Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis, spectroscopic, electrochemical and computational studies of rhenium(I) dicarbonyl complexes based on meridionally-coordinated 2,2′:6′,2″-terpyridine

Supporting Information

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1. Computational

5. Excitation and Emission Spectra

1. Computational

Table S1-A. Optimized geometry of *mer*,*cis*-Re(tpy-κ^3*N*)$(CO)_2$Cl (1) in the singlet ground state with E(B3LYP) = – 1508.5991 au.

Re	1.26104279	0.32410178	-0.22771282
C	1.82739943	0.19670334	-2.01960131
O	2.19834640	0.11732063	-3.13455134
C	3.08047316	0.31331409	0.34337271
O	4.19348166	0.30763315	0.72427902
Cl	0.51087918	0.50523548	2.25828532
N	-0.80621029	0.34963141	-0.61365748
C	-1.47888724	-0.82069153	-0.60910911
C	-1.42233357	1.54214255	-0.75605038
C	-2.86196567	-0.82693437	-0.81076405
C	-0.62748484	-2.00401350	-0.35458782
C	-2.80411243	1.58976111	-0.96071491
C	-0.51477904	2.70597225	-0.64902508
C	-3.51677501	0.39093836	-0.99608038
H	-3.42588213	-1.75506866	-0.81441304
C	-1.12838694	-3.30659146	-0.33672211
N	0.70209461	-1.75160688	-0.12602659
H	-3.32264193	2.53643466	-1.08107333
C	-0.95429309	4.02284652	-0.79185409
N	0.80247714	2.42123532	-0.39023386
H	-4.59279996	0.40678503	-1.15533601
C	-0.27385574	-4.37581563	-0.07948710
H	-2.18334802	-3.48576260	-0.52476685
C	1.51800584	-2.79469565	0.12746304
C	-0.04944211	5.07423111	-0.66756094
H	-2.00104879	4.22658937	-0.99960516
C	1.66790375	3.44787256	-0.26803931
C	1.07382599	-4.11244863	0.15792221
H	-0.65698625	-5.39384284	-0.06539274
H	2.55891307	-2.54380126	0.30678234
C	1.28587143	4.77886604	-0.39990123
H	-0.38458902	6.10326395	-0.77794376
H	2.69710846	3.17241363	-0.05942154
H	1.78195869	-4.91075123	0.36631979
H	2.03168758	5.56252158	-0.29106245

Table S2-B. Calculated singlet excited states of for *mer*,*cis*-Re(tpy-κ^3*N*)(CO)$_2$Cl (1) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	664.7	15.0	1.87	0.0258	91 →92(+98%)
2	581.6	17.2	2.13	0.0088	90 →92(+99%)
3	532.9	18.8	2.33	0.0056	91 →93(+86%) 89 →92(12%)
4	486.0	20.6	2.55	0.0031	90 →93(+91%) 89 →92(+25%)
5	461.0	21.7	2.69	0.0732	89 →92(+59%) 90 →93(+24%) 91 →93(+12)
6	430.0	23.3.	2.88	0.0149	89 →93(+98%)
7	378.7	26.4	3.27	0.0578	91 →94(+94%)
8	370.0	27.0	3.35	0.0137	91 →95(+77%) 90 →95(+19%)
9	352.9	28.3	3.51	0.0113	90 →94(+96%)
10	346.5	28.9	3.58	0.0167	90 →95(+79%) 91 →95(16%)
11	325.1	30.8	3.81	0.1230	88 →92(+67%) 86 →92(+21%) 89 →95(8%)
12	321.3	31.1	3.86	0.0255	89 →95(+90%)
13	321.0	31.1	3.86	0.0039	89 →94(+98%)
14	314.1	31.8	3.95	0.0175	87 →92(+95%)
15	310.1	32.2	4.00	0.1465	86 →92(+37%) 91 →96(33%) 91 →97(12%) 88 →92(12%)
16	309.7	32.3	4.00	0.1880	86 →92(+34%) 91 →96(+26%) 91 →97(+24%) 88 →92(8%)
17	300.6	33.3	4.12	0.0355	91 →97(+57%) 91 →96(38%)
18	293.7	34.0	4.22	0.0024	90 →97(+59%) 90 →96(+29%) 91 →98(+6%)
19	289.1	34.6	4.29	0.0285	86 →93(+66%) 88 →93(+31%)
20	287.8	34.8	4.31	0.0873	87 →93(+95%)
21	284.5	35.2	4.36	0.0025	90 →96(+49%) 91 →98(36%) 90 →97(8%)
22	282.3	35.4	4.39	0.0000	91 →98(+46%) 90 →97(27%) 90 →96(+18%)
23	277.3	36.1	4.47	0.1022	88 →93(+55%) 86 →93(30%) 89 →96(+9%)
24	272.6	36.7	4.55	0.0108	90 →98(+89%)
25	271.3	36.9	4.57	0.0013	91 →100(+57%) 89 →97(23%) 89 →96(6%)

26	268.6	37.2	4.62	0.0207	85 →92(+83%) 84 →92(+11%)
27	263.0	38.0	4.71	0.0426	89 →96(+64%) 84 →92(+19%) 91 →100(+8%)
28	255.9	39.1	4.84	0.1679	84 →92(+57%) 89 →96(11%) 91 →99(+8%) 85 →92(7%)
29	253.6	39.4	4.89	0.0334	85 →93(+88%) 88 →94(+6%)
30	251.8	39.7	4.92	0.0420	89 →98(+38%) 90 → 100(+29%) 89 →97(10%) 91 → 102(+6%) 89 →96(+6%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S1-C. Calculated triplet excited states of for *mer*,*cis*-Re(tpy-κ^3*N*)(CO)$_2$Cl (1) in acetonitrile.

