Electronic Supplementary Information for

Can a functionalized phosphine ligand promote room temperature luminescence of the $[Ru(bpy)(tpy)]^{2+}$ core?

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Computational details.

Density Functional Theory (DFT) calculations were performed using the Gaussian 09 package.[1] The choice of functional was based on the results of a number of benchmark calculations. The MPWB1K functional[2] was finally chosen as this functional outperformed the standard B3LYP functional[3] most commonly used in the studies of polypyridyl ruthenium complexes, and it gives reliable results for thermochemical kinetics.[2] In particular, there is a much better description of the Ru–P bond length (which is highly overestimated with B3LYP). Also it includes non-bonded interactions, which are important in these complexes. Time-dependent DFT was used to compute the absorption spectra using the B3LYP functional, which gives reliable excitation energies of polypyridyl ruthenium complexes.

The DFT and TD-DFT calculations were performed with a large basis set used in our previous studies of ruthenium polypyridine complexes.[4] It is made of a Stuttgart relativistic small-core effective potential[5] for ruthenium with its associated polarized basis set including one *f* polarization function (exponent of 0.96), a polarized double-ζ basis set (Ahlrichs pVDZ) for H atoms,[6] and a polarized triple-ζ basis set (Ahlrichs pVTZ) for C, N, and P atoms.[6]

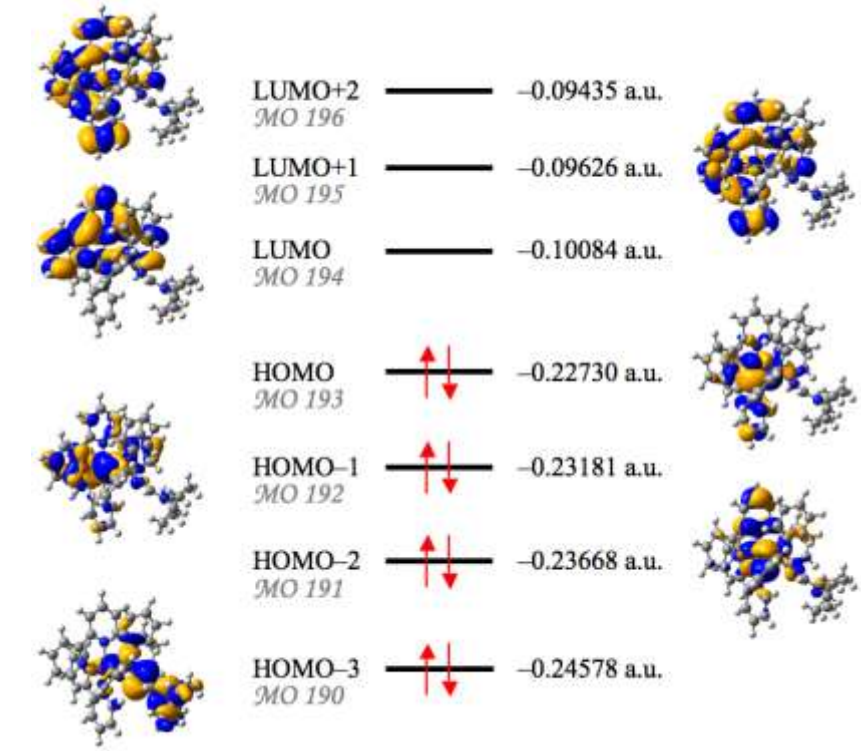
The triplet potential energy profiles of [Ru]**2** and [Ru]**P(*i*-Pr)$_3$** were constructed by optimizing the minima corresponding to the ^{3}MLCT and ^{3}MC states, as well as the transition state connecting them using unrestricted wavefunctions. The location of such transition state is very demanding as one needs to provide a good guess geometry (a structure close to the final transition state) and a reliable Hessian (information on the curvature of the potential energy surface) before starting the transition state search. In order to do that, we have performed linearly-interpolated transit path calculations. Intermediate geometries were constructed by interpolating between the ^{3}MLCT and ^{3}MC structures in internal coordinates. The triplet energies were computed at these intermediate structures and the structure corresponding to the maximum energy along this linearly-interpolated pathway was chosen as the starting geometry for a transition state optimization. The analytical Hessian was also computed at this starting geometry. This part of the calculation is time-consuming and requires access to a high-performance computing facility. To our knowledge, such computationally challenging calculations were recently performed only for the first time on a photochromic ruthenium sulfoxide complex in order to determine its photoisomerization mechanism.[7] Here we use this strategy to compute the potential energy profiles of two complexes in order to rationalize the difference of luminescence properties between [Ru]**2** and [Ru]**P(*i*-Pr)$_3$**. Analytical harmonic vibrational frequency calculations were performed at this same level of calculation to characterize the nature (minimum *vs.* transition state) of the stationary points found on the potential energy surface and to obtain the enthalpic and entropic corrections necessary to calculate the Gibbs energies. Mulliken spin density on the ruthenium atom was computed in order to highlight the MLCT (~1 e^-) or MC character (~2 e^-) of the triplet wavefunction. For transition states between the ^{3}MLCT and ^{3}MC states, the spin density on the ruthenium was found to be between 1.2 and 1.4 e^-, showing the mixing of the two electronic states occurring through the electron density at these structures. Spin contamination was found negligible in all cases.

Intrinsic reaction coordinate (IRC)[8] calculations, which provide a much more accurate description of the reaction pathway compared to the approximate linearly-interpolated pathway, were performed from the transition structures in order to connect all the stationary points (Figures S1-S2). Because of the very high computational demand to perform such calculations, we had to use a smaller basis set: a double-ζ quality LANL2DZ[9] basis set for all atoms but phosphorus, which was described by the 6-31G*[10] split valence Pople basis plus one polarization function. The complete triplet potential energy profile shown in Figure 2 of the article was deduced from the energies obtained at the optimized structures using MPWB1K with the large basis set, including corrections to take into account solvent effects using the polarized continuum model[11] for acetonitrile and the Gibbs energy contributions. The position of the transition states relative to the ^{3}MLCT and ^{3}MC minima along the ^{3}MLCT $\rightarrow$ ^{3}MC relaxation coordinate was determined based on the results of the IRC calculations.

Table S1. Ground-state optimized Cartesian coordinates, coordination distances, molecular orbitals and computed absorption spectrum of [Ru]**1**. The main low-energy ($d\pi \rightarrow \pi^*_{tpy/bpy}$) transition is shown in red.

C	2.80736354	0.30877172	-0.15430145
H	2.98293392	1.05135925	-0.93297118
C	5.19259423	0.53541896	0.08981710
H	5.91892860	0.08189203	0.75834545
C	5.57182277	0.17118079	-1.32738963
H	4.89160042	0.62061979	-2.05005765
H	5.56036646	-0.90651260	-1.47044100
H	6.57160328	0.53313541	-1.55367529
C	5.21032431	2.02741669	0.33113143
H	6.20207357	2.42606235	0.13317142
H	4.95258288	2.26105198	1.36162446
H	4.51483655	2.54898268	-0.32565631
N	3.90578928	-0.05890376	0.47216614
C	0.69163837	1.81859757	-1.72315383
C	0.36603996	3.02507070	-1.12558766
H	-0.17298814	3.02547647	-0.18973658
C	0.73426374	4.22053749	-1.70383367
H	0.47663448	5.15548796	-1.22838711
C	1.43260361	4.22125545	-2.89308515
H	1.71880692	5.15610293	-3.35178027
C	1.76829826	3.02629850	-3.49478171
H	2.31935303	3.02495414	-4.42360240
C	1.40497417	1.83029152	-2.91282487
H	1.67636643	0.90150529	-3.39276425
C	0.30229196	-0.98304572	-2.14587376
C	-0.39134124	-0.77417167	-3.32862793
H	-0.87048938	0.17794881	-3.51398223
C	-0.43941650	-1.75815325	-4.29036896
H	-0.95923090	-1.57864289	-5.22007314
C	0.19052304	-2.96844574	-4.07374391
H	0.16055717	-3.73642047	-4.83249699
C	0.87483989	-3.18549546	-2.89759944
H	1.38122021	-4.12538034	-2.73313229
C	0.93316327	-2.19570045	-1.93639364
H	1.47904172	-2.35752760	-1.01770273
C	-2.87612849	2.89792214	-0.30114761
H	-2.32472663	3.25966779	0.55293146
C	-3.66927291	3.74211691	-1.04282251
H	-3.74173086	4.78402173	-0.77356959
C	-4.35239012	3.22886376	-2.11990457
H	-4.97756063	3.86176006	-2.73133170
C	-4.23718757	1.88595965	-2.39920095
H	-4.77814699	1.45524344	-3.22603450
C	-3.43487355	1.09413983	-1.60767829
C	-3.31175804	-0.35614245	-1.79403953
C	-3.94995297	-1.11881847	-2.74980607
H	-4.59753670	-0.66488654	-3.48182067
C	-3.74435712	-2.48134402	-2.75400265
H	-4.22951854	-3.09488925	-3.49766699
C	-2.92917565	-3.06598614	-1.80891321
H	-2.77507810	-4.13225640	-1.80734763
C	-2.32065354	-2.25906925	-0.87120735
C	-1.45103602	-2.69940210	0.22528962
C	-1.13467817	-4.02007856	0.45305445
H	-1.53219047	-4.79191828	-0.18542999
C	-0.30232079	-4.34305176	1.50014749
H	-0.04795030	-5.37385174	1.69558006
C	0.20080459	-3.33289864	2.28752299
H	0.85843551	-3.54105212	3.11667400
C	-0.15438947	-2.03449635	2.00633983
H	0.22327575	-1.20595039	2.58383240
C	-4.38198090	-0.63368473	1.61141163
H	-4.43157189	-1.19957020	0.69486457
C	-5.43017859	-0.64291828	2.49833055
H	-6.31368811	-1.22218048	2.28129311
C	-5.31965420	0.09858615	3.65246509
H	-6.12173271	0.12056178	4.37467089
C	-4.16619579	0.81177584	3.87561743
H	-4.06224267	1.39326392	4.77586599
C	-3.14946853	0.77136672	2.94194146
C	-1.87420024	1.47191761	3.10961958
C	-1.58853272	2.23471857	4.22388474
H	-2.32151291	2.35730535	5.00301501
C	-0.35889069	2.83695934	4.34078263
H	-0.12481134	3.43869567	5.20593240
C	0.56341871	2.64489663	3.33915180
H	1.54752502	3.08408963	3.38557480
C	0.21475140	1.87476134	2.25562362
H	0.91943328	1.67968569	1.46540418
N	1.62327342	-0.12950527	0.11695393
N	-2.73925678	1.61047721	-0.57521721
N	-2.51781736	-0.94196705	-0.90156399
N	-0.97001010	-1.71932981	1.01310007
N	-3.26870458	0.05502696	1.82035571
N	-0.97975420	1.30686108	2.12169189
P	0.29520228	0.27872909	-0.82956265
Ru	-1.64770578	0.16632509	0.47227485
C	3.88055808	-1.07937720	1.51338694
H	2.83610472	-1.36922131	1.58607259
C	4.32368242	-0.50917234	2.84200710
H	4.24116760	-1.26544629	3.61900675
H	3.71057066	0.34204226	3.12999630
H	5.36327063	-0.18660236	2.81982194
C	4.69371222	-2.28807065	1.10640760
H	5.75289813	-2.05425645	1.01349092
H	4.35121109	-2.69241598	0.15659234
H	4.60385383	-3.06696760	1.85980137

Bonds	MPWB1K	X-ray
Ru1–P1	2.341 Å	2.325 Å
Ru1–N1	2.111 Å	2.113 Å
Ru1–N2	2.114 Å	2.122 Å
Ru1–N3	1.968 Å	1.964 Å
Ru1–N4	2.091 Å	2.096 Å
Ru1–N5	2.075 Å	2.073 Å



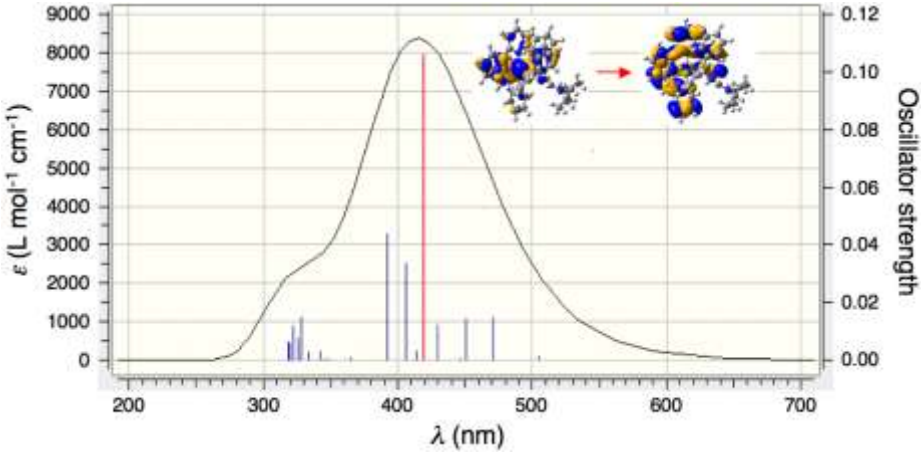


Table S2. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT state of [Ru]**1**.

C	2.80229822	0.32164684	-0.18152744
H	2.98754800	1.01850510	-0.99927392
C	5.18729528	0.53149696	0.05544022
H	5.90635969	0.09790275	0.74439825
C	5.55717943	0.09273298	-1.34279367
H	4.88724451	0.52163188	-2.08714054
H	5.52459545	-0.99003743	-1.43510555
H	6.56404430	0.42351269	-1.58441965
C	5.22693022	2.03248794	0.22511549
H	6.22367363	2.40619334	0.00522256
H	4.97705398	2.31957084	1.24392713
H	4.53701531	2.53210936	-0.45425811
N	3.88989840	-0.02330459	0.46798877
C	0.63342003	1.79805688	-1.79748759
C	0.24191170	3.00174635	-1.23408108
H	-0.32440221	3.00972214	-0.31459414
C	0.56459815	4.19581966	-1.84016383
H	0.24806491	5.12896113	-1.39858202
C	1.28552385	4.19724859	-3.01588086
H	1.53457987	5.13225661	-3.49542597
C	1.68700248	3.00473063	-3.58090748
H	2.25236739	3.00506492	-4.50097593
C	1.36566544	1.80857131	-2.97629715
H	1.68016688	0.88056868	-3.43057090
C	0.34904737	-1.04228142	-2.16331487
C	-0.31885116	-0.87946629	-3.36708569
H	-0.83328552	0.04615703	-3.58392373
C	-0.30671586	-1.88851471	-4.30299909
H	-0.81396845	-1.75275117	-5.24653406
C	0.36072038	-3.06881430	-4.04049421
H	0.37456251	-3.85582465	-4.77993375
C	1.02116784	-3.23652824	-2.84254749
H	1.55312706	-4.15490906	-2.64246694
C	1.01782058	-2.22531684	-1.90399836
H	1.54073307	-2.34871368	-0.96649344
C	-2.95628326	2.83835436	-0.05064856
H	-2.50101004	3.11125459	0.89001662
C	-3.66571968	3.74139427	-0.77317070
H	-3.79204015	4.74660640	-0.40606375
C	-4.22360967	3.33081310	-1.99303105
H	-4.77979064	4.02992671	-2.59854129
C	-4.07498796	2.04346302	-2.39762892
H	-4.51507491	1.70567989	-3.32255387
C	-3.36055932	1.13592513	-1.60736543
C	-3.24352839	-0.24946419	-1.84674666
C	-3.86064438	-1.00392823	-2.84427266
H	-4.47858762	-0.51494081	-3.58109521
C	-3.70583160	-2.35955266	-2.86892434
H	-4.19462224	-2.94456898	-3.63182510
C	-2.92997950	-3.00088564	-1.89235734
H	-2.82442769	-4.07295967	-1.89569129
C	-2.32546161	-2.24008702	-0.93790596
C	-1.51540503	-2.72030451	0.16601546
C	-1.18861176	-4.04553723	0.38317498
H	-1.53264627	-4.79972684	-0.30551566
C	-0.42775606	-4.38424045	1.47114823
H	-0.17003453	-5.41668748	1.65368870
C	0.00411462	-3.39061991	2.33289820
H	0.60130022	-3.61863099	3.20117240
C	-0.34968178	-2.09649992	2.07011475
H	-0.03322585	-1.28432287	2.70526966
C	-4.34754773	-0.62809535	1.61646869
H	-4.39593970	-1.15079785	0.67386824
C	-5.39205915	-0.65697842	2.50923116
H	-6.28447340	-1.21582659	2.27570689
C	-5.26742384	0.04090734	3.68874104
H	-6.06718597	0.04352840	4.41403844
C	-4.10893460	0.74093816	3.93574934
H	-4.00092948	1.29250386	4.85437853
C	-3.09967410	0.72455748	2.99501136
C	-1.82645435	1.43122768	3.15755574
C	-1.53315125	2.18818638	4.27177927
H	-2.25017490	2.28301893	5.06948419
C	-0.31855675	2.82734539	4.36082094
H	-0.08207786	3.42727865	5.22693150
C	0.58479478	2.68380690	3.33355887
H	1.55116961	3.16185273	3.35964020
C	0.23680436	1.91095703	2.25303614
H	0.92304983	1.74437470	1.43965768
N	1.60761226	-0.08852262	0.10681811
N	-2.76277691	1.57414727	-0.45184593
N	-2.47585866	-0.90111241	-0.92960711
N	-1.09299752	-1.76328879	1.01682544
N	-3.23262060	0.04183387	1.85756201
N	-0.94177681	1.30261990	2.15233776
P	0.31292065	0.25422211	-0.89602549
Ru	-1.60410677	0.18171517	0.48983526
C	3.85193238	-0.99536229	1.55627144
H	2.80221684	-1.25724486	1.65368778
C	4.32491877	-0.37758639	2.85255458
H	4.22798952	-1.09631177	3.66261224
H	3.73954381	0.50277254	3.10854339
H	5.37294352	-0.08678317	2.80776810
C	4.63267100	-2.23858624	1.19251288
H	5.69533528	-2.03268738	1.07624027
H	4.26785792	-2.67636989	0.26614052
H	4.53526766	-2.98095146	1.98087978

