Electronic Supplementary Information

Photo-release of nitric oxide (NO) on Ruthenium nitrosyl complexes with phenyl substituted terpyridines

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Table S1: yields (%) of the complexes 1-4, and ratio of *cis*/*trans* determined by ^{1}H NMR

R	*Cis* (isolated)	*Trans* (isolated)	cis/trans
NO_2	7	11	41/100
H	6	26	30/100
Br	12	57	25/100
OMe	16	58	28/100

[1c] (PF_6). ^{1}H NMR (δ ppm) (400 MHz, CD_3CN): 9.24 (2H, dd, *J* = 5.6; 1 Hz, (*H6, 6"*)), 8.93 (2H, s, (*H3', 5'*)), 8.80 (2H, d, *J* = 8 Hz, (*H3,3"*)), 8.58-8.55 (2H, m, (*H2ph,6ph*)), 8.54 (2H, dd, *J* = 7.8; 1.5 Hz, (*H4,4"*)), 8.35-8.27 (2H, m, (*H3ph,5ph*)), 8.02 (2H, ddd, *J* = 1.2, 3.7, 6.4 Hz, (*H5,5"*)). HRMS-ESI: m/z = 555.9521 $(M - PF_6)^+$ RMS difference = 0.72 ppm (pass). Elemental analysis (%): found C: 36.13; H: 2.00; N: 9.61; calc. C : 35.97; H: 2.01; N: 9.99.

[1t] (PF_6). ^{1}H NMR (δ ppm) (400 MHz, CD_3CN, TMS): 8.85 (2H, s, (*H3', 5'*)), 8.84 (2H, dd, *J* = 5.8; 0.8 Hz, (*H6, 6"*)), 8.76 (2H, d, *J* = 7.4 Hz, (*H3,3"*)), 8.56-8.51 (2H, m, (*H2ph,6ph*)), 8.45 (2H, dd, *J* = 8.7; 1.4 Hz, *H4,4"*)), 8.31-8.27 (2H, m, (*H3ph,5ph*)), 7.92 (2H, ddd, *J* = 6.6; 1.36 Hz, (*H5,5"*)). HRMS-ESI: m/z = 555.9528 (M -PF6)+ RMS difference = 1.98 ppm (pass). Elemental analysis (%): found C: 35.69; H: 2.25; N: 10.13; calc. C : 35.97; H: 2.01; N: 9.99.

[3c] (PF_6). ^{1}H NMR (δ ppm) (400 MHz; CD_3CN) 9.22 (2H, dd, *J* = 5.6; 1.2 Hz, (*H6, 6"*)), 8.86 (2H, s, (*H3', 5'*)), 8.78 (2H, d, *J* = 7.2 Hz, (*H3,3"*)), 8.52 (2H, dd, *J* = 8.0; 1.6 Hz, *H4,4"*)), 8.05 (2H, d, *J* = 8.8 Hz, (*H2ph,6ph*)), 8.00 (2H, ddd, *J* = 8.0; 5.6; 1.2 Hz, (*H5,5"*)).7.92 (2H, d, *J* = 8.4 Hz, (*H3ph,5ph*)). HRMS-ESI: m/z = 590.8758 $(M - PF_6)^+$ RMS difference = 0.59 ppm (pass) and m/z = 560.8774 $(M - PF_6 - NO)^+$ RMS difference = 0.53 ppm (pass). Elemental analysis (%): found C: 34.52; H: 1.71; N: 7.37; calc. C : 34.31; H: 1.92; N: 7.62.

[3t] (PF_6).: ^{1}H NMR (δ ppm) (400 MHz; CD_3CN) 8.81 (2H, dd, *J* = 5.6; 1.2 Hz, (*H6, 6"*)), 8.78 (2H, s, (*H3', 5'*)), 8.73 (2H, d, *J* = 8.0 Hz, (*H3,3"*)), 8.42 (2H, dd, *J* = 8.0; 1.6 Hz, *H4,4"*)), 8.01 (2H, d, *J* = 8.8 Hz, (*H2ph,6ph*)), 7.96 (2H, d, *J* = 8.4 Hz, (*H3ph,5ph*)), 7.90 (2H, ddd, *J* = 8.0; 5.6; 1.2 Hz, (*H5,5"*)), HRMS (ESI): m/z = 590.8762 $(M - PF_6)^+$ RMS difference = 1.07 ppm (pass) and m/z = 560.8777 $(M - PF_6 - NO)^+$ RMS difference = 1.03 ppm (pass). Elemental analysis (%): found C: 34.25; H: 1.63; N: 7.41; calc. C : 34.31; H: 1.92; N: 7.62.

[4c](PF_6) ^{1}H NMR (δ ppm) [400 MHz, CD_3CN): 9.22 (2H, dd, *J* = 5.6; 1.2 Hz, (*H6, 6"*)), 8.80 (2H, s, (*H3', 5'*)), *"*)), 8.82-8.76 (2H, m, (*H3,3"*)), 8.51 (2H, dd, *J* = 8.0; 1.6 Hz, (*H4,4"))*, 8.20-8.11 (2H, m, (*H2ph,6ph))*, 8.03-7.95 (2H, m, (*H5,5"*)), 7.30-7.23 (2H, m, (*H3ph,5ph*)), 3.97 (3H, s, *OMe*), HRMS (ESI): m/z = 540.9777 $(M - PF_6)^+$ RMS difference = 0.87 ppm (pass) and m/z = 510.9797 $(M - PF_6 - NO)^+$ RMS difference = 2.10 ppm (pass). Elemental analysis (%):found C: 38.45; H: 2.26; N: 8.38; calc. C : 38.50; H: 2.50; N: 8.16.