	E_{VER} [b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	716.7	14.0	1.73	0.0000	91 →92(+98%)
2	602.8	16.6	2.06	0.0000	90 →92(+99%)
3	585.8	17.1	2.12	0.0000	91 →93(+92%)
4	538.2	18.6	2.30	0.0000	89 →92(+96%)
5	494.6	20.2	2.51	0.0000	90 →93(+95%)
6	444.0	22.5	2.79	0.0000	89 →93(+97%)
7	409.4	24.4	3.03	0.0000	91 →95(+71%) 88 →93(10%)
8	402.2	24.9	3.08	0.0000	91 →94(+89%)
9	396.3	25.2	3.13	0.0000	88 →93(+55%) 91 →95(+19%)
10	383.4	26.1	3.23	0.0000	88 →92(+80%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] *f* is the oscillator strength. [d] Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S1-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-Re(tpy-κ^3*N*)(CO)$_2$Cl (1) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	Cl[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
85 (O)	-7.11	0.00	0.00	0.01	0.00	0.01	0.00	0.67	0.00	0.01	98.80	0.16	0.35
86 (O)	-6.78	0.67	0.62	0.02	2.53	7.48	0.07	0.09	0.12	0.00	3.39	10.39	74.92
87 (O)	-6.23	0.01	0.49	0.00	0.06	4.08	16.34	0.00	1.66	0.11	9.32	9.66	58.26
88 (O)	-6.10	0.00	0.00	1.55	0.01	0.15	0.01	12.40	0.05	0.07	7.94	1.78	76.05
89 (O)	-5.22	0.09	2.39	0.00	0.11	6.78	26.99	0.00	1.68	0.10	6.95	17.50	37.40
90 (O)	-5.13	0.00	0.00	5.14	0.02	0.03	0.24	2.17	0.22	60.40	6.63	23.92	1.23
91 (O)	-4.78	0.00	0.00	0.24	0.00	0.59	0.00	48.34	0.11	5.37	13.53	14.77	17.05
HOMO-LUMO gap: 2.284 eV (18422.7 cm^{-1})													
92 (V)	-2.50	0.01	0.42	0.01	1.07	1.18	1.60	0.01	0.08	0.01	88.99	4.26	2.37
93 (V)	-2.29	0.00	0.00	0.17	0.00	0.03	0.00	2.61	0.01	0.01	95.75	1.33	0.08
94 (V)	-1.31	0.00	0.02	0.00	0.46	0.04	0.00	0.00	0.01	0.00	99.32	0.01	0.12
95 (V)	-1.24	0.00	0.00	0.22	0.00	0.03	0.00	2.77	0.01	0.00	93.16	3.79	0.01
96 (V)	-0.58	0.00	0.05	0.00	0.12	0.06	0.18	0.00	0.02	0.00	98.29	1.18	0.09
97 (V)	0.41	0.00	0.00	0.04	0.00	0.00	0.00	0.21	0.00	0.01	99.62	0.10	0.01
98 (V)	0.58	-0.06	5.61	0.05	22.55	4.11	1.21	0.03	2.34	0.00	2.56	59.38	2.21
99 (V)	0.79	4.40	26.46	0.06	3.89	5.43	2.10	0.40	29.18	0.13	22.90	4.07	0.97
100 (V)	0.94	0.00	0.02	34.32	0.12	0.04	0.08	3.42	0.08	13.32	7.29	40.47	0.82
101 (V)	1.55	3.25	42.50	0.00	17.54	3.53	0.65	0.08	1.39	0.02	15.51	15.60	-0.08

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2"-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one chlorine (Cl) atom present as the chloro (Cl) ligand.

Table S3-A. Optimized geometry of *mer*,*cis*-[Re(tpy-κ^3*N*)$(CO)_2(NCCH_3)]^+$ (3) in the singlet ground state with E(B3LYP) = – 1180.9767 au.

Re	0.22738860	-0.24789843	-0.08697846
N	-1.89260719	-0.56616544	0.17308189
C	-2.79059754	-0.82912539	-0.79683687
C	-2.33618719	-0.47018519	1.46821349
C	-4.14790078	-1.00015701	-0.54239400
H	-2.38999495	-0.89738727	-1.80345946
C	-3.68583208	-0.63319694	1.78115119
C	-4.60566690	-0.89983420	0.76926782
H	-4.82453596	-1.20820889	-1.36752261
H	-4.01959191	-0.55144818	2.81173911
H	-5.65990655	-1.02621266	1.00584636
N	-0.05651009	-0.05010303	1.99390453
C	-1.30287935	-0.19349407	2.49223110
C	1.02366234	0.15597195	2.77695534
C	-1.51386917	-0.09144656	3.86989826
C	0.86454033	0.26578276	4.16108673
C	-0.41730248	0.14685020	4.69880262
H	-2.50670238	-0.19887043	4.29650521
H	1.71570881	0.43490088	4.81397468
H	-0.56155485	0.23143332	5.77367934
C	0.50565877	-0.58897820	-1.94893706
O	0.67848632	-0.81825968	-3.08616713
C	0.00047181	1.59886111	-0.49216837
O	-0.13578260	2.72892027	-0.76099498
C	2.30384429	0.22557865	2.03564528
C	3.52972890	0.44894773	2.66287590
N	2.22508318	0.05009143	0.67677838
C	4.69875582	0.49374841	1.90625773
H	3.57330438	0.58903945	3.73923771
C	3.36285876	0.09086726	-0.04439091
C	4.61194177	0.31021753	0.52830774
H	5.65787499	0.66908908	2.38866750
H	3.24831206	-0.05536718	-1.11394143
H	5.49431249	0.33450309	-0.10631760
N	0.49406222	-2.36819393	0.33196791
C	0.63698157	-3.49683122	0.54878571
C	0.81825917	-4.91711982	0.81003620
H	1.66795012	-5.06641169	1.48783357
H	-0.08700386	-5.33013419	1.27219588
H	1.01338502	-5.44496671	-0.13182556

Table S3-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NCCH$_3$)]$^+$ (3) in acetonitrile.