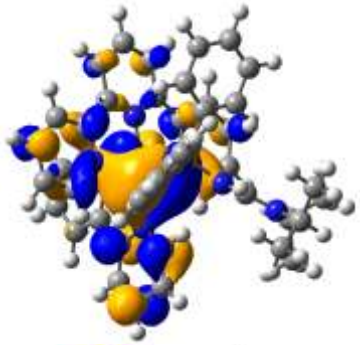
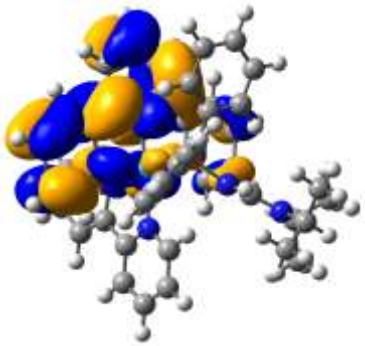
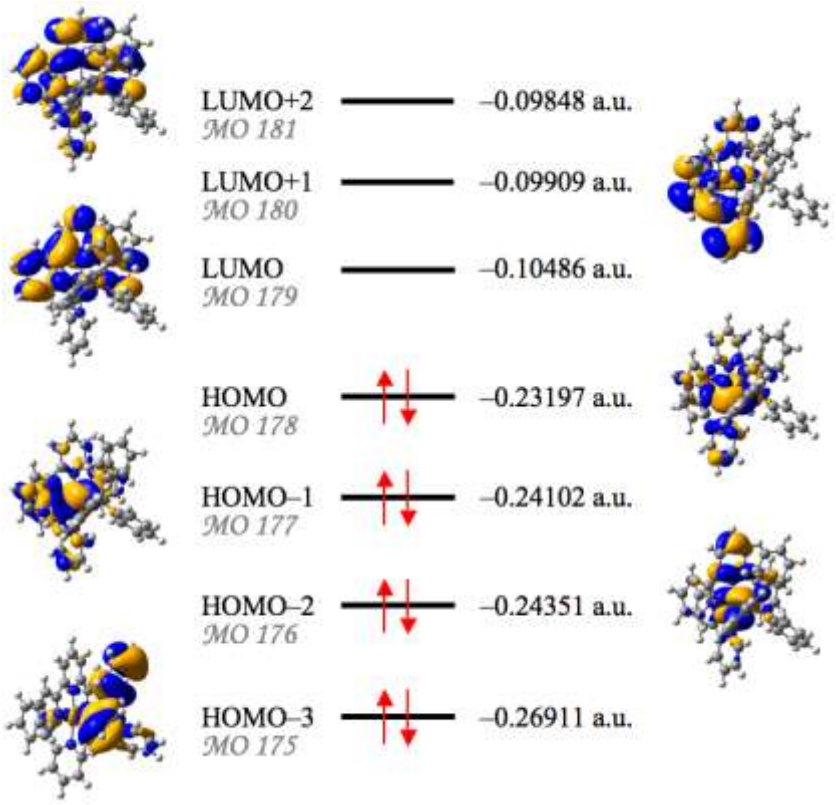
Energies (a.u.)	
$E(T_1)$	-2521.830847
$E(T_1$ in acetonitrile)	-2522.001933
$E(S_0)$	-2521.894568
$E(S_0$ in acetonitrile)	-2522.064654
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0197
Spin density on Ru	0.972

Table S3. Ground-state optimized Cartesian coordinates, coordination distances, molecular orbitals and computed absorption spectrum of [Ru]**PPh$_3$**. The main low-energy (d$\pi \rightarrow \pi^*_{tpy}$) and ($\pi_{PPh_3} \rightarrow \pi^*_{tpy}$) transitions are shown in red.

C	0.07463133	4.41229747	-0.46870942
C	1.41251284	4.35307158	-0.82050554
H	1.92077957	3.40127985	-0.82976891
C	2.09959548	5.49198866	-1.17915742
H	3.14017131	5.42975249	-1.46158145
C	1.45563780	6.71091665	-1.18156178
H	1.99105188	7.60625323	-1.46033313
C	0.12318683	6.78226673	-0.83515065
H	-0.38802806	7.73344654	-0.84466871
C	-0.56670849	5.64151764	-0.48559997
H	-1.61306657	5.71695556	-0.23217068
C	-1.48198086	2.42323265	-1.79060388
C	-1.47557289	1.11999256	-2.24842587
H	-1.00845014	0.35448618	-1.65192663
C	-2.04132141	0.79729432	-3.46476770
H	-2.02784477	-0.22429581	-3.81495295
C	-2.62024563	1.78285067	-4.23318122
H	-3.06380419	1.53621882	-5.18636356
C	-2.62925086	3.08900941	-3.78521310
H	-3.07958568	3.86375883	-4.38760687
C	-2.06384144	3.40957961	-2.57223046
H	-2.07640092	4.43539081	-2.23650962
C	-2.30830074	3.34349038	0.75225438
C	-2.24940555	4.27517129	1.77764645
H	-1.32002574	4.78092670	1.99747087
C	-3.38011709	4.59377831	2.49582911
H	-3.32981453	5.34228352	3.27307850
C	-4.57908232	3.97025930	2.21365914
H	-5.46823993	4.22992933	2.76895348
C	-4.64287609	3.03300938	1.20521480
H	-5.58239928	2.55618385	0.96760322
C	-3.51431301	2.72327432	0.47392507
H	-3.58094628	2.00629222	-0.33186223
C	1.27101684	-0.77639945	3.24591482
H	0.59561306	-0.17315896	3.83115335
C	1.92725615	-1.84348265	3.80801238
H	1.77028807	-2.08443072	4.84752669
C	2.77452002	-2.58447579	3.01592408
H	3.30600653	-3.43367988	3.41824267
C	2.93528176	-2.22683624	1.69858187
H	3.59255991	-2.79772845	1.06486107
C	2.24808956	-1.13798206	1.19981392
C	2.36904581	-0.67348326	-0.18374938
C	3.24247648	-1.24702168	-1.08515634
H	3.85861095	-2.08009329	-0.79196861
C	3.33308066	-0.74406726	-2.36131173
H	4.01372445	-1.18296131	-3.07514814
C	2.54404662	0.32938999	-2.70166654
H	2.57637360	0.76773841	-3.68672067
C	1.69244453	0.84966747	-1.75704492
H	1.05337178	1.68039704	-2.00164477
C	-1.51219237	-1.18021194	0.25093682
H	-0.77201978	-1.38238401	-0.50777506
C	-2.61707770	-1.98572671	0.39003172
H	-2.75320463	-2.82724114	-0.27078610
C	-3.52829128	-1.69066185	1.37760578
H	-4.41425092	-2.29306729	1.51032568
C	-3.27922791	-0.62544200	2.21109880
H	-3.96090452	-0.39110165	3.01208732
C	-2.14321400	0.13153198	2.02578491
C	-1.74656874	1.20209253	2.94644599
C	-2.44400051	1.62116678	4.05866532
H	-3.41349172	1.21448705	4.29316064
C	-1.87323942	2.57310404	4.87540523
H	-2.40199414	2.91459253	5.75221972
C	0.02046041	2.64103522	3.44975335
C	1.35716224	3.04193609	2.99803809
C	2.15904142	3.90837278	3.70746705
H	1.79446776	4.36951491	4.61084881
C	3.43584276	4.16829635	3.26377887
H	4.07656672	4.84364607	3.81025989
C	3.88130705	3.54058387	2.12470487
H	4.87979703	3.69723737	1.74813990
C	3.02290329	2.70016487	1.45546519
H	3.33230695	2.19398054	0.55407990
C	-0.62853887	3.08491658	4.58344438
H	-0.17706009	3.81929289	5.23005805
N	1.42264822	-0.42788166	1.97546038
N	1.59036240	0.36772314	-0.52178141
N	-1.28169983	-0.12807498	1.02356613
N	-0.55623238	1.73037755	2.66985817
N	1.78538159	2.46254069	1.85960260
P	-0.79927770	2.84204005	-0.14698584
Ru	0.39284809	1.13946783	1.04310194

Bonds	MPWB1K	X-ray
Ru1–P1	2.395 Å	2.344 Å
Ru1–N1	2.094 Å	2.089 Å
Ru1–N2	2.116 Å	2.116 Å
Ru1–N3	1.974 Å	1.971 Å
Ru1–N4	2.087 Å	2.065 Å
Ru1–N5	2.100 Å	2.095 Å



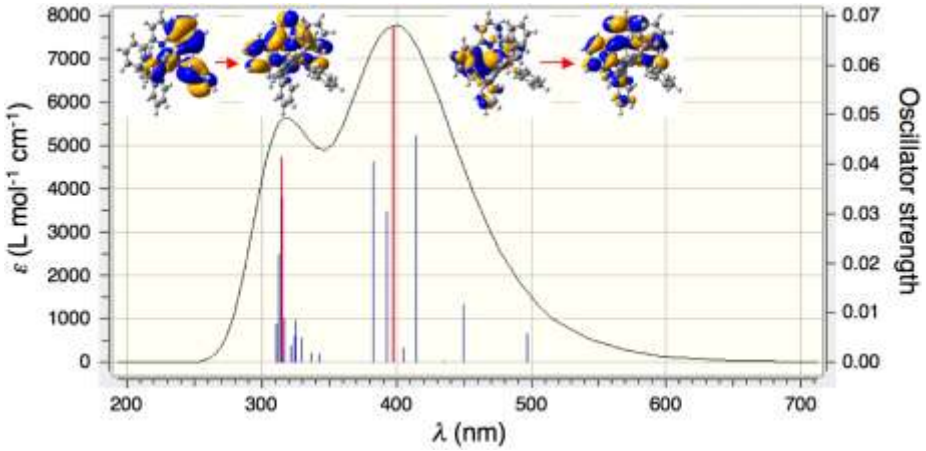


Table S4. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT state of [Ru]**PPh$_3$**.

C	0.00012395	4.43943212	-0.31037568
C	1.34358631	4.38150433	-0.64125717
H	1.85125088	3.42955024	-0.68621836
C	2.04196477	5.53219682	-0.93185437
H	3.08893039	5.47718016	-1.18997604
C	1.40152807	6.75297640	-0.89407620
H	1.94767685	7.65708192	-1.11858311
C	0.06035619	6.81755925	-0.58063515
H	-0.44716998	7.77049582	-0.56587384
C	-0.64334037	5.66727534	-0.29582366
H	-1.69776229	5.73133019	-0.07656264
C	-1.43033297	2.45673979	-1.78727487
C	-1.92869134	1.19157317	-2.05978038
H	-2.00785913	0.45869725	-1.27251790
C	-2.34503787	0.86221624	-3.33035474
H	-2.74315643	-0.12170877	-3.52956464
C	-2.25753822	1.79192699	-4.34656428
H	-2.58414544	1.53635359	-5.34360889
C	-1.75610336	3.04847611	-4.08535341
H	-1.68917606	3.77986085	-4.87697660
C	-1.34199694	3.38362306	-2.81260780
H	-0.95310895	4.37228198	-2.62470570
C	-2.44785588	3.31304751	0.77054897
C	-2.41422268	4.19405630	1.84056958
H	-1.48569158	4.66371037	2.12949248
C	-3.56887082	4.49446903	2.52560624
H	-3.53804812	5.19549050	3.34638261
C	-4.76418414	3.90898974	2.15964020
H	-5.67115236	4.15242980	2.69294198
C	-4.80177850	3.02883445	1.10019466
H	-5.73815779	2.58392912	0.79807048
C	-3.64909122	2.73302051	0.40257400
H	-3.70145153	2.06516761	-0.44323657
C	1.38964249	-0.70707977	3.21269639
H	0.72266032	-0.09663892	3.80144293
C	2.11738964	-1.72859540	3.77389143
H	2.02808179	-1.93674731	4.82841580
C	2.95096097	-2.46435957	2.96233848
H	3.53809108	-3.27504917	3.36712777
C	3.03240930	-2.15405932	1.62445840
H	3.68400456	-2.72051583	0.98069856
C	2.27497336	-1.11318523	1.12747390
C	2.29835869	-0.68514806	-0.27314504
C	3.09933065	-1.28304034	-1.22187919
H	3.73282166	-2.11209600	-0.95521399
C	3.09293952	-0.81127780	-2.51454895
H	3.71833970	-1.27173532	-3.26480159
C	2.28210563	0.25389408	-2.82856957
H	2.24358942	0.66328312	-3.82557983
C	1.50175626	0.80173894	-1.84000665
H	0.84406898	1.62654603	-2.05640808
C	-1.41842155	-1.25307295	0.39805589
H	-0.64952374	-1.45573425	-0.33238552
C	-2.51865598	-2.05152491	0.51284977
H	-2.62704927	-2.91322553	-0.12620604
C	-3.47884163	-1.72616931	1.46146237
H	-4.36661952	-2.33092776	1.56944172
C	-3.27888925	-0.64377560	2.27338110
H	-3.99863249	-0.38549776	3.03297408
C	-2.13074699	0.11781644	2.13064728
C	-1.74177342	1.19651017	3.00788219
C	-2.39627311	1.60941394	4.13139604
H	-3.33152537	1.16009750	4.42212608
C	-1.82140506	2.61264137	4.91624187
H	-2.32001858	2.94218532	5.81390337
C	0.03370035	2.71683572	3.41664875
C	1.31218475	3.09539593	2.94075673
C	2.13946064	4.06744743	3.50729352
H	1.76836351	4.67143892	4.32002926
C	3.40790589	4.23315294	3.04685935
H	4.05305171	4.97755403	3.48787480
C	3.87835335	3.41668254	2.01124177
H	4.88964738	3.49573571	1.64721980
C	3.02857313	2.51036829	1.46418330
H	3.34076508	1.87036640	0.65236969
C	-0.61385962	3.15466619	4.56452766
H	-0.15401566	3.90608532	5.18744687
N	1.46707469	-0.41305045	1.92479226
N	1.49764432	0.34972119	-0.58871466
N	-1.23327035	-0.17264435	1.16246842
N	-0.56150660	1.75404655	2.66086325
N	1.76166082	2.36288367	1.87580331
P	-0.90672515	2.88283466	-0.09191821
Ru	0.36671096	1.14560418	1.01032407

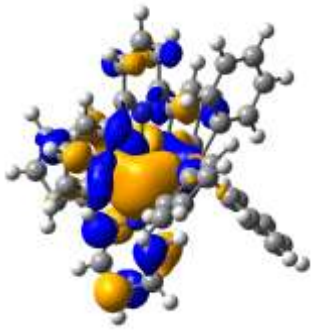
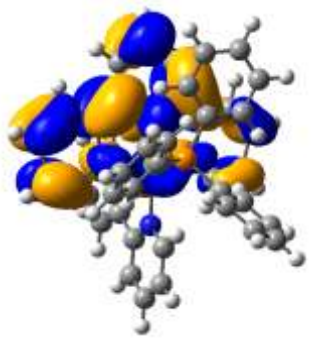
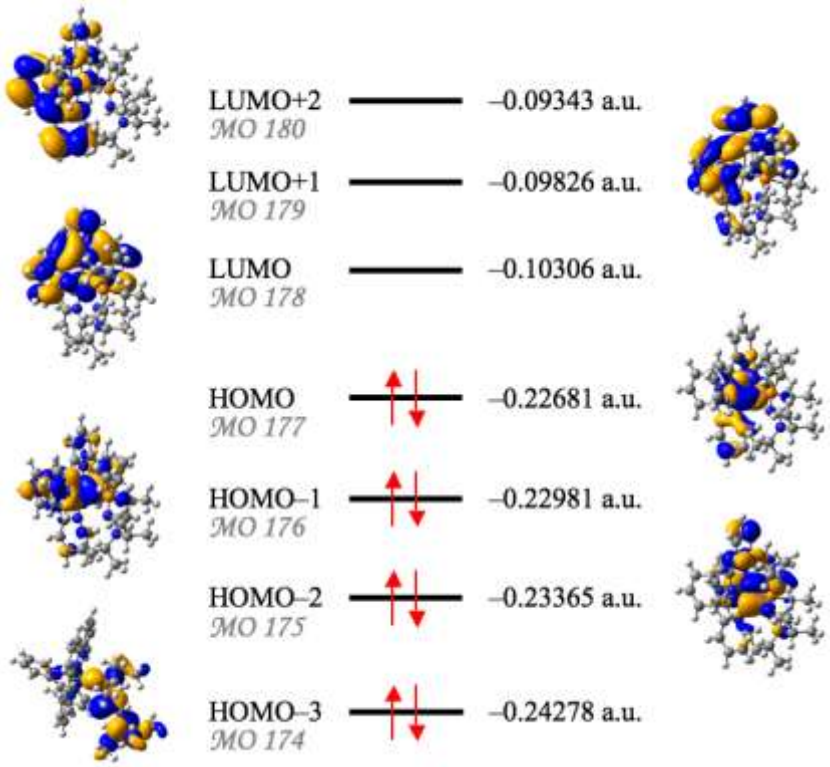
Energies (a.u.)	
$E(T_1)$	-2368.236576
$E(T_1$ in acetonitrile)	-2368.413268
$E(S_0)$	-2368.300159
$E(S_0$ in acetonitrile)	-2368.476860
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0217
Spin density on Ru	0.961

Table S5. Ground-state optimized Cartesian coordinates, coordination distances, molecular orbitals and computed absorption spectrum of [Ru]**2**. The main low-energy ($d\pi \rightarrow \pi^*_{tpy}$) transition is shown in red.