[4t](PF_6): ^{1}H NMR (δ ppm) (400 MHz, CD_3CN): 8.81-8.79 (2H, m, (*H6, 6"*)), 7.29-7.24 (2H, m, (*H3ph,5ph*)), 7.89 (2H, ddd, *J* = 8.0; 5.6; 1.6 Hz, (*H5,5"*)), 8.15-8.11 (2H, m, (*H2ph,6ph*)), 8.42 (2H, dd, *J* = 8.0; 1.2 Hz, (*H4,4"*)), 8.75-8.70 (2H, m, (*H3,3"*)), 8.71 (2H, s, (*H3', 5'*)), 3.97 (3H, s, *OMe*). HRMS (ESI): m/z = 540.9776 $(M - PF_6)^+$ RMS difference = 0.73 ppm (pass) and m/z = 510.9792 $(M - PF_6 - NO)^+$ RMS difference = 1.39 ppm (pass). Elemental analysis (%): found C: 38.39; H: 2.11; N: 8.35; calc. C : 38.50; H: 2.50; N: 8.16.

Table S2: DFT coordinates

$[1t]^+$

C	20.430530	3.440942	0.022990
H	20.793308	2.421034	-0.001371
C	21.312946	4.513656	0.048627
H	22.379984	4.323578	0.045847
C	20.801092	5.803304	0.076504
H	21.462050	6.663122	0.096846
C	19.421807	5.983106	0.077354
H	18.999310	6.980510	0.098186
C	18.590237	4.871808	0.051658
C	17.121766	4.947140	0.048951
C	16.349204	6.099861	0.075009
H	16.819390	7.074585	0.121567
C	14.370997	4.717532	0.046536
H	13.293313	4.611780	0.019264
C	15.188316	3.596064	0.022122
C	14.754367	2.191602	-0.013428
C	13.424708	1.792777	-0.023311
H	12.633025	2.532153	-0.005598
C	13.119565	0.436113	-0.056561
H	12.084753	0.111061	-0.065035
C	14.155068	-0.487600	-0.077807
H	13.966912	-1.554686	-0.102928
C	15.465973	-0.027802	-0.065773
H	16.299379	-0.718933	-0.079386
C	14.952247	5.992096	0.073720
C	14.106352	7.202074	0.100574
C	14.490175	8.348385	-0.609539
H	15.397148	8.345379	-1.205815
C	13.698141	9.486705	-0.590886
H	13.976382	10.375725	-1.143670
C	12.522912	9.467050	0.150842
C	12.116062	8.348294	0.868178
H	11.197291	8.375496	1.441296
C	12.913015	7.213704	0.836387
H	12.616593	6.343370	1.413280
N	18.677113	0.663997	-0.044530
N	19.105596	3.613827	0.025270
N	16.521184	3.747867	0.023913
N	15.758904	1.275504	-0.035290
Ru	17.670009	2.104571	-0.012558
Cl	17.585897	2.293709	-2.404121
Cl	17.571170	2.177129	2.384813
O	19.326840	-0.265382	-0.065156
N	11.686328	10.663710	0.177401
O	10.655530	10.623226	0.831015
O	12.064938	11.637094	-0.455510

$[1c]^+$

Ru	3.268683	0.084744	0.132644
Cl	3.194568	-0.085091	-2.221186
N	1.296156	-0.057651	0.060767
C	0.590271	1.075394	-0.071967
C	1.422345	2.291281	-0.170933
N	3.052117	-1.986466	0.169325
N	2.768785	2.090530	-0.118307
C	3.151947	4.420033	-0.398943
H	3.865312	5.231249	-0.487295
C	0.754811	-1.284709	0.085790
C	-0.626679	-1.409865	0.023423
H	-1.093424	-2.386347	0.072751
C	3.754132	-4.257493	0.217243
H	4.573081	-4.967146	0.239642
C	1.746747	-2.376029	0.154031
C	-1.417158	-0.256362	-0.079396
C	0.907105	3.569405	-0.333715
H	-0.163930	3.728026	-0.376266
C	-0.794542	0.998855	-0.138441
H	-1.389815	1.895099	-0.266033
C	3.610675	3.118002	-0.231415
H	4.666078	2.871959	-0.185592
C	4.028072	-2.894263	0.197365
H	5.039351	-2.502109	0.202166
C	1.413494	-3.722781	0.175579
H	0.374896	-4.031262	0.162979
C	2.430013	-4.674188	0.208434
H	2.182171	-5.730237	0.224851
C	1.783175	4.646016	-0.447855
H	1.392404	5.649891	-0.576088
Cl	5.691687	0.241765	-0.008219
N	3.465736	0.221408	1.867488
O	3.710274	0.317355	2.971564
C	-3.689778	0.586559	0.514290
H	-3.232982	1.388993	1.085026
C	-5.072787	0.490949	0.470268
H	-5.703532	1.210138	0.978388
C	-5.644574	-0.559341	-0.237939
C	-4.879102	-1.513359	-0.898013
H	-5.362451	-2.312131	-1.447193
C	-3.497065	-1.411021	-0.841198
H	-2.891076	-2.137019	-1.374010
C	-2.889229	-0.362063	-0.137276
N	-7.100556	-0.664309	-0.290090
O	-7.581736	-1.597747	-0.913157
O	-7.753547	0.187100	0.292889

$[2t]^+$

C	3.027965	0.081592	3.643139
H	2.740953	0.074560	4.687200
C	4.365214	0.115619	3.269195
H	5.130854	0.136745	4.036045
C	4.684146	0.120903	1.918329
H	5.718242	0.146807	1.591791
C	3.656952	0.091833	0.981237