	E_{VER} [b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	598.1	16.7	2.07	0.0187	93 →94(+98%)
2	550.2	18.2	2.25	0.0154	92 →94(+98%)
3	487.6	20.5	2.54	0.0051	93 →95(+90%) 91 →94(5%)
4	458.8	21.8	2.70	0.0012	92 →95(+85%) 91 →94(14%)
5	421.7	23.7	2.94	0.0851	91 →94(+76%) 92 →95(+10%) 93 →95(+8%)
6	392.0	25.5	3.16	0.0133	91 →95(+98%)
7	355.8	28.1	3.48	0.0224	93 →96(+91%) 90 →94(+5%)
8	351.7	28.4	3.53	0.0066	93 →97(+70%) 92 →97(28%)
9	340.3	29.4	3.64	0.0024	92 →96(+88%) 90 →94(+11%)
10	329.9	30.3	3.76	0.0333	92 →97(+69%) 93 →97(+24%)
11	314.4	31.8	3.94	0.5356	90 →94(+75%) 92 →96(8%) 93 →96(6%) 93 →99(6%)
12	309.1	32.4	4.01	0.0632	93 →99(+87%) 90 →94(+5%)
13	300.8	33.2	4.12	0.0019	92 →99(+52%) 91 →97(+40%)
14	299.2	33.4	4.14	0.0320	91 →97(+57%) 92 →99(37%)
15	298.8	33.5	4.15	0.0016	91 →96(+96%)
16	292.3	34.2	4.24	0.0327	93 →100(+84%) 91 →99(9%)
17	290.6	34.4	4.27	0.0163	93 →98(+88%)
18	279.4	35.8	4.44	0.0087	92 →98(+85%) 92 →101(+6%)
19	278.4	35.9	4.45	0.0037	92 →100(+76%) 91 →99(17%)
20	277.3	36.1	4.47	0.1507	90 →95(+88%)
21	271.9	36.8	4.56	0.0006	93 →101(+62%) 93 →103(+21%)
22	265.8	37.6	4.66	0.0039	92 →101(+59%) 92 →103(+20%) 92 →98(6%)
23	260.7	38.4	4.76	0.0029	91 →100(+91%)
24	259.1	38.6	4.79	0.0670	89 →94(+85%) 91 →98(+6%)
25	254.8	39.2	4.87	0.0030	93 →103(+52%) 93 →101(23%) 92 →103(10%)

26	248.3	40.3	4.99	0.1053	91 →98(+71%) 93 →104(+8%) 91 →99(+5%)
27	247.8	40.4	5.00	0.2539	89 →95(+91%)
28	241.4	41.4	5.14	0.0721	90 →97(+25%) 91 →99(+22%) 93 →104(11%) 93 →102(11%) 92 →106(+7%) 92 →104(6%)
29	241.1	41.5	5.14	0.0001	92 →103(+57%) 92 →101(24%) 93 →103(+5%)
30	240.8	41.5	5.15	0.0219	90 →97(+33%) 93 →104(+22%) 91 →99(10%) 93 →102(10%) 92 →104(+6%) 88 →94(6%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S3-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NCCH$_3$)]$^+$ (3) in acetonitrile.

	E_{VER} [b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	636.8	15.7	1.95	0.0000	93 →94(+96%)
2	572.9	17.5	2.16	0.0000	92 →94(+96%)
3	532.0	18.8	2.33	0.0000	93 →95(+79%) 92 →95(+9%) 90 →95(5%)
4	489.2	20.4	2.53	0.0000	91 →94(+88%)
5	473.1	21.1	2.62	0.0000	92 →95(+84%) 93 →95(10%)
6	407.4	24.5	3.04	0.0000	91 →95(+86%) 90 →94(+12%)
7	391.8	25.5	3.16	0.0000	90 →95(+58%) 89 →94(+8%) 93 →97(7%) 93 →95(+5%)
8	381.7	26.2	3.25	0.0000	90 →94(+66%) 91 →95(13%) 89 →95(+7%) 93 →96(+5%)
9	379.1	26.4	3.27	0.0000	93 →97(+72%) 90 →95(+12%) 92 →97(+9%)
10	374.3	26.7	3.31	0.0000	93 →96(+79%) 90 →94(9%) 92 →96(+7%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] *f* is the oscillator strength. [d] Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S3-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NCCH$_3$)]$^+$ (3) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	NCCH$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
89 (O)	-10.70	0.00	0.00	0.04	0.01	0.07	0.01	0.58	0.01	0.02	98.67	0.23	0.35
90 (O)	-9.94	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.05	0.49	99.18	0.10	0.16
91 (O)	-8.71	0.02	0.02	-0.01	1.08	7.54	0.39	44.77	2.03	1.71	12.22	22.97	7.26
92 (O)	-8.28	0.00	4.62	0.11	0.07	2.66	56.58	0.81	0.14	3.98	7.58	23.18	0.28
93 (O)	-8.21	0.00	0.04	0.00	0.00	0.20	3.64	1.52	6.15	51.85	15.75	13.03	7.85
HOMO-LUMO gap: 2.745 eV (22138.5 cm^{-1})													
94 (V)	-5.46	0.00	0.01	1.30	0.23	0.53	0.01	1.38	0.36	0.11	91.28	4.26	0.53
95 (V)	-5.18	0.00	0.06	0.00	0.00	0.00	0.01	0.03	0.16	1.83	96.81	0.78	0.31
96 (V)	-4.15	0.00	0.01	0.63	0.01	0.00	0.00	0.02	0.02	0.01	99.19	0.05	0.05
97 (V)	-4.10	0.00	0.10	0.00	0.00	0.00	0.01	0.03	0.17	1.89	94.38	3.34	0.08
98 (V)	-3.42	0.01	0.01	0.29	0.17	0.04	0.01	0.24	0.00	0.01	97.09	1.67	0.45
99 (V)	-3.21	0.00	8.76	0.08	0.00	0.03	2.92	0.04	0.01	0.05	1.43	25.92	60.75
100 (V)	-3.21	-0.04	0.03	1.51	8.19	2.48	0.06	0.11	0.45	0.07	2.47	28.73	55.95
101 (V)	-2.44	0.00	0.04	0.00	0.00	0.00	0.03	0.01	0.02	0.24	99.43	0.19	0.04
102 (V)	-2.21	0.07	0.69	28.65	0.09	0.52	0.03	1.43	1.17	0.03	1.51	46.51	19.29
103 (V)	-2.07	7.29	0.26	0.17	22.11	15.02	1.70	0.48	18.76	1.61	23.95	1.59	7.07
105 (V)	-1.65	9.80	0.32	41.51	10.21	0.52	0.14	0.26	0.99	0.16	2.04	17.34	16.72
107 (V)	-1.34	7.31	1.58	9.94	40.95	-0.04	0.36	1.99	10.75	1.41	11.84	13.49	0.43