C	3.14003873	-0.08668886	0.21552090
C	5.38255036	-0.12450067	-0.81977165
H	5.21509311	0.94260835	-0.75157693
C	5.56026872	-0.45361683	-2.28685241
H	5.78173633	-1.50640749	-2.45253493
H	6.39396572	0.11639938	-2.68932659
H	4.66941508	-0.19625011	-2.85681539
C	6.61847780	-0.44844243	-0.01107203
H	6.49016263	-0.17633879	1.03350574
H	7.46748470	0.10799635	-0.40028311
H	6.87890582	-1.50417374	-0.05747811
C	4.19931663	-2.23924010	-0.33541938
H	5.19691090	-2.47831645	-0.69157012
C	3.23483962	-2.80295605	-1.35141245
H	2.21111654	-2.57302388	-1.08210385
H	3.35395602	-3.88289788	-1.41117449
H	3.43476741	-2.38811423	-2.33660516
C	4.08238683	-2.86170604	1.03638845
H	4.85717428	-2.47682215	1.69568685
H	4.21465246	-3.93869619	0.96272294
H	3.11582408	-2.66893710	1.48563246
C	3.42378138	1.35771484	0.47530925
C	2.95035458	2.33003368	-0.38217761
H	2.36914991	2.04021238	-1.24410022
C	3.25670734	3.65924838	-0.17062491
H	2.91227471	4.40863692	-0.86846245
C	4.02323001	4.02667742	0.91393579
H	4.26986611	5.06495311	1.07866661
C	4.49968177	3.05821314	1.77524279
H	5.11422542	3.33943333	2.61744960
C	4.21678529	1.72997673	1.54783853
H	4.62349913	0.97465575	2.20315693
C	-0.23779031	2.98394491	0.13372675
H	0.56313699	2.48810892	0.64688546
C	-0.25306642	4.35356229	0.02370960
H	0.54259647	4.92850621	0.47021881
C	-1.29185066	4.94942091	-0.65033338
H	-1.34978512	6.02266433	-0.75140243
C	-2.25663725	4.14426026	-1.20763856
H	-3.07133304	4.58600613	-1.75561086
C	-2.17387542	2.77440659	-1.06339785
C	-3.14045506	1.86143009	-1.67292993
C	-4.19736316	2.28939321	-2.45211960
H	-4.36540656	3.33963180	-2.61912493
C	-5.03702399	1.36455704	-3.02398084
H	-5.86618418	1.68544797	-3.63628961
C	-4.79581765	0.02773746	-2.80575924
H	-5.42088788	-0.73751097	-3.23814638
C	-3.73026996	-0.32589306	-2.01521193
H	-3.51742329	-1.36491485	-1.82465357
C	-3.30594511	1.02231106	2.02500654
H	-2.87559203	1.99493868	1.84962687
C	-4.34875597	0.85973759	2.90742318
H	-4.73825909	1.71408804	3.43830425
C	-4.86939978	-0.39941937	3.09052676
H	-5.68294068	-0.56768265	3.77983100
C	-4.34331998	-1.44456169	2.36562365
H	-4.74659392	-2.43795589	2.47549484
C	-3.30279818	-1.21021699	1.49429418
C	-2.73521012	-2.25571110	0.63606262
C	-3.15027695	-3.56999988	0.57231255
H	-3.90892320	-3.94531284	1.23909396
C	-2.58296476	-4.39928368	-0.37106224
H	-2.88839023	-5.43273811	-0.43183711
C	-1.65195027	-3.90435286	-1.25861869
H	-1.23886343	-4.54108254	-2.02337971
C	-1.26947616	-2.58417168	-1.15031596
C	-0.37397756	-1.86238764	-2.05911076
C	0.21144892	-2.44808955	-3.15985987
H	0.05985068	-3.49554007	-3.36338106
C	0.99222276	-1.68525888	-3.99726910
H	1.45594044	-2.12911888	-4.86510240
C	1.16666545	-0.35212768	-3.70890373
H	1.76247840	0.28758461	-4.34087557
C	0.54771563	0.17006817	-2.59676922
H	0.63333063	1.21483152	-2.34475864
N	2.00806919	-0.65511233	0.44045055
N	4.18358860	-0.77636753	-0.27572205
N	-1.17568783	2.19587610	-0.37530402
N	-2.91955167	0.56173458	-1.45463969
N	-0.20586478	-0.55482199	-1.78810703
N	-1.78185403	-1.81965331	-0.18617506
N	-2.77193677	0.01926767	1.34556406
P	0.59970561	-0.32445280	1.28381129
Ru	-1.31450547	0.08963467	-0.15821765
C	1.00162794	0.94417904	2.59458819
C	1.98897486	0.44302041	3.63089818
C	-0.21783534	1.57597609	3.22927207
H	1.52464237	1.72159861	2.04078259
H	2.81187858	-0.10900815	3.18230161
H	2.41690351	1.29061823	4.16313744
H	1.52113878	-0.20014678	4.37113339
H	-0.81650648	2.10568214	2.49437975
H	-0.86347032	0.85174322	3.71870290
H	0.08985980	2.29882345	3.98328121
C	0.57096017	-1.87906714	2.31020659
C	0.52259360	-3.15720855	1.49749311
C	-0.45611982	-1.91329085	3.41988685
H	1.55805370	-1.82935028	2.76820617
H	1.03775383	-3.05992518	0.54648570
H	1.01123950	-3.95734798	2.05054790
H	-0.49814287	-3.48378830	1.32236985
H	-0.34789189	-1.10313125	4.13196555
H	-1.47235065	-1.88633757	3.03726815
H	-0.35045034	-2.84326600	3.97687058

Bonds	MPWB1K	X-ray
Ru1–P1	2.368 Å	2.350 Å
Ru1–N1	2.122 Å	2.128 Å
Ru1–N2	2.129 Å	2.119 Å
Ru1–N3	1.963 Å	1.960 Å
Ru1–N4	2.070 Å	2.064 Å
Ru1–N5	2.091 Å	2.101 Å



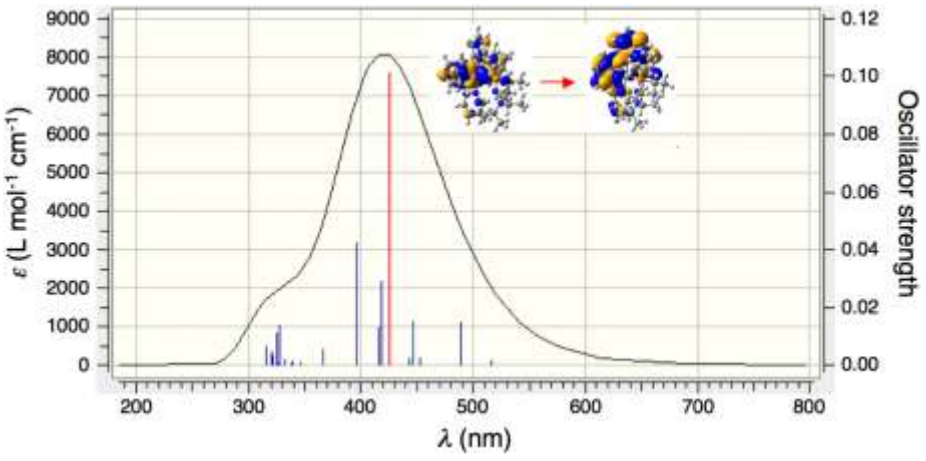


Table S6. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT state of [Ru]**2**.

C	2.80229822	0.32164684	-0.18152744
H	2.98754800	1.01850510	-0.99927392
C	5.18729528	0.53149696	0.05544022
H	5.90635969	0.09790275	0.74439825
C	5.55717943	0.09273298	-1.34279367
H	4.88724451	0.52163188	-2.08714054
H	5.52459545	-0.99003743	-1.43510555
H	6.56404430	0.42351269	-1.58441965
C	5.22693022	2.03248794	0.22511549
H	6.22367363	2.40619334	0.00522256
H	4.97705398	2.31957084	1.24392713
H	4.53701531	2.53210936	-0.45425811
N	3.88989840	-0.02330459	0.46798877
C	0.63342003	1.79805688	-1.79748759
C	0.24191170	3.00174635	-1.23408108
H	-0.32440221	3.00972214	-0.31459414
C	0.56459815	4.19581966	-1.84016383
H	0.24806491	5.12896113	-1.39858202
C	1.28552385	4.19724859	-3.01588086
H	1.53457987	5.13225661	-3.49542597
C	1.68700248	3.00473063	-3.58090748
H	2.25236739	3.00506492	-4.50097593
C	1.36566544	1.80857131	-2.97629715
H	1.68016688	0.88056868	-3.43057090
C	0.34904737	-1.04228142	-2.16331487
C	-0.31885116	-0.87946629	-3.36708569
H	-0.83328552	0.04615703	-3.58392373
C	-0.30671586	-1.88851471	-4.30299909
H	-0.81396845	-1.75275117	-5.24653406
C	0.36072038	-3.06881430	-4.04049421
H	0.37456251	-3.85582465	-4.77993375
C	1.02116784	-3.23652824	-2.84254749
H	1.55312706	-4.15490906	-2.64246694
C	1.01782058	-2.22531684	-1.90399836
H	1.54073307	-2.34871368	-0.96649344
C	-2.95628326	2.83835436	-0.05064856
H	-2.50101004	3.11125459	0.89001662
C	-3.66571968	3.74139427	-0.77317070
H	-3.79204015	4.74660640	-0.40606375
C	-4.22360967	3.33081310	-1.99303105
H	-4.77979064	4.02992671	-2.59854129
C	-4.07498796	2.04346302	-2.39762892
H	-4.51507491	1.70567989	-3.32255387
C	-3.36055932	1.13592513	-1.60736543
C	-3.24352839	-0.24946419	-1.84674666
C	-3.86064438	-1.00392823	-2.84427266
H	-4.47858762	-0.51494081	-3.58109521
C	-3.70583160	-2.35955266	-2.86892434
H	-4.19462224	-2.94456898	-3.63182510
C	-2.92997950	-3.00088564	-1.89235734
H	-2.82442769	-4.07295967	-1.89569129
C	-2.32546161	-2.24008702	-0.93790596
C	-1.51540503	-2.72030451	0.16601546
C	-1.18861176	-4.04553723	0.38317498
H	-1.53264627	-4.79972684	-0.30551566
C	-0.42775606	-4.38424045	1.47114823
H	-0.17003453	-5.41668748	1.65368870
C	0.00411462	-3.39061991	2.33289820
H	0.60130022	-3.61863099	3.20117240
C	-0.34968178	-2.09649992	2.07011475
H	-0.03322585	-1.28432287	2.70526966
C	-4.34754773	-0.62809535	1.61646869
H	-4.39593970	-1.15079785	0.67386824
C	-5.39205915	-0.65697842	2.50923116
H	-6.28447340	-1.21582659	2.27570689
C	-5.26742384	0.04090734	3.68874104
H	-6.06718597	0.04352840	4.41403844
C	-4.10893460	0.74093816	3.93574934
H	-4.00092948	1.29250386	4.85437853
C	-3.09967410	0.72455748	2.99501136
C	-1.82645435	1.43122768	3.15755574
C	-1.53315125	2.18818638	4.27177927
H	-2.25017490	2.28301893	5.06948419
C	-0.31855675	2.82734539	4.36082094
H	-0.08207786	3.42727865	5.22693150
C	0.58479478	2.68380690	3.33355887
H	1.55116961	3.16185273	3.35964020
C	0.23680436	1.91095703	2.25303614
H	0.92304983	1.74437470	1.43965768
N	1.60761226	-0.08852262	0.10681811
N	-2.76277691	1.57414727	-0.45184593
N	-2.47585866	-0.90111241	-0.92960711
N	-1.09299752	-1.76328879	1.01682544
N	-3.23262060	0.04183387	1.85756201
N	-0.94177681	1.30261990	2.15233776
P	0.31292065	0.25422211	-0.89602549
Ru	-1.60410677	0.18171517	0.48983526
C	3.85193238	-0.99536229	1.55627144
H	2.80221684	-1.25724486	1.65368778
C	4.32491877	-0.37758639	2.85255458
H	4.22798952	-1.09631177	3.66261224
H	3.73954381	0.50277254	3.10854339
H	5.37294352	-0.08678317	2.80776810
C	4.63267100	-2.23858624	1.19251288
H	5.69533528	-2.03268738	1.07624027
H	4.26785792	-2.67636989	0.26614052
H	4.53526766	-2.98095146	1.98087978

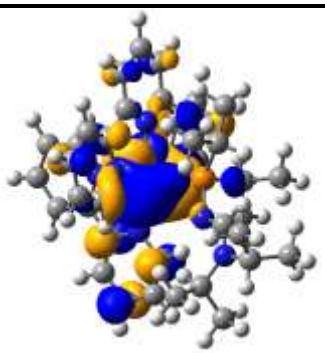
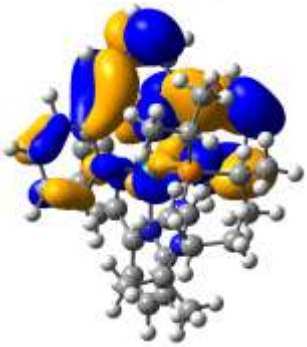
Energies (a.u.)	
$E(T_1)$	-2295.617175
Zero-point correction	0.815889
Sum of electronic and thermal Gibbs energies	-2294.879602
$E(T_1$ in acetonitrile)	-2295.790622
$G(T_1$ in acetonitrile)	-2295.053049
$E(S_0)$	-2295.676809
$E(S_0$ in acetonitrile)	-2295.849594
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0208
Spin density on Ru	0.975

Table S7. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT-^{3}MC transition state of [Ru]**2**.

