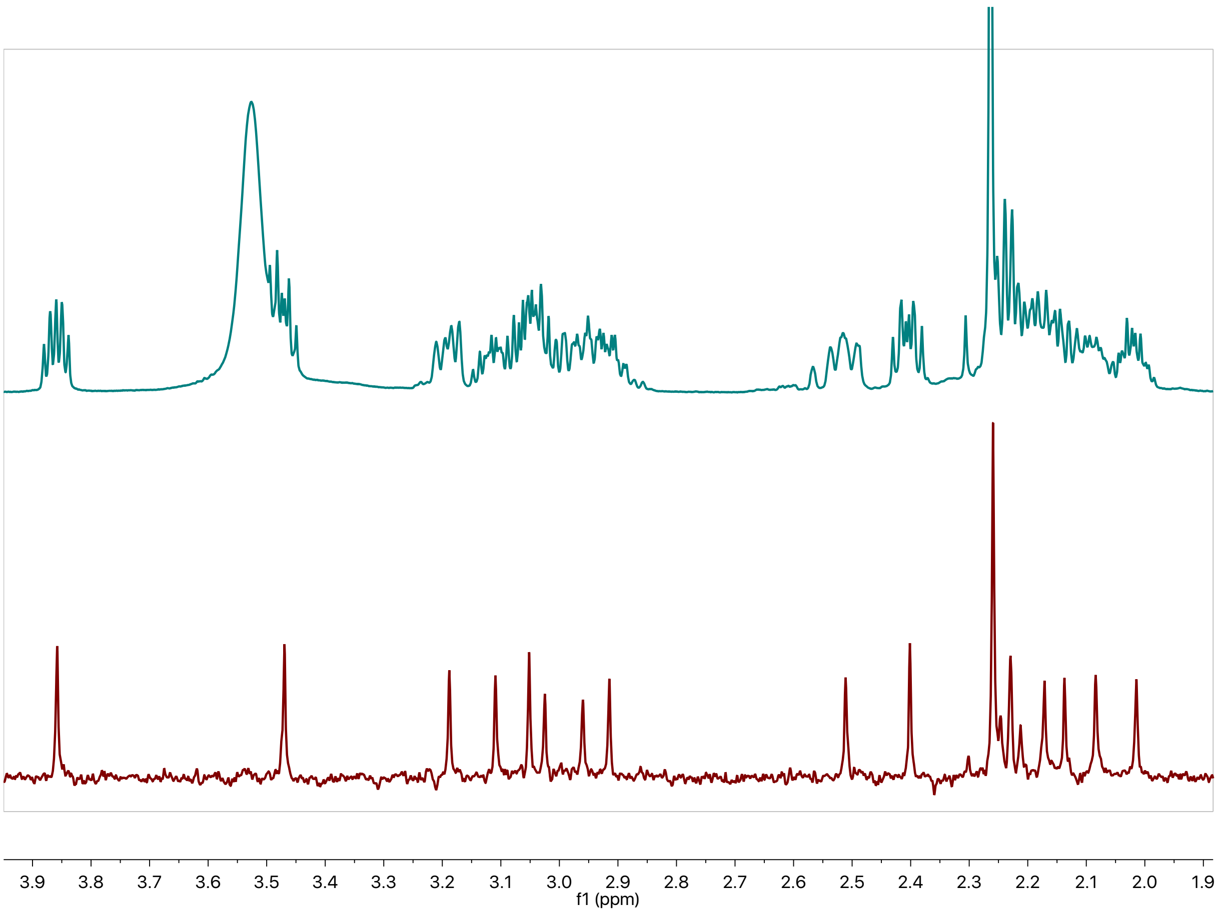
If the aqueous workup is avoided, a crystalline white powder can be isolated that we formulate as (^{Me,Pyr}CPy$_2$)LiI(THF) on the basis of the ^{1}H NMR spectrum (CD_2Cl_2, top) which contains one equivalent of THF and four signals for the pyrrolidine ring. The compound is sparingly soluble hot hexane (in contrast to ^{Me,Pyr}CPy$_2$), from which crystals formed. These crystals gave reasonable diffraction but only a partial data set was collected (bottom, enough to establish connectivity).

Figure S3. Temperature-dependence of ^{1}H NMR chemical shifts of $[(^{H,pyr}CPy_2)M(COD)]Cl$ (M = Rh, Ir).



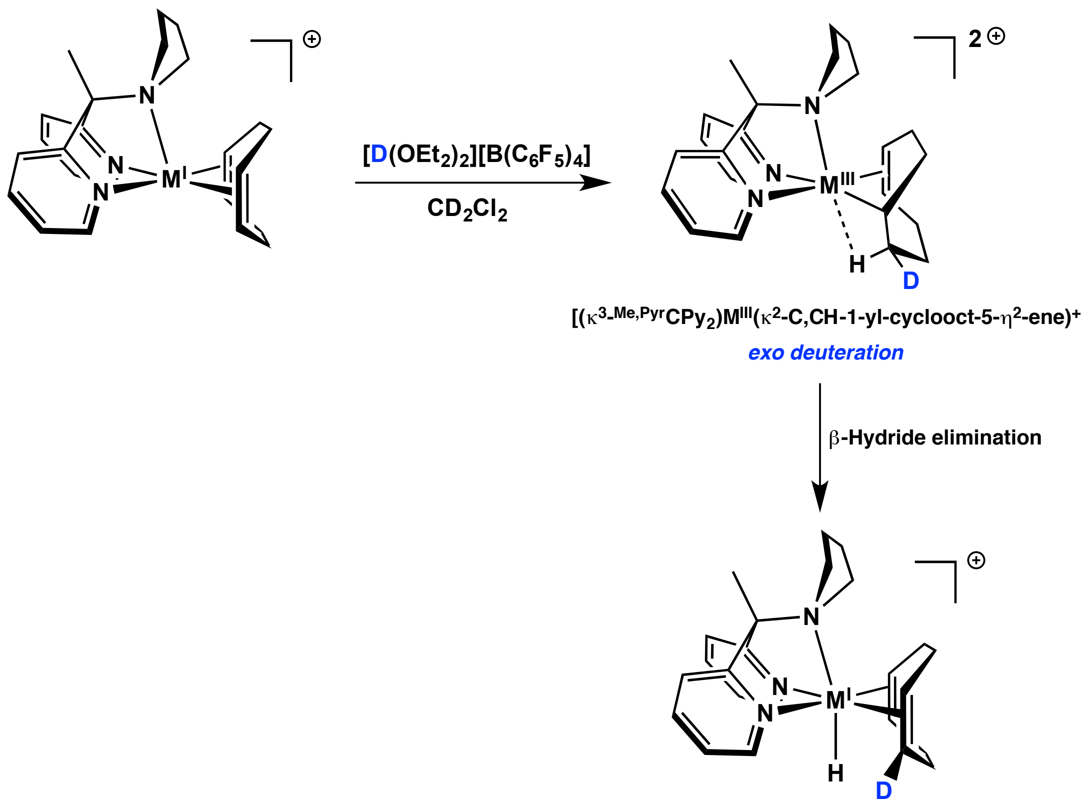
Top: Unabridged plot of the methine and aromatic protons of $[(^{H,pyr}CPy_2)M(COD)]Cl$ (M = Rh, Ir).
Bottom: Room-temperature (300 K, maroon) and low temperature (202 K, blue) ^{1}H NMR spectra of $[(^{H,pyr}CPy_2)Rh(COD)]Cl$, highlighting the mild (but structurally significant) changes in COD- and pyrrolidine-associated resonances.

Figure S4. Pure-Shift NMR Spectra of *cis*-[(κ^{3}-^{Me,Pyr}CPy$_2$)Ir^{III}H(COD)$^{+}$]



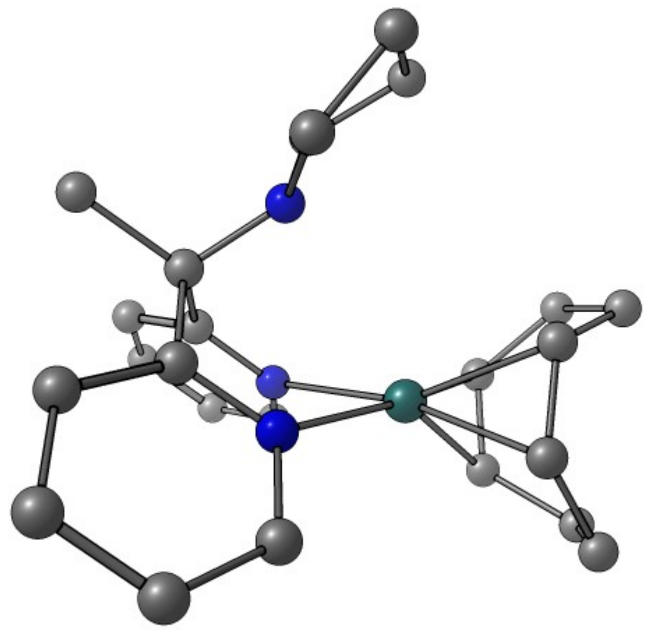
Standard ^{1}H (top) and Pure Shift ^{1}H (bottom) NMR spectra for the 3.9–1.9 ppm region of [*cis*-[(κ^{3}-^{Me,Pyr}CPy$_2$)Ir^{III}**H**(COD)$^{+}$]].[5–7] The broad resonance at 3.52 ppm corresponds to diethyl ether, which exhibits signs of dynamic exchange with residual [H(OEt$_2$)$_2$]$^{+}$.

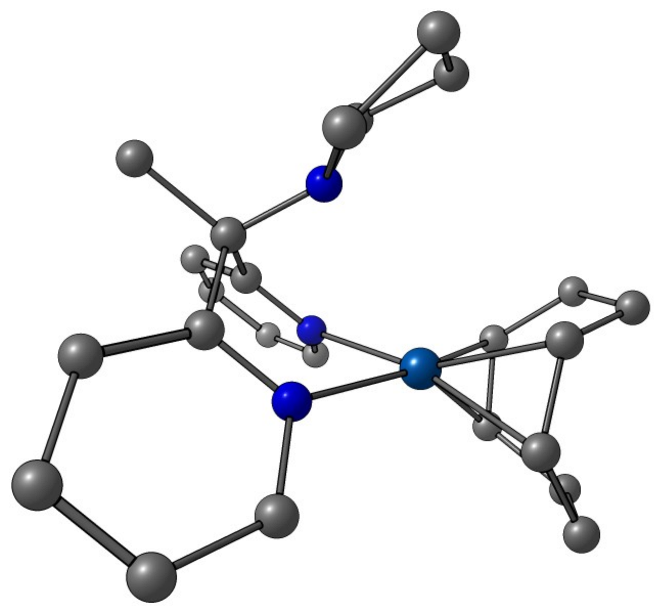
Scheme S1. Mechanistic Implications of Direct Protonation at COD



Exogenous addition of $[D(OEt_2)_2]^+$ to $[(^{Me,Pyr}CPy_2)M^I(COD)]^+$ should ultimately yield the *protio* hydride from β-hydride elimination, with deuterium incorporation in the η^2-alkene position. There was no measureable decrease in the ^{1}H NMR signal integration for the alkene protons in our experiments on the Rh and Ir complexes, and no signal was observed in that region of the ^{2}H NMR spectrum. Similarly, reversible access to the agostic structure would not directly lead to H/D scrambling, as the alkene portion of the nascent [κ^2-C,C**D**-1-yl-cyclooct-5-η^2-ene] ligand would have to dissociate first to provide access to the *exo*-portion of the alkyl.