H	3.881458	0.094509	-0.078645
C	2.338691	0.059376	1.415743
C	1.178251	0.026267	0.513008
C	1.205175	0.028915	-0.873248
H	2.149316	0.079373	-1.401725
C	0.000000	0.000000	-1.591947
C	-1.205175	-0.028915	-0.873248
H	-2.149316	-0.079373	-1.401725
C	-1.178251	-0.026267	0.513008
C	-2.338691	-0.059376	1.415743
C	-3.656952	-0.091833	0.981237
H	-3.881458	-0.094509	-0.078645
C	-4.684146	-0.120903	1.918329
H	-5.718242	-0.146807	1.591791
C	-4.365214	-0.115619	3.269195
H	-5.130854	-0.136745	4.036045
C	-3.027965	-0.081592	3.643139
H	-2.740953	-0.074560	4.687200
N	2.041046	0.054811	2.742389
N	0.000000	0.000000	1.155160
N	-2.041046	-0.054811	2.742389
Cl	0.067658	-2.395404	3.001315
Ru	0.000000	0.000000	3.158144
C	-1.012064	0.661061	-3.775673
H	-1.786979	1.204226	-3.241962
C	-1.007318	0.664213	-5.165621
H	-1.788979	1.191461	-5.704456
C	0.000000	0.000000	-5.863561
C	1.007318	-0.664213	-5.165621
H	1.788979	-1.191461	-5.704456
C	1.012064	-0.661061	-3.775673
H	1.786979	-1.204226	-3.241962
C	0.000000	0.000000	-3.064791
H	0.000000	0.000000	-6.949719
Cl	-0.067658	2.395404	3.001315
N	0.000000	0.000000	4.916315
O	0.000000	0.000000	6.050919

[2c]$^{+}$

Ru	3.273747	0.084313	0.132116
Cl	3.202838	-0.077099	-2.223759
N	1.302957	-0.056766	0.059798
C	0.594911	1.076035	-0.068688
C	1.427432	2.292284	-0.162476
N	3.055383	-1.987107	0.161616
N	2.773855	2.091420	-0.110873
C	3.158175	4.422273	-0.379077
H	3.871674	5.233849	-0.462951
C	0.758223	-1.282975	0.079888
C	-0.622204	-1.406720	0.018587
H	-1.087451	-2.383866	0.067389
C	3.756775	-4.258500	0.202512
H	4.575236	-4.968780	0.222835
C	1.749675	-2.375319	0.144925
C	-1.418764	-0.254312	-0.081957

C	0.913022	3.571816	-0.318374
H	-0.158051	3.730516	-0.359313
C	-0.788493	0.999906	-0.137982
H	-1.381262	1.897600	-0.266440
C	3.616213	3.119508	-0.218120
H	4.671507	2.872856	-0.172979
C	4.031124	-2.895623	0.186939
H	5.042500	-2.503735	0.193078
C	1.416268	-3.722333	0.162135
H	0.377386	-4.029814	0.148091
C	2.432127	-4.674227	0.192164
H	2.183741	-5.730229	0.205174
C	1.789208	4.648623	-0.427001
H	1.398750	5.653318	-0.549955
Cl	5.699561	0.241337	-0.006652
N	3.470807	0.214410	1.866293
O	3.717069	0.306279	2.970845
C	-3.691604	0.622113	0.458731
H	-3.233679	1.449246	0.994056
C	-5.077112	0.520821	0.410072
H	-5.688572	1.279364	0.889572
C	-5.677625	-0.553146	-0.244793
C	-4.886497	-1.529644	-0.847755
H	-5.349227	-2.363056	-1.367882
C	-3.500630	-1.437381	-0.792755
H	-2.894432	-2.189920	-1.289187
C	-2.887451	-0.358195	-0.140257
H	-6.760354	-0.628944	-0.285377

$[3t]^+$

C	20.435118	3.435330	0.015608
H	20.797989	2.415379	-0.006487
C	21.317365	4.508013	0.037279
H	22.384449	4.318204	0.033330
C	20.805094	5.797706	0.062791
H	21.465908	6.657741	0.079934
C	19.425932	5.977152	0.065538
H	19.003020	6.974417	0.084483
C	18.594146	4.865783	0.043954
C	17.125512	4.940693	0.044092
C	16.353482	6.092407	0.070959
H	16.825611	7.066177	0.116712
C	14.376618	4.710852	0.050264
H	13.299179	4.602931	0.023724
C	15.193185	3.590200	0.026707
C	14.758837	2.185648	-0.005985
C	13.429120	1.786529	-0.011763
H	12.637753	2.526194	0.007834
C	13.123716	0.430047	-0.043099
H	12.088815	0.105115	-0.048368
C	14.159064	-0.494008	-0.066710
H	13.970659	-1.561079	-0.090651
C	15.469802	-0.034247	-0.058640
H	16.303166	-0.725417	-0.074515
C	14.954347	5.989108	0.073648

C	14.110568	7.196068	0.100430
C	14.511296	8.361011	-0.567943
H	15.435616	8.376031	-1.137893
C	13.717160	9.500024	-0.550684
H	14.026952	10.392832	-1.082413
C	12.515165	9.478167	0.151070
C	12.096209	8.336234	0.827969
H	11.162599	8.335748	1.379499
C	12.893055	7.199470	0.794729
H	12.573194	6.319821	1.345492
Br	11.434069	11.024590	0.185385
N	18.681736	0.657369	-0.044664
N	19.109961	3.607996	0.019514
N	16.526808	3.739826	0.023736
N	15.762988	1.269240	-0.029790
Ru	17.674554	2.098064	-0.012695
Cl	17.586305	2.280401	-2.405413
Cl	17.583538	2.172152	2.385714
O	19.331633	-0.272257	-0.065292

