

ELECTRONIC SUPPLEMENTARY INFORMATION

Reactivity of Vinylidene Complexes of Ruthenium with Hydrazines and Hydroxylamines

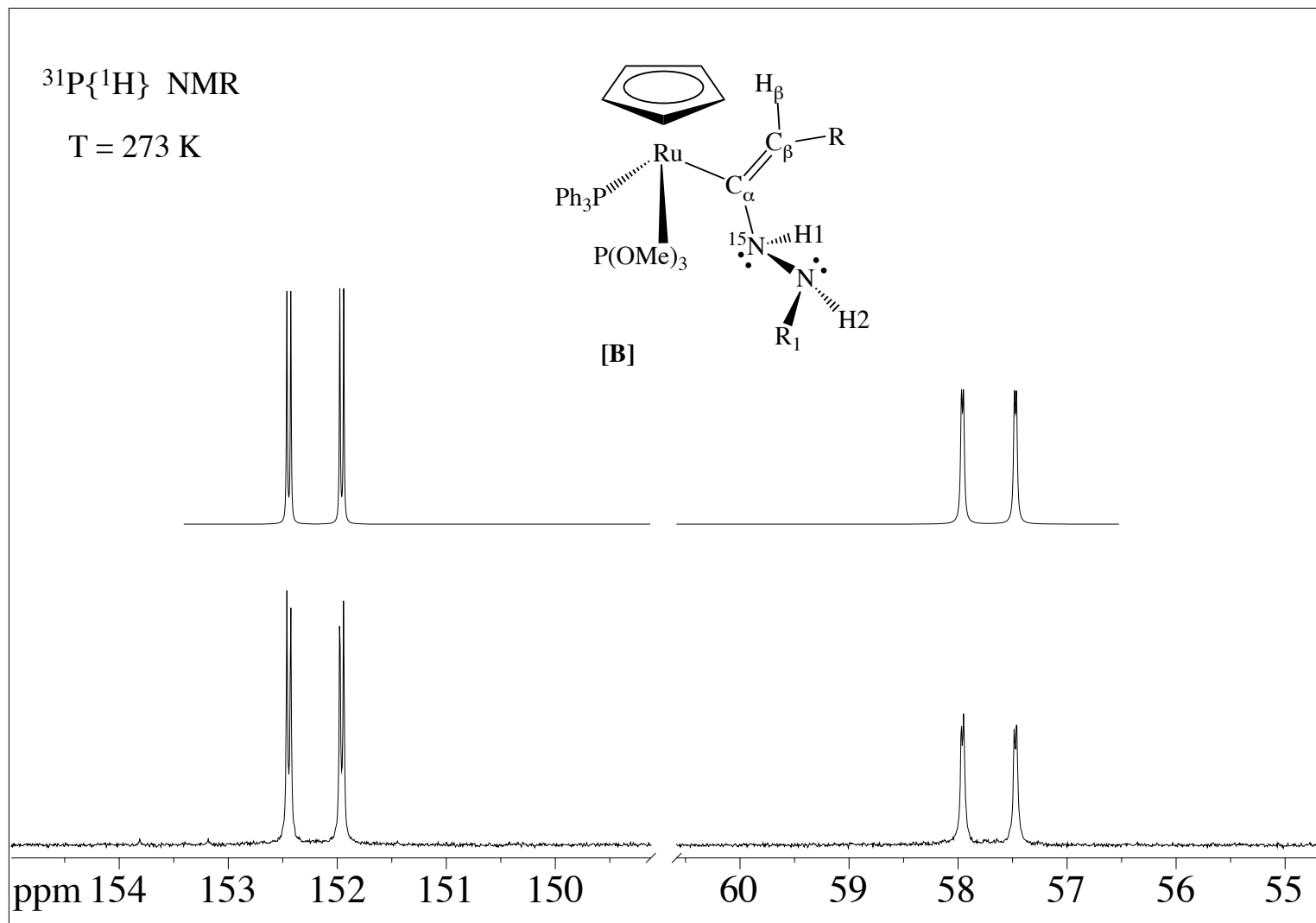
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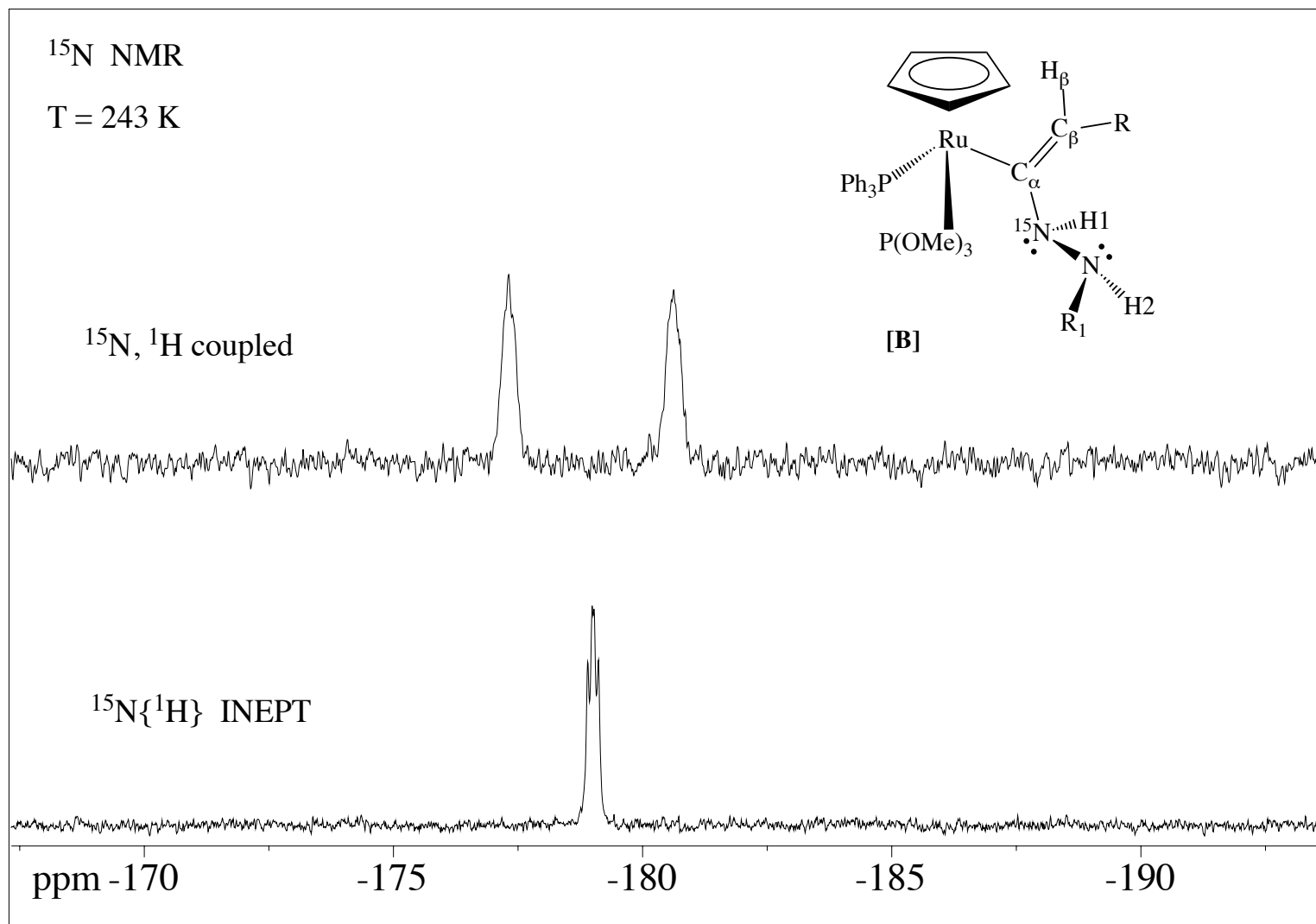
Dorsoduro 2137, 30123 Venezia, Italy