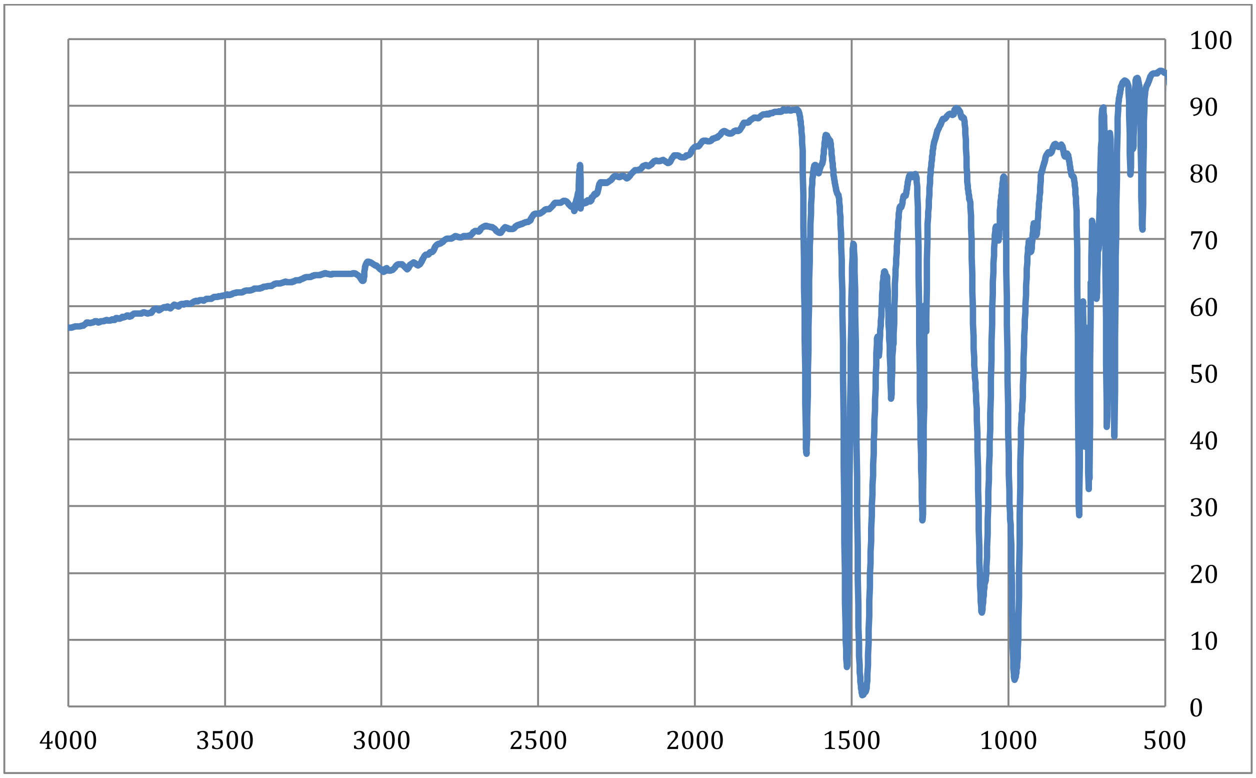
Figure S5. Computed structures of [(^{Me,pyr}CPy$_2$)Rh(COD)]$^+$ and [(^{Me,pyr}CPy$_2$)Ir (COD)]$^+$ with Constrained M–N$_{pyr}$ Distances





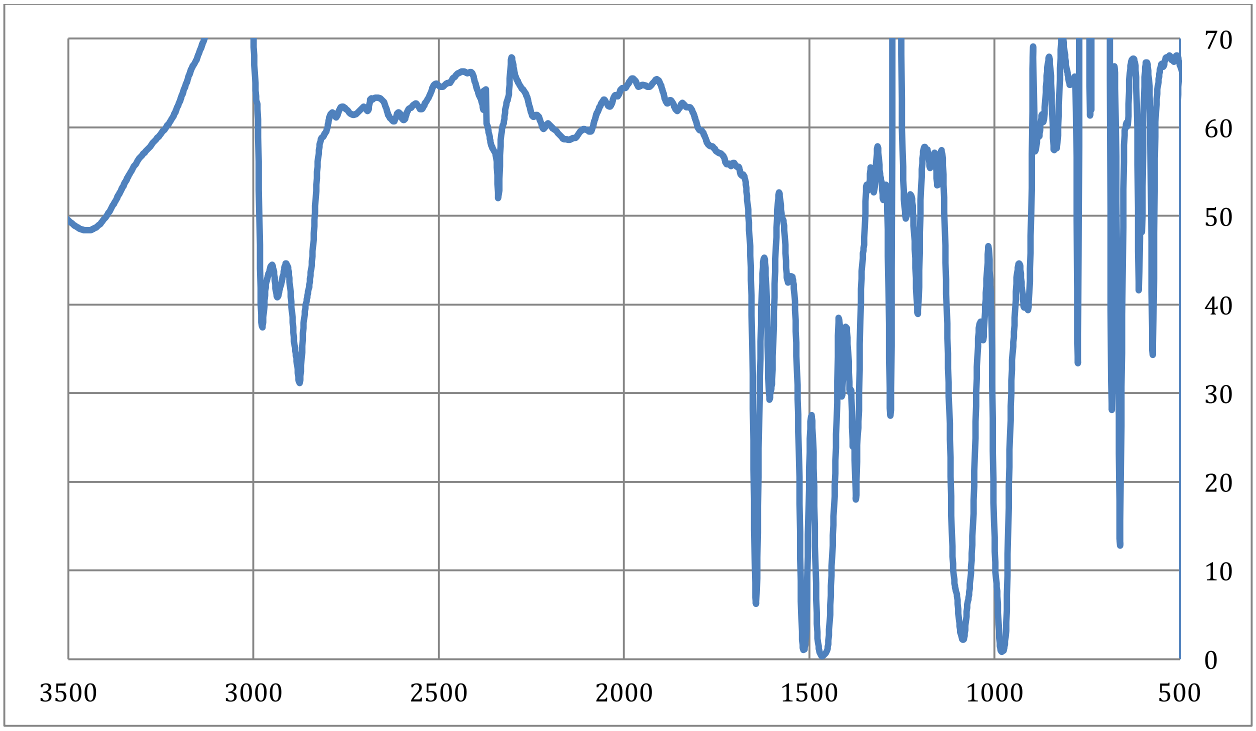
Calculated structures of [(^{Me,pyr}CPy$_2$)M(COD)]$^+$ (M = Rh (top), Ir (bottom)) where the M–N$_{pyr}$ distances have both been constrained to 2.936 Å.

Figure S6. IR Spectrum of [(^{Me,pyrH}CPy$_2$)Rh(COD)]$^+$ in in CH_2Cl_2/Et_2O



Artefacts from solvent subtraction are visible, but we could not see stretches consistent with the expected N-H in the protonated complex. Based on the DFT calculations, we suspect the N-H stretch occurs at lower frequency than ‘normal’ N-H stretches due to NH-M hydrogen bonding and overlaps with aliphatic stretches that have been partially removed via solvent subtraction.

Figure S7. IR Spectrum of $[(^{Me,pyr}CPy_2)Ir(H)(COD)]^+$ in CH_2Cl_2/Et_2O



Although artefacts from solvent subtraction and the presence of excess $[H(OEt_2)_2]^+$ are visible, a sharp, medium-intensity stretch is apparent at 2339 cm^{-1} which has been assigned as the Ir–H stretch.

Figure S8. ^{1}H and ^{13}C NMR Spectra of $^{H,pyr}CPy_2$ in CD_2Cl_2

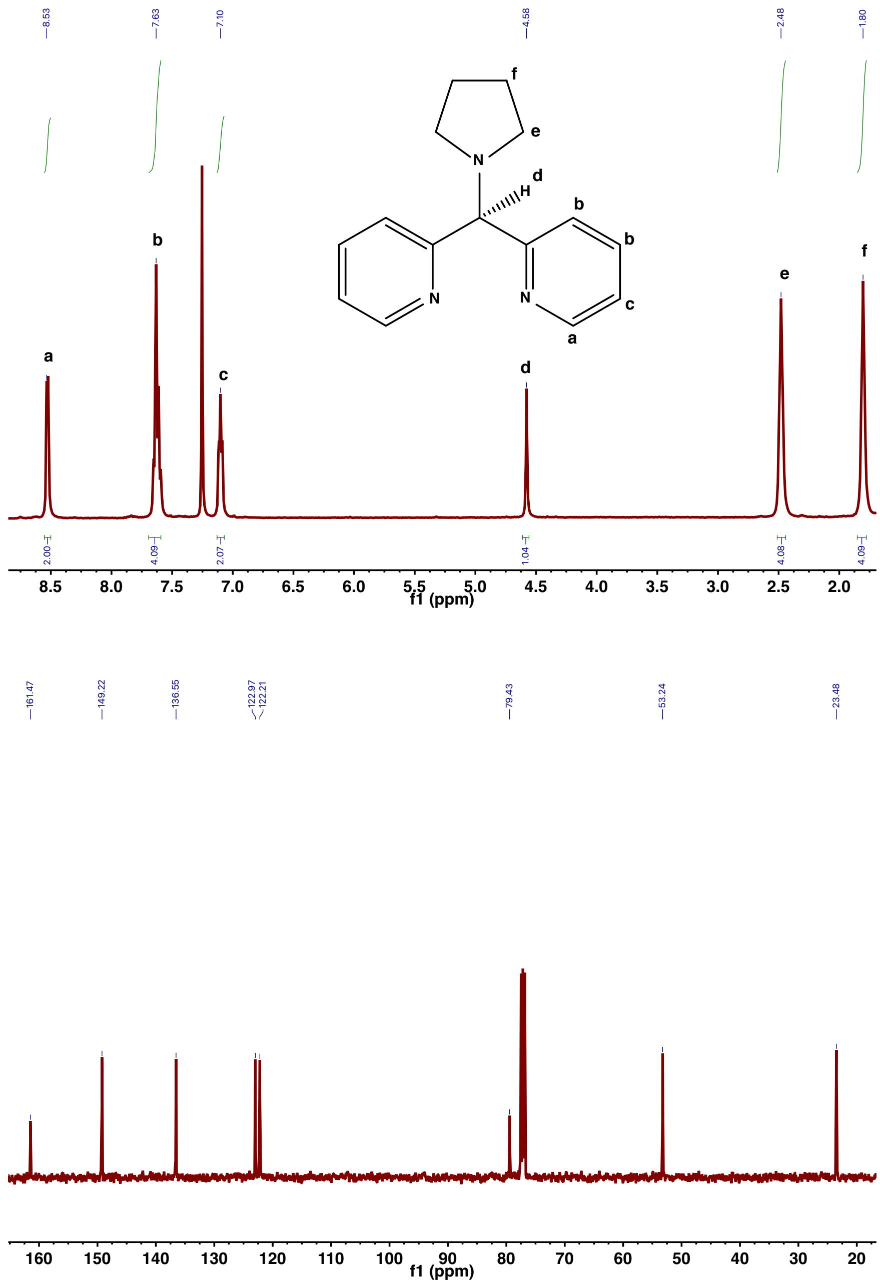
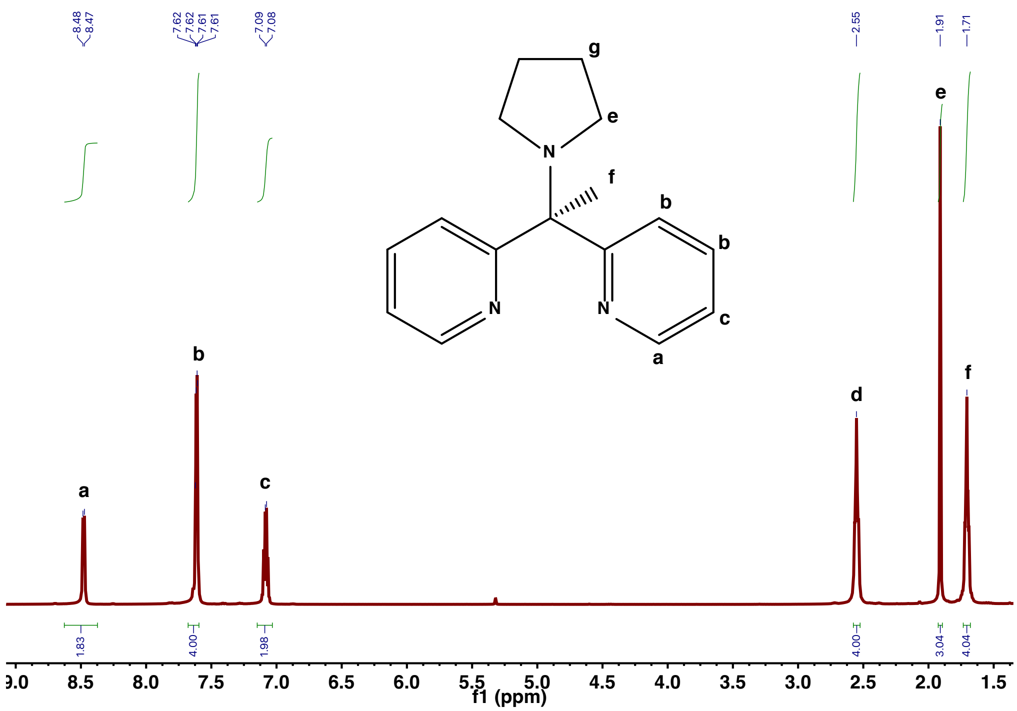