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one nitrogen (N) atom, two carbon, and three hydrogen atoms present in the acetonitrile ($NCCH_3$) ligand.

Table S4-A. Optimized geometry of *mer,cis*-Re(tpy-κ^3*N*)$(CO)_2$CN (4) in the singlet ground state with E(B3LYP) = – 1141.2383 au.

Re	0.23479359	-0.29059109	-0.07952503
N	-1.88618599	-0.59177930	0.18308657
C	-2.78553327	-0.85953394	-0.78549199
C	-2.33260169	-0.48906808	1.47685605
C	-4.14257039	-1.02679986	-0.53255324
H	-2.38432842	-0.93617420	-1.78792967
C	-3.68427150	-0.64843708	1.78845402
C	-4.60342891	-0.91891306	0.77840502
H	-4.81581073	-1.23887284	-1.35564847
H	-4.01740183	-0.56177682	2.81557929
H	-5.65515861	-1.04294990	1.01359817
N	-0.05452465	-0.06974512	2.00067362
C	-1.30187888	-0.20853464	2.49959087
C	1.02350865	0.14128074	2.78646102
C	-1.51494215	-0.09849502	3.87666658
C	0.86149312	0.25883834	4.16995809
C	-0.42059203	0.14311129	4.70708892
H	-2.50598401	-0.20323189	4.30025714
H	1.70964700	0.43015536	4.82107280
H	-0.56617304	0.23236937	5.77830917
C	0.51846855	-0.66533617	-1.92871397
O	0.69627535	-0.92128819	-3.06353883
C	0.00817710	1.58185008	-0.51544068
O	-0.12231456	2.70470060	-0.82345810
C	2.30339677	0.20765134	2.04831188
C	3.52901377	0.43639525	2.67687522
N	2.22625469	0.02514617	0.69015361
C	4.69937133	0.47909506	1.92412861
H	3.56925692	0.58094791	3.74965213
C	3.36759369	0.06361350	-0.02718237
C	4.61437757	0.28795937	0.54616446
H	5.65472363	0.65708434	2.40628029
H	3.25605867	-0.09052671	-1.09279605
H	5.49534534	0.30893907	-0.08560560
C	0.49972503	-2.38774965	0.31952690
N	0.64302846	-3.53026148	0.54269775

Table S4-B. Calculated singlet excited states of for *mer,cis*-Re(tpy-κ^3*N*)(CO)$_2$CN (4) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	637.1	15.7	1.95	0.0262	89 →90(+98%)
2	578.0	17.3	2.14	0.0085	88 →90(+99%)
3	529.7	18.9	2.34	0.0075	89 →91(+89%) 87 →90(8%)
4	494.0	20.2	2.51	0.0007	88 →91(+91%) 87 →90(8%)
5	447.9	22.3	2.77	0.0829	87 →90(+78%) 89 →91(+9%) 89 →93(6%) 88 →91(+6%)
6	428.0	23.4	2.90	0.0179	87 →91(+98%)
7	376.4	26.6	3.29	0.0646	89 →92(+92%)
8	368.8	27.1	3.36	0.0108	89 →93(+59%) 88 →93(38%)
9	358.1	27.9	3.46	0.0223	88 →92(+94%)
10	348.6	28.7	3.56	0.0336	88 →93(+61%) 89 →93(+33%)
11	320.2	31.2	3.87	0.0001	87 →93(+95%)
12	319.2	31.3	3.88	0.0051	87 →92(+98%)
13	311.1	32.1	3.98	0.4534	86 →90(+81%) 89 →95(+6%)
14	307.5	32.5	4.03	0.0744	89 →95(+77%) 89 →94(+9%) 86 →90(6%)
15	304.6	32.8	4.07	0.0194	89 →94(+83%) 89 →95(12%)
16	298.0	33.6	4.16	0.0309	88 →95(+89%)
17	290.4	34.4	4.27	0.0068	88 →94(+97%)
18	285.5	35.0	4.34	0.0156	89 →96(+78%) 87 →95(17%)
19	278.3	35.9	4.46	0.1199	86 →91(+87%) 87 →94(+9%)
20	271.5	36.8	4.57	0.0013	89 →98(+85%) 89 →101(8%)
21	270.6	36.9	4.58	0.0016	88 →96(+67%) 87 →95(20%)
22	264.1	37.9	4.69	0.0014	88 →98(+84%) 87 →96(+5%)
23	262.0	38.2	4.73	0.0000	85 →90(+77%) 83 →90(14%)
24	261.2	38.3	4.75	0.0760	87 →94(+75%) 83 →90(14%)
25	258.0	38.8	4.81	0.0001	87 →96(+79%) 84 →90(+11%)