Jesús Castro

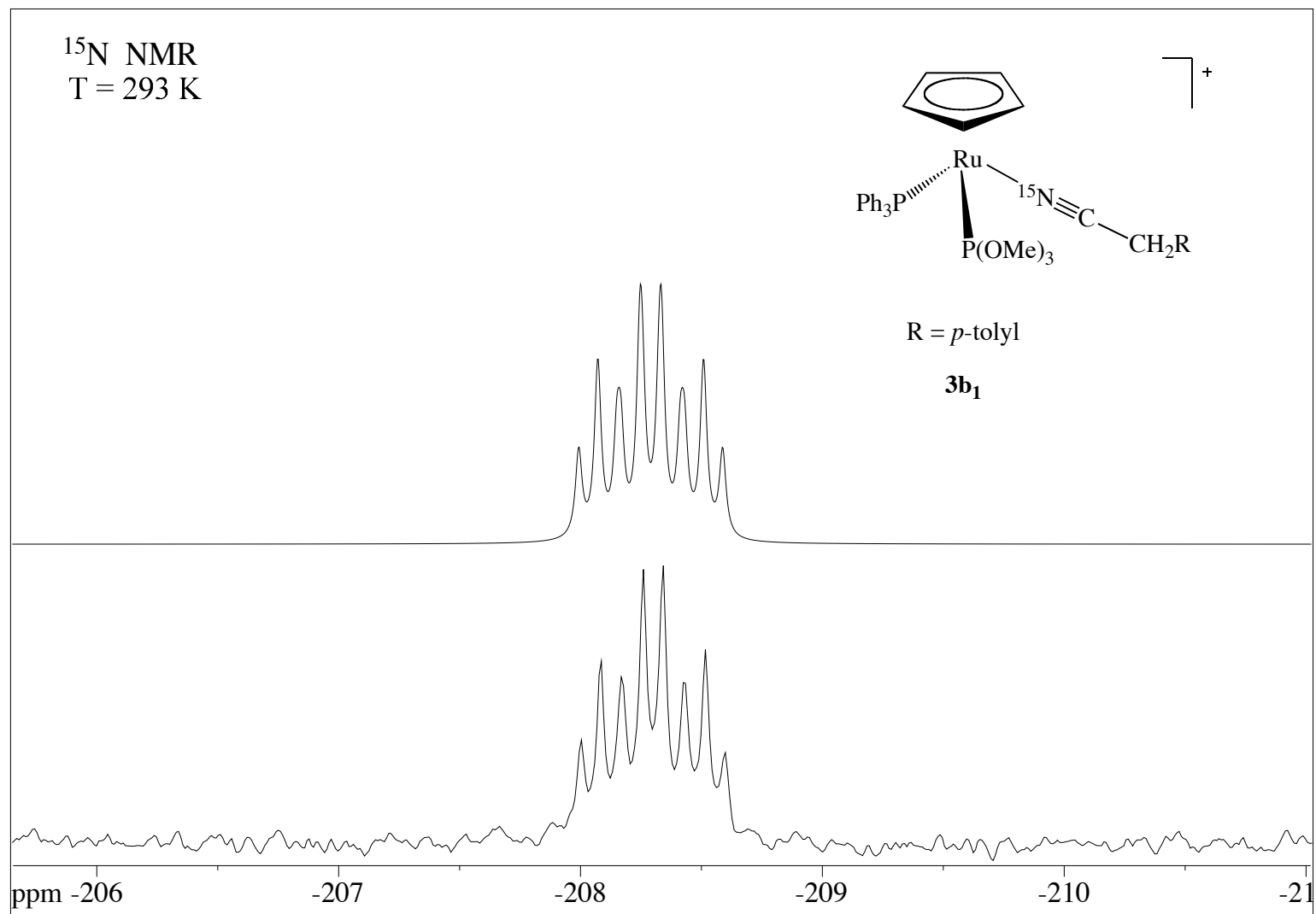
Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain



Calculated (upper) and experimental (lower) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CD_2Cl_2 of intermediate **[B]**, formed from reaction of **1b** and $\text{PhNH}^{15}\text{NH}_2$ (ratio 1:2).