$[3c]^{+}$

Ru	3.274547	0.084536	0.132885
Cl	3.204527	-0.077267	-2.222612
N	1.303415	-0.056874	0.059355
C	0.595957	1.076081	-0.069588
C	1.428346	2.292320	-0.163684
N	3.056676	-1.986777	0.162763
N	2.774739	2.091433	-0.111276
C	3.158807	4.422082	-0.381406
H	3.872300	5.233618	-0.465776
C	0.759540	-1.283328	0.079288
C	-0.621076	-1.407473	0.017348
H	-1.086061	-2.384745	0.066288
C	3.758333	-4.258054	0.204685
H	4.576954	-4.968134	0.225786
C	1.751103	-2.375441	0.145117
C	-1.416030	-0.254574	-0.082694
C	0.913731	3.571521	-0.320987
H	-0.157311	3.730276	-0.362712
C	-0.787699	1.000005	-0.138647
H	-1.380424	1.897725	-0.267144
C	3.616996	3.119456	-0.219031
H	4.672318	2.873005	-0.173281
C	4.032508	-2.895058	0.189047
H	5.043830	-2.503017	0.195877
C	1.417794	-3.722404	0.162313
H	0.379043	-4.030310	0.147528
C	2.433869	-4.674126	0.193349
H	2.185688	-5.730168	0.206359
C	1.789916	4.648345	-0.430227
H	1.399419	5.652861	-0.554420
Cl	5.699599	0.241694	-0.004801
N	3.470455	0.215615	1.867450
O	3.715533	0.308028	2.972071
C	-3.690311	0.615929	0.464480

H	-3.238405	1.442583	1.004855
C	-5.075152	0.521381	0.421509
H	-5.691451	1.271722	0.904200
C	-5.661161	-0.552802	-0.241942
C	-4.884450	-1.531357	-0.855791
H	-5.353564	-2.357482	-1.378539
C	-3.500519	-1.432275	-0.797437
H	-2.900524	-2.185146	-1.300045
C	-2.884745	-0.358526	-0.140205
Br	-7.542547	-0.684823	-0.310618

$[4t]^{+}$

C	-2.999624	-2.964387	0.119921
H	-4.033682	-2.643548	0.131041
C	-2.668170	-4.312675	0.152466
H	-3.458290	-5.053594	0.190536
C	-1.328127	-4.674169	0.133778
H	-1.034188	-5.718107	0.156885
C	-0.359706	-3.677547	0.084258
H	0.692299	-3.936027	0.068272
C	-0.752040	-2.345886	0.055779
C	0.185961	-1.214195	0.005089
C	1.568927	-1.284768	-0.009565
H	2.063753	-2.246710	0.041366
C	2.331291	-0.103564	-0.052230
C	1.643890	1.123288	-0.076777
H	2.195782	2.052611	-0.142739
C	0.259376	1.139501	-0.054096
C	-0.606009	2.328459	-0.080079
C	-0.130112	3.632308	-0.123690
H	0.936378	3.822563	-0.140688
C	-1.034042	4.688773	-0.144400
H	-0.674993	5.711800	-0.178538
C	-2.394452	4.413358	-0.119988
H	-3.136669	5.203081	-0.134055
C	-2.810305	3.089104	-0.075497
H	-3.862839	2.835810	-0.053805
N	-2.068489	-2.006565	0.072798
N	-0.422247	-0.017052	-0.015584
N	-1.941307	2.073689	-0.056563
Cl	-2.309005	-0.037525	-2.384271
Ru	-2.421378	0.046931	0.014191
C	4.560107	0.879931	0.492389
H	4.070884	1.718375	0.979720
C	5.947697	0.840374	0.490108
H	6.501596	1.649196	0.952410
C	6.608578	-0.245532	-0.097287
C	5.857319	-1.283256	-0.671262
H	6.382540	-2.112196	-1.135032
C	4.477736	-1.237570	-0.650906
H	3.922156	-2.040645	-1.126460
C	3.795856	-0.151434	-0.070555
O	7.943697	-0.383412	-0.159905
H	8.578343	1.599315	-0.100379
C	8.753119	0.639322	0.398286

H	8.572509	0.744789	1.474010
H	9.783943	0.326061	0.232401
Cl	-2.230086	0.121048	2.407991
N	-4.179109	0.096675	0.042381
O	-5.313681	0.120734	0.062621

