Supporting Information

Synthesis and Reactivity of a Ru(I) Dimer Devoid of pi-acid Ligands

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Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 5.5 suite[1] programs. Geometry optimizations were performed with the B3LYP[2-5] functional and the 6-31G** basis set. The transition metals were represented using the Los Alamos LACVP** basis[6-8] that includes relativistic effective core potentials. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ξ basis set[9] cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP**, designated as LACV3P**, in which the exponents were decontracted to match the effective core potential with the triple-ξ.

References

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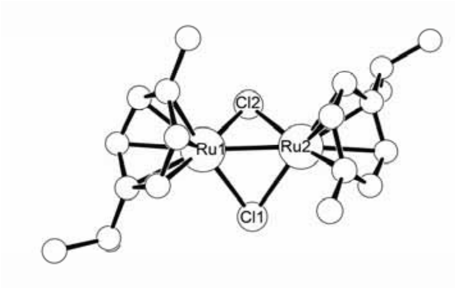
$(\mathrm{CymRuCl})_2$

Ru	-0.338556734	-0.137362626	1.295755948
Ru	0.168359533	0.306537983	-1.265699670
Cl	1.748868494	-0.931245202	0.219908258
Cl	-1.384603858	-1.479325454	-0.516305394
C	-1.925016412	1.179963908	2.165580289
C	-0.666759034	1.852098025	2.223119615
H	-0.547591609	2.819500075	1.747935474
C	0.452190535	1.229559231	2.841251160
H	1.423368293	1.708763656	2.791274706
C	0.343973143	-0.056000683	3.480730389
C	-0.914058997	-0.702817129	3.485247797
H	-1.028717559	-1.689527705	3.913495768
C	-1.995138177	-0.121765494	2.757769879
H	-2.908048943	-0.695167322	2.634915573
C	-3.128078702	1.790287509	1.496002397
H	-3.754809529	2.317837092	2.226023424
H	-3.741032614	1.019792684	1.021266255
H	-2.831672395	2.508703825	0.727198022
C	1.588896640	-0.665630848	4.110193060
H	2.440601270	-0.282551314	3.534724403
C	1.737673674	-0.170839888	5.564519211
H	1.746118722	0.922268786	5.619796643
H	2.672361984	-0.539260605	5.999680741
H	0.911208507	-0.532579453	6.186007938
C	1.640759379	-2.197752669	4.035892418
H	1.507184947	-2.547537255	3.009146950
H	0.873634737	-2.661904376	4.665017398
H	2.610918265	-2.553135051	4.396534697
C	1.088981626	2.310975404	-1.647820798
C	-0.333411641	2.428750649	-1.676714977
H	-0.834391566	3.124008495	-1.011963682
C	-1.106796496	1.590468034	-2.526444826
H	-2.188902874	1.625135639	-2.468000324
C	-0.490616829	0.662121458	-3.441393443
C	0.919123313	0.571739901	-3.453394177
H	1.423823400	-0.147961501	-4.084693894
C	1.675519982	1.326505282	-2.505915274
H	2.740235452	1.138095672	-2.416078337
C	1.947111700	3.150868969	-0.738762115
H	2.411743573	3.975079571	-1.293925388
H	2.746990518	2.550975967	-0.296591426
H	1.357737636	3.585182607	0.073117176
C	-1.379304404	-0.186607065	-4.339181314
H	-2.344941116	-0.272114835	-3.825538195

C	-0.854799440	-1.612182987	-4.566445046
H	-0.674483284	-2.119044827	-3.615234384
H	0.075900203	-1.618362025	-5.144379266
H	-1.590333353	-2.192235546	-5.132550077
C	-1.619856781	0.543008185	-5.677367131
H	-2.038331604	1.542396210	-5.521670491
H	-2.319003359	-0.023540764	-6.301079253
H	-0.683687933	0.653219589	-6.235360533



Ru1-Ru2: 2.649 Ru1-Cl1: 2.497 Ru1-Cl2: 2.482 Ru2-Cl1: 2.479 Ru2-Cl2: 2.486

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Figure 1. ^{1}H NMR spectrum of [(terpy)$_2$ Ru]Cl$_2$.