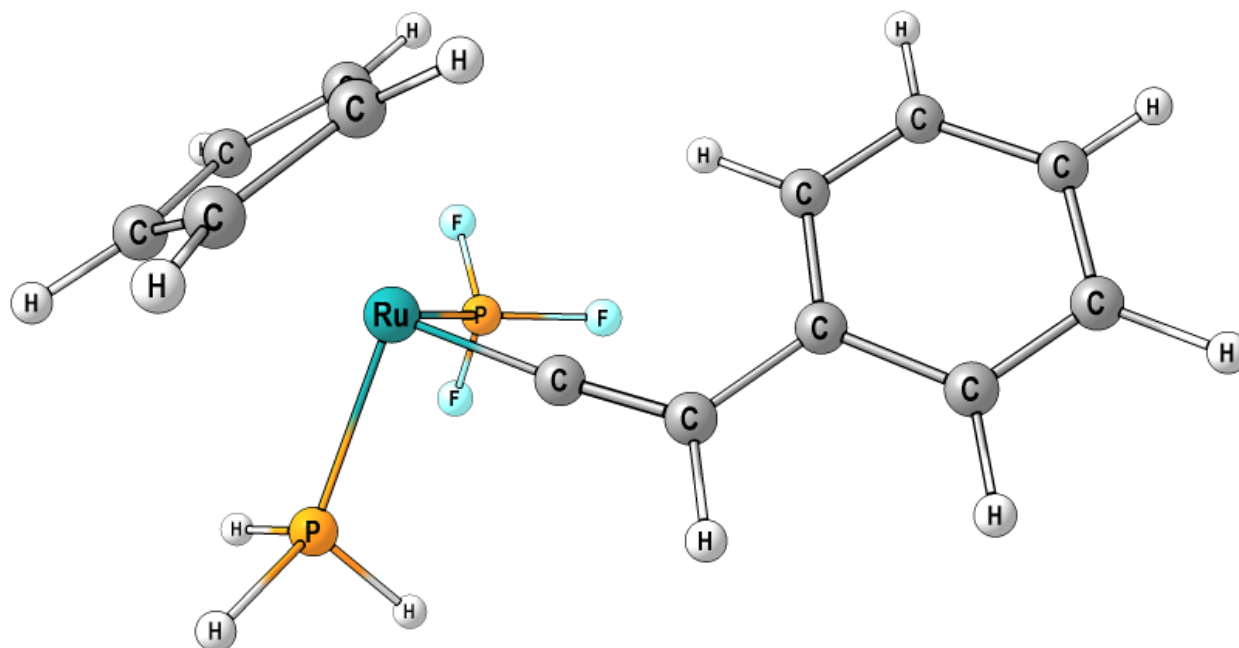


^{15}N NMR spectra in CD_2Cl_2 of intermediate [B].



Calculated (upper) and experimental (lower) ^{15}N NMR spectra in CD_2Cl_2 of complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(^{15}\text{N}\equiv\text{CCH}_2\text{-}p\text{-tolyl})(\text{PPh}_3)\{\text{P}(\text{OMe})_3\}]\text{BPh}_4$ (**3b₁**).

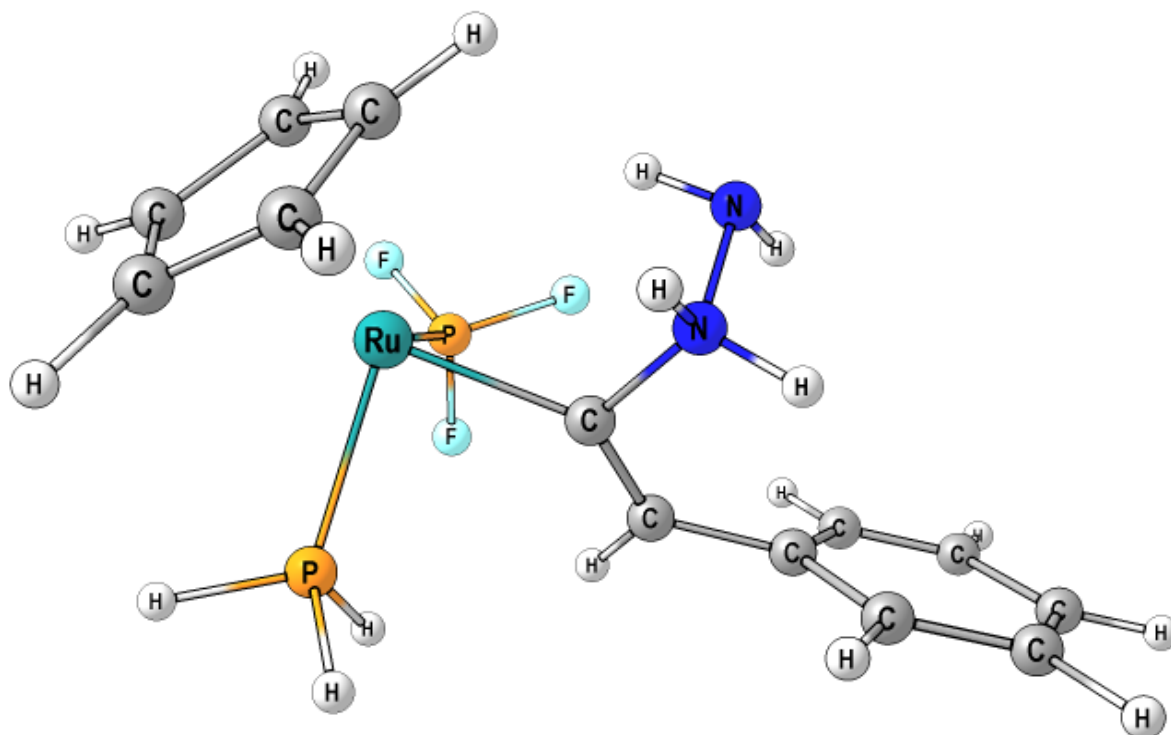
Figure S1. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.141331000	-0.421387000	0.092930000	F	-0.463403000	2.428246000	-0.309348000
H	1.418134000	-3.377326000	0.510493000	F	1.728465000	2.813384000	0.492510000
C	1.564567000	-2.618159000	-0.244439000	C	-0.539642000	-0.418918000	0.918670000
C	2.782987000	-1.910010000	-0.502024000	C	-1.751527000	-0.496216000	1.397250000
H	-0.412708000	-2.532314000	-1.278411000	H	-1.809380000	-0.719290000	2.466445000
H	3.704892000	-2.024866000	0.052983000	C	-3.006405000	-0.325381000	0.657967000
C	2.576312000	-1.034234000	-1.583051000	C	-5.425674000	-0.018892000	-0.698308000
H	3.306741000	-0.366623000	-2.017487000	C	-4.216817000	-0.373321000	1.350521000
C	1.213602000	-1.184025000	-2.006142000	C	-3.021977000	-0.122306000	-0.725935000
H	0.744862000	-0.663872000	-2.830657000	C	-4.223186000	0.029704000	-1.395496000
C	0.610236000	-2.189121000	-1.201233000	C	-5.418062000	-0.220002000	0.674631000
P	0.945501000	1.733931000	-0.349305000	H	-4.210908000	-0.531566000	2.425344000
P	2.234448000	0.040349000	2.138062000	H	-2.085004000	-0.082774000	-1.276979000
H	2.521472000	-1.078550000	2.936799000	H	-4.223882000	0.185567000	-2.469624000
H	1.582659000	0.885713000	3.049433000	H	-6.352856000	-0.259069000	1.224815000
H	3.496676000	0.651357000	2.046625000	H	-6.366259000	0.099191000	-1.226537000
F	1.390637000	2.205766000	-1.781829000				