Figure S8. ^{1}H and ^{13}C NMR Spectra of $^{Me,pyr}CPy_2$ in CD_2Cl_2



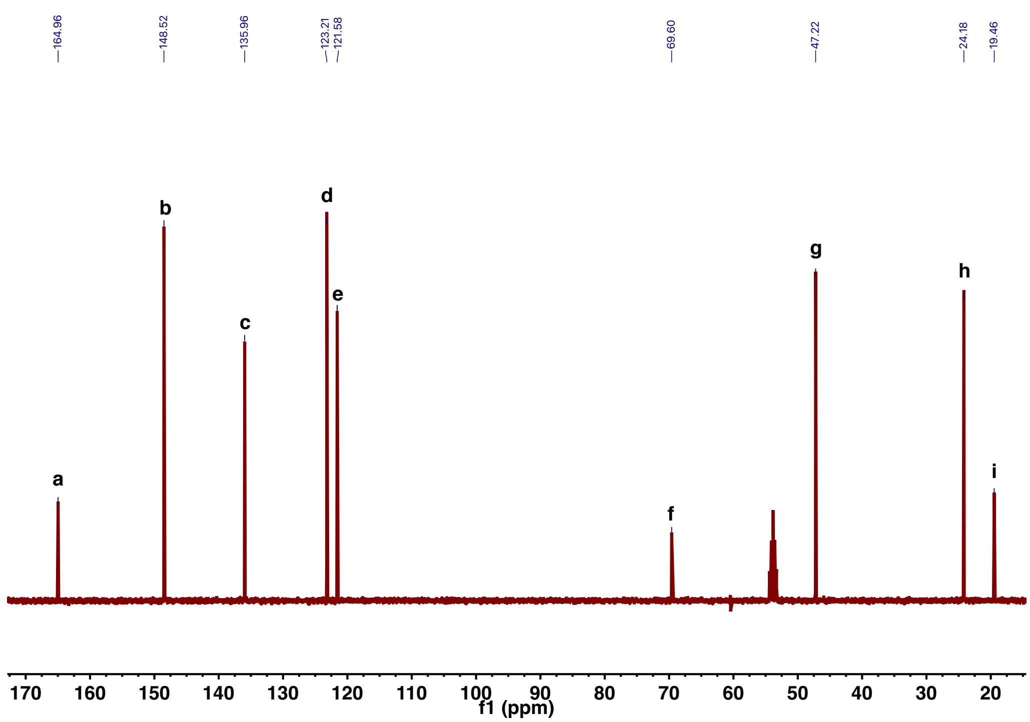
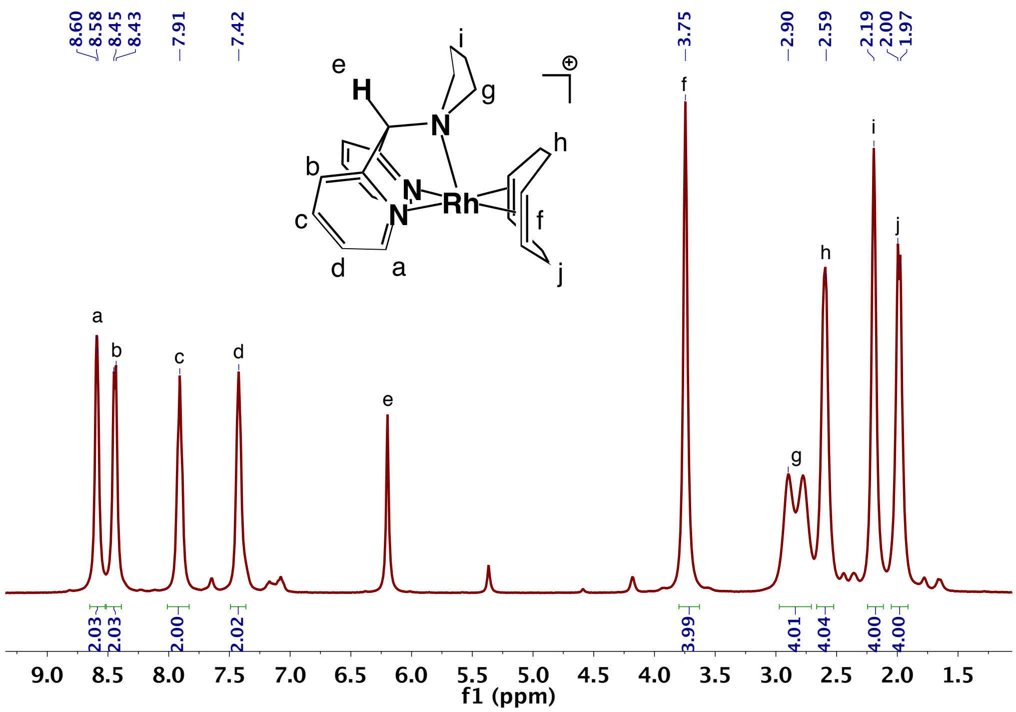


Figure S9. ^{1}H and ^{13}C NMR Spectra of $[(^{H,pyr}CPy_2)Rh(COD)]Cl$ in CD_2Cl_2



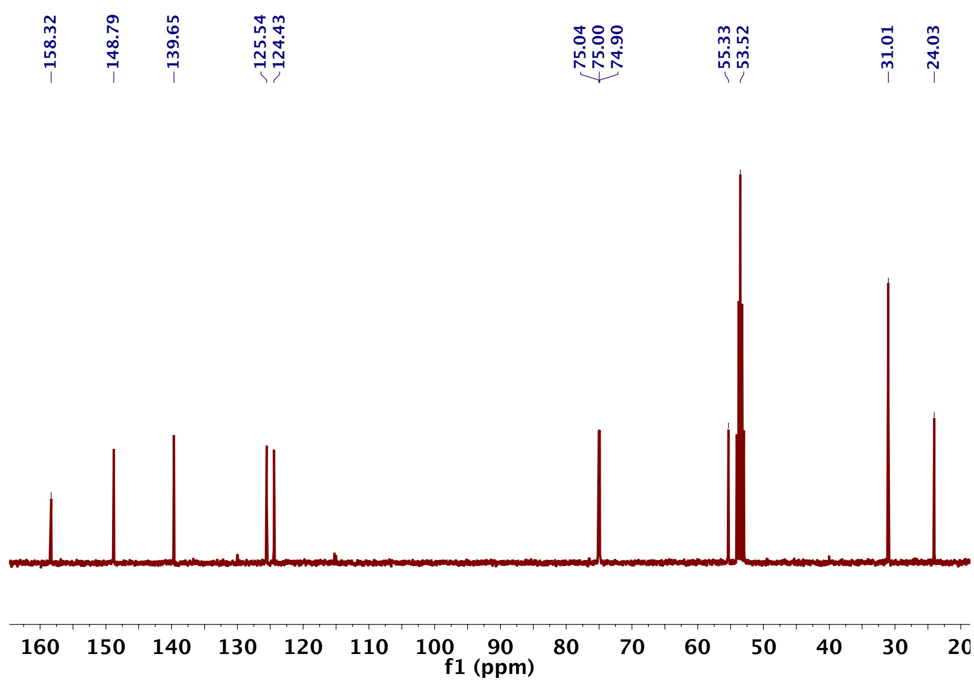
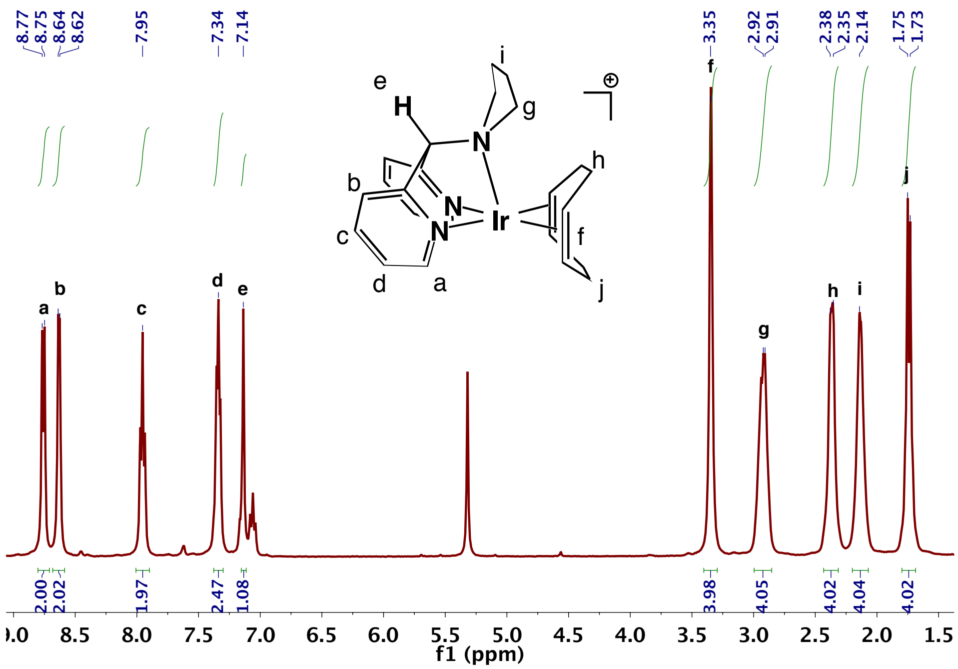


Figure S9. ^{1}**H and** ^{13}**C NMR Spectra of [(^{H,pyr}CPy$_2$)Ir(COD)]Cl in CD$_2$Cl$_2$**



(note: crystalline samples bear residual fluorobenzene, visible at 7.10 ppm)

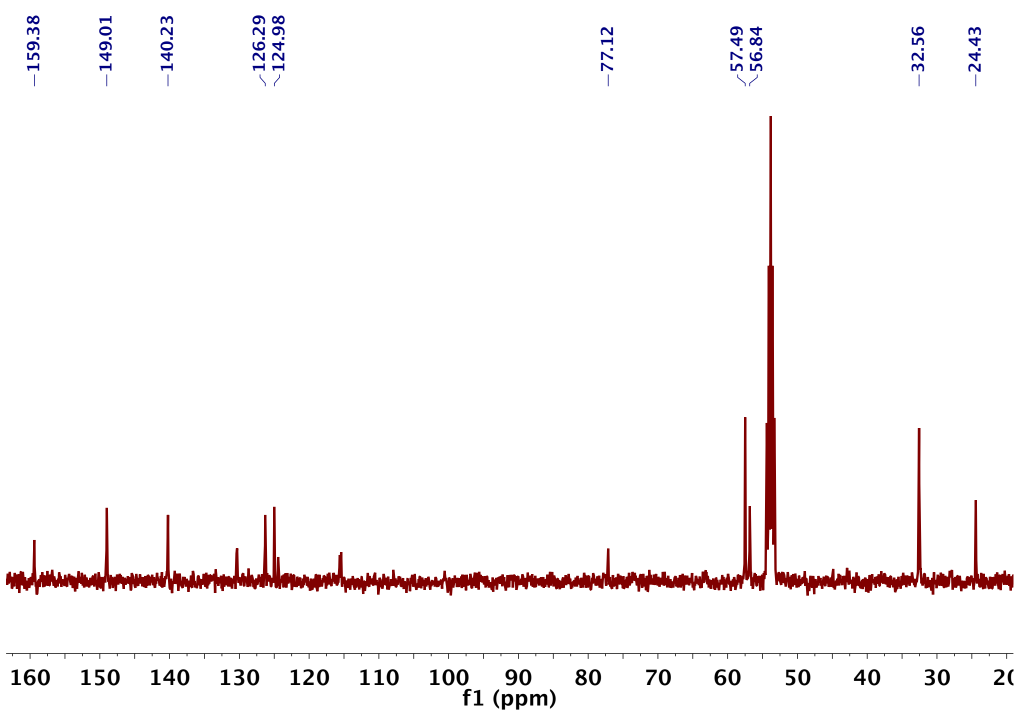
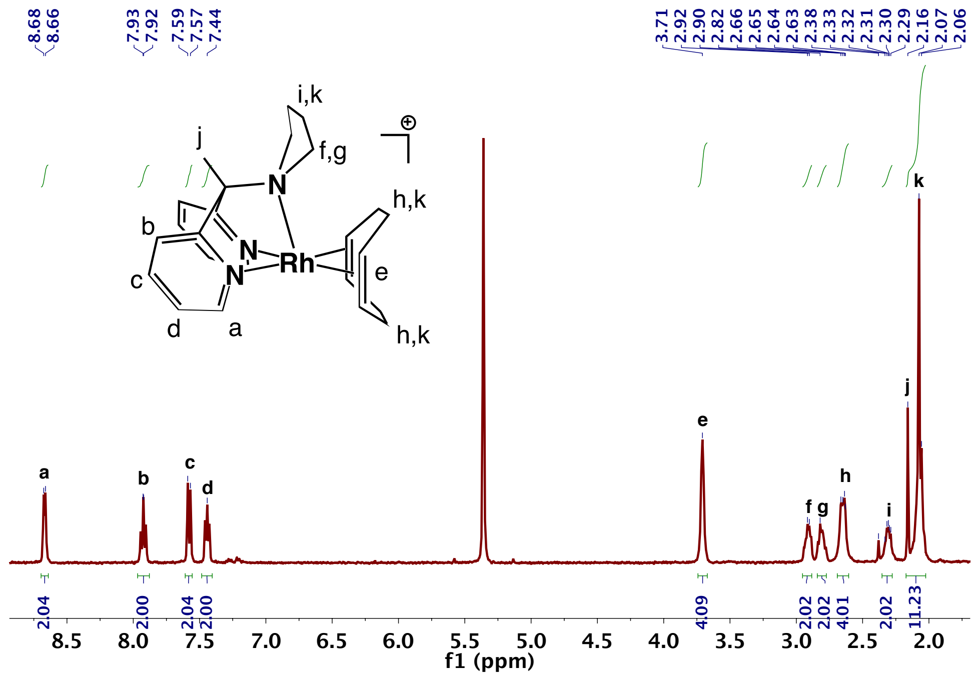


Figure S10. ^{1}H **and** ^{13}C **NMR Spectra of [(** ^{Me,pyr} **CPy** $_2$ **)Rh(COD)][B(** C_6F_5 **)** $_4$ **] in** CD_2Cl_2