Ru	-0.98837914	-0.26100601	-0.20632002
P	0.84724286	0.92949099	0.75707289
N	-2.42330876	1.31614526	-0.00622915
N	2.24563489	0.55903552	-0.09229426
N	-2.66155056	-1.21914263	-1.22540158
C	0.77391572	-4.26768989	0.08435261
H	1.35915938	-4.90489453	-0.55958190
N	-0.48109961	-2.28051350	0.34710131
C	-3.19794830	3.46617340	-0.62937065
H	-3.37329033	4.18551361	-1.41357705
N	4.54944530	0.45295982	-0.27726649
C	-3.34997918	2.77330153	1.64056006
H	-3.61028850	2.95756813	2.67120629
C	-2.21803237	-1.89635217	3.52006178
H	-2.07796552	-2.83360813	4.03391058
C	4.53135877	-0.07379408	-1.63688071
H	3.48107508	-0.24207929	-1.85262794
N	-0.46694228	-0.19561939	-2.25552750
C	1.60841158	3.59430217	1.29541378
H	2.63188583	3.32422553	1.03240691
H	1.49788470	3.52399471	2.37361044
H	1.48313157	4.64169266	1.02725217
C	3.43874295	0.71482276	0.37758851
H	3.62938562	1.07524353	1.38690091
C	-1.17930885	-0.57926913	-4.48848791
H	-1.93625087	-0.92522590	-5.17155689
C	0.23982847	1.29797077	3.51349697
H	-0.49891390	0.53396069	3.73706696
H	-0.27982197	2.18333529	3.15072384
H	0.71249121	1.56576098	4.45645378
C	-0.26029632	-3.78648850	2.16915784
H	-0.47054241	-4.03425150	3.19731118
C	-2.80589714	1.55368473	1.26788239
C	-4.78707694	-2.16182788	-2.67428966
H	-5.62379724	-2.52887198	-3.24949714
C	-3.68958633	-1.63282228	-3.31156786
H	-3.66642131	-1.58425991	-4.38710282
C	-3.54302159	3.73839219	0.68919815
H	-3.96510238	4.69457552	0.95841761
C	0.97250741	0.30960746	-4.07708372
H	1.93049402	0.68234712	-4.40403555
C	-4.80209908	-2.21804338	-1.29855738
H	-5.64112272	-2.62978455	-0.76019411
C	0.64263571	3.10064672	-0.93935021
H	0.39610821	4.15056043	-1.08193468
H	-0.06156930	2.51513581	-1.52433395
H	1.63870099	2.93425375	-1.34614737
C	0.60142796	2.75654508	0.53533848
H	-0.40101467	2.96380383	0.91768147
C	0.50674647	-4.61946589	1.39619513
H	0.89708341	-5.53794024	1.80776997
C	5.25005727	-1.40217746	-1.71500870
H	6.31457792	-1.30659284	-1.50991294
H	5.15480097	-1.81282381	-2.71719546
H	4.82965584	-2.11887581	-1.01335144
C	0.69446343	0.24646271	-2.73267540
H	1.42185173	0.53473811	-1.98686381
C	6.01190044	2.16392911	0.73486601
H	5.83591101	2.80970569	-0.12213925
H	7.02275583	2.34420790	1.09133603
H	5.33398014	2.46005624	1.53491217
C	-1.39869271	-0.62508003	-3.12850206
N	-1.75599758	-0.49453304	1.67191878
C	-3.71635698	-1.72889139	-0.61320312
H	-3.68559055	-1.74184914	0.46555365
C	-3.26653657	0.23531450	3.34554506
H	-3.95612086	0.97883914	3.71252315
C	-2.64007768	2.25656965	-0.92807350
H	-2.35577715	2.00463159	-1.93979323
C	6.07267692	-0.22004447	1.53782836
H	5.36739451	-0.02203175	2.34484122
H	7.07241700	-0.07948148	1.94083055
H	5.97022027	-1.26072605	1.24039530
C	0.01499761	-0.09966440	-4.97351258
H	0.19354307	-0.05835600	-6.03763279
C	-3.05270350	-0.92787210	4.04736679
H	-3.56319532	-1.10224925	4.98180251
C	5.84606502	0.70725391	0.36630507
H	6.58401492	0.47439172	-0.39588509
C	-0.75435176	-2.61780692	1.61726071
C	1.78004818	-0.59394754	2.93219488
H	2.24943443	-0.55586036	3.91383754
H	2.50902640	-0.99503966	2.23223859
H	0.95846998	-1.30022805	2.99937807
C	5.07999700	0.94050767	-2.61529157
H	4.52503629	1.87517946	-2.56970786
H	5.01844043	0.55333430	-3.62983053
H	6.12851190	1.16074071	-2.42207595
C	1.28903644	0.78475552	2.54784683
H	2.13612596	1.46913407	2.60995846
C	-2.63043650	-1.17049764	-2.55451627
C	-2.61660337	0.42965851	2.14425470
C	0.26669326	-3.09092671	-0.39643146
H	0.44743509	-2.77324966	-1.41253068
C	-1.59401530	-1.66567626	2.31759423

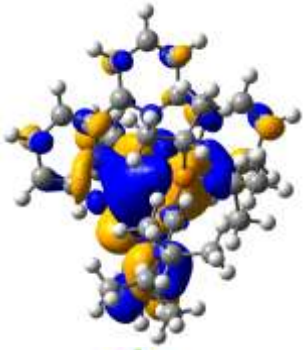
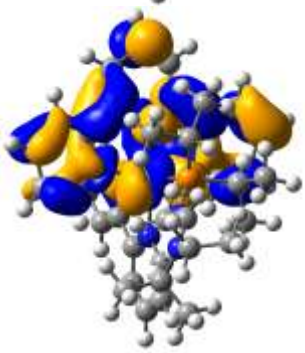
Energies (a.u.)	
$E(T_1)$	-2295.611070
Zero-point correction	0.814831
Sum of electronic and thermal Gibbs energies	-2294.874113
$E(T_1$ in acetonitrile)	-2295.782964
$G(T_1$ in acetonitrile)	-2295.046007
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0292
Spin density on Ru	1.349

Table S8. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MC state of [Ru]**2**.

Ru	-1.00360835	-0.33240188	-0.16575935
P	0.83433325	0.87382233	0.79033276
N	-2.59473677	1.41162085	0.18021986
N	2.24532159	0.56208816	-0.07558003
N	-2.62837315	-1.28424778	-1.15983315
C	0.45982502	-4.59410659	0.53325736
H	1.02806505	-5.30650521	-0.04396807
N	-0.56592275	-2.46789252	0.66088457
C	-3.35796603	3.59520532	-0.31993734
H	-3.54374917	4.35394836	-1.06391293
N	4.55013921	0.50929921	-0.28160172
C	-3.39870798	2.80253564	1.91819660
H	-3.60286272	2.95652915	2.96535506
C	-2.33343843	-1.82262470	3.77947884
H	-2.19551781	-2.73484110	4.33414327
C	4.53323916	0.06194851	-1.66849038
H	3.48616984	-0.12584003	-1.88351493
N	-0.46700738	-0.24570742	-2.20985317
C	1.61520247	3.53975843	1.33468195
H	2.62595464	3.28119532	1.01732486
H	1.55920049	3.44827133	2.41581312
H	1.47156200	4.59156478	1.09373146
C	3.43620043	0.71408205	0.39327782
H	3.62902049	1.02094112	1.41980657
C	-1.18953138	-0.62136586	-4.44134423
H	-1.94496354	-0.97393860	-5.12278922
C	0.28233199	1.21722342	3.56584846
H	-0.46761012	0.46263183	3.78449454
H	-0.22468975	2.12108924	3.23184829
H	0.77107581	1.45385799	4.50904836
C	-0.68247998	-3.93490644	2.50793356
H	-1.00872372	-4.14523433	3.51261115
C	-2.89205256	1.60308191	1.45889815
C	-4.71961707	-2.34226756	-2.59631408
H	-5.53985576	-2.75408222	-3.16472428
C	-3.64034593	-1.78653597	-3.24020885
H	-3.61092200	-1.76355066	-4.31639953
C	-3.62799613	3.81420367	1.01223647
H	-4.02041569	4.76350943	1.34510987
C	0.94398899	0.31499377	-4.03559114
H	1.88976427	0.71481586	-4.36621556
C	-4.73322370	-2.36811829	-1.21979108
H	-5.55626533	-2.79898733	-0.67186880
C	0.53883337	3.06983416	-0.85698927
H	0.27452714	4.11861382	-0.97631739
H	-0.18711293	2.47948484	-1.41135905
H	1.51402062	2.91963175	-1.31727100
C	0.57910114	2.70537754	0.61275919
H	-0.40453660	2.90037410	1.04705769
C	0.04404691	-4.87590572	1.81504494
H	0.28265622	-5.82319160	2.27498020
C	5.29056846	-1.23683516	-1.83308851
H	6.35510909	-1.11984805	-1.63927777
H	5.19084871	-1.59343942	-2.85535426
H	4.90462484	-2.00499046	-1.16717968
C	0.67888400	0.23112651	-2.68942211
H	1.40400909	0.52886263	-1.94473233
C	5.97891036	2.19415065	0.81889565
H	5.77944160	2.88398667	0.00225081
H	6.98836280	2.37829928	1.17748457
H	5.30102796	2.42669028	1.63968189
C	-1.39403347	-0.68809872	-3.08025774
N	-1.90076908	-0.53239445	1.83982190
C	-3.66824124	-1.82578153	-0.54371141
H	-3.64065034	-1.82063876	0.53395195
C	-3.30731329	0.32073391	3.54782824
H	-3.95494414	1.10404109	3.90453958
C	-2.83450195	2.37602995	-0.68777373
H	-2.59549433	2.16345307	-1.72097767
C	6.10297486	-0.22939887	1.48187504
H	5.39675776	-0.09754166	2.30153036
H	7.10092478	-0.08583099	1.88842590
H	6.02606355	-1.25344177	1.12501037
C	-0.01048534	-0.10744767	-4.92920702
H	0.15842578	-0.04867373	-5.99406971
C	-3.11248160	-0.81522291	4.29416014
H	-3.58535364	-0.92702456	5.25819388
C	5.84404261	0.75759942	0.36696048
H	6.58230070	0.58788009	-0.41155729
C	-0.97213085	-2.73112800	1.89484340
C	1.77965179	-0.68695915	2.91866973
H	2.21347263	-0.69828031	3.91730441
H	2.53072522	-1.05962910	2.22643972
H	0.95355739	-1.39222137	2.91752745
C	5.04014806	1.14693238	-2.59227102
H	4.45875527	2.06037275	-2.48674281
H	4.97872314	0.81808262	-3.62727787
H	6.08400153	1.38649579	-2.39618206
C	1.30940074	0.70899282	2.57381050
H	2.16682469	1.37864788	2.64402498
C	-2.60157655	-1.26594777	-2.49346784
C	-2.68198562	0.43473157	2.32294274
C	0.12940322	-3.37150992	-0.00443361
H	0.43162911	-3.10160327	-1.00668166
C	-1.75175515	-1.66112656	2.53722350

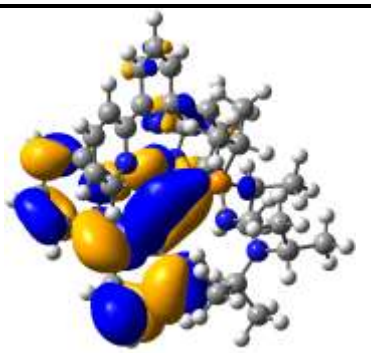
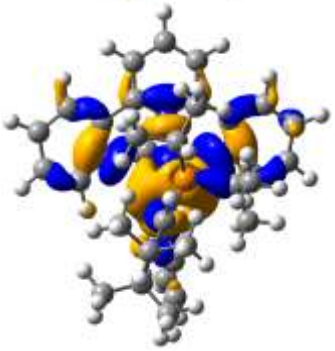
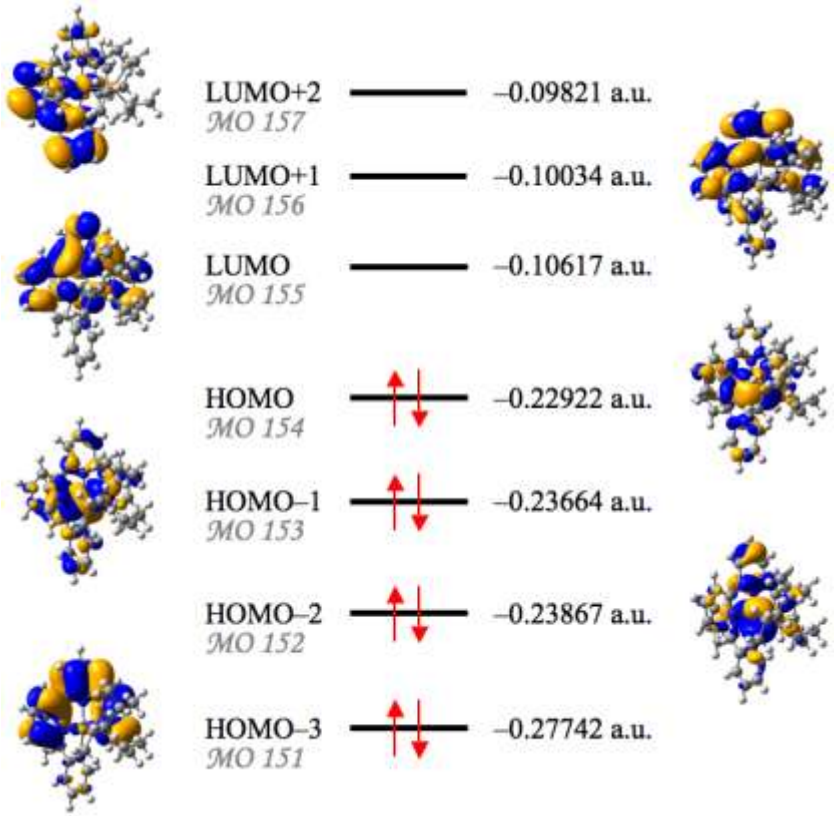
Energies (a.u.)	
$E(T_1)$	-2295.622035
Zero-point correction	0.817314
Sum of electronic and thermal Gibbs energies	-2294.885278
$E(T_1$ in acetonitrile)	-2295.793340
$G(T_1$ in acetonitrile)	-2295.056583
$E(S_0)$	-2295.644600
$E(S_0$ in acetonitrile)	-2295.816141
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0131
Spin density on Ru	1.839

Table S9. Ground-state optimized Cartesian coordinates, coordination distances, molecular orbitals and computed absorption spectrum of [Ru]**P(*i*-Pr)$_3$**. The main low-energy (d$\pi\rightarrow\pi^*_{tpy}$) and (d$\pi\rightarrow\pi^*_{bpy}$) transitions are shown in red.

C	0.83366106	1.92968097	2.84820929
H	-0.10109590	1.82653981	3.40128703
C	1.46736865	3.22654427	3.32099594
H	1.58825503	3.18155331	4.40177712
H	0.87152174	4.10496858	3.10095698
H	2.45743125	3.37716560	2.89851037
C	1.72368202	0.75785194	3.20609144
H	2.67111070	0.79004530	2.67275468
H	1.25401509	-0.19432699	2.98412061
H	1.95168634	0.77805229	4.27031007
C	-1.29870042	2.87972323	1.03873375
H	-1.64737308	2.74112335	0.01365377
C	-2.33296033	2.27069992	1.96329190
H	-2.11076428	2.48921456	3.00650692
H	-2.41028226	1.19362477	1.85203834
H	-3.31368250	2.69516225	1.75775895
C	-1.20247639	4.37059605	1.29608980
H	-2.17752507	4.82065900	1.11566546
H	-0.49423233	4.88220341	0.65223568
H	-0.94893500	4.58816562	2.32974697
C	1.47246803	3.08323555	0.27771036
H	1.39115614	3.93380168	0.95188394
C	2.91722349	2.63188147	0.29513819
H	3.10726768	1.86071299	-0.44441466
H	3.23682997	2.25396951	1.26082831
H	3.56268251	3.47344240	0.04821572
C	1.07696843	3.56263285	-1.10531055
H	1.55168840	4.52140857	-1.30578779
H	0.00516500	3.70527952	-1.22597343
H	1.42068890	2.87944861	-1.87639757
C	-1.17581509	-0.91075422	2.88912090
H	-0.94250086	0.12373913	3.05382937
C	-1.72096604	-1.66766846	3.89716577
H	-1.91479093	-1.21718366	4.85789833
C	-2.00378955	-2.98975951	3.64880812
H	-2.42981131	-3.62215995	4.41299601
C	-1.73690827	-3.49108029	2.39753342
H	-1.95946036	-4.52090217	2.17614963
C	-1.19325945	-2.67024695	1.42987291
C	-0.92083739	-3.13763888	0.07047651
C	-1.14309171	-4.43672738	-0.34159047
H	-1.51731497	-5.17435955	0.34758822
C	-0.88367602	-4.79006246	-1.64386787
H	-1.05370745	-5.80225269	-1.97857536
C	-0.40739161	-3.83101827	-2.50793360
H	-0.19236561	-4.05675213	-3.54047615
C	-0.20400651	-2.56043794	-2.02918766
H	0.17087634	-1.78727065	-2.67948851
C	2.51261198	-1.64918316	1.03309365
H	1.91112114	-1.92617092	1.88370022
C	3.81578140	-2.07539019	0.91956869
H	4.24740877	-2.68854652	1.69501141
C	4.53824743	-1.70441872	-0.18965787
H	5.56555176	-2.01337716	-0.31047129
C	3.92140821	-0.94349810	-1.15698274
H	4.45872737	-0.65920629	-2.04703081
C	2.61112194	-0.55713886	-0.98289054
C	1.86194797	0.18970241	-2.00045759
C	2.34243404	0.60665151	-3.22485444
H	3.37524403	0.46033420	-3.49522939
C	1.47164099	1.20551718	-4.10986791
H	1.82855826	1.53950427	-5.07230232
C	0.14142988	1.35313341	-3.78149480
H	-0.54709627	1.78681496	-4.48783228
C	-0.28562110	0.92915328	-2.54054097
C	-1.67046927	0.91981433	-2.05956918
C	-2.72349303	1.40703500	-2.80122616
H	-2.54468121	1.88530691	-3.75047890
C	-4.00877689	1.26922237	-2.32621158
H	-4.84456519	1.64817198	-2.89479766
C	-4.20537670	0.62353990	-1.12862539
H	-5.19451380	0.46765029	-0.72747296
C	-3.10748516	0.17379807	-0.43125533
H	-3.22066812	-0.33549687	0.51259142
N	-0.90416001	-1.38190860	1.67665999
N	-0.44947443	-2.21371612	-0.77243319
N	1.91982623	-0.88970003	0.12472131
N	0.58492794	0.39753000	-1.68278921
N	-1.86567831	0.33566157	-0.85987295
P	0.28304590	1.88824857	1.05868743
Ru	-0.08856182	-0.30306267	0.02968278