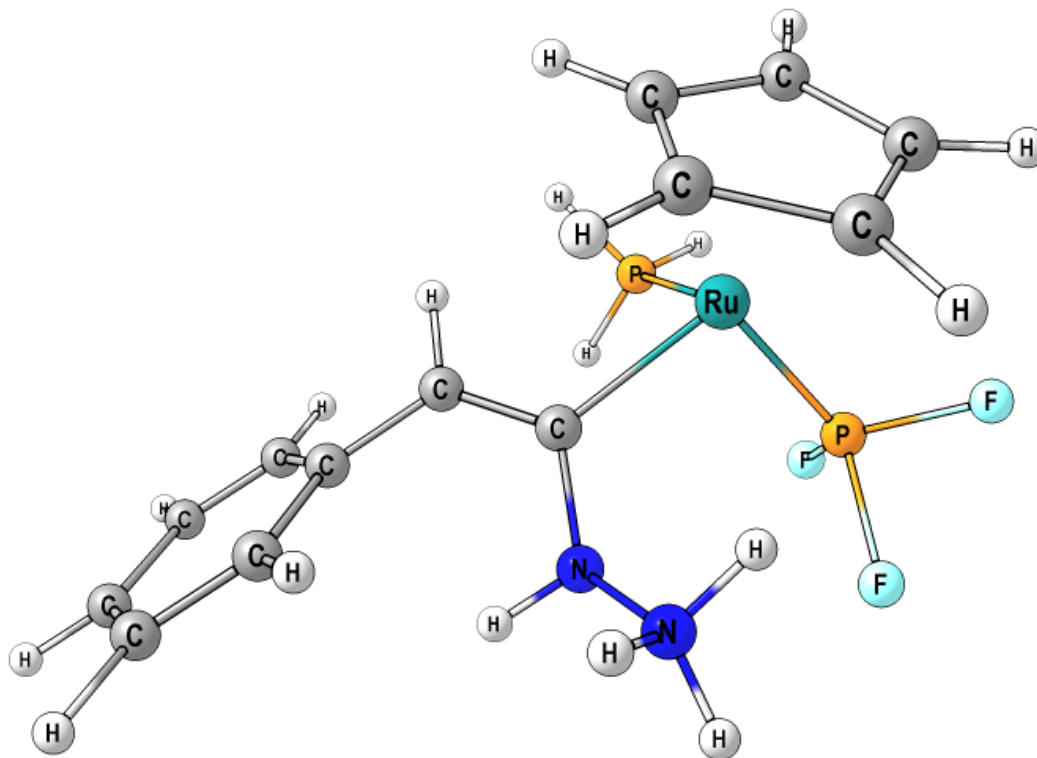
Figure S2. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}_2\text{NH}_2)=\text{C}(\text{H})\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.421074000	-0.341257000	0.142440000	C	-1.685016000	0.083361000	0.710980000
H	3.263070000	-2.277724000	1.484228000	H	-1.423224000	0.818644000	1.471781000
C	3.041516000	-1.877426000	0.503158000	C	-3.134305000	-0.050357000	0.448992000
C	3.640792000	-0.727741000	-0.077572000	C	-5.868835000	-0.230213000	-0.098787000
H	1.538077000	-3.331260000	-0.265942000	C	-3.814871000	-1.259170000	0.616018000
H	4.406249000	-0.109856000	0.368535000	C	-3.848664000	1.071078000	0.018685000
C	3.064394000	-0.559814000	-1.366732000	C	-5.204023000	0.981061000	-0.253582000
H	3.313856000	0.220879000	-2.073072000	C	-5.173439000	-1.347929000	0.337098000
C	2.123937000	-1.605602000	-1.585386000	H	-3.281743000	-2.127708000	0.997731000
H	1.596124000	-1.796738000	-2.510673000	H	-3.325779000	2.016475000	-0.105429000
C	2.107701000	-2.424131000	-0.415412000	H	-5.745959000	1.858921000	-0.590737000
P	1.094612000	1.782544000	-0.222245000	H	-5.689358000	-2.293024000	0.473351000
P	1.116613000	-0.195658000	2.455919000	H	-6.930348000	-0.299333000	-0.313057000
H	0.389948000	-1.234818000	3.071359000	N	-1.174251000	-1.387235000	-1.079729000
H	0.462592000	0.912590000	3.029001000	H	-2.163006000	-1.647002000	-0.946743000
H	2.282646000	-0.212252000	3.246799000	H	-0.652736000	-2.265551000	-1.111907000
F	2.298585000	2.651188000	-0.772108000	N	-1.082366000	-0.781003000	-2.384199000
F	0.022160000	2.265102000	-1.293142000	H	-0.147245000	-0.368945000	-2.416459000
F	0.628238000	2.785581000	0.917928000	H	-1.731516000	0.006992000	-2.362884000
C	-0.682825000	-0.519357000	0.055045000				