26	257.3	38.9	4.82	0.0160	84 →90(+84%) 87 →96(9%)
27	252.8	39.6	4.90	0.1995	85 →91(+85%) 86 →92(+6%)
28	251.9	39.7	4.92	0.1001	82 →90(+31%) 83 →90(30%) 89 →97(16%)
29	249.1	40.1	4.98	0.0347	82 →90(+60%) 89 →97(+22%) 83 →90(+13%)
30	246.7	40.5	5.03	0.0774	89 →97(+54%) 83 →90(23%) 85 →90(10%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S4-C. Calculated triplet excited states of for *mer*,*cis*-Re(tpy-κ^3*N*)(CO)$_2$CN (4) in acetonitrile.

	E_{VER} [b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	685.2	14.6	1.81	0.0000	89 →90(+97%)
2	596.5	16.8	2.08	0.0000	88 →90(+98%)
3	587.2	17.0	2.11	0.0000	89 →91(+90%)
4	524.7	19.1	2.36	0.0000	87 →90(+95%)
5	505.8	19.8	2.45	0.0000	88 →91(+94)
6	444.6	22.5	2.79	0.0000	87 →91(+97%)
7	410.5	24.4	3.02	0.0000	89 →93(+74%) 86 →91(+7%)
8	402.6	24.8	3.08	0.0000	89 →92(+88%)
9	392.8	25.5	3.16	0.0000	86 →91(+65%) 89 →93(+14%) 85 →90(+7%)
10	375.2	26.7	3.30	0.0000	86 →90(+79%) 85 →91(+7%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S4-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-Re(tpy-κ^3*N*)(CO)$_2$CN (4) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	CN[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
82 (O)	-7.94	0.00	0.00	0.05	0.01	0.08	0.01	0.85	0.01	0.02	97.37	0.40	1.19
83 (O)	-7.21	0.00	0.09	0.00	0.00	0.00	0.00	0.02	0.13	1.35	92.18	0.22	6.02
84 (O)	-7.06	0.97	0.05	2.16	0.06	2.57	0.00	1.45	2.79	0.46	1.54	8.52	79.43
85 (O)	-6.98	0.52	0.00	0.50	0.86	0.01	0.05	5.28	0.14	0.02	7.86	4.24	80.52
86 (O)	-6.94	0.00	1.30	0.03	0.02	0.00	0.05	0.08	0.41	4.05	13.65	0.48	79.94
87 (O)	-5.43	0.02	0.03	0.03	1.05	4.12	0.50	43.23	0.93	1.30	11.45	21.01	16.34
88 (O)	-5.17	0.00	4.70	0.11	0.07	2.50	53.88	0.65	0.03	6.60	7.44	23.36	0.68
89 (O)	-4.92	0.00	0.00	0.00	0.00	0.37	7.11	1.65	5.98	46.01	15.48	14.07	9.35
HOMO-LUMO gap: 2.384 eV (19230.4 cm^{-1})													
90 (V)	-2.53	0.04	0.01	0.83	0.22	0.21	0.04	2.92	0.08	0.09	89.44	4.70	1.43
91 (V)	-2.38	0.00	0.11	0.00	0.00	0.00	0.00	0.04	0.24	2.55	95.71	1.24	0.10
92 (V)	-1.39	0.00	0.01	0.58	0.02	0.00	0.00	0.04	0.00	0.00	99.29	0.03	0.03
93 (V)	-1.31	0.00	0.22	0.00	0.00	0.00	0.00	0.05	0.27	2.85	92.65	3.93	0.02
94 (V)	-0.66	0.00	0.00	0.27	0.03	0.01	0.01	0.25	0.00	0.01	98.20	1.19	0.03
95 (V)	0.33	0.00	0.07	0.00	0.00	0.00	0.03	0.00	0.02	0.15	99.28	0.37	0.07
96 (V)	0.37	-0.41	0.70	2.51	24.29	10.62	0.61	0.90	3.00	0.18	8.62	43.47	5.49
97 (V)	0.57	0.00	28.99	0.65	0.43	0.39	8.60	0.02	0.14	5.90	5.53	42.26	7.10
98 (V)	0.90	13.76	0.02	4.53	4.26	5.75	0.97	0.15	15.57	1.41	24.31	27.28	1.97
101 (V)	1.55	0.00	51.60	1.16	0.79	0.22	4.80	0.10	0.05	0.02	19.44	21.62	0.19

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one carbon and one nitrogen atom present in the cyano (CN) ligand.

Table S5-A. Optimized geometry of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2(NC_5H_5)]^+$ (5) in the singlet ground state with E(B3LYP) = – 1296.5071 au.