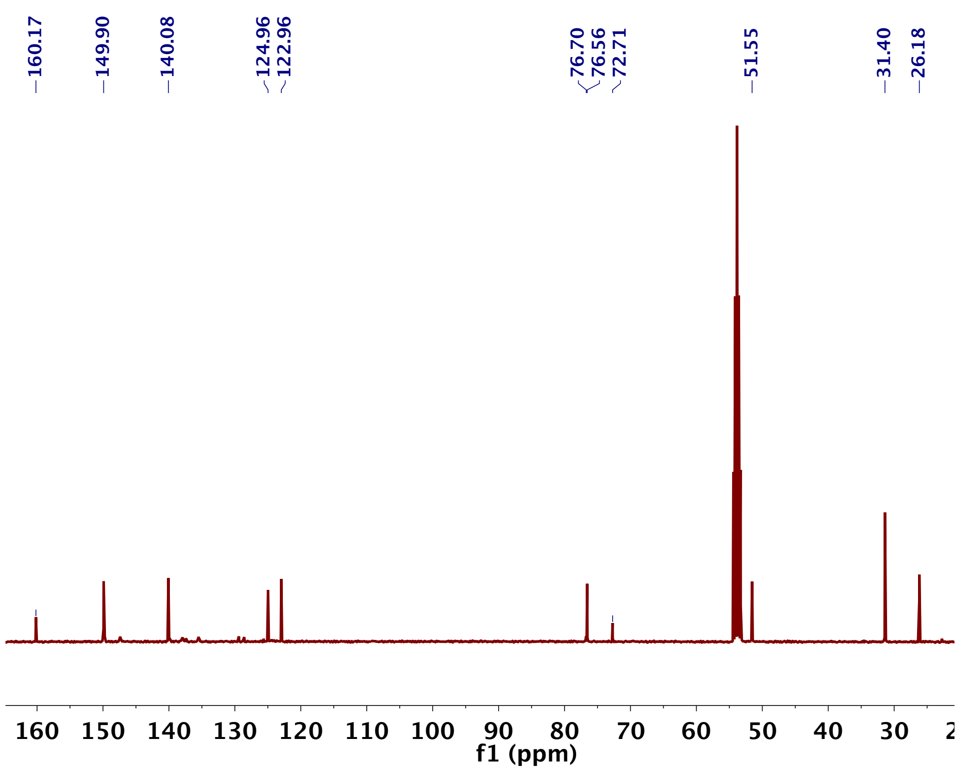
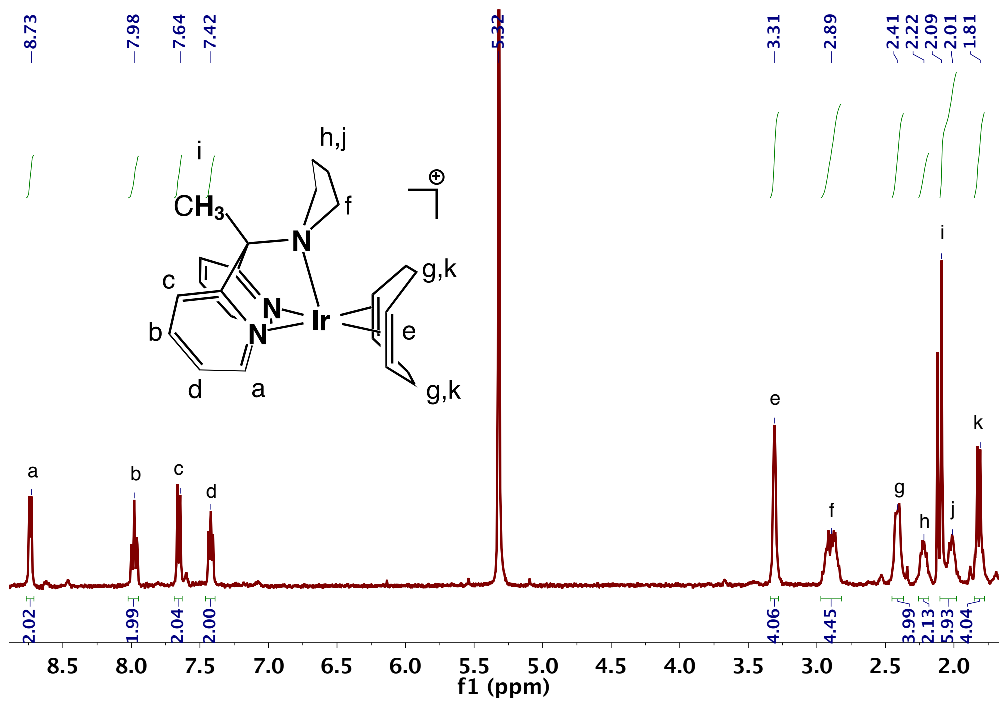


Figure S11. ^{1}H and ^{13}C NMR Spectra of $[(^{Me,pyr}CPy_2)Ir(COD)][B(C_6F_5)_4]$ in CD_2Cl_2



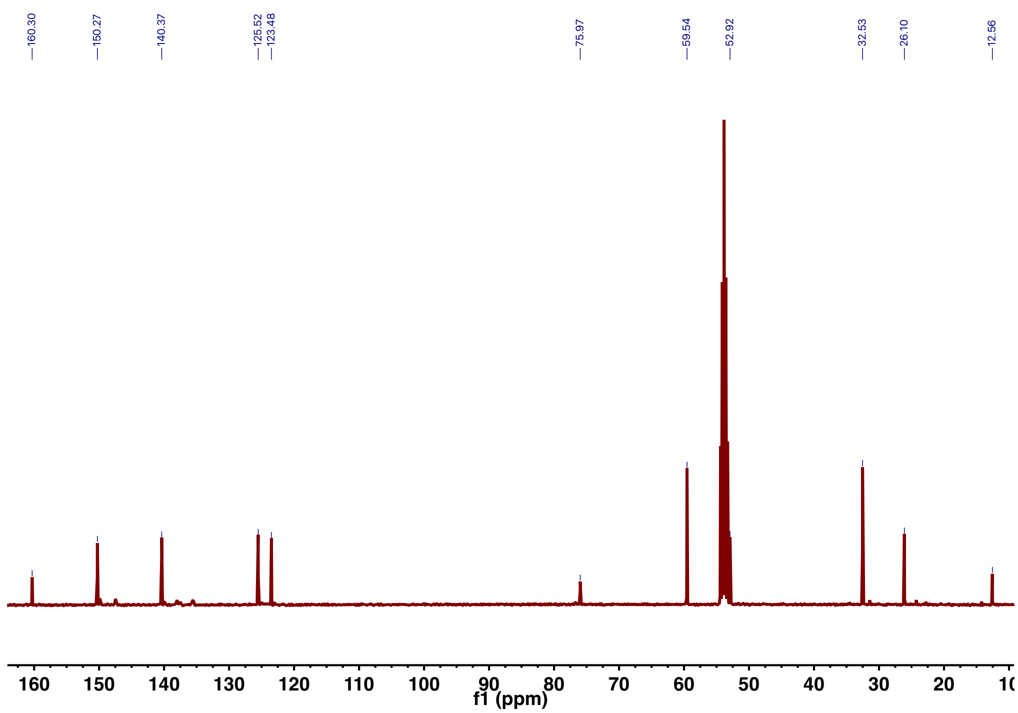
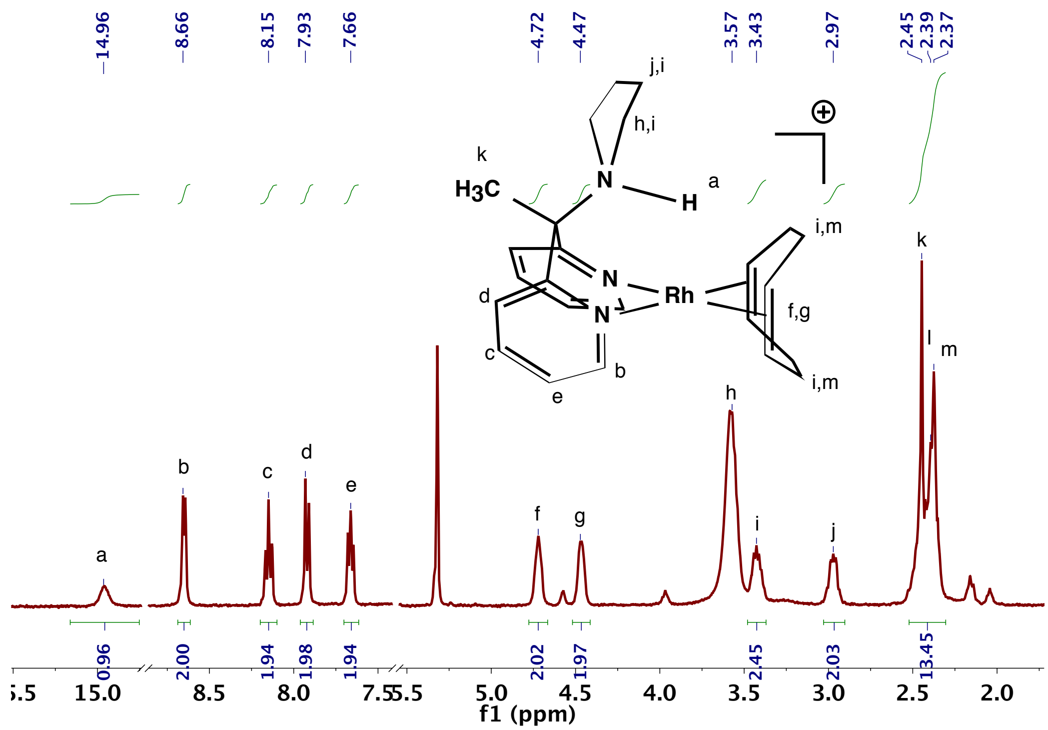


Figure S12. **[1]H and [13]C NMR Spectra of [(^{Me,pyrH}CPy$_2$)Rh(COD)][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$**