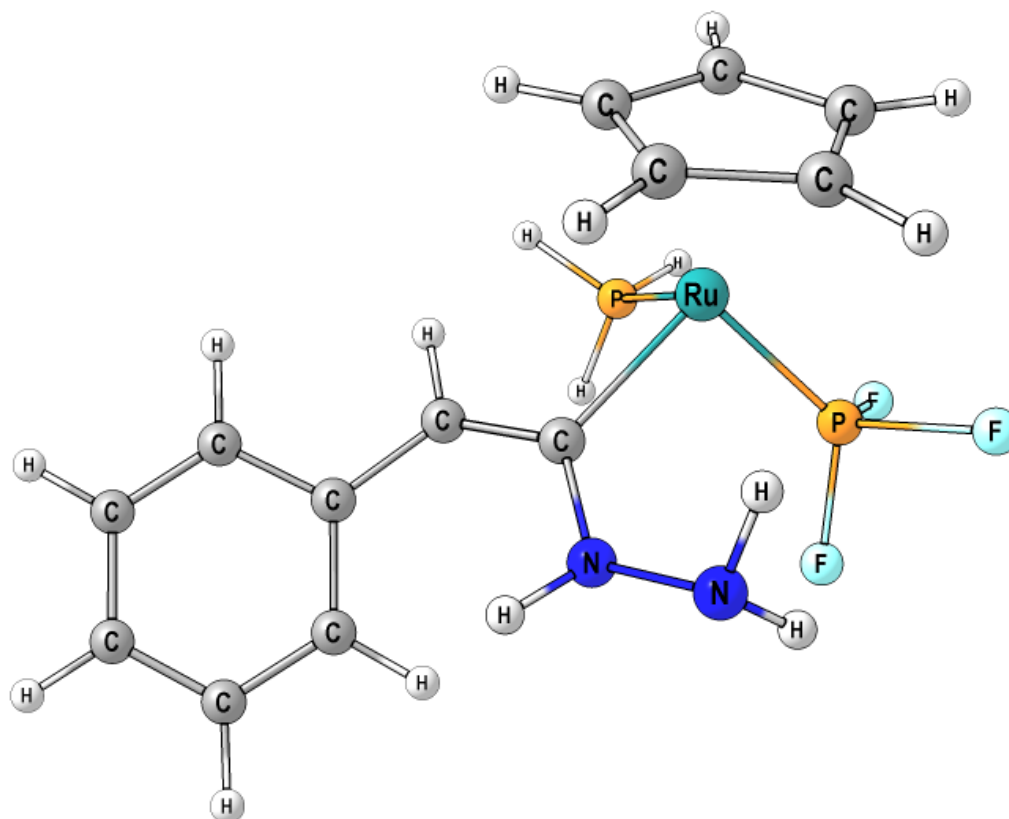
Figure S3. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NHNH}_3)=\text{C}(\text{H})\text{Ph}\}-(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.191388000	-0.518108000	0.037821000	N	-1.105709000	1.339809000	-0.798027000
H	0.348030000	-3.351422000	0.234343000	H	-2.101814000	1.536372000	-0.911833000
C	1.052248000	-2.719751000	-0.290283000	C	-1.871961000	-0.573090000	0.378656000
C	2.396964000	-2.421617000	0.123023000	H	-1.662866000	-1.415194000	1.038225000
H	-0.079247000	-2.125252000	-2.117089000	C	-3.305880000	-0.263610000	0.206653000
H	2.877024000	-2.777737000	1.024184000	C	-6.042295000	0.288769000	-0.064676000
C	2.978744000	-1.592284000	-0.854239000	C	-3.887417000	-0.112212000	-1.056492000
H	3.980728000	-1.186192000	-0.832558000	C	-4.131555000	-0.155065000	1.329522000
C	2.009042000	-1.374202000	-1.890237000	C	-5.483792000	0.119343000	1.196211000
H	2.174904000	-0.825825000	-2.807752000	C	-5.240226000	0.168261000	-1.190944000
C	0.839186000	-2.095750000	-1.545776000	H	-3.280052000	-0.258803000	-1.947634000
P	2.066009000	1.468760000	0.186543000	H	-3.696159000	-0.283831000	2.317665000
P	0.716846000	-0.491217000	2.319421000	H	-6.106495000	0.202678000	2.081668000
H	0.141980000	-1.674831000	2.827855000	H	-5.672010000	0.277085000	-2.181099000
H	-0.200595000	0.456024000	2.814614000	H	-7.101115000	0.503265000	-0.168706000
H	1.764690000	-0.327013000	3.248488000	N	-0.498572000	1.412266000	-2.089858000
F	1.733061000	2.661403000	-0.838559000	H	-0.406916000	2.386492000	-2.391569000
F	1.924124000	2.360651000	1.497090000	H	-0.979313000	0.868945000	-2.820065000
F	3.642149000	1.604770000	0.041776000	H	0.451128000	1.009357000	-1.968311000
C	-0.826364000	0.100130000	-0.138349000				

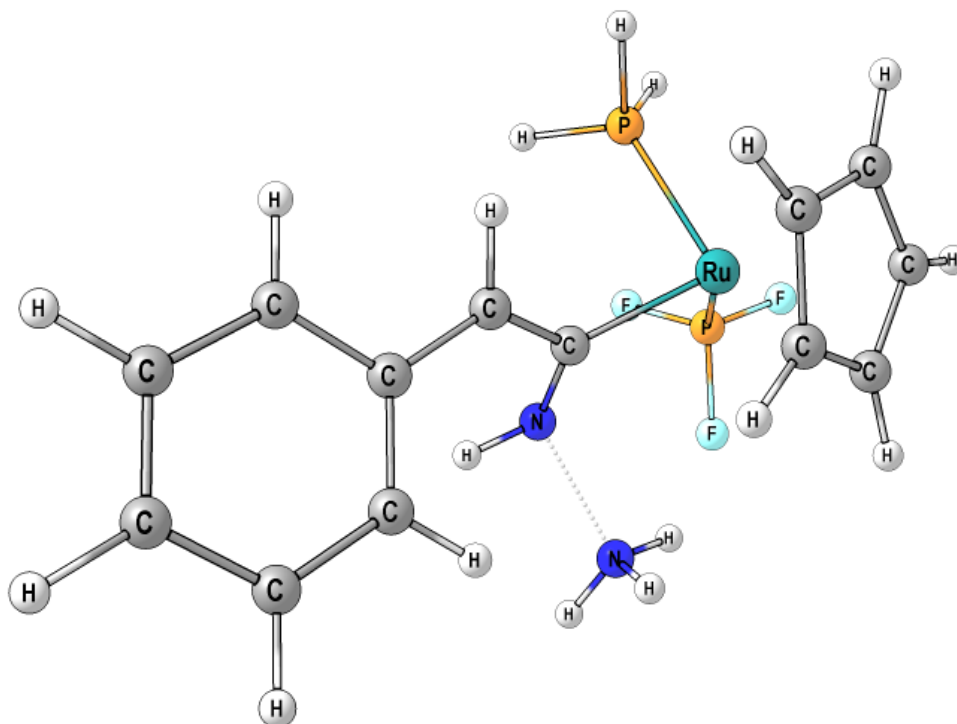
Figure S4. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NHNH}_2)=\text{C}(\text{H})\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]$