Bonds	MPWB1K	X-ray
Ru1–P1	2.449 Å	2.428 Å
Ru1–N1	2.103 Å	2.117 Å
Ru1–N2	2.131 Å	2.116 Å
Ru1–N3	1.969 Å	1.957 Å
Ru1–N4	2.087 Å	2.078 Å
Ru1–N5	2.094 Å	2.084 Å



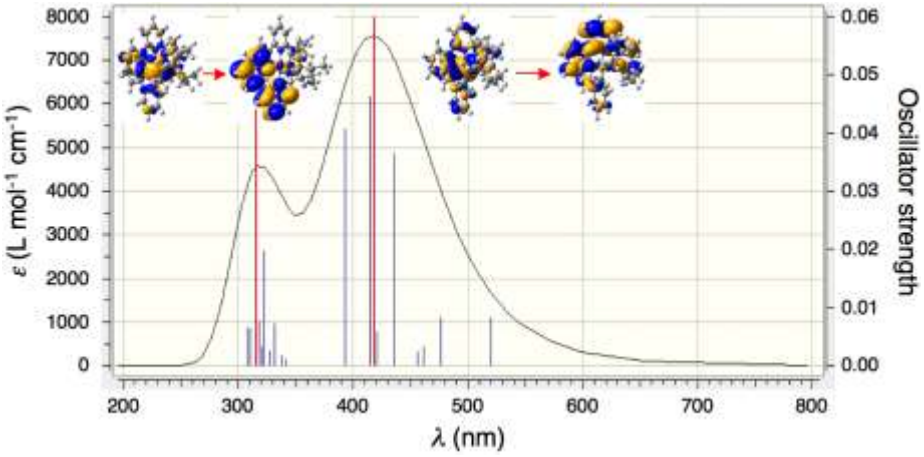


Table S10. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT state of [Ru]**P(*i*-Pr)$_3$**.

C	0.84981858	1.94811575	2.81991152
H	-0.08412823	1.81512984	3.36737026
C	1.45099467	3.25305166	3.31286370
H	1.57195237	3.19403113	4.39283079
H	0.82994125	4.11728637	3.10533977
H	2.43600411	3.43645969	2.89266081
C	1.76680508	0.78659081	3.14734950
H	2.70510039	0.84108488	2.60039451
H	1.31396737	-0.17514279	2.92429395
H	2.01026142	0.79685165	4.20808911
C	-1.30401018	2.86848867	0.98411649
H	-1.63460811	2.70824271	-0.04339770
C	-2.32687908	2.24231653	1.90978773
H	-2.10638548	2.45868731	2.95393692
H	-2.40241365	1.16546247	1.78815766
H	-3.31035081	2.65838970	1.70346817
C	-1.23110646	4.36315811	1.22829726
H	-2.21543345	4.79048703	1.04468939
H	-0.53531901	4.87885350	0.57443983
H	-0.97845046	4.59622458	2.25901950
C	1.49482379	3.12297208	0.24112963
H	1.39204491	3.97160960	0.91746547
C	2.94292942	2.68580930	0.27673205
H	3.13324878	1.87337464	-0.41670705
H	3.27799593	2.37942381	1.26202649
H	3.57136864	3.51970314	-0.03156146
C	1.10439779	3.58976021	-1.14686867
H	1.54777764	4.56628191	-1.33155112
H	0.03080580	3.68888977	-1.28921559
H	1.48678175	2.91799686	-1.90802723
C	-1.16250066	-0.91831300	2.93516682
H	-0.91630264	0.11291387	3.10508606
C	-1.70935498	-1.67860400	3.93806827
H	-1.89235318	-1.23745281	4.90514061
C	-2.00933150	-2.99463541	3.67474699
H	-2.43727887	-3.62972863	4.43598552
C	-1.76022292	-3.48949096	2.41637175
H	-1.99706926	-4.51456817	2.18750618
C	-1.21561949	-2.66824841	1.45131148
C	-0.96489940	-3.12356428	0.08368504
C	-1.23800446	-4.40183984	-0.35827528
H	-1.64124867	-5.14348381	0.31020477
C	-0.99437551	-4.72575722	-1.67274062
H	-1.20435270	-5.72132022	-2.03410096
C	-0.48666156	-3.76435202	-2.51638102
H	-0.28731526	-3.97281572	-3.55567368
C	-0.23386207	-2.51284894	-2.00909254
H	0.16159086	-1.72675281	-2.63209776
C	2.45137048	-1.75971487	0.98758099
H	1.80701550	-2.08724375	1.78840911
C	3.75890886	-2.15244165	0.92596355
H	4.16241752	-2.79906394	1.68873153
C	4.53514047	-1.70489392	-0.12919587
H	5.57343237	-1.99110591	-0.20532466
C	3.96626255	-0.90834215	-1.08837391
H	4.54518058	-0.56484719	-1.93029444
C	2.63500414	-0.55144674	-0.97898969
C	1.90464160	0.21382763	-1.97191469
C	2.37296730	0.61425637	-3.18798686
H	3.39416311	0.42702417	-3.47671832
C	1.49090807	1.24514970	-4.07685676
H	1.84408202	1.56508359	-5.04435267
C	0.17633260	1.40213734	-3.74028886
H	-0.51679358	1.83007299	-4.44753693
C	-0.27951826	0.97422183	-2.49566846
C	-1.61432813	0.92540443	-2.04110730
C	-2.72208318	1.45182933	-2.71395735
H	-2.57068110	2.02714860	-3.61351625
C	-3.97588223	1.22731256	-2.24104898
H	-4.83250559	1.62808645	-2.76132020
C	-4.15100527	0.45433289	-1.08490942
H	-5.13263575	0.22677627	-0.70290225
C	-3.04864210	-0.01237313	-0.44505236
H	-3.13452115	-0.60541525	0.45252039
N	-0.90765372	-1.38547813	1.71631622
N	-0.46281906	-2.20423469	-0.74183028
N	1.90057690	-0.95489115	0.07877557
N	0.62454885	0.45145556	-1.61679249
N	-1.80093187	0.23739414	-0.86778152
P	0.30954405	1.94266646	1.03350299
Ru	-0.07682845	-0.29291601	0.08628546

Energies (a.u.)	
$E(T_1)$	-2028.913015
Zero-point correction	0.690999
Sum of electronic and thermal Gibbs energies	-2028.289517
$E(T_1$ in acetonitrile)	-2029.095689
$G(T_1$ in acetonitrile)	-2028.472191
$E(S_0)$	-2028.973959
$E(S_0$ in acetonitrile)	-2029.155923
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0203
Spin density on Ru	0.954

Table S11. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MLCT-^{3}MC transition state of [Ru]**P(*i*-Pr)$_3$**.

C	0.86661467	1.92544978	2.81001705
H	-0.04905055	1.78813933	3.38661688
C	1.47581148	3.23159197	3.28983473
H	1.62858515	3.16831985	4.36554132
H	0.84411108	4.09355042	3.10522960
H	2.44716308	3.42303160	2.84253589
C	1.79812191	0.76516017	3.10224378
H	2.71840872	0.82856154	2.52590997
H	1.34419771	-0.19780686	2.88424429
H	2.07491623	0.76892276	4.15483479
C	-1.35866390	2.80177370	1.02713234
H	-1.69280273	2.67236855	-0.00459861
C	-2.37032725	2.12446660	1.92846497
H	-2.13164680	2.26842843	2.98122921
H	-2.45884950	1.05902749	1.73584858
H	-3.35228898	2.56409191	1.76778925
C	-1.31278082	4.28733236	1.32577668
H	-2.30445203	4.70595808	1.16304311
H	-0.62759887	4.83953013	0.69042266
H	-1.05864058	4.48350000	2.36408017
C	1.41426047	3.12913718	0.22875274
H	1.31642899	3.97032646	0.91431419
C	2.86957343	2.71521860	0.22004240
H	3.05211598	1.91429906	-0.48829197
H	3.23392773	2.39709971	1.19091528
H	3.47845366	3.56259496	-0.09090842
C	0.98252481	3.60365569	-1.14466282
H	1.40221755	4.59064009	-1.32912200
H	-0.09617385	3.68614358	-1.26011670
H	1.36214771	2.95002276	-1.92402611
C	-1.14726843	-0.90822479	2.93222035
H	-0.89188147	0.12324312	3.08020936
C	-1.68081438	-1.64427834	3.95952833
H	-1.84030621	-1.18310305	4.92135454
C	-1.99817076	-2.96143126	3.72619834
H	-2.41841569	-3.57941347	4.50552221
C	-1.77264056	-3.47916455	2.47324449
H	-2.01904357	-4.50661705	2.26678145
C	-1.23589821	-2.68274063	1.48273114
C	-0.99696272	-3.18270256	0.12777940
C	-1.27350499	-4.47606857	-0.27114735
H	-1.67825714	-5.19681771	0.41893290
C	-1.02716574	-4.84188715	-1.57363964
H	-1.23763391	-5.84820253	-1.90347814
C	-0.51317787	-3.90968627	-2.44678782
H	-0.30895582	-4.15454001	-3.47722306
C	-0.26133423	-2.64329324	-1.97699977
H	0.14100730	-1.87818408	-2.62266696
C	2.48805099	-1.83219089	0.91443304
H	1.82891117	-2.24315732	1.66503113
C	3.82822191	-2.10291058	0.92114915
H	4.24483239	-2.74331052	1.68238616
C	4.62301061	-1.54610184	-0.06768785
H	5.68707276	-1.72774526	-0.08192148
C	4.04101300	-0.76983938	-1.03560324
H	4.63962732	-0.33021413	-1.81742095
C	2.67386304	-0.55617783	-1.00072965
C	1.92551308	0.17164856	-2.00321247
C	2.40351389	0.54575573	-3.23515132
H	3.42895767	0.34847518	-3.50306523
C	1.54570306	1.14178447	-4.14337078
H	1.90310981	1.42310435	-5.12173280
C	0.22353416	1.32002075	-3.80965916
H	-0.47233454	1.72745120	-4.52577616
C	-0.21707114	0.93852287	-2.55891217
C	-1.57736874	0.97423242	-2.10564019
C	-2.59971125	1.70223586	-2.69694999
H	-2.38490505	2.36202881	-3.52297491
C	-3.87523095	1.57668462	-2.21928650
H	-4.68400625	2.13275990	-2.66833537
C	-4.11836016	0.71353753	-1.15552578
H	-5.11687900	0.55575157	-0.77977854
C	-3.06838054	0.04820442	-0.59437361
H	-3.21155737	-0.63005616	0.23413406
N	-0.91730149	-1.39479162	1.71540114
N	-0.49529365	-2.29291290	-0.72393548
N	1.91761194	-1.06323059	-0.01087205
N	0.64621118	0.42143776	-1.65810599
N	-1.81333776	0.18074896	-1.03367660
P	0.27698206	1.91010461	1.03757567
Ru	-0.08544574	-0.31077915	0.08426010

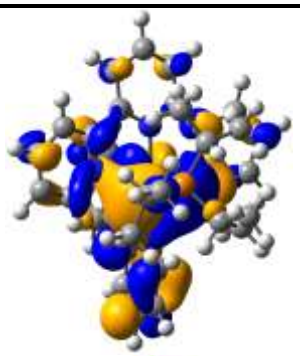
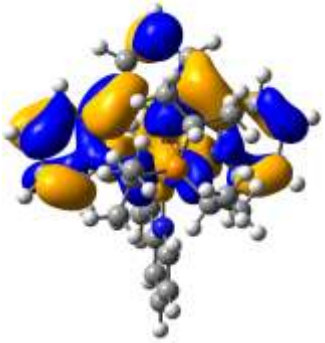
Energies (a.u.)	
$E(T_1)$	-2028.909147
Zero-point correction	0.689189
Sum of electronic and thermal Gibbs energies	-2028.288198
$E(T_1$ in acetonitrile)	-2029.090143
$G(T_1$ in acetonitrile)	-2028.469194
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0291
Spin density on Ru	1.278

Table S12. Optimized Cartesian coordinates, energies and electronic structure of the ^{3}MC state of [Ru]**P(*i*-Pr)$_3$**.

C	0.87165719	1.91921879	2.79842365
H	-0.05609369	1.82940942	3.36682031
C	1.53943032	3.19532490	3.27957532
H	1.68876319	3.12727903	4.35558272
H	0.94982105	4.08652500	3.09298086
H	2.51968000	3.33934513	2.83276538
C	1.74921010	0.72078540	3.10945783
H	2.70126910	0.77793569	2.58589831
H	1.28399358	-0.22266909	2.83332584
H	1.96918101	0.68362529	4.17486474
C	-1.31939770	2.82026184	0.99928491
H	-1.60412944	2.76995381	-0.05470084
C	-2.38927639	2.09871454	1.79158648
H	-2.19943239	2.14968120	2.86305293
H	-2.48733308	1.05479862	1.50697752
H	-3.35285337	2.57602987	1.62509947
C	-1.26402647	4.27536946	1.41757252
H	-2.23326097	4.73637983	1.23521763
H	-0.52676018	4.85891667	0.87460033
H	-1.06647292	4.37471011	2.48234241
C	1.45484832	3.12066913	0.23593415
H	1.39621110	3.94609707	0.94322976
C	2.89313409	2.65203134	0.20276307
H	3.04870692	1.90267608	-0.56593193
H	3.23092502	2.23616480	1.14665393
H	3.54403299	3.49250694	-0.03266133
C	1.03270920	3.65830629	-1.11583683
H	1.55556399	4.59418122	-1.30460300
H	-0.03181397	3.86925251	-1.18659836
H	1.30630088	2.98218273	-1.92012608
C	-1.23953604	-0.83659370	2.90847788
H	-0.93729278	0.18101583	3.06198653
C	-1.87456901	-1.53153336	3.90599153
H	-2.06788657	-1.05234249	4.85266844
C	-2.24944401	-2.83218588	3.66326574
H	-2.75246897	-3.41627939	4.41931458
C	-1.96913334	-3.37929670	2.43408375
H	-2.25265191	-4.39631173	2.22338567
C	-1.32449697	-2.62447399	1.47617778
C	-0.98802643	-3.15275601	0.15684115
C	-1.27204005	-4.44375381	-0.24287457
H	-1.77508564	-5.12817830	0.41887419
C	-0.90313704	-4.85605845	-1.50072723
H	-1.11787079	-5.86179127	-1.82918260
C	-0.25480784	-3.96724583	-2.32813937
H	0.05686201	-4.24631457	-3.32229172
C	-0.00634392	-2.69940879	-1.86342564
H	0.49884899	-1.97392478	-2.47935539
C	2.90204738	-1.66850650	0.65137011
H	2.35775785	-2.03729088	1.50930901
C	4.23881632	-1.94906655	0.48965365
H	4.76299769	-2.54033103	1.22404343
C	4.87652487	-1.45767295	-0.62722705
H	5.92604646	-1.65099897	-0.79161428
C	4.15803671	-0.71972146	-1.53959149
H	4.64722018	-0.33516676	-2.41864600
C	2.81739910	-0.48424561	-1.30219003
C	1.95154909	0.26031000	-2.23100800
C	2.40918896	0.71421519	-3.45246011
H	3.43905362	0.58171370	-3.73611123
C	1.52944923	1.31619224	-4.31861735
H	1.86443263	1.66788024	-5.28280249
C	0.21097445	1.42926416	-3.95323289
H	-0.50948786	1.84624472	-4.63650708
C	-0.18329679	0.98003944	-2.70888820
C	-1.59161338	1.01601769	-2.29223262
C	-2.55451025	1.76444862	-2.94001062
H	-2.29476744	2.43172586	-3.74542261
C	-3.86548940	1.65330587	-2.53280652
H	-4.63705556	2.22838537	-3.02272098
C	-4.17776598	0.79491577	-1.50284098
H	-5.19506081	0.66216977	-1.16926690
C	-3.15197032	0.10633915	-0.89555735
H	-3.34564198	-0.56791779	-0.07208069
N	-0.96088236	-1.35029542	1.71366883
N	-0.36474460	-2.29512138	-0.65350695
N	2.21412940	-0.94876251	-0.21662449
N	0.68224265	0.43030144	-1.85509113
N	-1.89264459	0.22502181	-1.27058574
P	0.29682458	1.89745048	1.01750570
Ru	-0.02388564	-0.34063625	0.09297360

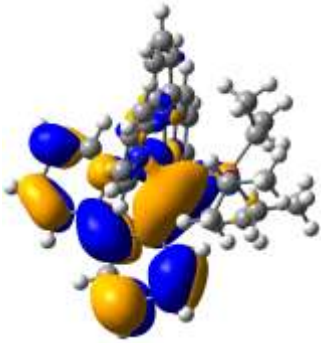
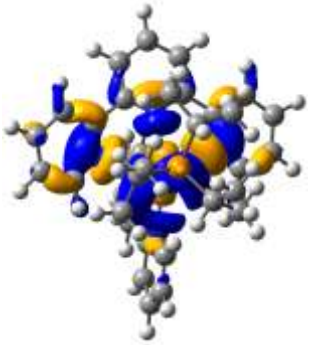
Energies (a.u.)	
$E(T_1)$	-2028.922494
Zero-point correction	0.691701
Sum of electronic and thermal Gibbs energies	-2028.301179
$E(T_1$ in acetonitrile)	-2029.102817
$G(T_1$ in acetonitrile)	-2028.481502
$E(S_0)$	-2028.944307
$E(S_0$ in acetonitrile)	-2029.124754
Electronic structure (in vacuo)	
SOMO (hole β)	
SOMO (electron α)	
$< S^2 >$	2.0124
Spin density on Ru	1.831

Figure S1: Intrinsic reaction coordinate (IRC) for ^{3}MLCT → ^{3}MC of [Ru]**2**. IRC performed at the MPWB1K using LANL2DZ and 6-31G* basis sets. The energy of the lowest triplet excited state *E* is represented as a function of the intrinsic reaction coordinate. Structures (Tables S6-S8 for Cartesian coordinates optimized at the MPWB1K and a large basis set level) and the transition vector are shown.