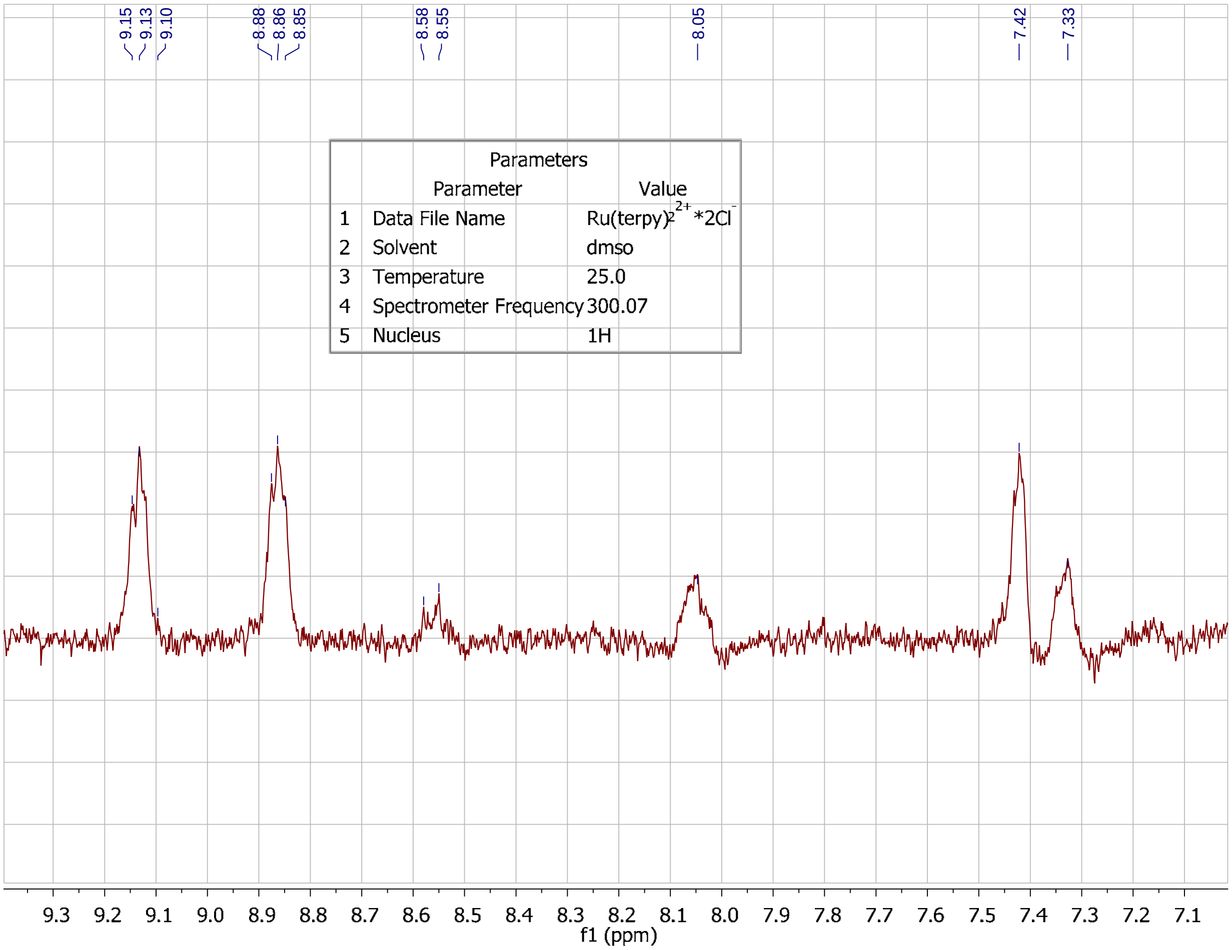
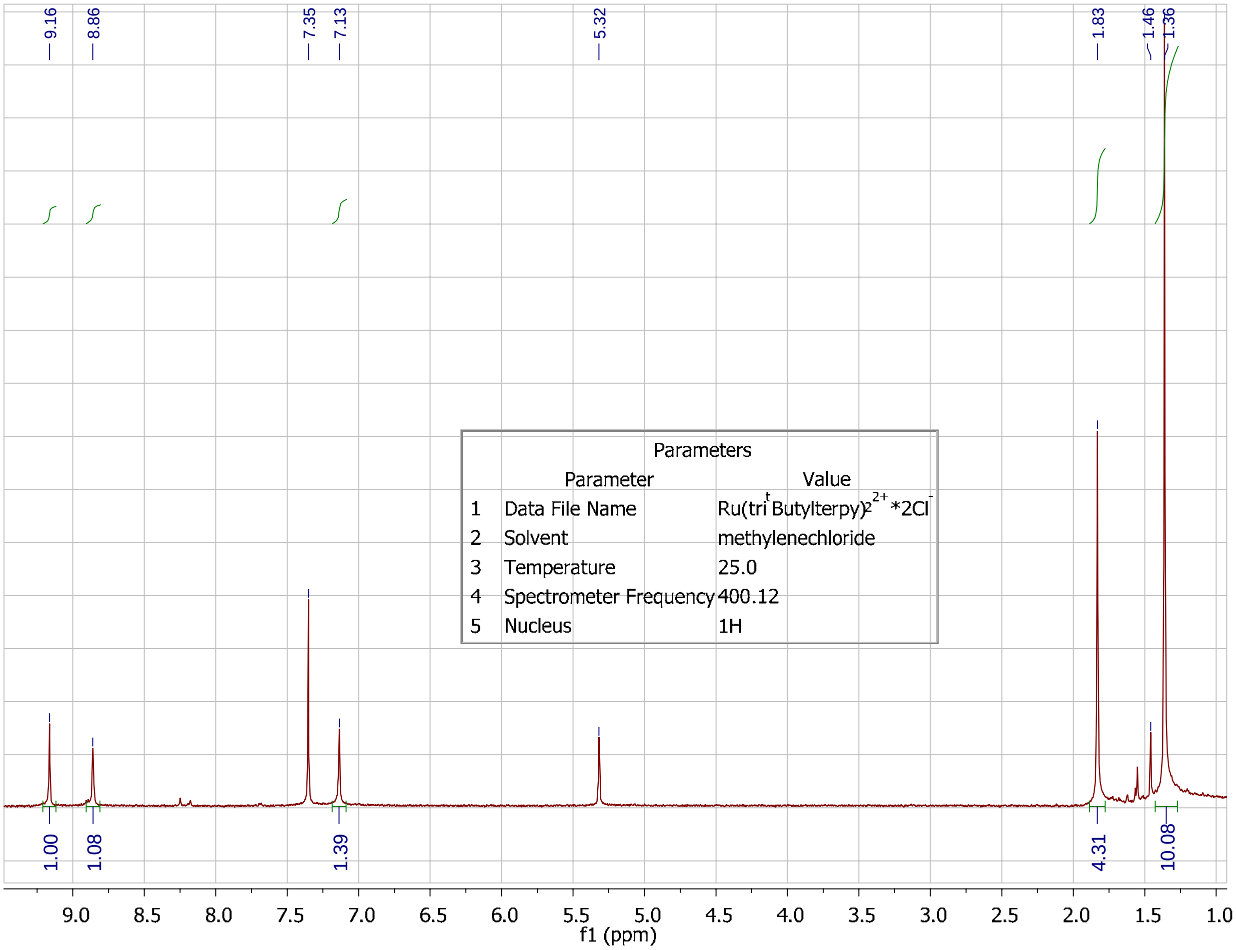


Figure 2. ^{1}H NMR spectrum of [(^{t}Bu$_3$-terpy)$_2$ Ru]Cl$_2$.



Single Crystal structure determination of [(terpy)$_2$ Ru]Cl$_2$

A red crystal (approximate dimensions 0.17 × 0.15 × 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K. The data collection was carried out using Mo K α radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 6.0 cm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 4 were collected. Four major sections of frames were collected with 0.50º ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 3110 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2] The space group P2$_1$/c was determined based on intensity statistics and of systematic absences. The structure was solved using SIR-2004[3] and refined with SHELXL-97.[4] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Disordered solvent was refined with a set of restraints and constraints. The final full matrix least squares refinement converged to R1 = 0.0381 and wR2 = 0.0985 (F^2, all data). The remaining electron density is located near the solvent chlorines.

1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
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3 Sir2004, A Program for Automatic Solution and Refinement of Crystal Structures.
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