Coordinates (Å)

Ru	1.257494000	0.308773000	0.009377000	C	-0.791530000	-0.170882000	0.301508000
H	0.552516000	3.181324000	0.147712000	C	-1.756848000	0.559497000	-0.338644000
C	1.265922000	2.473374000	0.547213000	H	-1.418993000	1.390725000	-0.954603000
C	2.553139000	2.160305000	-0.008463000	C	-3.211043000	0.466684000	-0.253317000
H	0.267060000	1.749836000	2.408484000	C	-6.043498000	0.436386000	-0.186102000
H	2.969642000	2.579688000	-0.914563000	C	-3.974381000	1.604231000	-0.578149000
C	3.177555000	1.218074000	0.831398000	C	-3.928083000	-0.697513000	0.077811000
H	4.156995000	0.782945000	0.688533000	C	-5.316394000	-0.706011000	0.113758000
C	2.287341000	0.939370000	1.921044000	C	-5.356463000	1.593495000	-0.542510000
H	2.494213000	0.274583000	2.749394000	H	-3.450968000	2.515501000	-0.860989000
C	1.128831000	1.736463000	1.754247000	H	-3.398397000	-1.626715000	0.263090000
P	1.906196000	-1.744569000	-0.211121000	H	-5.834255000	-1.626769000	0.368789000
P	0.758006000	0.422529000	-2.252962000	H	-5.906953000	2.495726000	-0.795059000
H	0.240182000	1.653021000	-2.712265000	H	-7.128480000	0.425961000	-0.154115000
H	-0.191971000	-0.451158000	-2.819920000	N	-1.172814000	-1.139819000	1.217518000
H	1.810031000	0.266381000	-3.182284000	H	-2.105669000	-1.003939000	1.595186000
F	2.963079000	-2.309204000	0.842414000	N	-0.331417000	-1.644534000	2.225718000
F	0.961099000	-3.037550000	-0.196010000	H	0.397323000	-0.967806000	2.441188000
F	2.710022000	-2.204276000	-1.515438000	H	0.121511000	-2.489129000	1.889132000

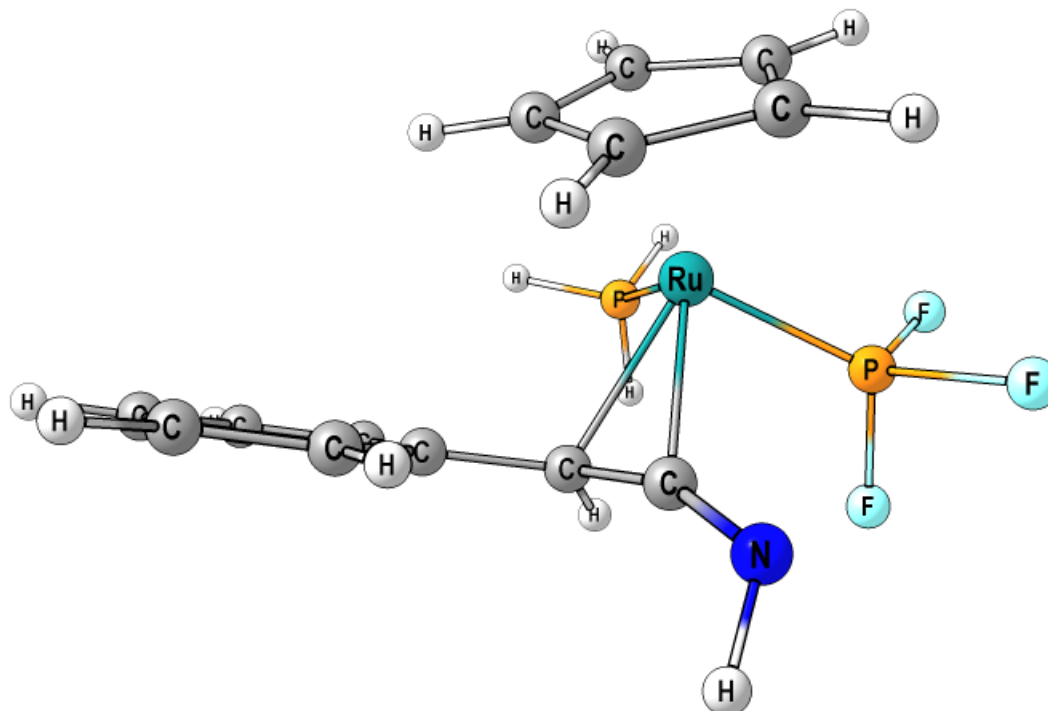
Figure S5. Transition-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}\cdots\text{NH}_3)=\text{C}(\text{H})\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.134984000	-0.576014000	-0.083995000	N	-0.853844000	1.673713000	0.275906000
H	-0.182706000	-3.168490000	-0.748871000	H	-1.838347000	1.951999000	0.377646000
C	0.554773000	-2.472874000	-1.126429000	C	-1.831574000	-0.416050000	0.575128000
C	1.971394000	-2.528628000	-0.889454000	H	-1.653742000	-1.340632000	1.128804000
H	-0.656594000	-1.097192000	-2.400908000	C	-3.227789000	-0.152297000	0.327016000
H	2.478838000	-3.252263000	-0.265936000	C	-5.964433000	0.216653000	-0.103100000
C	2.578781000	-1.480967000	-1.603017000	C	-3.685818000	0.655644000	-0.728917000
H	3.634685000	-1.249118000	-1.624737000	C	-4.178113000	-0.796400000	1.137346000
C	1.545860000	-0.759688000	-2.294860000	C	-5.531199000	-0.601756000	0.933210000
H	1.693469000	0.089964000	-2.948074000	C	-5.038828000	0.833513000	-0.940100000
C	0.313011000	-1.400403000	-2.025858000	H	-2.976626000	1.111041000	-1.411380000
P	2.193864000	1.244777000	0.431799000	H	-3.834082000	-1.443741000	1.939013000
P	1.112883000	-1.261816000	2.136501000	H	-6.252653000	-1.094495000	1.576053000
H	0.770592000	-2.614435000	2.349073000	H	-5.379497000	1.447893000	-1.766581000
H	0.214372000	-0.653798000	3.041166000	H	-7.026465000	0.363452000	-0.270094000
H	2.285977000	-1.207339000	2.917209000	N	-0.657735000	2.487163000	-1.537770000
F	2.074134000	2.570799000	-0.464037000	H	-1.182971000	3.356877000	-1.560497000
F	1.993877000	1.972842000	1.831544000	H	-0.918835000	1.887603000	-2.316914000
F	3.783924000	1.249293000	0.451637000	H	0.340958000	2.676615000	-1.549218000
C	-0.696605000	0.332205000	0.266743000				