$[4c]^{+}$

Ru	3.304985	0.076010	0.115179
Cl	3.199126	-0.066928	-2.241524
N	1.333961	-0.047227	0.071377
C	0.631514	1.091353	-0.043589
C	1.472731	2.301208	-0.143144
N	3.067645	-1.993521	0.133166
N	2.817901	2.089234	-0.107487
C	3.218558	4.418064	-0.370207
H	3.937821	5.224110	-0.458234
C	0.776017	-1.268273	0.088799
C	-0.604486	-1.379739	0.042942
H	-1.073350	-2.354845	0.093607
C	3.750420	-4.271036	0.151753
H	4.562730	-4.988599	0.156147
C	1.758445	-2.369995	0.134012
C	-1.398517	-0.220821	-0.042836
C	0.967276	3.585660	-0.289780
H	-0.102913	3.753114	-0.319048
C	-0.751458	1.028097	-0.099672
H	-1.332288	1.933935	-0.222916
C	3.667392	3.111219	-0.219089
H	4.721119	2.856081	-0.186496
C	4.035984	-2.910587	0.138821
H	5.050485	-2.526842	0.131431
C	1.414307	-3.714464	0.149474
H	0.372871	-4.013465	0.149732
C	2.422085	-4.675021	0.159570
H	2.164800	-5.728947	0.171391
C	1.850864	4.655580	-0.403903
H	1.467492	5.663853	-0.519744
Cl	5.731927	0.211549	-0.060920
N	3.534069	0.192129	1.845971
O	3.805521	0.274454	2.945779
C	-3.664336	0.709513	0.436612
H	-3.207478	1.572586	0.912424
C	-5.050262	0.631541	0.409088
H	-5.634777	1.435619	0.841100
C	-5.669628	-0.485606	-0.164360
C	-4.879098	-1.515203	-0.698579
H	-5.372197	-2.369192	-1.152085
C	-3.501776	-1.430455	-0.654117
H	-2.915757	-2.228587	-1.100645
C	-2.861355	-0.312578	-0.087431
O	-6.999317	-0.661880	-0.249297
C	-7.846496	0.352813	0.265455
H	-8.865376	0.008418	0.087082
H	-7.691086	0.490631	1.341604
H	-7.686469	1.304103	-0.254402

X-ray crystallographic data.

Table S3 : Crystal data and structure refinement for [2c](Cl)

Colorless crystals were obtained by diffusion of Et2O in a solution of the complex in MeCN

Empirical formula	C21 H15 Cl2 N4 O Ru, Cl, H2 O	
Formula weight	564.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 28.0160(14) Å	α= 90°.
	b = 8.6148(5) Å	β= 90°.
	c = 20.3292(10) Å	γ = 90°.
Volume	4906.5(4) $Å^3$	
Z	8	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	0.990 mm^{-1}	
F(000)	2256	
Crystal size	0.060 x 0.020 x 0.010 mm^3	
Theta range for data collection	1.454 to 25.348°.	
Index ranges	-33<=h<=33, -10<=k<=10, -24<=l<=24	
Reflections collected	82713	
Independent reflections	4494 [R(int) = 0.1628]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4494 / 2 / 290	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0715	
R indices (all data)	R1 = 0.0761, wR2 = 0.0844	
Largest diff. peak and hole	0.508 and -0.512 $e.Å^{-3}$	

Table S4 : Crystal data and structure refinement for [2t] (PF_6)

Pale yellow crystals were obtained by diffusion of Et2O in a solution of the complex in MeCN

Empirical formula	C21 H15 Cl2 N4 O Ru, F6 P
Formula weight	656.31
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	a = 14.023(6) A alpha = 90 deg. b = 7.125(4) A beta = 105.620(17) deg. c = 25.620(12) A gamma = 90 deg.
Volume	2465(2) A^3
Z, Calculated density	4, 1.768 Mg/m^3
Absorption coefficient	0.986 mm^-1
F(000)	1296
Crystal size	0.08 x 0.04 x 0.02 mm
Theta range for data collection	1.90 to 28.31 deg.
Limiting indices	-18<=h<=18, -9<=k<=9, -34<=l<=33
Reflections collected / unique	79983 / 6106 [R(int) = 0.0800]
Completeness to theta = 28.31	99.3 %
Max. and min. transmission	0.7457 and 0.6954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6106 / 0 / 325
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0701
R indices (all data)	R1 = 0.0557, wR2 = 0.0779
Largest diff. peak and hole	0.576 and -0.765 e.A^-3

Table S5 : Crystal data and structure refinement for [3c] (PF_6)

Orange crystals were obtained by diffusion of Et2O in a solution of the complex in MeCN

Empirical formula	C21 H14 Br Cl2 N4 O Ru, F6 P

Formula weight	735.20
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	a = 10.8897(9) A alpha = 90 deg. b = 17.2969(13) A beta = 105.353(3) deg. c = 13.3346(10) A gamma = 90 deg.
Volume	2422.0(3) A^3
Z, Calculated density	4, 2.016 Mg/m^3
Absorption coefficient	2.655 mm^-1
F(000)	1432
Crystal size	0.12 x 0.06 x 0.04 mm
Theta range for data collection	1.97 to 26.73 deg.
Limiting indices	-13<=h<=13, -21<=k<=21, -16<=l<=16
Reflections collected / unique	50815 / 5140 [R(int) = 0.0629]
Completeness to theta = 26.73	100.0 %
Max. and min. transmission	0.7461 and 0.6853
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5140 / 108 / 390
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0772
R indices (all data)	R1 = 0.0494, wR2 = 0.0837
Largest diff. peak and hole	1.636 and -0.585 e.A^-3

Table S6 : Crystal data and structure refinement for [4c](PF_6)

Orange crystals were obtained by diffusion of Et2O in a solution of the complex in MeCN

Empirical formula	2(C22 H17 Cl2 N4 O2 Ru), 2(F6 P), C4 H10 O, C2 H3 N
Formula weight	1487.85
Temperature	100(2) K
Wavelength	0.71073 A

Crystal system, space group monoclinic, P 21/c

Unit cell dimensions a = 21.673(2) A alpha = 90 deg.

b = 25.105(3) A beta = 97.922(3) deg.

c = 11.5618(12) A gamma = 90 deg.

Volume 6230.8(11) A^3

Z, Calculated density 4, 1.586 Mg/m^3

Absorption coefficient 0.794 mm^-1

F(000) 2976

Crystal size 0.18 x 0.12 x 0.02 mm

Theta range for data collection 1.90 to 25.35 deg.