Re	0.21559986	-0.27124996	-0.05394064
N	-1.91286043	-0.52691381	0.18433331
C	-2.80329692	-0.80248078	-0.79037739
C	-2.38145108	-0.33314739	1.46170225
C	-4.17295145	-0.88508623	-0.56051631
H	-2.38508831	-0.95274573	-1.78073233
C	-3.74472053	-0.40292587	1.74854335
C	-4.65476891	-0.67854151	0.73020315
H	-4.84100905	-1.10815713	-1.38866155
H	-4.09592397	-0.24205799	2.76385768
H	-5.71950133	-0.73217920	0.94606520
N	-0.09287840	-0.01476473	2.01464066
C	-1.35434126	-0.06976088	2.49537362
C	0.98227675	0.17144689	2.81056493
C	-1.58328398	0.09059543	3.86446037
C	0.80556497	0.33368803	4.18709719
C	-0.48936867	0.29647168	4.70534218
H	-2.58761272	0.05001699	4.27538990
H	1.65304011	0.48474589	4.84904469
H	-0.64655661	0.42285225	5.77417793
C	0.49446892	-0.66030822	-1.90279843
O	0.66212607	-0.92162093	-3.03616555
C	0.01612836	1.56296187	-0.50219755
O	-0.09864620	2.69113256	-0.79915570
C	2.27355508	0.18890421	2.08694926
C	3.49550410	0.38894302	2.72911065
N	2.20714553	0.01124645	0.72679395
C	4.67459064	0.41611173	1.98734558
H	3.52778880	0.52605062	3.80620270
C	3.35513094	0.04470994	0.01969027
C	4.60048291	0.24466081	0.60723917
H	5.63055499	0.57229305	2.48224096
H	3.25257233	-0.08907883	-1.05295234
H	5.48967240	0.26212235	-0.01793631
C	1.59341514	-3.13931562	-0.11141953
C	-0.31628079	-3.21261739	1.18448169
C	1.84851751	-4.48752393	0.11132059
H	2.25835732	-2.54329164	-0.72958521
C	-0.13159502	-4.56432702	1.45687018
H	-1.17094569	-2.68434718	1.59558049
C	0.97120708	-5.21945091	0.91133327
H	2.72439524	-4.94772247	-0.33988724
H	-0.84816694	-5.08533175	2.08739114
H	1.14339465	-6.27660098	1.10456920

N	0.52624634	-2.49627152	0.41189992

Table S5-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NC$_5$H$_5$)]$^+$ (5) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	623.1	16.0	1.99	0.0217	103 →104(+98%)
2	571.4	17.5	2.17	0.0130	102 →104(+98%)
3	501.5	19.9	2.47	0.0054	103 →105(+89%) 101 →104(8%)
4	471.6	21.2	2.63	0.0004	102 →105(+86%) 101 →104(+13%)
5	435.3	23.0	2.85	0.0831	101 →104(+74%) 102 →105(10%) 103 →105(+9%)
6	402.8	24.8	3.08	0.0137	101 →105(+98%)
7	375.9	26.6	3.30	0.0297	103 →106(+88%) 102 →106(+8%)
8	362.0	27.6	3.42	0.0317	103 →107(+88%) 100 →104(+6%)
9	359.2	27.8	3.45	0.0112	102 →106(+43%) 103 →108(43%) 102 →108(10%)
10	352.8	28.3	3.51	0.0164	102 →106(+46%) 103 →108(+23%) 102 →108(+21%)
11	346.4	28.9	3.58	0.0059	102 →107(+88%) 100 →104(7%)
12	337.0	29.7	3.68	0.0254	102 →108(+62%) 103 →108(24%)
13	316.7	31.6	3.91	0.5232	100 →104(+81%) 103 →107(7%)
14	313.9	31.9	3.95	0.0030	103 →109(+84%) 103 →111(5%)
15	312.9	32.0	3.96	0.0886	101 →106(+79%) 101 →108(8%)
16	305.2	32.8	4.06	0.0228	101 →107(+85%) 101 →108(10%)
17	302.9	33.0	4.09	0.0357	101 →108(+79%) 101 →107(+11%) 101 →106(+7%)
18	299.4	35.8	4.14	0.0040	102 →109(+77%) 102 →111(12%) 103 →109(6%)
19	292.8	34.2	4.23	0.0083	103 →110(+83%) 103 →111(9%)
20	286.7	34.9	4.33	0.0204	103 →111(+74%) 103 →110(+13%)
21	282.6	35.4	4.39	0.0020	99 →104(+99%)
22	281.2	35.6	4.41	0.0053	102 →111(+45%) 102 →110(35%) 102 →109(+8%) 103 →111(6%)
23	279.1	35.8	4.44	0.0053	102 →110(+53%) 102 →111(+28%) 100 →105(6%)
24	278.3	35.9	4.46	0.1274	100 →105(+81%)