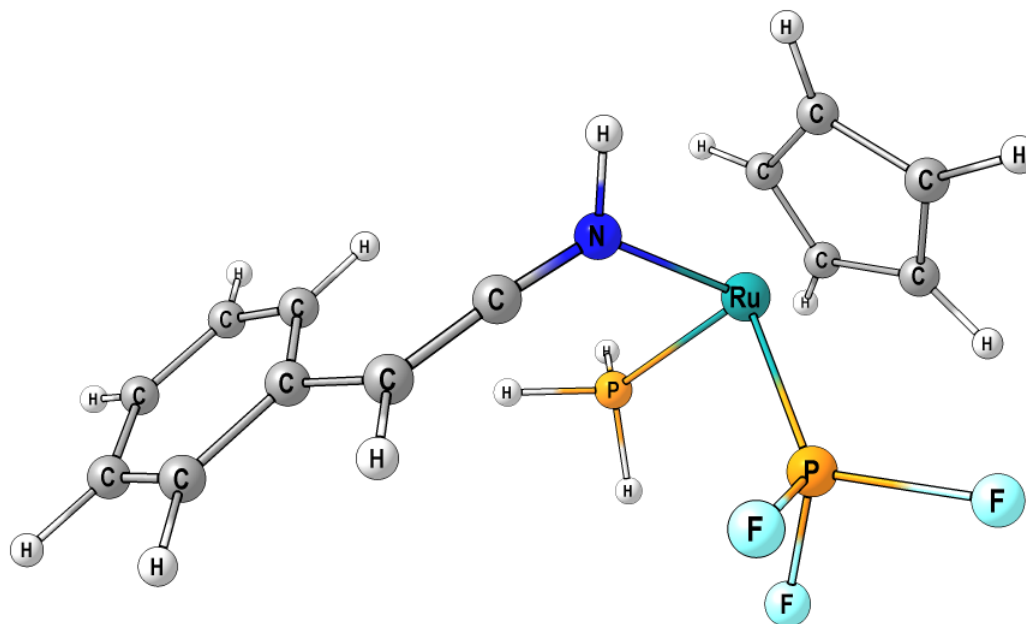
Figure S6. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-(C,C)NH=C=C(H)Ph}\}\text{(PH}_3\text{)}(\text{PF}_3)]^+$



Coordinates (Å)

Ru	0.549043000	0.389342000	-0.179006000	F	3.549138000	-0.767239000	-0.863724000
H	-1.840493000	2.100827000	-0.703145000	C	-0.134709000	-0.787264000	1.525433000
C	-0.803500000	2.176618000	-0.403325000	N	0.269314000	-0.699897000	2.686914000
C	0.312315000	2.363218000	-1.271210000	H	-0.230806000	-1.320037000	3.333360000
H	-0.896649000	2.032366000	1.827865000	C	-0.917629000	-1.214254000	0.462920000
H	0.268776000	2.435478000	-2.350105000	H	-0.623782000	-2.173600000	0.035084000
C	1.490012000	2.412530000	-0.488317000	C	-2.339632000	-0.844192000	0.320265000
H	2.495977000	2.550356000	-0.859299000	C	-5.027822000	-0.157563000	-0.018688000
C	1.105394000	2.270921000	0.884225000	C	-2.998031000	-0.059746000	1.270204000
H	1.769292000	2.284379000	1.737925000	C	-3.059110000	-1.308007000	-0.782782000
C	-0.306792000	2.148107000	0.929286000	C	-4.391472000	-0.964601000	-0.952237000
P	2.388600000	-0.762968000	0.199731000	C	-4.328973000	0.283902000	1.097894000
P	0.263534000	-0.697625000	-2.253746000	H	-2.469385000	0.275848000	2.158464000
H	-0.981969000	-0.459708000	-2.865693000	H	-2.577731000	-1.961980000	-1.505689000
H	0.325485000	-2.103399000	-2.303048000	H	-4.936362000	-1.333867000	-1.815007000
H	1.146476000	-0.351873000	-3.292972000	H	-4.826481000	0.893746000	1.845097000
F	3.250786000	-0.383073000	1.456487000	H	-6.069704000	0.114395000	-0.152104000
F	2.313629000	-2.319002000	0.445611000				