Limiting indices -26<=h<=26, -30<=k<=30,

-13<=l<=13

Reflections collected / unique 157097 / 11384 [R(int) = 0.1119]

Completeness to theta = 25.35 99.9 %

Max. and min. transmission 0.7454 and 0.6445

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 11384 / 237 / 826

Goodness-of-fit on F^2 1.163

Final R indices [I>2sigma(I)] R1 = 0.1009, wR2 = 0.2276

R indices (all data) R1 = 0.1220, wR2 = 0.2379

Largest diff. peak and hole 2.002 and -1.702 e.A^-3

Table S7 : Crystal data and structure refinement for [4t] (PF_6)

Orange crystals were obtained by slow concentration of a solution of the complex in acetone

Empirical formula	C22 H17 Cl2 N4 O2 Ru, F6 P, C3 H6 O
Formula weight	744.41
Temperature	100(2) K
Wavelength	0.71073 A

Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 6.9624(6) A alpha = 88.839(2) deg. b = 14.2674(10) A beta = 80.540(2) deg. c = 14.4225(11) A gamma = 83.493(2) deg.
Volume	1404.08(19) A^3
Z, Calculated density	2, 1.761 Mg/m^3
Absorption coefficient	0.882 mm^-1
F(000)	744
Crystal size	0.18 x 0.06 x 0.02 mm
Theta range for data collection	1.44 to 30.55 deg.
Limiting indices	-9<=h<=9, -20<=k<=20, -20<=l<=20
Reflections collected / unique	53554 / 8556 [R(int) = 0.0496]
Completeness to theta = 30.55	99.5 %
Max. and min. transmission	0.7461 and 0.6995
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8556 / 0 / 382
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0293, wR2 = 0.0652
R indices (all data)	R1 = 0.0386, wR2 = 0.0695
Largest diff. peak and hole	0.569 and -0.652 e.A^-3

Table S8: Crystal data of complex [4i](PF_6)

Orange crystals were obtained by diffusion of Et_2O in a solution of the complex in MeCN

Empirical formula	C24 H20 Cl2 N4 O Ru, F6 P
Formula weight	697.38
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 7.6187(8) A alpha = 90 deg. b = 25.999(3) A beta = 103.433(11) deg. c = 13.6071(12) A gamma = 90 deg.

Volume	2621.6(5) A^3
Z, Calculated density	4, 1.767 Mg/m^3
Absorption coefficient	0.933 mm^-1
F(000)	1388
Crystal size	0.2 x 0.08 x 0.02 mm
Theta range for data collection	2.93 to 24.71 deg.
Limiting indices	-8<=h<=8, -28<=k<=30, -15<=l<=16
Reflections collected / unique	26342 / 4454 [R(int) = 0.1051]
Completeness to theta = 24.71	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9987 and 0.6765
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4454 / 4 / 364
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0766, wR2 = 0.1344
R indices (all data)	R1 = 0.1127, wR2 = 0.1479
Largest diff. peak and hole	0.870 and -0.614 e.A^-3

Table S9: Crystal data of complex [3i](PF_6)

Red crystals were obtained by slow concentration of a solution of the complex in MeCN

Empirical formula	C23 H17 Br Cl2 N4 Ru, F6 P, 2(C2 H3 N)
Formula weight	828.35
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	a = 9.9381(6) A alpha = 90 deg.

b = 9.8000(6) A beta = 98.325(3) deg.
c = 31.5878(19) A gamma = 90 deg.

Volume 3044.0(3) A^3

Z, Calculated density 4, 1.808 Mg/m^3

Absorption coefficient 2.123 mm^-1

F(000) 1636

Crystal size 0.26 x 0.06 x 0.04 mm

Theta range for data collection 2.93 to 35.84 deg.

Limiting indices -16<=h<=16, -16<=k<=16, -51<=l<=50

Reflections collected / unique 171898 / 14207 [R(int) = 0.0438]

Completeness to theta = 35.84 99.7 %

Max. and min. transmission 0.7470 and 0.6107

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 14207 / 129 / 456

Goodness-of-fit on F^2 1.144

Final R indices [I>2sigma(I)] R1 = 0.0326, wR2 = 0.0667

R indices (all data) R1 = 0.0417, wR2 = 0.0693

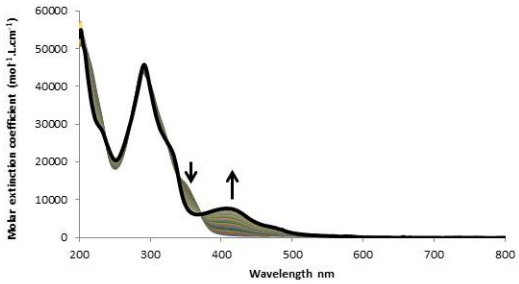
Largest diff. peak and hole 1.172 and -1.049 e.A^-3

Table S 10: Selected bond lengths and angles for two photoproducts: [4i](PF_6) and [3i](PF_6)

Selected bonds (Å)	[4i](PF_6)	[3i](PF_6)
Ru(1)-N(1)	2.064(8)	2.0837(14)
Ru(1)-N(2)	1.951(7)	2.0735(13)
Ru(1)-N(3)	2.081(6)	1.923(12)
Ru(1)-N(4)	2.082(6)	2.0661(13)
Ru(1)-Cl(1)	2.314(2)	2.3248(4)
Ru(1)-Cl(2)	2.352(2)	2.3223(4)