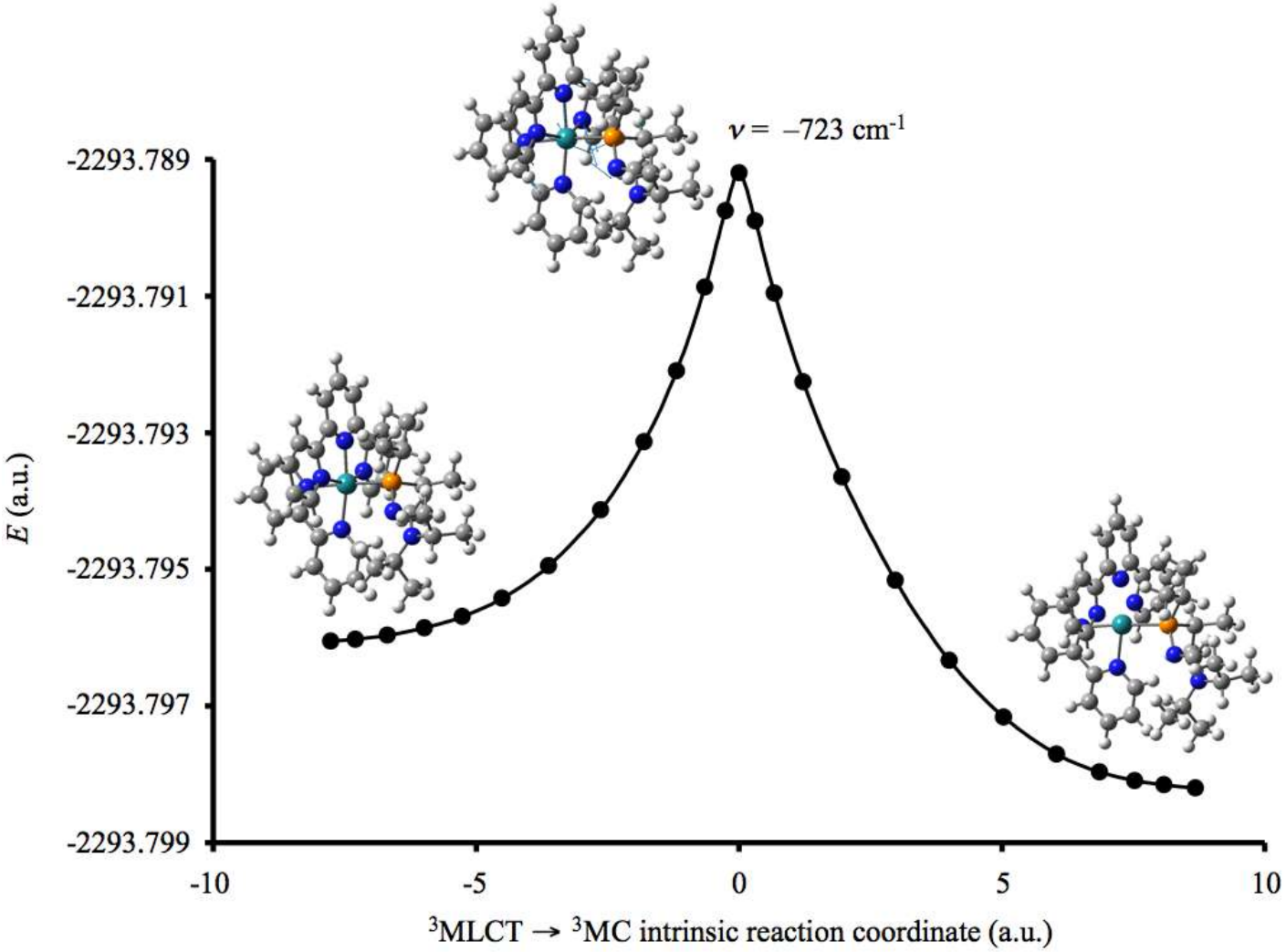
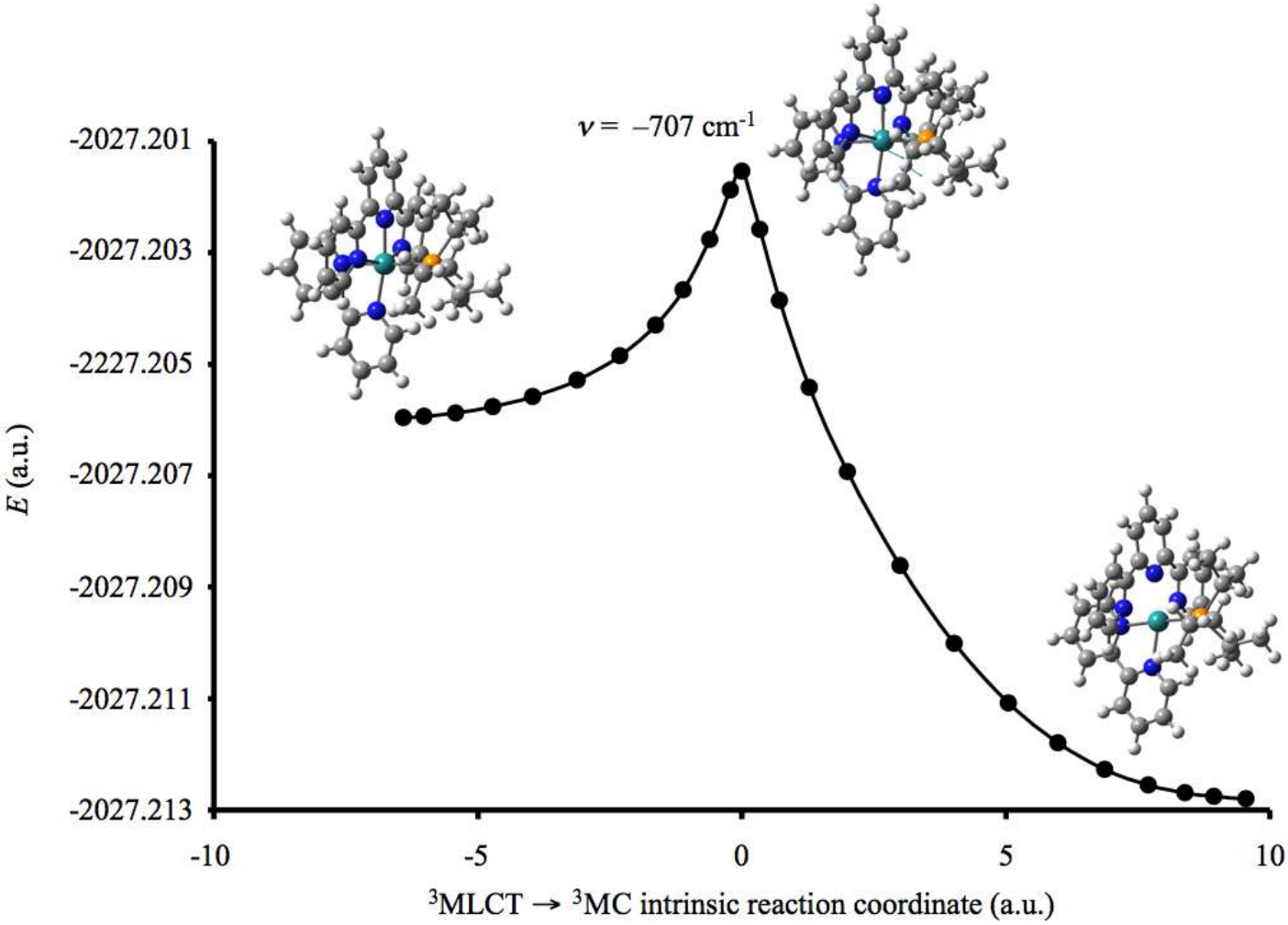


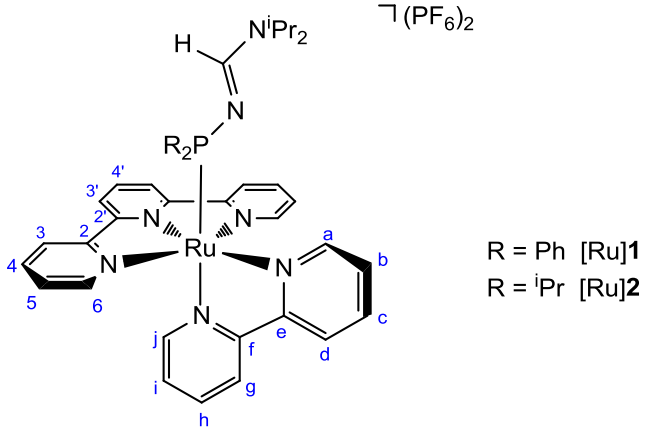
Figure S2: Intrinsic reaction coordinate (IRC) for ^{3}MLCT → ^{3}MC of [Ru]**P(*i*-Pr)$_3$**. IRC performed at the MPWB1K using LANL2DZ and 6-31G* basis sets. The energy of the lowest triplet excited state *E* is represented as a function of the intrinsic reaction coordinate. Structures (Tables S10-S12 for Cartesian coordinates optimized at the MPWB1K and a large basis set level) and the transition vector are shown.



Experimental details

Ligands **1, 2** were synthesized according to the method we described previously.[12,13] [Ru(bpy)(tpy)(NCCH$_3$)](PF$_6$)$_2$ was synthesized from [Ru(bpy)(tpy)Cl](PF$_6$) according to the method described for [Ru(tpy)(phen)(NCCH$_3$)](PF$_6$)$_2$.[14] The abbreviations bpy and tpy stand for 2,2'-bipyridine and 2,2':6',2"-terpyridine respectively, and [Ru] stands for [Ru(bpy)(tpy)](PF$_6$)$_2$. All solvents were dried and distilled by standard methods. Column chromatography was performed on silica gel from SDS (70–200 μm). NMR spectra were performed on a Bruker AV300 spectrometer, in (CD$_3$)$_2$CO unless otherwise stated. Elemental analyses were carried out with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

The electrochemical measurements were obtained using an Autolab PGSTAT 100 potentiostat using tetrabutylammonium hexafluorophosphate as the supporting electrolyte in freshly distilled acetonitrile and a platinum working electrode. Electrospray mass spectrometry analyses were performed on a Perkin Elmer Sciex API-365 spectrometer in positive mode. Melting points were determined in capillaries using an Electrothermal melting point apparatus. Absorption spectra were recorded in acetonitrile solutions using a Perkin-Elmer Lambda 35 spectrophotometer. Luminescence experiments were conducted in air-equilibrated acetonitrile solutions at room temperature, and in an EtOH–MeOH 1 : 4 v/v matrix at 77 K. Uncorrected emission spectra and emission lifetimes were obtained with an Edinburgh FLS-920 spectrofluorimeter. Emission spectra at 77 K were recorded using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen.



[Ru]**1**

[Ru(bpy)(tpy)(NCCH$_3$)](PF$_6$)$_2$ (148 mg, 0.18 mmol) and **1** (568 mg, 1.8 mmol) were placed in a closed Schlenck tube with 4 mL of acetone and irradiated for 2h. After cooling, the reaction mixture was poured into a tenfold excess of diethylether to precipitate the complexes. The precipitate was recovered by filtration, washed with diethylether and purified by chromatography on silica gel (acetone-H_2O-saturated aqueous KNO_3 (v/v) 90/5/0.5). In a final step the nitrate counter ions were exchanged by hexafluorophosphate ions to ensure solubility in organic solvents. Complex [Ru]**1** was isolated as an orange solid in 98% yield (194 mg).

NMR ^{1}H (300 MHz, acetone d$_6$) : δ (ppm) = 9.80 (d, 1H, H$_a$, ^3J=5.7 Hz), 8.93 (d, 1H, H$_d$, ^3J=8.1 Hz), 8.74 (d, 1H, H$_g$, ^3J=8.1 Hz), 8.50 (d, 2H, H$_{3'}$, ^3J=8.1 Hz), 8.48-8.38 (m, 3H, H$_3$+H$_c$), 8.22 (t, 1H, H$_{4'}$, ^3J=8.1 Hz), 8.19 (d, 1H, H$_6$, ^3J=5.7 Hz), 8.10-8.01 (m, 3H, H$_4$+H$_h$), 7.90 (ddd, 1H, H$_b$, ^3J=7.2 Hz, ^3J=6.0 Hz, ^4J=1.2 Hz), 7.48 (ddd, 2H, H$_5$, ^3J=7.4 Hz, ^3J=5.9 Hz, ^4J=1.5 Hz), 7.45-7.37 (m, 3H, H$_p$+H$_i$), 7.33 (d, 1H, H$_j$, ^3J=6.60 Hz), 7.26 (ddd, 4H, H$_m$, ^3J=7.2 Hz, ^3J=7.8 Hz, $^5J_{HP}$=2.1 Hz), 7.04 (d, N=C<u>H</u>, $^3J_{HP}$=22.8 Hz), 7.03-6.96 (m, 4H, H$_o$), 4.62 (sept, 1H, C<u>H</u>CH$_3$, ^3J=6.9 Hz), 3.64 (sept, 1H, C<u>H</u>CH$_3$, ^3J=6.9 Hz), 1.19 (d, 6H, CHC<u>H</u>$_3$, ^3J=6.9 Hz), 0.95 (d, 6H, CHC<u>H</u>$_3$, ^3J=6.9 Hz).
NMR ^{13}C {^{1}H} (75 MHz, acetone d$_6$) : δ (ppm) = 157.98 (C$_2$), 157.19 (d, C$_e$, $^3J_{CP}$=1.8 Hz), 156.87 (C$_{2'}$), 155.91 (d, C$_a$, $^3J_{CP}$=3.2 Hz), 155.54(C$_f$), 154.58 (N=<u>C</u>H, $^2J_{CP}$=6.3 Hz), 153.90 (C$_6$), 148.77 (C$_i$), 138.80 (C$_h$), 138.30 (C$_c$), 138.19 (C$_4$), 136.13 (C$_{4'}$), 131.68 (C$_{ipso}$, $^1J_{CP}$=38.6 Hz), 131.39 (d, C$_o$, $^2J_{CP}$=10.0 Hz), 130.40 (d, C$_p$, $^4J_{CP}$=2.2 Hz), 128.68 (d, C$_m$, $^3J_{CP}$=8.9 Hz), 127.78 (C$_5$), 127.30 (d, C$_j$, $^3J_{CP}$=2.3 Hz), 127.21 (C$_b$), 124.79 (C$_d$), 124.09 (C$_3$), 123.75 (d, C$_g$, $^4J_{CP}$=2.0 Hz), 123.48 (C$_{3'}$), 45.83 (<u>C</u>HCH$_3$), 45.76 (<u>C</u>HCH$_3$), 23.39 (CH<u>C</u>H$_3$), 19.18 (CH<u>C</u>H$_3$).
NMR ^{31}P (121.5 MHz, acetone d$_6$) : δ (ppm) = 74.5, -144.2 (sept, $^1J_{PF}$=709 Hz).
ES$^+$-MS: *m/z* = 948.1 ([M-PF$_6$]$^+$), 490.1 ([M-{^{i}Pr$_2$N-C(H)=NPPh$_2$}-2PF$_6$]$^+$), 401.9 ([M-2PF$_6$]$^{2+}$).
mp : 132 °C (decomposition).