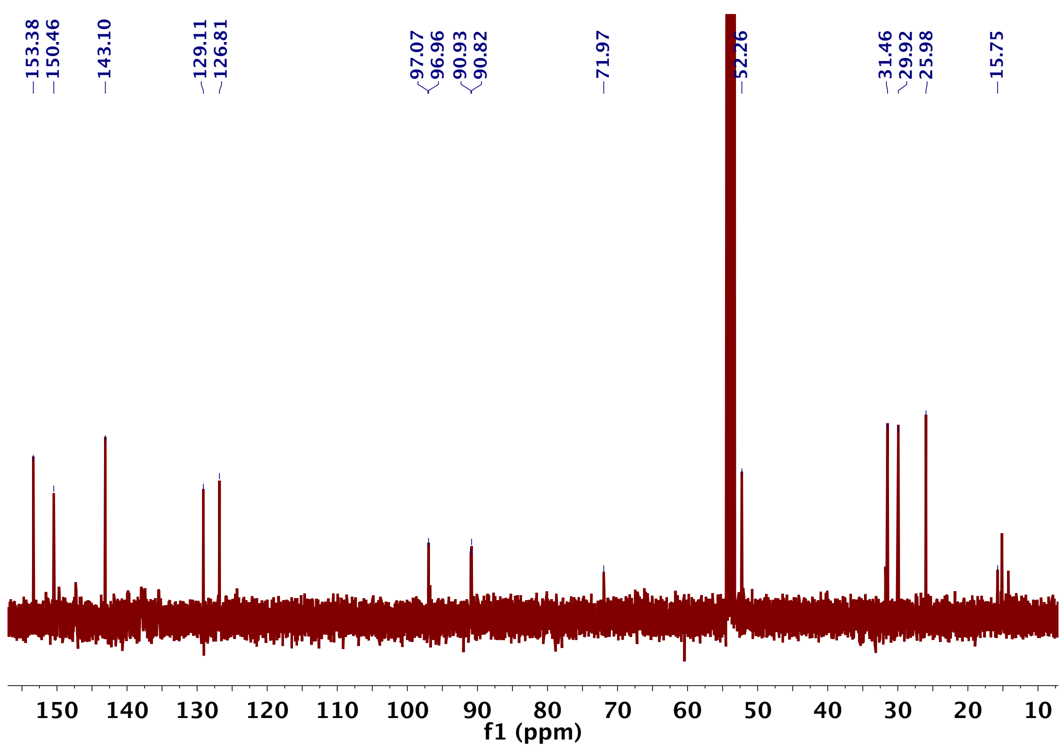
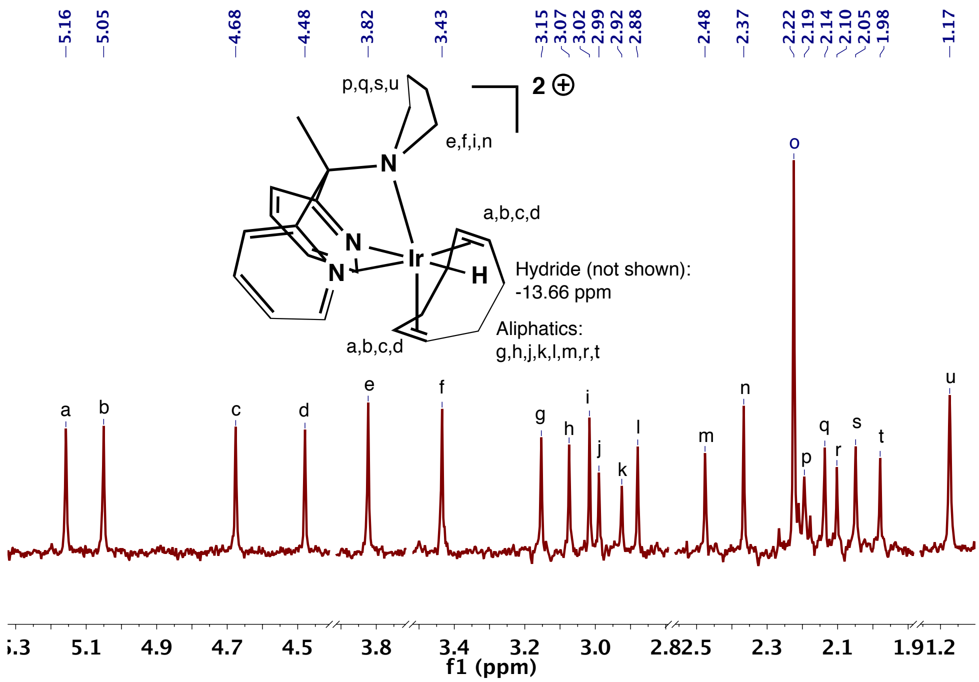
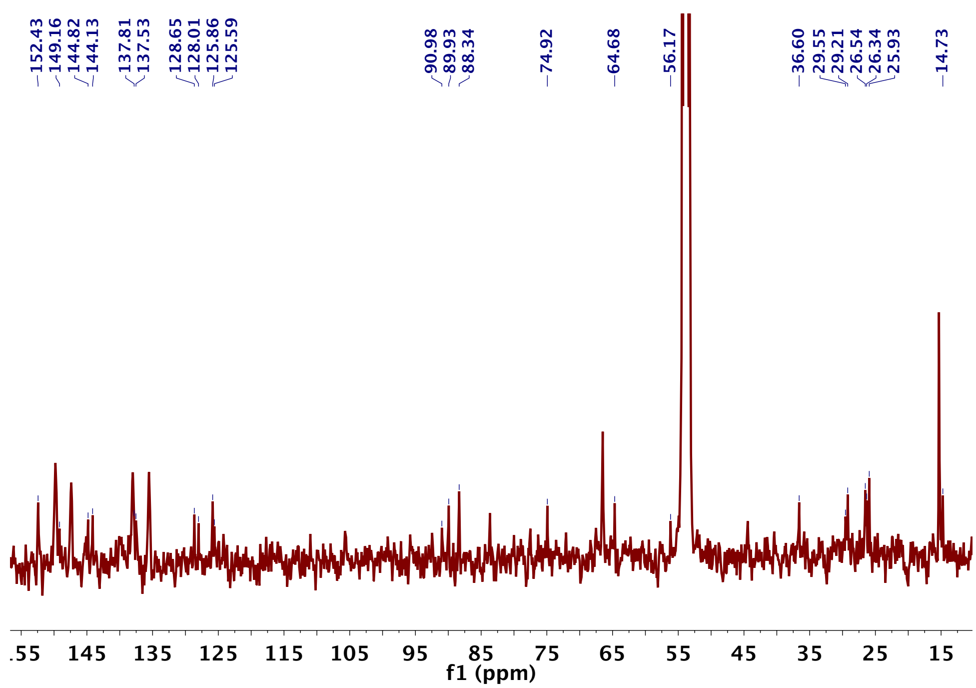


Figure S11. ^{1}H (PureShift) and ^{13}C NMR Spectra of [(^{Me,pyr}CPy$_2$)Ir(H)(COD)][B(C_6F_5)$_4$] in CD_2Cl_2





XYZ-Coordinates for Computed Structures.

Et_2O

8	-0.521010000	2.129129000	0.081121000
6	0.881004000	2.049421000	-0.096352000
1	1.153933000	2.494851000	-1.063871000
1	1.403550000	2.629619000	0.675031000
6	1.289653000	0.604523000	-0.032552000
1	0.798418000	0.024508000	-0.812724000
1	2.365917000	0.504771000	-0.161249000
1	1.023968000	0.168620000	0.929877000
6	-1.044768000	3.429838000	-0.121897000
1	-0.716619000	3.808410000	-1.099908000
1	-2.126995000	3.301129000	-0.174339000
6	-0.685323000	4.410893000	0.969467000
1	0.384004000	4.616266000	0.999101000
1	-1.195129000	5.359536000	0.806016000
1	-0.984813000	4.030877000	1.945909000

$[H(OEt_2)]^+$

1	-0.576392000	0.268921000	-0.838206000
8	-1.113859000	-0.323705000	-0.291320000
6	-2.204828000	0.458639000	0.388086000
1	-2.570500000	1.107988000	-0.402517000
1	-1.722655000	1.053110000	1.161895000
6	-3.236023000	-0.486401000	0.899974000
1	-2.850504000	-1.138093000	1.681600000
1	-4.038686000	0.102587000	1.339205000
1	-3.657291000	-1.090645000	0.100100000
6	-0.225136000	-1.184551000	0.582638000
1	0.784240000	-0.841275000	0.374334000
1	-0.486622000	-0.917949000	1.603661000
6	-0.455005000	-2.616461000	0.243004000
1	-1.479447000	-2.922068000	0.440472000
1	-0.215820000	-2.821510000	-0.797430000
1	0.202929000	-3.220708000	0.865207000

$[H(OEt_2)_2]^+$

8	0.430415000	1.669865000	-0.469859000
6	-0.332295000	2.724444000	-1.129503000
1	-1.120899000	2.191722000	-1.658133000
1	-0.793254000	3.343345000	-0.356599000
6	0.530286000	3.520786000	-2.060104000
1	-0.087533000	4.249923000	-2.580547000
1	1.304507000	4.071961000	-1.528455000
1	1.002471000	2.882071000	-2.804032000
6	1.423067000	2.102929000	0.515886000
1	1.202445000	1.545250000	1.426646000
1	1.242913000	3.157895000	0.721254000
6	2.808870000	1.833285000	0.014743000

1	3.025483000	2.397567000	-0.889865000
1	3.531320000	2.122481000	0.775970000
1	2.948182000	0.774701000	-0.196233000
1	-0.275457000	0.788988000	-0.071238000
8	-0.996941000	-0.103073000	0.282055000
6	-1.559682000	0.097455000	1.611007000
1	-1.701007000	1.175002000	1.684867000
1	-0.810020000	-0.201955000	2.346547000
6	-2.849090000	-0.648736000	1.771873000
1	-2.704988000	-1.726349000	1.708136000
1	-3.266983000	-0.433640000	2.753226000
1	-3.574502000	-0.347872000	1.018556000
6	-0.456731000	-1.433573000	-0.005273000
1	0.578570000	-1.281326000	-0.311350000
1	-0.447558000	-1.989683000	0.931626000
6	-1.269986000	-2.102022000	-1.071289000
1	-2.299864000	-2.251693000	-0.752850000
1	-1.273016000	-1.513513000	-1.986709000
1	-0.839360000	-3.075537000	-1.298752000

[(κ^{3}–^{Me,Pyr}CPy$_{2}$)Rh(COD)$^{+}$]

45	2.254462000	2.838122000	4.642120000
7	4.131443000	3.572772000	3.879249000
7	3.287211000	0.836107000	4.231407000
7	2.286210000	2.371923000	2.234439000
6	1.735840000	4.723393000	5.309210000
1	2.400606000	5.465203000	4.867967000
6	2.254640000	3.948265000	6.396355000
1	3.281747000	4.136820000	6.700273000
6	0.819995000	1.724644000	5.759982000
1	0.928421000	0.685138000	5.460591000
6	0.150030000	2.557787000	4.854705000
1	-0.177281000	2.083996000	3.934482000
6	4.116326000	1.624928000	0.681589000
1	5.149858000	1.295465000	0.620777000
1	3.502147000	0.832284000	0.261188000
1	4.020409000	2.503483000	0.048544000
6	3.705308000	1.934971000	2.114677000
6	4.565262000	3.049071000	2.715553000
6	5.742780000	3.491658000	2.133987000
1	6.076511000	3.071055000	1.198207000
6	6.485250000	4.483009000	2.752281000
1	7.403337000	4.835135000	2.301406000
6	6.032432000	5.013554000	3.945227000
1	6.575200000	5.788099000	4.466811000
6	4.850394000	4.532993000	4.469230000
1	4.459963000	4.926940000	5.397380000
6	3.868365000	0.720051000	3.029796000
6	4.592452000	-0.410155000	2.682831000
1	5.045756000	-0.496029000	1.706904000
6	4.723492000	-1.437106000	3.602474000
1	5.283927000	-2.326354000	3.347064000
6	4.133281000	-1.306677000	4.846442000

1	4.219005000	−2.077847000	5.598352000
6	3.421722000	−0.153801000	5.116764000
1	2.945703000	−0.004754000	6.078059000
6	1.945584000	3.603092000	1.495029000
1	2.288614000	3.555988000	0.454593000
1	2.413677000	4.467388000	1.967454000
6	0.437363000	3.613741000	1.549482000
1	−0.002651000	4.279136000	0.810270000
1	0.111230000	3.950038000	2.534022000
6	0.075962000	2.147355000	1.323466000
1	−0.067655000	1.954213000	0.261132000
1	−0.849833000	1.862866000	1.821160000
6	1.279665000	1.352511000	1.839531000
1	1.047320000	0.727419000	2.703383000
1	1.667149000	0.685757000	1.065983000
6	1.373445000	3.422447000	7.511981000
1	0.495923000	4.061470000	7.624945000
1	1.902853000	3.482746000	8.462695000
6	0.969115000	1.980946000	7.232709000
1	1.741251000	1.310523000	7.616963000
1	0.050451000	1.704768000	7.763021000
6	−0.606451000	3.813282000	5.233782000
1	−1.027203000	3.694251000	6.233615000
1	−1.463555000	3.921683000	4.568286000
6	0.275778000	5.059865000	5.155624000
1	0.142233000	5.542063000	4.185628000
1	−0.034475000	5.806308000	5.895916000

[(*exo*-κ^2–^{Me,Pyr}CPy$_2$)Rh(COD)$^+$]

45	2.339687000	2.726615000	4.919732000
7	4.159534000	3.476804000	3.922932000
7	3.054229000	0.818796000	4.076961000
7	4.113359000	1.708822000	0.666714000
6	1.782837000	4.721813000	5.332836000
1	2.497831000	5.364234000	4.824438000
6	2.210624000	4.107371000	6.522789000
1	3.235585000	4.290987000	6.834039000
6	0.862716000	1.745471000	6.086065000
1	0.963497000	0.675203000	5.938656000
6	0.239751000	2.442591000	5.039769000
1	−0.008196000	1.859287000	4.156584000
6	2.174117000	2.576228000	1.918056000
1	1.456946000	1.771276000	1.773566000
1	1.853985000	3.145479000	2.792099000
1	2.101811000	3.255892000	1.071508000
6	3.609165000	2.026811000	2.008052000
6	4.555812000	3.004403000	2.722867000
6	5.814793000	3.308795000	2.224148000
1	6.131428000	2.872207000	1.290381000
6	6.652629000	4.151914000	2.931193000
1	7.633831000	4.392809000	2.543882000
6	6.217073000	4.676707000	4.133746000
1	6.828495000	5.346615000	4.720335000

6	4.971981000	4.304124000	4.592355000
1	4.605278000	4.672744000	5.540503000
6	3.721369000	0.792787000	2.907415000
6	4.601746000	-0.238630000	2.607305000
1	5.171884000	-0.186727000	1.692756000
6	4.762178000	-1.287660000	3.492354000
1	5.446921000	-2.093784000	3.264412000
6	4.048402000	-1.276290000	4.676006000
1	4.142393000	-2.066124000	5.406987000
6	3.223259000	-0.202492000	4.933055000
1	2.692351000	-0.135666000	5.871397000
6	3.374989000	0.636504000	-0.035718000
1	2.335213000	0.570383000	0.305025000
1	3.824844000	-0.339993000	0.145985000
6	3.416785000	1.026408000	-1.500328000
1	2.628426000	0.546986000	-2.076653000
1	4.371932000	0.735454000	-1.941976000
6	3.305980000	2.537135000	-1.436294000
1	2.273956000	2.827148000	-1.224708000
1	3.609518000	3.043747000	-2.350516000
6	4.202673000	2.865834000	-0.258574000
1	5.237255000	2.985301000	-0.595613000
1	3.932203000	3.798583000	0.239543000
6	1.290036000	3.668583000	7.637946000
1	0.393456000	4.288005000	7.638480000
1	1.775688000	3.854075000	8.595411000
6	0.934292000	2.189832000	7.517435000
1	1.702337000	1.592129000	8.012450000
1	-0.000569000	1.964455000	8.042330000
6	-0.528288000	3.733435000	5.204472000
1	-0.964212000	3.769397000	6.203274000
1	-1.371539000	3.736800000	4.514438000
6	0.350144000	4.957239000	4.947699000
1	0.326835000	5.201692000	3.884520000
1	-0.047514000	5.838215000	5.462894000