25	274.3	36.5	4.52	0.0014	103 ⟶113(+53%) 103 ⟶ 112(+30%)
26	269.3	37.1	4.60	0.0025	101 ⟶109(+63%) 103 ⟶114(11%) 103 ⟶112(+9%) 101 ⟶111(5%)
27	268.2	37.3	4.62	0.0058	102 ⟶113(+54%) 102 ⟶ 112(+29%)
28	263.0	38.0	4.71	0.0089	103 ⟶114(+28%) 101 ⟶ 109(+26%) 103 ⟶112(19%) 101 ⟶ 111(+11%) 103 ⟶113(+8%)
29	260.6	38.4	4.76	0.0568	98 ⟶104(+78%) 101 ⟶110(+6%)
30	259.5	38.5	4.78	0.0036	99 ⟶105(+95%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# ⟶MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S5-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NC$_5$H$_5$)]$^+$ (5) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	669.9	14.9	1.85	0.0000	103 →104(+97%)
2	594.9	16.8	2.08	0.0000	102 →104(+97%)
3	550.0	18.2	2.25	0.0000	103 →105(+84%) 102 →105(6%)
4	508.6	19.7	2.44	0.0000	101 →104(+93%)
5	483.6	20.7	2.56	0.0000	102 →105(+89%) 103 →105(+7%)
6	418.5	23.9	2.96	0.0000	101 →105(+91%) 100 →104(+6%)
7	399.4	25.0	3.10	0.0000	103 →106(+50%) 103 →108(18%) 100 →105(+11%)
8	393.0	25.4	3.15	0.0000	100 →105(+45%) 103 →106(29%) 98 →104(+6%)
9	385.4	25.9	3.22	0.0000	103 →107(+36%) 100 → 104(+35%) 98 →105(+5%)
10	384.0	26.0	3.23	0.0000	103 →108(+36%) 103 →107(23%) 100 →104(+13%) 103 → 106(+10%) 100 →105(+8%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S5-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NC$_5$H$_5$)]$^+$ (5) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	NC$_5$H$_5$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
98 (O)	-10.67	0.00	0.00	0.03	0.00	0.03	0.00	0.029	0.00	0.05	99.26	0.04	0.29
99 (O)	-10.50	0.00	-0.01	0.00	0.00	0.08	0.11	0.01	0.04	0.00	1.69	1.04	97.06
100 (O)	-9.99	0.00	-0.02	1.20	-0.01	0.47	0.00	0.73	0.02	0.35	98.98	0.04	0.58
101 (O)	-8.56	0.01	0.00	0.14	0.57	8.29	0.19	41.65	1.79	3.75	18.50	20.42	4.69
102 (O)	-8.36	0.05	2.81	0.06	0.26	5.67	57.09	0.89	0.74	2.21	9.32	20.21	0.68
103 (O)	-7.86	0.03	-0.03	-0.03	-0.01	0.15	1.45	2.50	4.31	45.18	26.39	9.75	10.30
HOMO-LUMO gap: 2.578 eV (20793.1 cm^{-1})													
104 (V)	-5.28	0.01	0.02	1.57	0.58	0.58	0.00	1.48	0.16	0.11	83.91	10.31	1.28
105 (V)	-5.03	0.00	0.06	0.01	0.01	0.00	0.01	0.03	0.11	1.92	93.98	0.63	3.23
106 (V)	-4.38	0.00	1.16	0.01	0.98	-0.02	0.38	0.10	0.16	0.71	7.12	12.10	77.30
107 (V)	-4.18	0.00	0.01	0.82	0.09	0.06	0.01	0.44	0.01	0.03	96.56	1.00	0.96
108 (V)	-4.04	-0.02	1.15	0.06	0.03	0.09	0.09	0.04	0.23	1.59	64.44	16.36	1.59
109 (V)	-3.83	0.11	0.21	0.25	0.02	0.19	0.22	1.00	0.09	0.22	22.87	14.56	60.26
110 (V)	-3.45	-0.01	0.05	0.23	0.38	0.14	0.00	0.11	0.05	0.01	84.53	3.37	11.14
111 (V)	-3.24	0.04	4.97	0.16	0.04	0.32	17.91	0.11	0.27	0.09	7.91	65.09	3.09
112 (V)	-3.13	0.49	0.34	2.69	3.10	0.39	0.04	0.64	0.00	0.23	-0.42	83.51	8.99
113 (V)	-2.82	0.12	5.16	2.30	2.09	0.55	0.06	6.84	0.92	12.38	13.00	51.68	4.90
114 (V)	-2.61	0.03	1.13	0.11	3.48	1.12	0.07	5.41	0.25	1.44	58.59	24.87	3.50

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one nitrogen (N) atom, five carbon, and five hydrogen atoms present in the pyridine (NC_5H_5) ligand.

Table S6-A. Optimized geometry of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2(PMe)_3]^+$ (6) in the singlet ground state with E(B3LYP) = – 1509.3025 au.

Re	2.50953762	2.88071548	-3.04804345
N	2.61699589	4.97919603	-3.07361029
C	2.46127401	5.65622744	-1.91071219
C	2.83847657	5.60818159	-4.25272466
C	2.53079078	7.05233551	-1.90465485
C	2.22025302	4.78799071	-0.73930099
C	2.91513644	7.00333148	-4.29256070
C	2.97245198	4.69230420	-5.40493572
C	2.75875577	7.72168557	-3.10708326
H	2.40830319	7.61368923	-0.98612344
C	1.99832905	5.28823554	0.54568413
N	2.21045563	3.43572494	-0.98673846
H	3.09050577	7.52670810	-5.22483946
C	3.16937005	5.13941174	-6.71338807
N	2.87696651	3.35094619	-5.11940902
H	2.81288554	8.80535982	-3.12061312
C	1.75318338	4.41482575	1.60157157
H	2.00863217	6.35804692	0.71927741
C	1.96708665	2.59954155	0.04590286
C	3.26415839	4.22294576	-7.75691872
H	3.24023557	6.20149639	-6.91756508
C	2.96646889	2.47255696	-6.14179721
C	1.73454097	3.04504746	1.34231440
H	1.57484130	4.79735049	2.60117957
H	1.95705433	1.54514860	-0.20027939
C	3.15685608	2.86446505	-7.46218017
H	3.41203538	4.56410327	-8.77627720
H	2.87338052	1.42872527	-5.86926664
H	1.54012952	2.32196859	2.12706969
H	3.21543123	2.10937432	-8.23864031
C	2.54328888	0.96072208	-3.00277158
O	2.61545571	-0.20572216	-2.96700989
C	0.59373782	2.79778140	-3.35547080
O	-0.54779696	2.70339226	-3.53796329
P	4.99719579	2.66511249	-2.64493464
C	6.00223422	4.21537192	-2.54374642
H	5.91333218	4.78100393	-3.47658300
H	5.64005071	4.84467384	-1.72470985
H	7.05931721	3.98811716	-2.37061516
C	5.89006685	1.68106156	-3.92593843
H	5.45251733	0.67974628	-3.98365917
H	5.78859939	2.15837208	-4.90516335
H	6.95417012	1.59094777	-3.68370536
C	5.44306670	1.78478873	-1.08512043