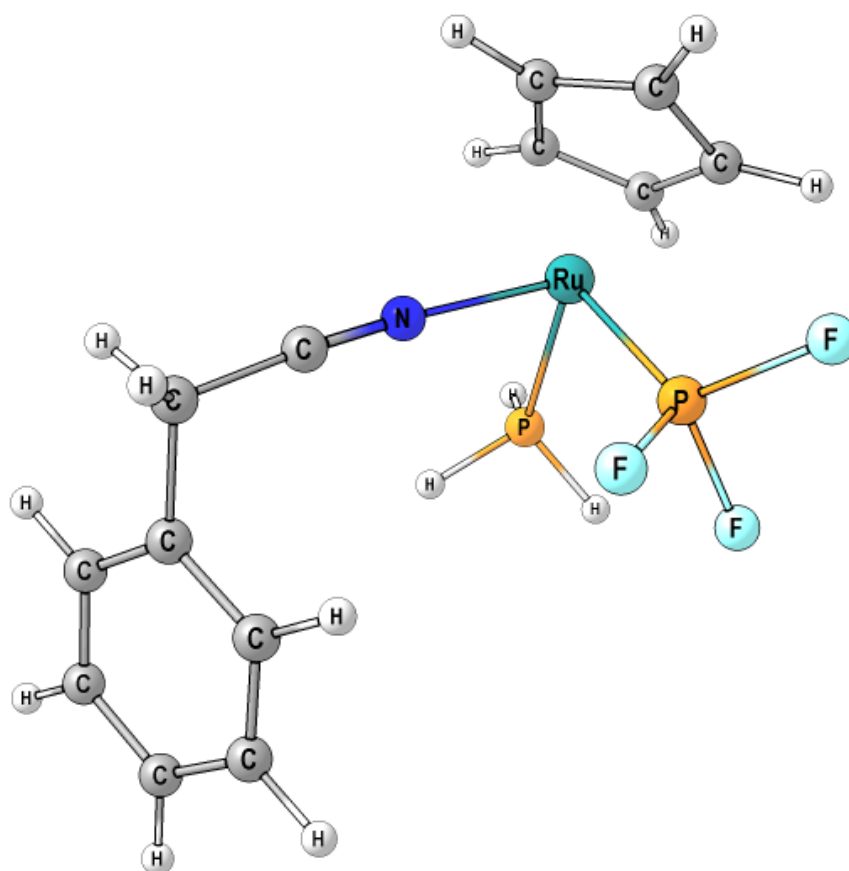
Figure S7. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^1\text{-NH}=\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.427017000	-0.468248000	-0.063724000	F	1.215687000	2.403364000	1.596448000
H	1.629745000	-3.437650000	-0.029559000	C	-1.316001000	0.279835000	-1.336422000
C	2.223497000	-2.543454000	-0.154630000	N	-0.230169000	-0.293654000	-1.456498000
C	2.886379000	-1.810518000	0.884093000	C	-2.432840000	0.909188000	-1.108957000
H	2.160069000	-2.201549000	-2.357572000	H	-2.440447000	1.970063000	-1.357188000
H	2.875967000	-2.047393000	1.939146000	C	-3.654498000	0.307731000	-0.569271000
C	3.582482000	-0.730466000	0.285021000	C	-5.999317000	-0.767441000	0.492481000
H	4.191022000	-0.003378000	0.804823000	C	-3.756266000	-1.065250000	-0.324301000
C	3.364116000	-0.787274000	-1.131286000	C	-4.743810000	1.130892000	-0.284588000
H	3.776809000	-0.113626000	-1.868662000	C	-5.908751000	0.594511000	0.243841000
C	2.534943000	-1.906144000	-1.385744000	C	-4.919468000	-1.595671000	0.204998000
P	1.503052000	1.720360000	0.196764000	H	-2.922967000	-1.722580000	-0.562713000
P	-0.107249000	-0.771639000	1.696281000	H	-4.672476000	2.197458000	-0.478278000
H	-0.024809000	-2.010359000	2.360913000	H	-6.749371000	1.245241000	0.461665000
H	-1.488662000	-0.739952000	1.402138000	H	-4.988627000	-2.662839000	0.389618000
H	-0.078959000	0.099306000	2.801717000	H	-6.911163000	-1.186591000	0.905219000
F	2.893842000	2.419856000	-0.074946000	H	-0.060906000	-0.733255000	-2.365277000
F	0.604625000	2.696687000	-0.669698000				

Figure S8. Ground-state DFT-optimized geometry of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{N}=\text{CCH}_2\text{Ph}\}(\text{PH}_3)(\text{PF}_3)]^+$



Coordinates (Å)

Ru	1.487322000	-0.415346000	0.090041000	F	2.339168000	2.561574000	-0.886415000
H	2.230384000	-3.214031000	0.758639000	N	-0.337285000	-0.833289000	-0.821599000
C	2.625319000	-2.307306000	0.323106000	C	-1.375538000	-1.017041000	-1.276810000
C	3.296843000	-1.251479000	1.021293000	C	-2.720418000	-1.186086000	-1.784844000
H	2.156584000	-2.543876000	-1.845538000	H	-2.901864000	-2.253711000	-1.944291000
H	3.487778000	-1.210306000	2.084997000	H	-2.775627000	-0.701917000	-2.767757000
C	3.682687000	-0.271514000	0.073015000	C	-3.724210000	-0.593852000	-0.819031000
H	4.222524000	0.640362000	0.287899000	C	-5.568047000	0.508579000	0.946674000
C	3.265315000	-0.717999000	-1.225386000	C	-4.726254000	-1.385913000	-0.274002000
H	3.429950000	-0.202668000	-2.161034000	C	-3.644121000	0.753127000	-0.474224000
C	2.624975000	-1.968580000	-1.058083000	C	-4.563327000	1.302268000	0.405972000
P	1.154979000	1.746235000	-0.233423000	C	-5.648634000	-0.833587000	0.605620000
P	0.308149000	-0.419898000	2.131980000	H	-4.787747000	-2.437668000	-0.539737000
H	0.706072000	-1.398684000	3.062398000	H	-2.858824000	1.374630000	-0.899816000
H	-1.081239000	-0.659478000	2.082796000	H	-4.497849000	2.352978000	0.669404000
H	0.334763000	0.725534000	2.949085000	H	-6.431365000	-1.456733000	1.026036000
F	-0.005427000	2.262452000	-1.176444000	H	-6.288271000	0.938537000	1.635282000
F	0.875048000	2.740031000	0.966510000				