[(^{Me,PyrH}CPy$_2$)Rh^I(COD)]$^+$

45	2.558928000	2.615656000	5.173173000
7	4.254472000	3.441612000	4.104051000
7	3.328092000	0.774322000	4.338906000
7	2.300882000	2.465592000	2.134367000
6	1.601429000	4.531246000	5.092136000
1	2.226532000	5.158524000	4.461660000
6	2.038673000	4.310397000	6.398817000
1	2.993999000	4.740671000	6.683605000
6	1.179849000	1.684428000	6.521155000
1	1.503640000	0.657721000	6.657020000
6	0.520478000	1.961061000	5.317481000
1	0.425515000	1.120380000	4.634531000
6	4.205722000	1.659311000	0.780356000
1	5.230075000	1.299628000	0.774117000
1	3.588476000	0.896615000	0.313188000
1	4.173648000	2.547368000	0.156847000
6	3.751448000	1.947818000	2.198368000

6	4.602381000	3.035003000	2.865143000
6	5.708557000	3.574471000	2.228782000
1	5.977422000	3.257015000	1.233932000
6	6.477249000	4.531801000	2.869955000
1	7.339855000	4.954278000	2.373169000
6	6.121405000	4.933103000	4.140720000
1	6.688161000	5.673274000	4.686076000
6	5.002066000	4.367990000	4.716421000
1	4.685295000	4.660121000	5.707605000
6	3.772720000	0.684659000	3.067390000
6	4.292586000	−0.504606000	2.580767000
1	4.629978000	−0.577158000	1.559837000
6	4.388751000	−1.611210000	3.407080000
1	4.794048000	−2.538272000	3.026306000
6	3.972040000	−1.500033000	4.716491000
1	4.044915000	−2.322744000	5.412421000
6	3.446203000	−0.295994000	5.137557000
1	3.118012000	−0.170603000	6.158269000
6	2.129425000	3.815524000	1.457013000
1	2.994338000	3.990485000	0.823306000
1	2.118956000	4.583063000	2.227507000
6	0.854366000	3.680822000	0.653539000
1	0.842449000	4.370887000	−0.185580000
1	−0.016147000	3.899155000	1.273205000
6	0.853146000	2.218541000	0.238755000
1	1.559724000	2.044919000	−0.573776000
1	−0.120117000	1.864683000	−0.090217000
6	1.298706000	1.513682000	1.496809000
1	0.482799000	1.404896000	2.209544000
1	1.760229000	0.539478000	1.361056000
6	1.121799000	3.972346000	7.545821000
1	0.124104000	4.363030000	7.346548000
1	1.467470000	4.484761000	8.442379000
6	1.083504000	2.469797000	7.793039000
1	1.922975000	2.183259000	8.428027000
1	0.183269000	2.183094000	8.346185000
6	−0.474756000	3.081536000	5.109464000
1	−1.032797000	3.239334000	6.032558000
1	−1.211695000	2.763936000	4.372658000
6	0.178687000	4.384039000	4.638172000
1	0.157829000	4.429125000	3.548047000
1	−0.404256000	5.250608000	4.966203000
1	2.030110000	2.593530000	3.139968000

***trans*-[(κ^{3}-^{Me,Pyr}CPy$_{2}$)Rh^{III}H(COD)]$^{+}$**

45	2.359739000	2.494133000	4.919787000
7	4.100083000	3.304305000	4.051311000
7	3.183523000	0.660324000	4.289267000
7	1.979545000	2.462962000	2.533293000
6	1.378363000	4.450371000	5.106395000
1	1.961500000	5.109010000	4.469906000
6	1.914653000	4.174754000	6.355365000
1	2.884565000	4.604282000	6.573519000

6	1.022049000	1.491018000	6.416466000
1	1.374027000	0.467903000	6.459805000
6	0.279332000	1.835880000	5.298630000
1	0.151696000	1.045959000	4.567039000
6	3.580803000	1.668292000	0.724845000
1	4.595986000	1.328349000	0.535971000
1	2.909403000	0.897857000	0.354780000
1	3.429721000	2.569358000	0.137032000
6	3.357955000	1.907745000	2.208518000
6	4.350048000	2.909655000	2.787943000
6	5.450115000	3.395004000	2.105483000
1	5.636910000	3.085537000	1.088733000
6	6.303875000	4.287681000	2.732257000
1	7.163373000	4.676507000	2.203606000
6	6.043563000	4.670853000	4.034146000
1	6.686672000	5.356126000	4.566112000
6	4.928602000	4.157609000	4.663224000
1	4.687636000	4.423066000	5.682362000
6	3.537837000	0.612815000	2.993085000
6	4.090623000	−0.538660000	2.458567000
1	4.361245000	−0.579601000	1.415511000
6	4.300036000	−1.639560000	3.271230000
1	4.729446000	−2.542534000	2.859501000
6	3.968105000	−1.561540000	4.609664000
1	4.136398000	−2.384093000	5.288775000
6	3.411633000	−0.393101000	5.084350000
1	3.154620000	−0.282624000	6.127159000
6	1.774310000	3.805437000	1.861468000
1	2.632402000	4.026891000	1.229455000
1	1.733072000	4.596749000	2.601990000
6	0.505784000	3.694810000	1.031724000
1	0.546530000	4.335753000	0.154428000
1	−0.364970000	4.002133000	1.612733000
6	0.411668000	2.216064000	0.703268000
1	1.055898000	1.958790000	−0.135728000
1	−0.596669000	1.898064000	0.448550000
6	0.885030000	1.582889000	1.993751000
1	0.064536000	1.588809000	2.707286000
1	1.234787000	0.554757000	1.910511000
6	1.109440000	3.740307000	7.551522000
1	0.107768000	4.159822000	7.468852000
1	1.547606000	4.186117000	8.442411000
6	1.056100000	2.227011000	7.718722000
1	1.928647000	1.889596000	8.278204000
1	0.188055000	1.929494000	8.314348000
6	−0.692932000	2.986754000	5.229388000
1	−1.150847000	3.117755000	6.209081000
1	−1.505880000	2.713164000	4.558372000
6	−0.065387000	4.295084000	4.741669000
1	−0.156113000	4.359880000	3.658982000
1	−0.624717000	5.153529000	5.125609000
1	3.089438000	2.349696000	6.269267000

***cis*-[(κ^{3}-^{Me,Pyr}CPy$_{2}$)Rh^{III}H(COD)]$^{+}$**

7	3.993486000	3.697547000	3.962411000
7	3.347833000	1.042907000	4.592809000
7	2.046700000	2.430874000	2.573472000
6	2.039659000	4.255146000	6.476920000
1	2.786398000	5.018781000	6.305081000
6	2.482788000	2.996420000	6.871537000
1	3.557371000	2.862246000	6.951795000
6	0.517659000	1.612243000	5.390680000
1	0.442840000	0.858955000	4.615913000
6	-0.024476000	2.868252000	5.142144000
1	-0.486484000	3.035622000	4.174734000
6	3.774670000	1.555873000	0.918495000
1	4.808463000	1.237068000	0.817487000
1	3.154480000	0.720702000	0.606436000
1	3.628219000	2.386747000	0.234780000
6	3.480744000	1.957539000	2.350013000
6	4.374088000	3.098945000	2.816776000
6	5.533746000	3.480995000	2.168181000
1	5.824151000	3.000750000	1.246681000
6	6.317741000	4.485888000	2.709410000
1	7.225757000	4.793770000	2.209436000
6	5.923698000	5.083867000	3.890762000
1	6.504523000	5.866669000	4.355416000
6	4.751286000	4.665704000	4.485687000
1	4.411811000	5.113918000	5.407336000
6	3.740998000	0.813804000	3.327551000
6	4.428434000	-0.338321000	2.988043000
1	4.723466000	-0.521491000	1.966322000
6	4.742651000	-1.255017000	3.977869000
1	5.278352000	-2.160273000	3.726838000
6	4.383889000	-0.985737000	5.284201000
1	4.637000000	-1.655154000	6.093126000
6	3.681942000	0.173589000	5.549118000
1	3.391920000	0.423621000	6.559423000
6	1.678224000	3.635119000	1.740208000
1	2.540343000	4.291225000	1.640830000
1	0.920851000	4.175383000	2.301429000
6	1.098247000	3.128613000	0.425798000
1	1.820448000	3.183780000	-0.385001000
1	0.258111000	3.752804000	0.131859000
6	0.670240000	1.680749000	0.697000000
1	1.172276000	0.986930000	0.027829000
1	-0.396797000	1.535775000	0.548084000
6	1.023543000	1.418500000	2.157967000
1	0.144273000	1.591150000	2.773682000
1	1.386545000	0.413881000	2.370572000
6	1.620367000	2.025463000	7.643503000
1	0.970796000	2.599119000	8.305698000
1	2.257988000	1.438694000	8.303064000
6	0.788639000	1.082411000	6.765649000
1	1.276944000	0.114586000	6.675401000
1	-0.171624000	0.869138000	7.245031000
6	-0.438932000	3.794495000	6.259856000

1	-0.742276000	3.183931000	7.111058000
1	-1.328162000	4.340617000	5.951906000
6	0.649097000	4.784665000	6.664208000
1	0.553624000	5.693862000	6.072146000
1	0.528481000	5.092406000	7.707269000
1	1.488906000	4.296074000	4.412266000
45	2.151605000	2.928928000	4.701776000

[(κ^3-^{Me,Pyr}CPy$_2$)Rh^{III}(κ^2-C,CH-1-yl-cyclooct-5-η^2-ene)]$^+$

45	2.230611000	2.653635000	4.586819000
7	4.051317000	3.405314000	3.886442000
7	3.220446000	0.659184000	4.215801000
7	2.103332000	2.270899000	2.429287000
6	1.637179000	4.518372000	5.223849000
1	2.311877000	5.282468000	4.841057000
6	2.116614000	3.885977000	6.482435000
1	2.938555000	4.455492000	6.922960000
6	0.635817000	1.577839000	5.741702000
1	0.786226000	0.535632000	5.477460000
6	-0.004963000	2.378001000	4.814684000
1	-0.289797000	1.902570000	3.886798000
6	3.809835000	1.585725000	0.664195000
1	4.818706000	1.204664000	0.531986000
1	3.135014000	0.851315000	0.234466000
1	3.740222000	2.502518000	0.085996000
6	3.538693000	1.827227000	2.138313000
6	4.443698000	2.905338000	2.701745000
6	5.614281000	3.338017000	2.105617000
1	5.917481000	2.935903000	1.151031000
6	6.388574000	4.291959000	2.744221000
1	7.304943000	4.639769000	2.287561000
6	5.976646000	4.791718000	3.966301000
1	6.551336000	5.532964000	4.501389000
6	4.796470000	4.326892000	4.505392000
1	4.434672000	4.692674000	5.455482000
6	3.747976000	0.575966000	2.988125000
6	4.441465000	-0.546250000	2.571743000
1	4.853789000	-0.604697000	1.575748000
6	4.592977000	-1.602685000	3.455885000
1	5.130025000	-2.490309000	3.150487000
6	4.052914000	-1.508096000	4.725402000
1	4.154562000	-2.307381000	5.444709000
6	3.368612000	-0.357381000	5.066585000
1	2.929114000	-0.236373000	6.048469000
6	1.700520000	3.511085000	1.685260000
1	2.123656000	3.475345000	0.680439000
1	2.092654000	4.394119000	2.185189000
6	0.197459000	3.425893000	1.613571000
1	-0.199510000	4.059486000	0.824623000
1	-0.255728000	3.760518000	2.544796000
6	-0.061121000	1.943155000	1.368134000
1	-0.072268000	1.734282000	0.299686000
1	-1.019765000	1.614479000	1.764660000

6	1.106448000	1.211117000	2.023416000
1	0.834815000	0.630114000	2.900951000
1	1.580431000	0.512745000	1.338552000
6	1.122494000	3.352284000	7.507824000
1	0.249058000	4.000280000	7.536127000
1	1.568829000	3.409107000	8.498325000
6	0.767834000	1.900822000	7.203490000
1	1.536138000	1.254005000	7.630307000
1	-0.163086000	1.609709000	7.699389000
6	-0.724818000	3.662607000	5.133241000
1	-1.166993000	3.586930000	6.126045000
1	-1.562762000	3.769712000	4.445485000
6	0.195072000	4.876805000	5.025521000
1	0.101168000	5.334094000	4.039988000
1	-0.098945000	5.660413000	5.731966000
1	2.786434000	2.931031000	6.242366000