Elemental analysis Calcd. for $C_{44}H_{44}F_{12}N_7P_3Ru$ (1092.84): C, 48.36; H, 4.06; N, 8.97. Found: C, 48.55; H, 3.92; N, 8.77.

[Ru]**2**

$[Ru(bpy)(tpy)(NCCH_3)](PF_6)_2$ (78 mg, 0.095 mmol) and **2** (232 mg, 0.95 mmol) were placed in a closed Schlenck tube with 4 mL of acetone and irradiated for 2h. After cooling, the reaction mixture was poured into a tenfold excess of diethylether to precipitate the complexes. The precipitate was recovered by filtration, washed with diethylether and purified by chromatography on silica gel (acetone-H_2O-saturated aqueous KNO_3 (v/v) 90/5/0.5). In a final step the nitrate counter ions were exchanged by hexafluorophosphate ions to ensure solubility in organic solvents. According to ^{31}P NMR on the crude reaction mixture, conversion of $[Ru(bpy)(tpy)(NCCH_3)](PF_6)_2$ into [Ru]**2** was quantitative and isolated as a red solid in 33% yield (30 mg) after purification by chromatography. The isolated yield was not optimized.

NMR ^{1}H (300 MHz, acetone d_6) : δ (ppm) = 10.44 (d, 1H, H_a, ^3J=5.4 Hz), 8.92-8.84 (m, 3H, $H_{3'}$+H_d), 8.72 (d, 2H, H_3, ^3J=8.7 Hz), 8.66 (d, 1H, H_g, ^3J=8.1 Hz), 8.52-8.39 (m, 2H, $H_{4'}$+H_c), 8.19-8.11 (m, 4H, H_4+H_6), 8.08 (dd, 1H, H_b, ^3J=6.3 Hz, ^4J=1.2 Hz), 8.00 (dd, 1H, H_h, ^3J= 7.8 Hz, ^4J=1.5 Hz), 7.58-7.51 (m, 2H, H_5), 7.44 (d, 1H, N=C<u>H</u>, $^3J_{HP}$=17.4 Hz), 7.30 (dd, 1H, H_i, ^3J=6.6 Hz, ^4J=1.5 Hz), 7.09 (d, 1H, H_j, ^3J=5.7 Hz), 4.77 (sept, 1H, NC<u>H</u>CH_3, ^3J=6.9 Hz), 3.70 (sept, 1H, NC<u>H</u>CH_3, ^3J=6.9 Hz), 2.20-2.05 (m, 2H, PC<u>H</u>CH_3), 1.33 (d, 6H, NCHC<u>H</u>$_3$, ^3J=6.9 Hz), 1.20 (d, 6H, NCHC<u>H</u>$_3$, ^3J=6.9 Hz), 0.84 (d, 3H, PCHC<u>H</u>$_3$, ^3J=6.9 Hz), 0.79 (d, 3H, PCHC<u>H</u>$_3$, ^3J=6.9 Hz), 0.67 (d, 3H, PCHC<u>H</u>$_3$, ^3J=6.9 Hz), 0.63 (d, 3H, PCHC<u>H</u>$_3$, ^3J=6.9 Hz).
NMR ^{13}C {^{1}H} (75 MHz, acetone d_6) : δ (ppm) = 158.41 (C_2), 158.38 ($C_{2'}$), 157.05 (d, C_e, $^3J_{CP}$=2.26 Hz), 156.68 (C_a), 155.56 (C_f), 153.70 (C_6), 153.49 (d, N=<u>C</u>H, $^2J_{CP}$=4.23 Hz), 147.34 (C_j), 138.63 (C_h), 138.43 (C_4), 138.25 (C_c), 136.50 ($C_{4'}$), 128.25 (C_5), 127.35 (d, C_i, $^4J_{CP}$=1.96 Hz), 126.93 (C_b), 124.60 (C_d), 124.52 (C_3), 124.04 ($C_{3'}$), 123.58 (d, C_g, $^4J_{CP}$=1.81 Hz), 46.87 (N<u>C</u>HCH_3), 45.16 (N<u>C</u>HCH_3), 27.82 (P<u>C</u>HCH_3), 27.53 (P<u>C</u>HCH_3), 23.15 (NCH<u>C</u>H_3), 19.30 (NCH<u>C</u>H_3), 18.01 (PCH<u>C</u>H_3), 16.63 (PCH<u>C</u>H_3).
NMR ^{31}P (121.5 MHz, acetone d_6) : δ (ppm) = 75.4, -140.8 (sept, $^1J_{PF}$=707 Hz).
ES$^+$-MS : *m/z* = 880.1 ($[M\text{-}PF_6]^+$), 490.1 ($[M\text{-}\{^iPr_2N\text{-}C(H)=NP^iPr_2\}\text{-}2PF_6]^+$), 367.8 ($[M\text{-}2PF_6]^{2+}$).
mp : 122 °C (decomposition).
Elemental analysis Calcd. for $C_{38}H_{48}F_{12}N_7P_3Ru$ (1024.81): C, 44.54; H, 4.72; N, 9.57. Found: C, 44.69; H, 4.54; N, 9.48.

X-ray diffraction

Monocrystals of [Ru]**1** and [Ru]**2** were obtained by the slow liquid diffusion of diethylether into an acetone solution of the complex. Data for [Ru]**1** (CCDC 836294) were collected at low temperature (180 K) on a IPDS STOE diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. Data for [Ru]**2** (CCDC 836293) were collected at low temperature (180 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) and equipped with an Oxford Instrument Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92[15] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[16] included in the software package WinGX version 1.63.[17] The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography.[18] 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 $P=(Fo^2+2Fc^2)/3$. Drawings of molecules are performed with the program ORTEP32[19] [5] with 30% probability displacement ellipsoids for non-hydrogen atoms. For both compounds, it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON (Spek, 1990) resulted in a smooth refinement. Since a few low order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for D(calc), F(000) and the molecular weight are only valid for the ordered part of the structure.

Table S13. Crystal data and structure refinement for [Ru]**1** and [Ru]**2**.

	[Ru]**1**	[Ru]**2**
Identification code	CCDC 836294	CCDC 836293
Empirical formula	C44 H44 N7 P Ru, 2(F6 P)	C38 H48 N7 P Ru, 2(F6 P)
Formula weight	1092.84	1024.81
Temperature	180(2) K	180(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/n 1	Monoclinic, P 21/c
Unit cell dimensions	a = 17.2051(17) Å α = 90 deg.	a = 13.0299(8) Å α = 90 deg.
	b = 14.2527(8) Å β = 99.011(12) deg.	b = 17.0758(12) Å β = 104.414(5) deg.
	c = 23.982(2) Å γ = 90 deg.	c = 21.0409(12) Å γ = 90 deg.
Volume	5808.2(9) $Å^3$	4534.2(5) $Å^3$
Z, Calculated density	4, 1.250 Mg/m^3	4, 1.501 Mg/m^3
Absorption coefficient	0.424 mm^{-1}	0.537 mm^{-1}
F(000)	2216	2088
Crystal size	0.2 x 0.075 x 0.025 mm	0.5 x 0.2 x 0.15 mm
θ range for data collection	2.13 to 25.68 deg.	3.10 to 32.27 deg.
Limiting indices	20<=h<=20 -17<=k<=17 -29<=l<=29	-19<=h<=18 -25<=k<=23 -29<=l<=31
Reflections collected / unique	44287 / 11025 [R(int) = 0.0820]	44527 / 15022 [R(int) = 0.1055]
Completeness to θ	= 25.68 99.9 %	= 32.27 93.1 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.987 and 0.931	0.918 and 0.703
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11025 / 12 / 609	15022 / 0 / 558
Goodness-of-fit on F^2	0.817	0.896
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1314	R1 = 0.0578, wR2 = 0.1248
R indices (all data)	R1 = 0.1161, wR2 = 0.1506	R1 = 0.1120, wR2 = 0.1381
Largest diff. peak and hole	0.610 and -0.553 e. $Å^{-3}$	2.334 and -1.016 e. $Å^{-3}$

Cyclic voltammograms in acetonitrile solution for ligands **1** and **2** and for complexes [Ru]**1** and [Ru]**2**, at 100 $mV.s^{-1}$ scan rate, with n-Bu_4NPF_6 as supporting electrolyte, platinum working and counter electrodes and using the standard calomel electrode as reference. The arrow indicates the direction of the scan.

Figure S3. Oxidation cyclic voltammogram of **1** at 100 $mV.s^{-1}$ scan rate

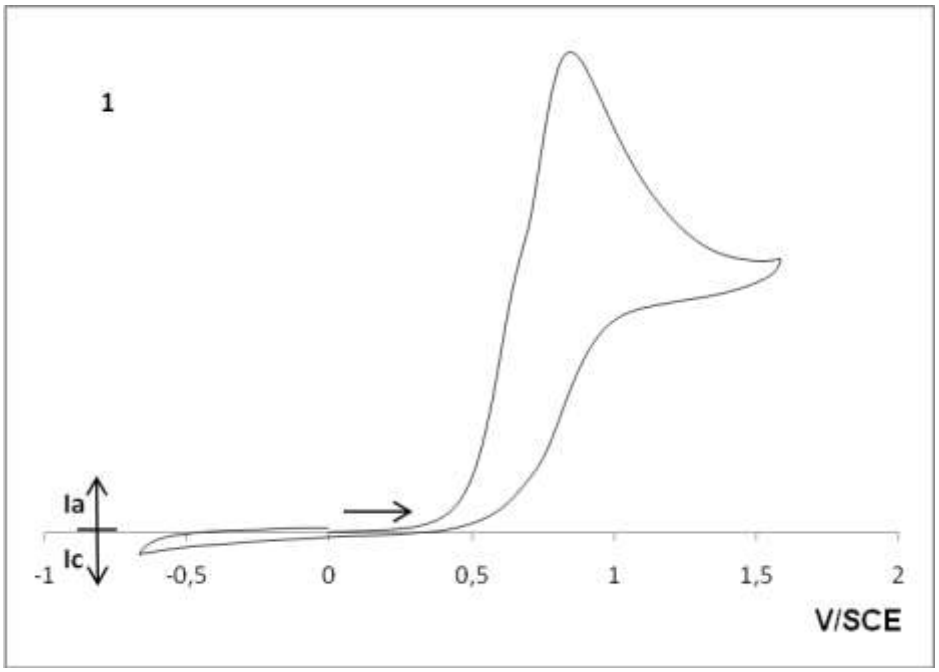


Figure S4. Square wave oxidation voltammogram of **1** at 20 Hz 20 $5mV.s^{-1}$ corresponding to 100 $mV.s^{-1}$ scan rate

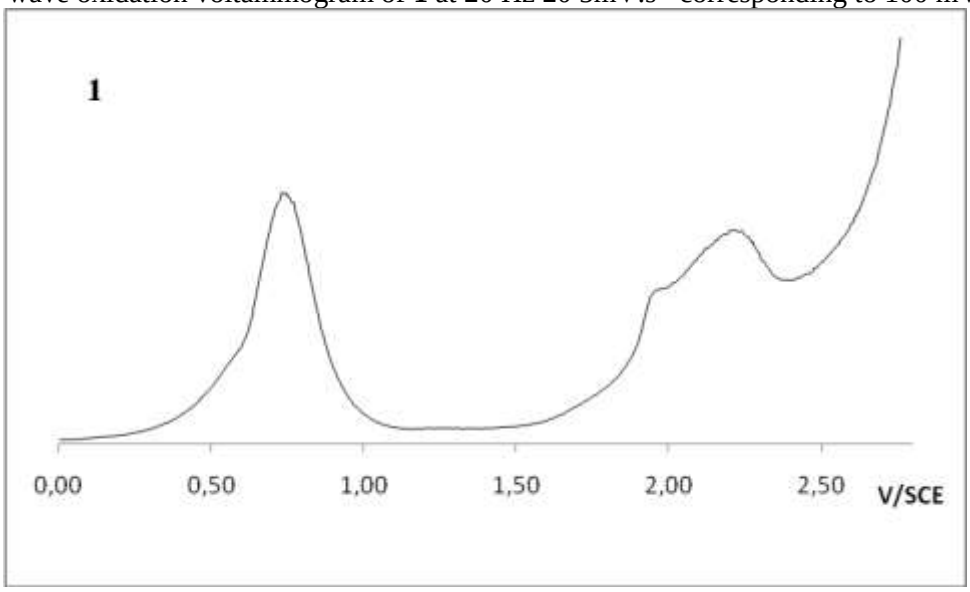


Figure S5. Oxidation (solid line) and reduction (dashed line) cyclic voltammograms of [Ru]**1** at 100 mV.s^{-1} scan rate

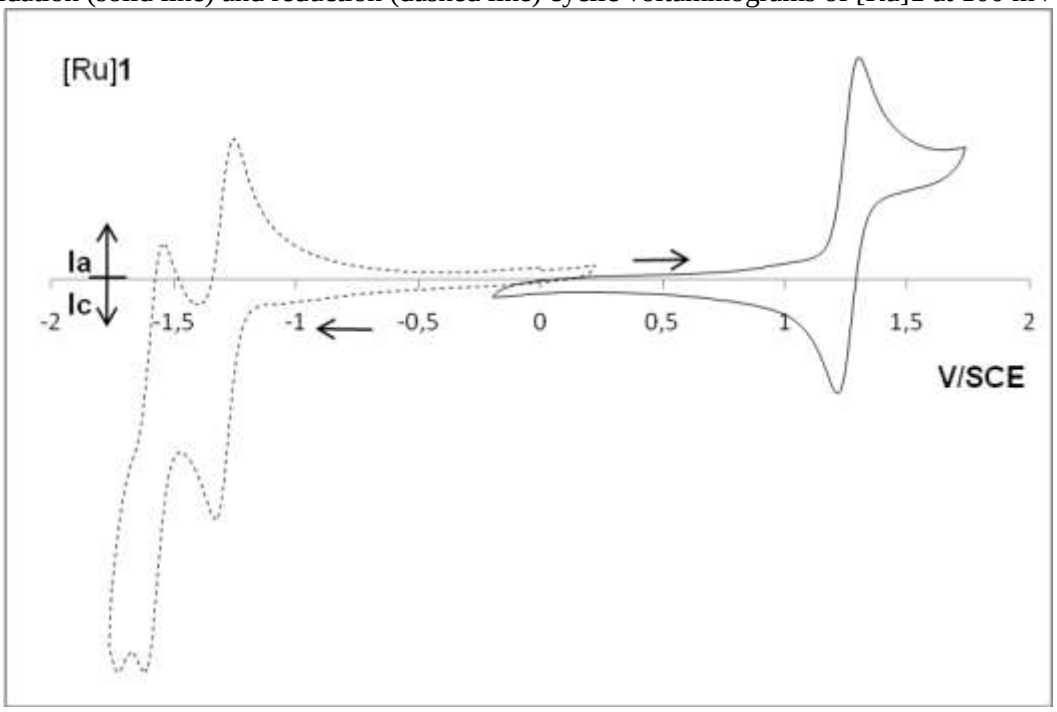


Figure S6. Oxidation cyclic voltammogram of **2** at 100 mV.s^{-1} scan rate

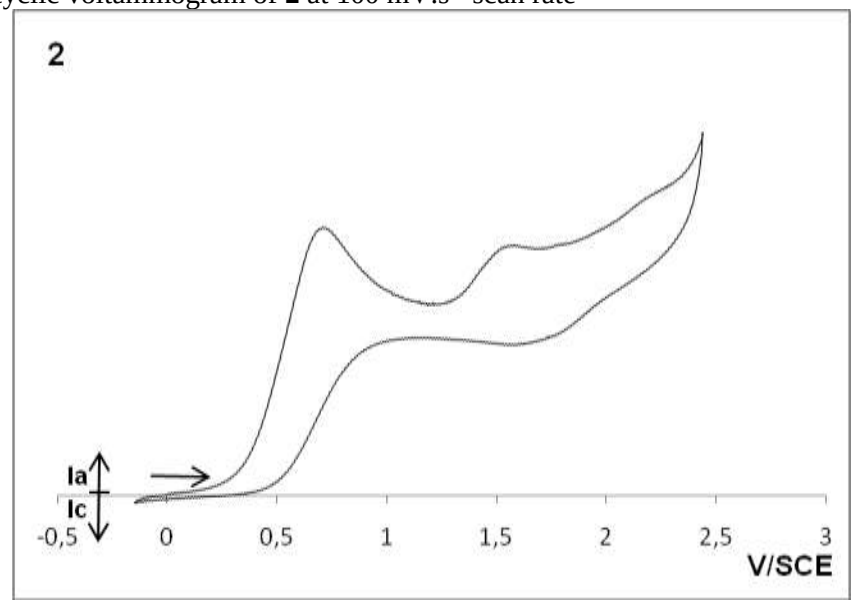


Figure S7. Square wave oxidation voltammogram of **2** at 20 Hz 20 5mV.s^{-1} corresponding to 100 mV.s^{-1} scan rate