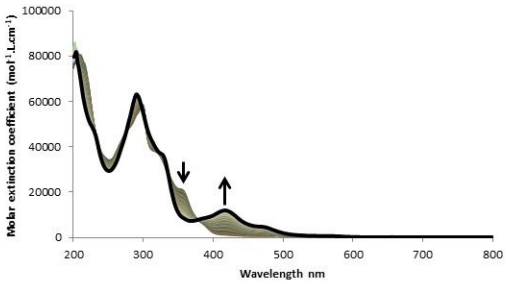
Selected angles (°)		
N(3)-Ru(1)-N(1)	176.2(3)	176.5(5)
N(3)-Ru(1)-N(4)	79.4(3); 80.8(3)	79.67(5)
Cl(2)-Ru(1)-Cl(1)	178.99(9)	179.02(15)
Cl(1)-Ru(1)-N(1)	92.9(2); 87.8(2)	90.80(4)

[1c](PF6)



Isosbestic points
374 nm
340 nm
326 nm
298 nm
288 nm
272 nm
236 nm

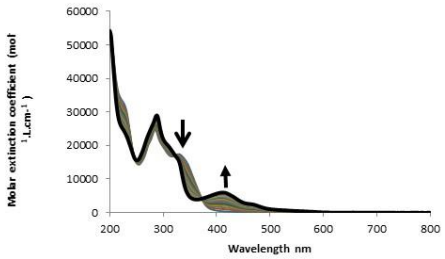
[1t](PF6)



Isosbestic points
380 nm
336 nm
306 nm
298 nm
276 nm
236 nm

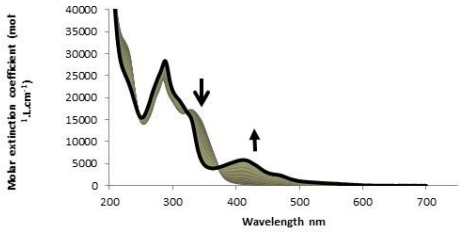
Fig. S1: Irradiation of a solution of [1c(PF_6)](left) or [1t(PF_6)](right) in MeCN at 365 nm for 30 min.

[2c](PF6)



Isosbestic points
372 nm
324 nm
248 nm

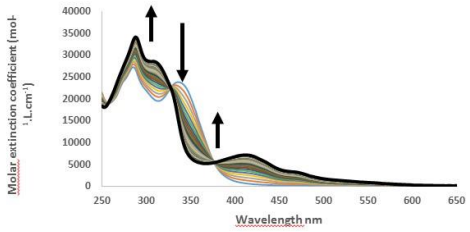
[2t](PF6)



Isosbestic points
374 nm
326 nm
246 nm

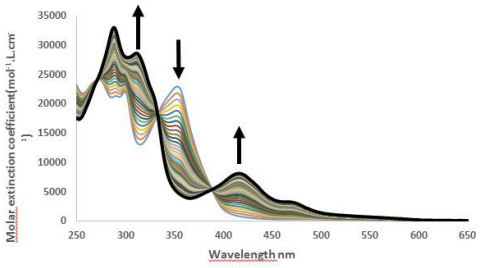
Fig. S2 Irradiation of a solution of [2c(PF_6)](left) or [2t(PF_6)](right) in MeCN at 365 nm for 30 min.

[3c](PF6)



Isosbestic points
380 nm
328 nm
258 nm

[3t](PF6)



Isosbestic points
386 nm
332 nm
272 nm

Fig. S3 Irradiation of a solution of [3c(PF_6)](left) or [3t(PF_6)](right) in MeCN at 365 nm for 30 min.

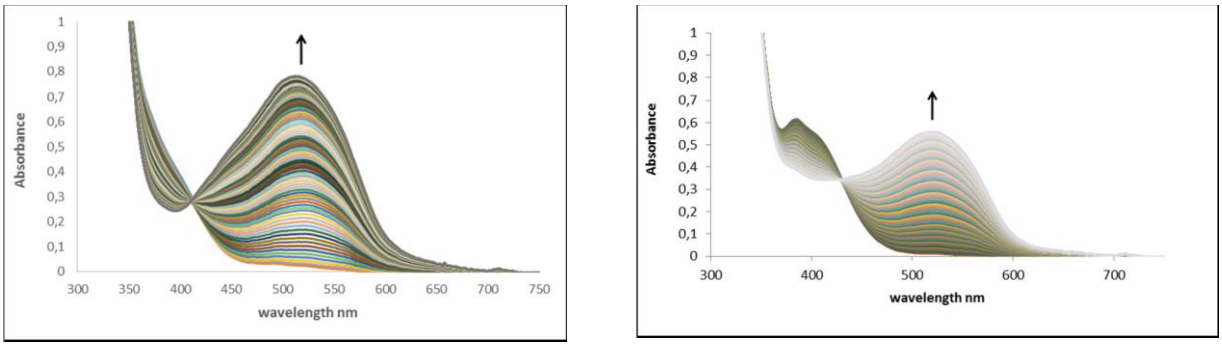


Fig. S4: Spectral changes of a solution 10^{-5}M of [4c](PF_6) (left) and [4t](PF_6) (right) in MeCN with irradiation at 365 nm in the presence of Griess reagent.