[(^{Me,Pyr}CPy(PyH))Rh^{I}(COD)]$^{+}$ - pyridine-protonated isomer

45	-1.11782	0.20014	-0.08544
7	0.27033	1.69346	0.56019
7	1.31251	-1.10806	1.42548
7	0.66213	-0.18898	-1.34586
6	-2.91020	1.19744	0.44963
1	-2.66286	2.25601	0.46013
6	-2.49512	0.42365	1.54106
1	-1.94265	0.93563	2.32492
6	-1.85826	-1.79614	-0.00407
1	-1.02574	-2.44472	-0.26795
6	-2.50359	-1.11626	-1.04440
1	-2.10940	-1.25765	-2.04832
6	3.10080	0.45600	-1.47696
1	4.00052	0.65868	-0.90311
1	3.30132	-0.41437	-2.09545
1	2.93126	1.31281	-2.12215
6	1.89861	0.22978	-0.56829
6	1.55863	1.51120	0.19792
6	2.53551	2.42258	0.55912
1	3.56358	2.26109	0.27319
6	2.18970	3.54392	1.29371
1	2.94740	4.26193	1.57605
6	0.86932	3.72668	1.65826
1	0.55144	4.58437	2.23230
6	-0.05550	2.77939	1.27453
1	-1.09787	2.87896	1.54493
6	2.22335	-0.85797	0.46128
6	3.39863	-1.58122	0.49954
1	4.15655	-1.41801	-0.24960
6	3.60468	-2.52486	1.49635
1	4.52528	-3.09170	1.51048
6	2.64112	-2.73810	2.46628
1	2.77782	-3.45904	3.25719
6	1.48084	-2.00488	2.40555
1	0.67128	-2.09843	3.11357
6	0.35423	0.77154	-2.47119

1	0.67709	1.77402	−2.19560
1	−0.73184	0.80330	−2.57286
6	0.99457	0.22656	−3.74291
1	1.91125	0.76072	−3.98339
1	0.32380	0.36769	−4.58674
6	1.27332	−1.25524	−3.47027
1	2.32877	−1.48859	−3.59566
1	0.73373	−1.90452	−4.15558
6	0.80621	−1.50887	−2.03921
1	−0.17675	−1.97338	−2.04753
1	1.45984	−2.16446	−1.46737
6	−3.15656	−0.87050	1.95305
1	−4.21047	−0.84059	1.67871
1	−3.13700	−0.95220	3.03868
6	−2.46736	−2.08745	1.33740
1	−1.67770	−2.43656	2.00361
1	−3.16283	−2.92901	1.25205
6	−3.92828	−0.62328	−0.97278
1	−4.50695	−1.26489	−0.30865
1	−4.39110	−0.72061	−1.95365
6	−3.99403	0.83605	−0.52400
1	−3.88645	1.48552	−1.39378
1	−4.97482	1.07214	−0.09824
1	0.40509	−0.61152	1.36819

[(κ^{3}–^{Me,Pyr}CPy$_2$)Ir(COD)$^{+}$]

77	2.270207000	2.827895000	4.636024000
7	4.141092000	3.564484000	3.871171000
7	3.283896000	0.841027000	4.216760000
7	2.295578000	2.371238000	2.237796000
6	1.733726000	4.716383000	5.290777000
1	2.381728000	5.493932000	4.883920000
6	2.268200000	3.939436000	6.392391000
1	3.275009000	4.186150000	6.725478000
6	0.844299000	1.720233000	5.769742000
1	0.915987000	0.669662000	5.495685000
6	0.167782000	2.548303000	4.847126000
1	−0.196329000	2.049200000	3.953511000
6	4.123151000	1.623884000	0.670715000
1	5.155800000	1.291207000	0.611050000
1	3.507098000	0.833258000	0.249545000
1	4.031141000	2.503399000	0.038611000
6	3.717270000	1.932091000	2.104160000
6	4.576761000	3.046113000	2.703764000
6	5.750847000	3.496019000	2.123715000
1	6.085895000	3.079211000	1.186702000
6	6.488016000	4.489421000	2.745166000
1	7.404065000	4.847716000	2.295210000
6	6.033097000	5.014602000	3.940100000
1	6.572674000	5.790406000	4.462901000
6	4.855203000	4.528406000	4.465558000
1	4.461150000	4.914181000	5.394979000
6	3.873433000	0.718446000	3.017466000

6	4.593235000	−0.415349000	2.677911000
1	5.053480000	−0.502735000	1.705382000
6	4.710889000	−1.442463000	3.598833000
1	5.267902000	−2.335256000	3.348880000
6	4.112107000	−1.306202000	4.838508000
1	4.188197000	−2.076490000	5.592268000
6	3.407473000	−0.149832000	5.106193000
1	2.929884000	0.006882000	6.064598000
6	1.952875000	3.601535000	1.490676000
1	2.289124000	3.538025000	0.449818000
1	2.430004000	4.466528000	1.951554000
6	0.445663000	3.618042000	1.554786000
1	0.005268000	4.282588000	0.815166000
1	0.126241000	3.958455000	2.540065000
6	0.077820000	2.152260000	1.334034000
1	−0.078625000	1.957754000	0.273866000
1	−0.842371000	1.871267000	1.843538000
6	1.284100000	1.353118000	1.836985000
1	1.057344000	0.719975000	2.695577000
1	1.672204000	0.698093000	1.054726000
6	1.378293000	3.431241000	7.514920000
1	0.507103000	4.080362000	7.623192000
1	1.906387000	3.493604000	8.466321000
6	0.958732000	1.992351000	7.245208000
1	1.710765000	1.314116000	7.655567000
1	0.022444000	1.737741000	7.754663000
6	−0.604034000	3.797376000	5.231415000
1	−1.029470000	3.666169000	6.228065000
1	−1.459078000	3.901549000	4.562368000
6	0.267612000	5.052395000	5.169212000
1	0.116965000	5.555670000	4.211848000
1	−0.037310000	5.778926000	5.930834000

[(*exo*-κ^{2}–^{Me,Pyr}CPy$_{2}$)Ir(COD)$^{+}$]

77	2.422051000	2.677334000	5.012687000
7	4.225515000	3.391144000	4.008973000
7	3.055881000	0.787347000	4.075333000
7	4.171918000	1.777918000	0.675562000
6	1.561841000	4.597025000	4.961186000
1	2.139093000	5.208542000	4.269655000
6	2.117957000	4.388603000	6.246669000
1	3.066630000	4.879264000	6.442220000
6	1.159451000	1.832118000	6.491977000
1	1.417883000	0.790068000	6.655738000
6	0.400442000	2.112636000	5.331774000
1	0.185835000	1.268327000	4.680831000
6	2.239510000	2.661055000	1.909915000
1	1.619887000	2.051620000	1.256440000
1	1.712193000	2.741654000	2.860162000
1	2.303926000	3.663878000	1.490360000
6	3.642414000	2.045158000	2.022622000
6	4.615378000	2.949928000	2.792174000
6	5.893773000	3.217603000	2.322218000
1	6.197646000	2.810945000	1.370974000

6	6.765881000	3.980855000	3.075694000
1	7.760962000	4.191876000	2.707161000
6	6.347430000	4.458947000	4.303245000
1	6.987809000	5.059193000	4.932429000
6	5.080705000	4.133194000	4.732586000
1	4.727152000	4.457042000	5.699845000
6	3.682108000	0.769272000	2.875567000
6	4.459440000	-0.318416000	2.503860000
1	5.024928000	-0.265253000	1.588073000
6	4.531974000	-1.435823000	3.314898000
1	5.139525000	-2.281766000	3.023021000
6	3.823127000	-1.444011000	4.499898000
1	3.832388000	-2.292934000	5.167608000
6	3.119713000	-0.311078000	4.846220000
1	2.599660000	-0.262008000	5.790490000
6	3.440239000	0.755033000	-0.105392000
1	2.437963000	0.580162000	0.300146000
1	3.951423000	-0.207750000	-0.076266000
6	3.354416000	1.295806000	-1.523002000
1	2.502085000	0.890707000	-2.064650000
1	4.252840000	1.029096000	-2.082630000
6	3.299030000	2.797320000	-1.314752000
1	2.297829000	3.102071000	-1.001589000
1	3.558338000	3.374107000	-2.200492000
6	4.287269000	2.984532000	-0.180631000
1	5.306015000	3.050571000	-0.576767000
1	4.118829000	3.896135000	0.392139000
6	1.284351000	4.135821000	7.484485000
1	0.307917000	4.609143000	7.376126000
1	1.751442000	4.624295000	8.338935000
6	1.142277000	2.642542000	7.757781000
1	1.975838000	2.306427000	8.376728000
1	0.237005000	2.429245000	8.335886000
6	-0.567835000	3.272457000	5.224908000
1	-0.988989000	3.485243000	6.208039000
1	-1.411236000	2.978961000	4.601123000
6	0.095333000	4.519059000	4.636421000
1	-0.006297000	4.506746000	3.549840000
1	-0.414367000	5.427771000	4.972965000

[(^{Me,PyrH}CPy$_2$)Ir^{I}(COD)]$^{+}$

77	2.577847000	2.609739000	5.185393000
7	4.266894000	3.430988000	4.108271000
7	3.313545000	0.766530000	4.338543000
7	2.297161000	2.458929000	2.112449000
6	1.626408000	4.518324000	5.093227000
1	2.230209000	5.169569000	4.464814000
6	2.081843000	4.305052000	6.407537000
1	3.015588000	4.784983000	6.687271000
6	1.211304000	1.697701000	6.552626000
1	1.494324000	0.661277000	6.712250000
6	0.542530000	1.967566000	5.339882000

1	0.409059000	1.112653000	4.680991000
6	4.212783000	1.647046000	0.779777000
1	5.238148000	1.289987000	0.780513000
1	3.599068000	0.881386000	0.313135000
1	4.180151000	2.531620000	0.151501000
6	3.747428000	1.942302000	2.193344000
6	4.596640000	3.033006000	2.858437000
6	5.686285000	3.590333000	2.209720000
1	5.941777000	3.283729000	1.208228000
6	6.457039000	4.550857000	2.843437000
1	7.305333000	4.985921000	2.333328000
6	6.121657000	4.938694000	4.123921000
1	6.690921000	5.680244000	4.664627000
6	5.018963000	4.360284000	4.715831000
1	4.714487000	4.640677000	5.713867000
6	3.761189000	0.679710000	3.064650000
6	4.271751000	-0.513301000	2.578822000
1	4.613246000	-0.585405000	1.559435000
6	4.354494000	-1.624874000	3.399945000
1	4.754236000	-2.553086000	3.016401000
6	3.930199000	-1.517337000	4.707205000
1	3.989488000	-2.344676000	5.398827000
6	3.415339000	-0.311559000	5.133008000
1	3.080856000	-0.185377000	6.151253000
6	2.129119000	3.806850000	1.433308000
1	2.994569000	3.981595000	0.799920000
1	2.116660000	4.575373000	2.203140000
6	0.854462000	3.671638000	0.629076000
1	0.842484000	4.361373000	-0.210308000
1	-0.015919000	3.889947000	1.248876000
6	0.854215000	2.209178000	0.214617000
1	1.561765000	2.035948000	-0.597217000
1	-0.118517000	1.854677000	-0.115280000
6	1.299652000	1.504948000	1.473220000
1	0.482902000	1.392916000	2.184488000
1	1.763291000	0.531722000	1.337026000
6	1.161588000	3.992536000	7.564146000
1	0.172365000	4.406512000	7.368049000
1	1.522050000	4.502673000	8.456078000
6	1.088158000	2.492114000	7.820002000
1	1.903567000	2.194359000	8.480925000
1	0.166190000	2.226261000	8.346546000
6	-0.459701000	3.086980000	5.143962000
1	-1.007214000	3.245007000	6.073388000
1	-1.204324000	2.768851000	4.415252000
6	0.191809000	4.388127000	4.666288000
1	0.153037000	4.438098000	3.576318000
1	-0.377608000	5.256322000	5.011767000
1	2.024829000	2.590476000	3.121880000