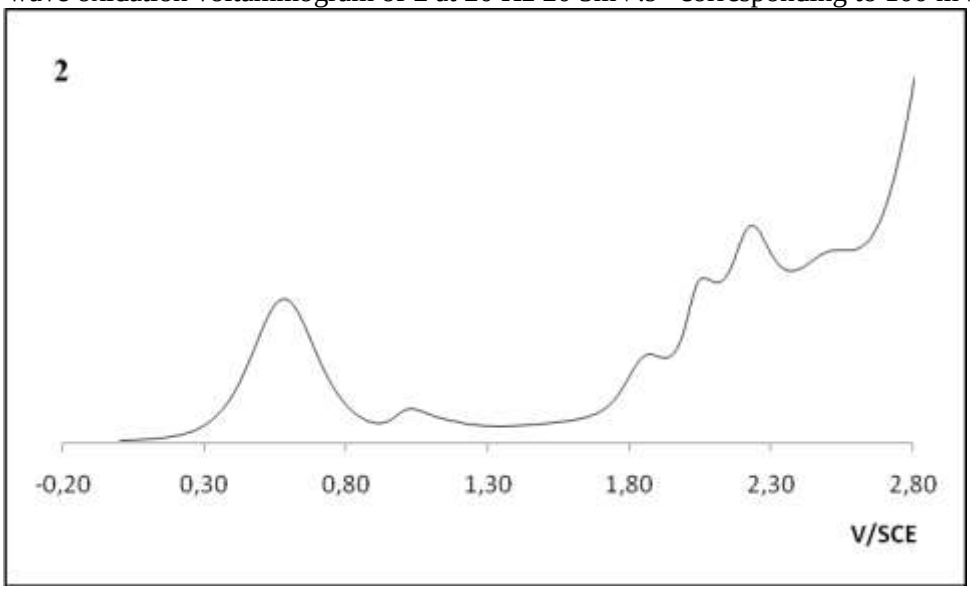


Figure S8. Oxidation (solid line) and reduction (dashed line) cyclic voltammograms of [Ru]**2**, in at 100 mV.s^{-1} scan rate

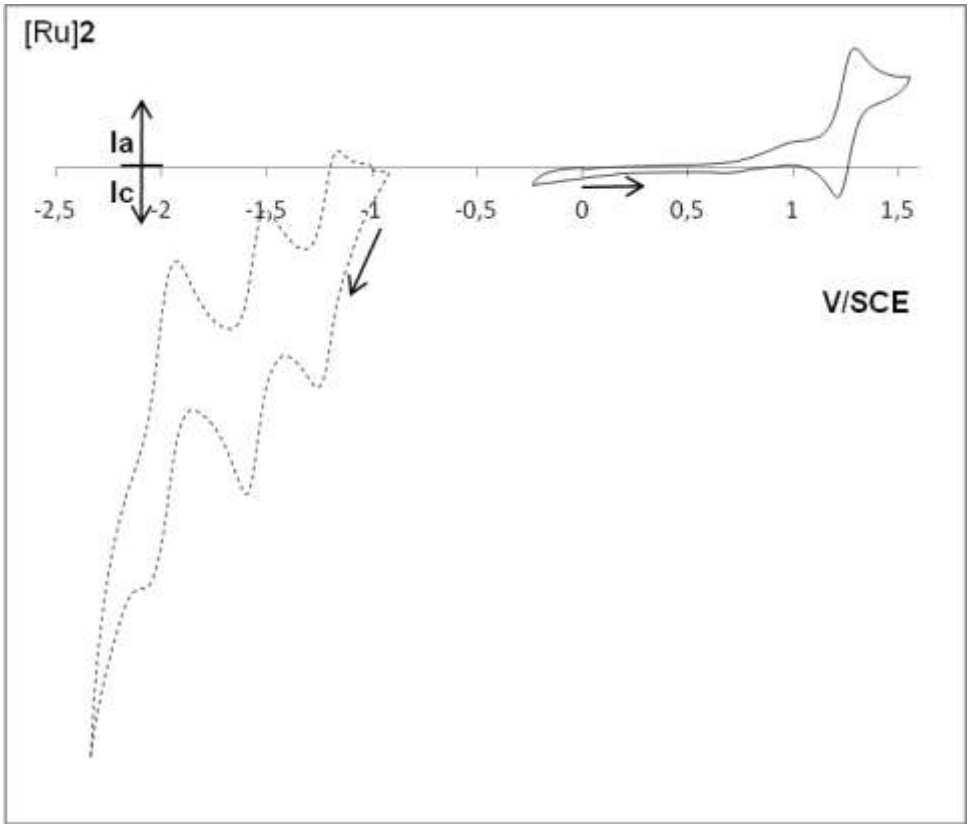


Figure S9. Oxidation (solid line) and reduction (dashed line) voltammograms of [Ru]**PPh$_3$** at 100 mV.s^{-1} scan rate

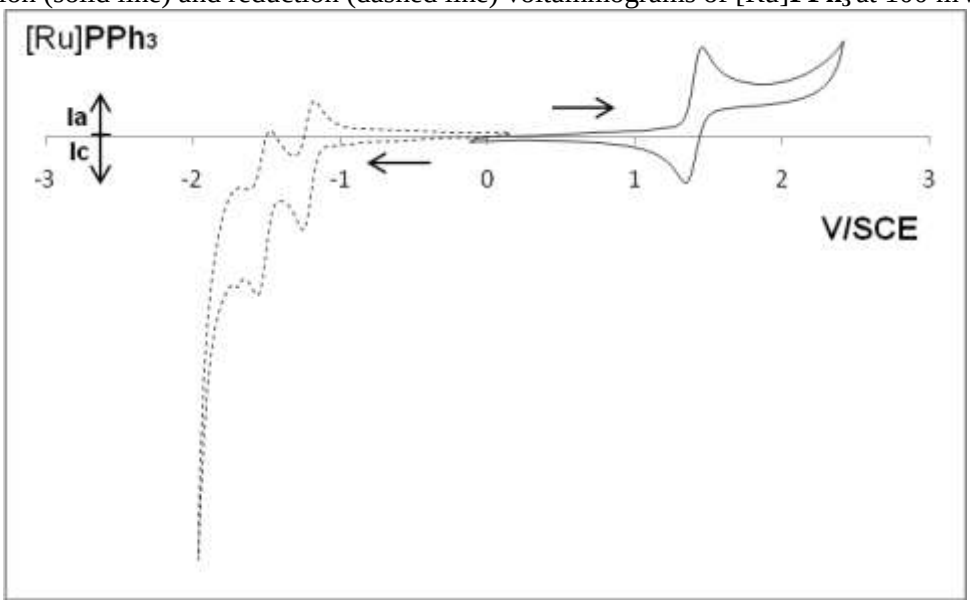
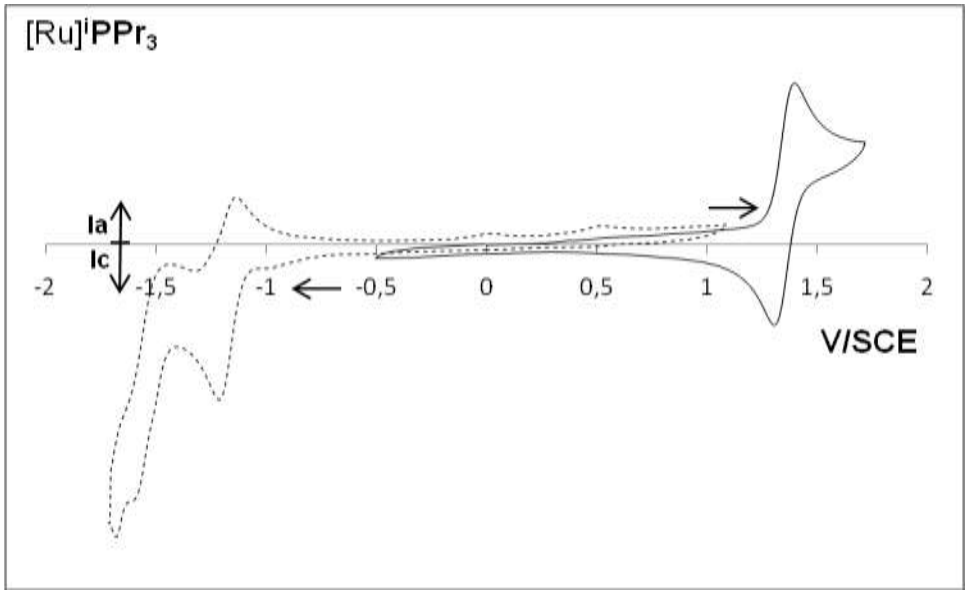


Figure S10. Cyclic voltammogram of [Ru]**P^{i}Pr$_3$**, in oxidation (solid line) and reduction (dashed line), at 100 mV.s^{-1} scan rate



Absorption spectra (solid line) in acetonitrile solution at room temperature. Uncorrected emission spectra at 77 K (dotted line, arbitrary units) in EtOH/MeOH 1:4 v/v matrix and at 298 K (dashed line, arbitrary units) in acetonitrile solution for complexes [Ru]**1** and [Ru]**2**.

Figure S11. Absorption and emission spectra of [Ru]**1**

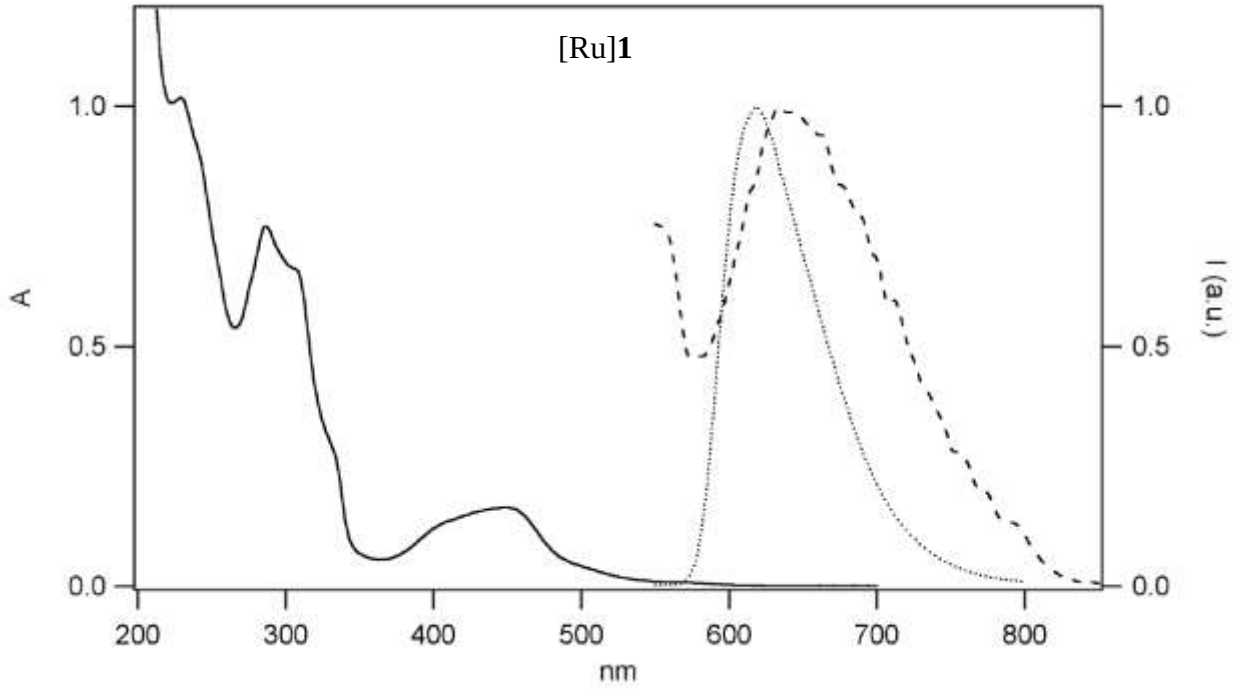
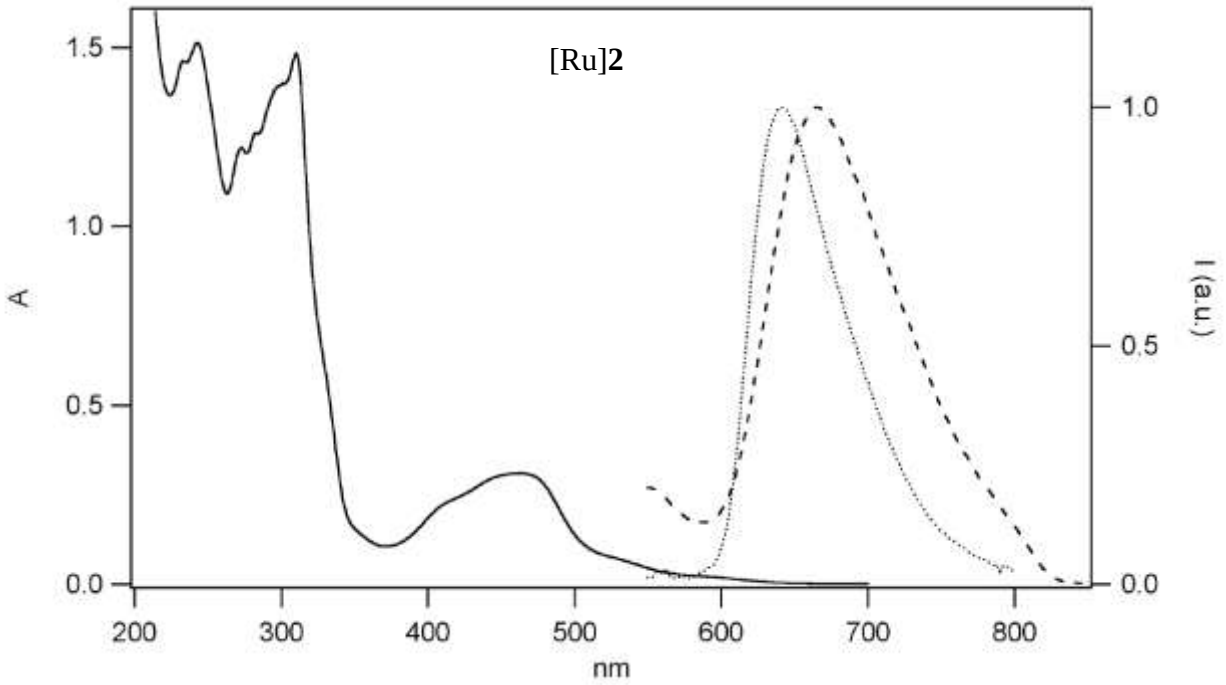


Figure S12. Absorption and emission spectra of [Ru]**2**



Discussion on the σ-donating and π-donating properties of phosphine ligands 1 and 2

The values of the σ-donating capacity of the formamidino phosphine ligands **1** and **2**, as illustrated by the P-Se coupling constant measured by ^{31}P NMR spectroscopy for the corresponding selenides (744 Hz for **1**Se, 716 for **2**Se), are identical to the ones for the reference ligands **PPh$_3$** (745 Hz) and **P(*i*-Pr)$_3$** (716 Hz). Therefore, according to $J_{P\text{-}Se}$, similar σ-donating effects are expected for the formamidino diphenylphosphine **1** and its model phosphine **PPh$_3$**; idem for **2** and P(*i*-Pr)$_3$. Therefore, the difference between **1**, **2** and their model phosphines should lie in their respective π-donating properties.

In all cases, the HOMO, HOMO–1 and HOMO–2 are essentially metallic orbitals. The complexes differ mostly in the energy and localization of their HOMO–3: in the case of [Ru]**P(*i*-Pr)$_3$**, which contains a phosphorus ligand with no π-donating character, HOMO–3 is localized on the tpy ligand and is well separated in energy from the metallic MOs. In the case of [Ru]**PPh$_3$**, HOMO–3 is localized on PPh$_3$ and the gap between the metallic MOs and HOMO–3 decreases. In the case of [Ru]**1** and [Ru]**2**, HOMO–3 is located throughout the phosphorus ligand and the gap between the metallic MOs and HOMO–3 decreases further, illustrating a more pronounced π-donating character for ligands **1** and **2**. A stronger donor character is also consistent with a destabilization of all the frontier orbitals for complexes [Ru]**1** and [Ru]**2** compared to the model compounds.

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