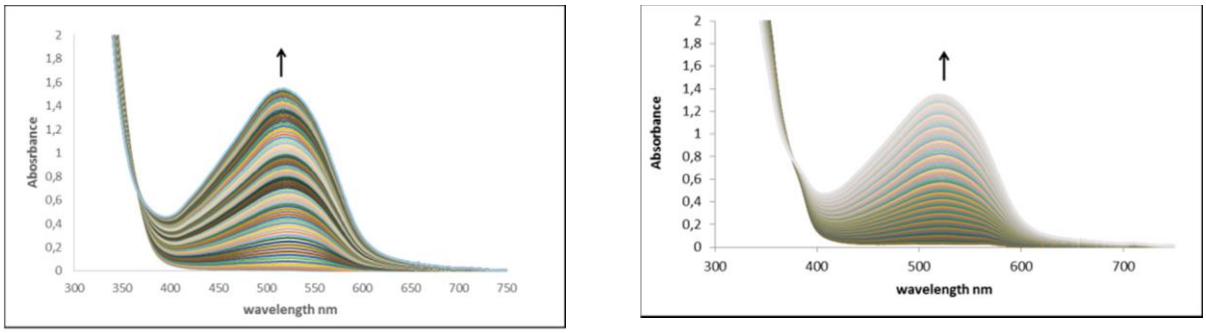
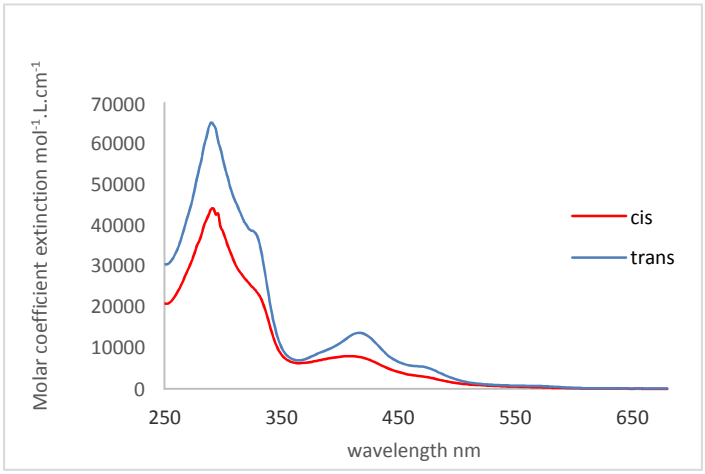
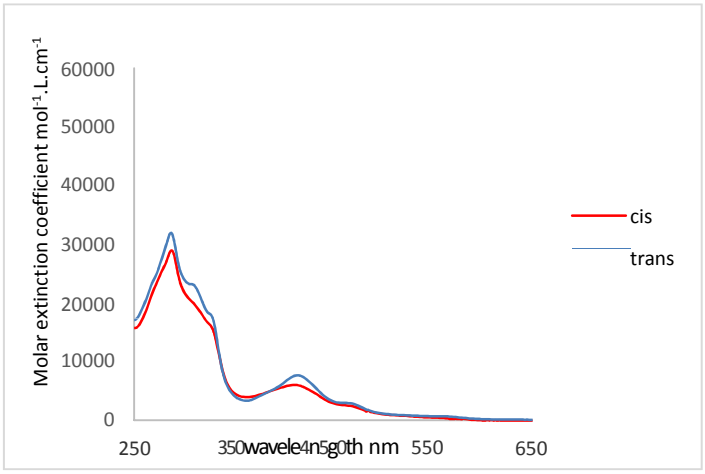


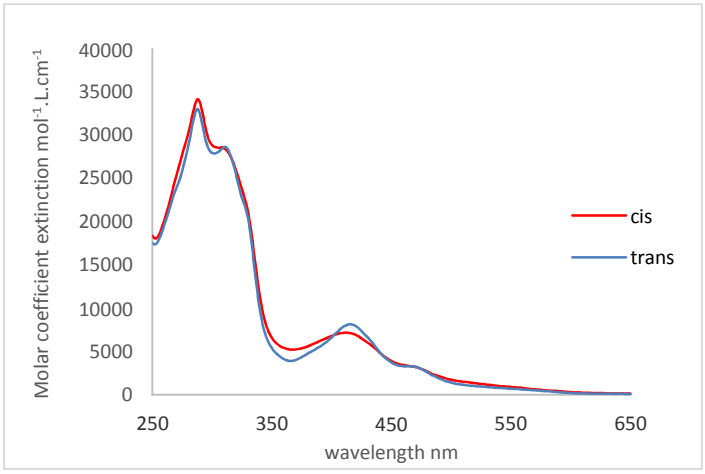
Fig. S5: Spectral changes of a solution 10^{-5}M of [2c](PF_6) (left) and [2t](PF_6) (right) in MeCN with irradiation at 365 nm in the presence of Griess reagent.



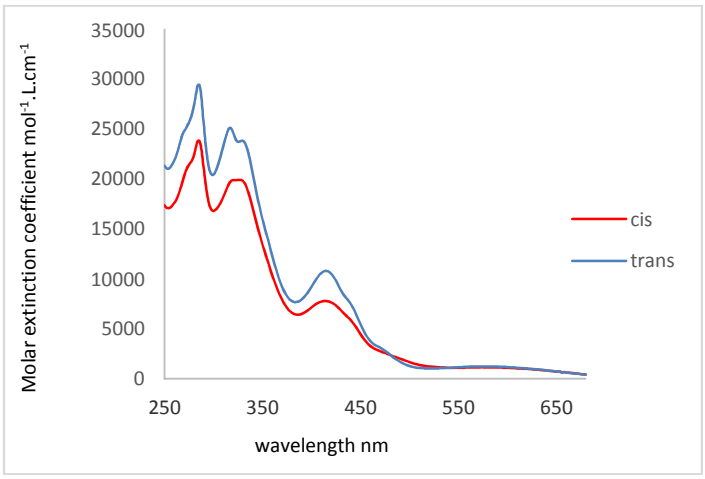
(a)



(b)



(c)



(d)

Fig S6: UV-visible spectra of the photoproducts after release of NO by irradiation at 365nm after 30 min, 10^{-5}M in MeCN (a) [1](PF_6), (b) [2](PF_6), (c) [3](PF_6) and (d) [4](PF_6).