***trans*-[(κ^3-^{Me,Pyr}CPy$_2$)Ir^{III}H(COD)]$^+$**

77	2.363935000	2.493737000	4.935224000
7	4.107574000	3.306698000	4.047879000

7	3.180958000	0.655570000	4.280300000
7	1.987502000	2.466564000	2.551079000
6	1.371289000	4.436453000	5.082629000
1	1.933443000	5.128198000	4.461812000
6	1.917032000	4.167017000	6.338703000
1	2.869729000	4.631209000	6.562175000
6	1.041689000	1.499077000	6.414901000
1	1.365761000	0.467268000	6.479588000
6	0.295914000	1.838387000	5.285202000
1	0.136751000	1.026904000	4.583482000
6	3.575032000	1.675719000	0.721950000
1	4.590452000	1.340662000	0.525758000
1	2.905491000	0.901959000	0.355765000
1	3.416318000	2.577212000	0.136916000
6	3.365818000	1.909511000	2.207389000
6	4.360564000	2.909850000	2.783493000
6	5.461377000	3.392177000	2.102156000
1	5.649294000	3.080185000	1.086450000
6	6.315668000	4.284617000	2.728755000
1	7.176381000	4.671396000	2.200707000
6	6.053738000	4.670645000	4.029735000
1	6.696818000	5.356824000	4.560420000
6	4.938182000	4.161541000	4.659106000
1	4.693712000	4.428997000	5.676720000
6	3.545316000	0.611832000	2.984654000
6	4.100646000	−0.536662000	2.449181000
1	4.379389000	−0.571761000	1.408108000
6	4.302546000	−1.641927000	3.257838000
1	4.734520000	−2.543206000	2.845255000
6	3.958658000	−1.570305000	4.593860000
1	4.119025000	−2.397310000	5.269374000
6	3.400917000	−0.404867000	5.071739000
1	3.134083000	−0.298667000	6.112194000
6	1.776922000	3.810101000	1.874173000
1	2.640083000	4.033557000	1.250641000
1	1.725004000	4.600221000	2.613890000
6	0.514654000	3.691582000	1.036438000
1	0.564872000	4.321908000	0.152025000
1	−0.358532000	4.009583000	1.607482000
6	0.415858000	2.210137000	0.722548000
1	1.054724000	1.941616000	−0.116517000
1	−0.594624000	1.893607000	0.474812000
6	0.886348000	1.585799000	2.017782000
1	0.068145000	1.603887000	2.732593000
1	1.232706000	0.555857000	1.944129000
6	1.106948000	3.749965000	7.541247000
1	0.107925000	4.175276000	7.455093000
1	1.546953000	4.201088000	8.428474000
6	1.044300000	2.237963000	7.717776000
1	1.903098000	1.899346000	8.297606000
1	0.161047000	1.947742000	8.293520000
6	−0.697395000	2.977557000	5.224516000
1	−1.156550000	3.096632000	6.205217000
1	−1.507892000	2.694668000	4.554364000
6	−0.084011000	4.293769000	4.743550000

1	-0.194138000	4.372680000	3.663270000
1	-0.633152000	5.147289000	5.150834000
1	3.148420000	2.317661000	6.283538000

***cis*-[(κ^{3}-^{Me,Pyr}CPy$_2$)Ir^{III}H(COD)]$^{+}$**

7	3.996333000	3.694238000	3.955847000
7	3.334941000	1.057147000	4.582544000
7	2.047978000	2.434249000	2.568198000
6	2.054877000	4.237126000	6.481608000
1	2.806831000	5.005304000	6.356193000
6	2.491210000	2.962034000	6.862307000
1	3.563849000	2.836255000	6.978103000
6	0.526649000	1.618480000	5.383864000
1	0.407691000	0.862751000	4.616892000
6	-0.015104000	2.886584000	5.144967000
1	-0.512081000	3.046579000	4.193397000
6	3.781727000	1.553050000	0.910352000
1	4.815997000	1.234026000	0.814558000
1	3.162703000	0.716444000	0.600103000
1	3.638103000	2.380760000	0.222542000
6	3.485410000	1.959689000	2.338487000
6	4.377210000	3.102656000	2.804524000
6	5.531985000	3.493408000	2.154338000
1	5.821678000	3.018075000	1.230104000
6	6.311600000	4.500906000	2.697292000
1	7.215958000	4.816359000	2.195537000
6	5.917737000	5.092297000	3.882468000
1	6.495638000	5.877169000	4.347086000
6	4.751214000	4.666261000	4.481008000
1	4.408735000	5.108360000	5.404174000
6	3.741382000	0.821545000	3.321231000
6	4.434577000	-0.330398000	2.996906000
1	4.741020000	-0.517729000	1.979379000
6	4.739833000	-1.240427000	3.995490000
1	5.280373000	-2.145800000	3.755879000
6	4.365521000	-0.964720000	5.296303000
1	4.610500000	-1.629417000	6.111456000
6	3.659725000	0.193724000	5.549720000
1	3.357596000	0.450287000	6.554106000
6	1.676612000	3.631159000	1.719939000
1	2.536306000	4.290615000	1.620797000
1	0.913861000	4.169503000	2.275110000
6	1.106242000	3.110380000	0.408261000
1	1.832545000	3.157877000	-0.399223000
1	0.267488000	3.731126000	0.103409000
6	0.677122000	1.665312000	0.691618000
1	1.179890000	0.964946000	0.029901000
1	-0.389592000	1.519676000	0.541111000
6	1.023649000	1.416152000	2.155459000

1	0.144533000	1.597487000	2.768624000
1	1.386113000	0.413785000	2.379065000
6	1.618802000	2.000537000	7.642658000
1	0.981943000	2.580734000	8.311377000
1	2.253200000	1.404127000	8.296961000
6	0.772247000	1.075906000	6.762474000
1	1.241679000	0.098158000	6.672415000
1	-0.195887000	0.881766000	7.232913000
6	-0.428204000	3.800334000	6.276633000
1	-0.739059000	3.181057000	7.118898000
1	-1.312105000	4.358128000	5.974613000
6	0.669492000	4.773702000	6.696592000
1	0.577699000	5.697211000	6.126033000
1	0.558607000	5.056597000	7.747289000
1	1.501495000	4.344475000	4.372450000
77	2.143489000	2.942728000	4.703632000

[(^{Me,Pyr}CPy(PyH))Ir^{I}(COD)]$^{+}$ - pyridine-protonated isomer

7	0.25451	1.73239	0.51058
7	1.29849	-1.14194	1.39328
7	0.65175	-0.17262	-1.36576
6	-2.91855	1.20124	0.48347
1	-2.71862	2.26955	0.52542
6	-2.46524	0.41318	1.56252
1	-1.93408	0.93223	2.35681
6	-1.86381	-1.77107	-0.02283
1	-1.06247	-2.44653	-0.31532
6	-2.53339	-1.07319	-1.05012
1	-2.18150	-1.23750	-2.06688
6	3.09999	0.47403	-1.47375
1	3.99004	0.68675	-0.88943
1	3.31879	-0.39430	-2.08776
1	2.93131	1.32983	-2.11986
6	1.89253	0.23641	-0.57473
6	1.55168	1.51777	0.19352
6	2.53536	2.40233	0.59861
1	3.56977	2.21345	0.35676
6	2.19076	3.53171	1.32072
1	2.95604	4.22669	1.63759
6	0.86123	3.75312	1.62681
1	0.54310	4.62044	2.18595
6	-0.07253	2.83061	1.20971
1	-1.12141	2.95539	1.43865
6	2.21991	-0.85831	0.44930
6	3.41480	-1.54838	0.50432
1	4.18287	-1.35930	-0.22810
6	3.62848	-2.49318	1.49883
1	4.56502	-3.03298	1.52679
6	2.65337	-2.74125	2.44827
1	2.79541	-3.46385	3.23677
6	1.47335	-2.04146	2.36835
1	0.65252	-2.16495	3.05881
6	0.39761	0.76756	-2.52792

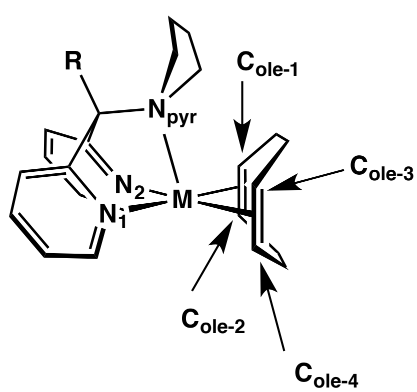
1	0.72578	1.77073	-2.26108
1	-0.68317	0.81302	-2.66791
6	1.07149	0.18207	-3.76359
1	1.99978	0.70016	-3.99348
1	0.42516	0.30622	-4.62876
6	1.32499	-1.29474	-3.44398
1	2.38306	-1.53952	-3.50834
1	0.81672	-1.95640	-4.14123
6	0.77835	-1.51049	-2.03724
1	-0.22417	-1.92668	-2.09266
1	1.37026	-2.18619	-1.42374
6	-3.12801	-0.88339	1.97313
1	-4.18947	-0.83712	1.72991
1	-3.07774	-0.98468	3.05598
6	-2.47232	-2.09596	1.31299
1	-1.68771	-2.48807	1.96096
1	-3.19006	-2.91482	1.20139
6	-3.96640	-0.60376	-0.93665
1	-4.52109	-1.27309	-0.27866
1	-4.44834	-0.68261	-1.90987
6	-4.04484	0.84109	-0.44449
1	-3.99594	1.51688	-1.29941
1	-5.00726	1.04057	0.03723
1	0.36918	-0.67389	1.31029
77	-1.12600	0.22599	-0.09786

Table S2. Pressure-Corrected Boiling Points for Selected Solvents and Reagents

Solvent	ΔH_{vap} (kJ/mol)	T_{boil} (ºC, 1 atm)	T_{boil} (K, 1 atm)	T_{boil} (ºC, 0.77 atm)	T_{boil} (K, 0.77 atm)
dichloromethane	29.2	39.6	312.8	32	305.5
diethyl ether	28.1	34.6	307.8	27	300.4
THF	30.8	66	339.2	58	331.0
fluorobenzene	31.2	84.5	357.7	76	348.8
benzene	33.83	80.1	353.3	72	345.2
toluene	33.5	111	384.2	101	374.6
hexane	31.52	69	342.2	61	334.1
pentane	26.42	36	309.2	28	301.3
water	43.99	100	373.2	93	366.2
ethanol	40.5	78.37	351.5	72	344.9
methanol	35.4	64.7	337.9	58	330.8
1,2-dichloroethane	34.8	84	357.2	76	349.2
isopropanol	39.8	82.6	355.8	76	348.8
acetone	31.1	56.05	329.2	48	321.6
DMSO	48.6	189	462.2	179	452.6
DMF	56.7	153	426.2	146	419.1
MTBE	29.6	55.2	328.4	47	320.4
heptane	36.57	98.4	371.6	90	363.3
octane	41.56	125.5	398.7	117	390.3
chloroform	30.9	61.15	334.3	53	326.4
acetonitrile	33.3	81.7	354.9	73	346.6
o-difluorobenzene	32.2	92	365.2	83	356.2

Table S3. Comparison of Calculated and Experimental Bond Length and Angles for [(κ^3–^{Me,Pyr}CPy$_2$)M(COD)][B(C$_6$F$_5$)$_4$] (M = Rh, Ir) and [(κ^3–^{H,Pyr}CPy$_2$)Ir(COD)$^+$]Cl

Metric	[(^{Me,Pyr}CPy$_2$)M(COD)$^+$] (Calc.)		[(^{Me,Pyr}CPy$_2$)Rh(COD)$^+$] (Exp.)	[(^{H,Pyr}CPy$_2$)Ir(COD)$^+$] (Exp.)
	M = Rh	M = Ir		
M-N$_{pyr}$ (Å)	2.45261	2.44145	2.3645(10)	2.299(3)
M-N$_1$ (Å)	2.28983	2.26958	2.2470(10)	2.199(3)
M-N$_2$ (Å)	2.15517	2.15123	2.1021(10)	2.105(3)
M-C$_{ole-1}$ (Å)	2.06597	2.06952	2.0711(12)	2.068(4)
M-C$_{ole-2}$ (Å)	2.07600	2.07855	2.0795(12)	2.087(3)
M-C$_{ole-3}$ (Å)	2.13364	2.13141	2.1582(13)	2.138(3)
M-C$_{ole-4}$ (Å)	2.13240	2.13200	2.1480(12)	2.131(3)
C$_{ole-1}$-C$_{ole-2}$ (Å)	1.43243	1.45012	1.4350(19)	1.464(6)
C$_{ole-3}$-C$_{ole-4}$ (Å)	1.40090	1.41230	1.399(2)	1.520(6)
N$_1$-M-N$_{pyr}$ (°)	69.628	69.522	71.81(3)	74.07(10)
N$_2$-M-N$_{pyr}$ (°)	72.904	72.888	75.86(3)	75.87(10)
N$_1$-M-N$_2$ (°)	80.894	81.120	81.38(4)	81.84(11)
N$_1$-M-C$_{ole-3}$ (°)	110.355	110.122	112.69(5)	111.09(13)
N$_1$-M-C$_{ole-4}$ (°)	86.611	86.682	86.74(5)	86.00(13)
N$_2$-M-C$_{ole-1}$ (°)	91.253	91.460	90.52(5)	90.95(14)
N$_2$-M-C$_{ole-2}$ (°)	96.705	96.786	96.32(5)	96.09(14)



note: for [(κ^3–^{H,Pyr}CPy$_2$)Ir(COD)$^+$]Cl, data for one of the two molecules in the asymmetric unit are shown

References.

(1) Bruker. *Apex II*. 2009, p Bruker AXS Inc., Madison, Wisconsin, USA.

(2) Sheldrick, G. M. *SADABS, Programs for Scaling and Absorption Correction of Area Detector Data*. 1997, p University of Göttingen: Göttingen, Germany.

(3) Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64* (1), 112.

(4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42* (2), 339.

(5) Zangger, K.; Sterk, H. *J. Magn. Reson.* **1997**, *124* (124), 486.

(6) Aguilar, J. A.; Faulkner, S.; Nilsson, M.; Morris, G. A. *Angew. Chemie - Int. Ed.* **2010**, *49* (23), 3901.

(7) Zangger, K. *Prog. Nucl. Magn. Reson. Spectrosc.* **2015**, *86–87*, 1.