H	6.52909627	1.68954192	-0.98228781
H	5.05148333	2.32904766	-0.22059060
H	4.99808220	0.78508499	-1.09364045

Table S6-B. Calculated singlet excited states of for *mer*,*cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PMe$_3$)]$^+$ (6) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	596.0	16.8	2.08	0.0153	103 →104(+98%)
2	557.2	17.9	2.23	0.0138	102 →104(+98%)
3	494.1	20.2	2.51	0.0046	103 →105(+89%) 101 →104(+5%)
4	470.5	21.3	2.64	0.0021	102 →105(+85%) 101 →104(13%)
5	432.4	23.6	2.93	0.0922	101 →104(+76%) 102 →105(+9%) 103 →105(8%)
6	403.5	24.8	3.07	0.0204	101 →105(+98%)
7	359.9	27.8	3.44	0.0277	103 →106(+89%) 102 →106(+6%)
8	356.2	28.1	3.48	0.0047	103 →107(+63%) 102 → 107(+35%)
9	346.8	28.8	3.58	0.0192	102 →106(+88%) 100 →104(8%)
10	333.6	30.0	3.72	0.0388	102 →107(+61%) 103 →107(31%)
11	312.8	32.0	3.96	0.4840	100 →104(+79%) 101 →107(+7%) 103 →106(5%)
12	305.7	32.7	4.06	0.0093	101 →106(+91%)
13	305.5	32.7	4.06	0.0192	101 →107(+83%) 101 →106(+5%)
14	301.2	33.2	4.12	0.0333	102 →109(+90%)
15	298.1	33.5	4.16	0.0050	103 →109(+90%)
16	291.7	34.3	4.25	0.0280	103 →108(+88%)
17	284.6	35.1	4.36	0.0209	103 →110(+86%) 101 →109(+8%)
18	283.1	35.3	4.38	0.0088	102 →108(+92%)
19	278.0	36.0	4.46	0.1370	100 →105(+89%)
20	275.3	36.3	4.50	0.0295	99 →104(+95%)
21	272.8	36.7	4.54	0.0002	103 →111(+85%)
22	271.9	36.8	4.56	0.0016	102 →110(+64%) 101 →109(24%)
23	268.2	37.3	4.62	0.0065	102 →111(+85%)
24	258.6	38.7	4.79	0.0081	99 →105(+97%)
25	257.3	38.9	4.82	0.0212	98 →104(+73%) 101 →108(+20%)

26	256.0	39.1	4.84	0.0012	101 ⟶110(+93%)
27	250.2	40.0	4.96	0.2169	101 ⟶108(+68%) 98 ⟶104(15%)
28	247.1	40.5	5.02	0.2476	98 ⟶105(+94%)
29	241.5	41.4	5.13	0.0156	100 ⟶107(+29%) 102 ⟶113(+20%) 103 ⟶112(+18%) 101 ⟶109(+12%) 103 ⟶113(6%)
30	240.4	41.6	5.16	0.0359	102 ⟶113(+24%) 100 ⟶107(23%) 103 ⟶112(14%) 101 ⟶109(+13%) 103 ⟶113(8%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# ⟶MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S6-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PMe$_3$)]$^+$ (6) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	636.6	15.7	1.95	0.0000	103 →104(+92%) 102 →104(6%)
2	579.5	17.3	2.14	0.0000	102 →104(+93%) 103 →104(+6%)
3	544.9	18.4	2.28	0.0000	103 →105(+76%) 102 →105(13%)
4	504.9	19.8	2.46	0.0000	101 →104(+92%)
5	486.1	20.6	2.55	0.0000	102 →105(+81%) 103 → 105(+16%)
6	422.2	23.7	2.94	0.0000	101 →105(+94%)
7	394.2	25.4	3.15	0.0000	100 →105(+37%) 103 →107(26%) 102 →107(+6%) 103 →105(+6%) 98 →104(6%)
8	384.4	26.0	3.23	0.0000	103 →106(+63%) 102 →106(11%) 100 →104(+9%)
9	383.3	26.1	3.24	0.0000	103 →107(+49%) 100 → 105(+34%) 102 →107(8%)
10	375.6	26.6	3.30	0.0000	100 →104(+72%) 103 →106(15%) 98 →105(5%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S6-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PMe$_3$)]$^+$ (6) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	PMe$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
98 (O)	-10.72	0.02	0.15	-0.01	0.00	0.01	0.00	0.02	0.08	0.88	98.01	0.36	0.47
99 (O)	-10.21	1.66	3.92	0.00	0.10	1.25	0.60	0.06	6.29	2.44	6.31	14.27	63.10
100 (O)	-9.95	0.00	0.00	0.00	0.01	0.07	0.83	0.02	0.02	0.00	98.64	0.19	0.23
101 (O)	-8.74	0.00	-0.09	0.20	0.00	0.01	0.02	1.43	0.08	54.83	17.04	23.00	3.47
102 (O)	-8.27	0.00	0.08	0.00	3.20	1.84	30.09	29.91	1.08	0.53	11.80	21.13	0.34
103 (O)	-8.16	0.00	0.03	0.00	1.51	2.99	27.78	34.09	0.55	1.20	14.58	15.80	1.46
HOMO-LUMO gap: 2.594 eV (20924.8 cm^{-1})													
104 (V)	-5.56	0.00	0.97	0.05	0.02	0.05	0.02	0.08	0.04	3.05	88.16	4.74	2.81
105 (V)	-5.25	0.00	0.00	0.00	0.03	0.23	2.61	0.06	0.07	0.01	95.69	1.14	0.16
106 (V)	-4.16	0.00	0.58	0.00	0.01	0.02	0.00	0.00	0.00	0.03	98.99	0.03	0.05
107 (V)	-4.09	0.00	0.01	0.00	0.25	0.19	2.11	0.10	0.05	0.01	93.19	3.76	0.34
108 (V)	-3.46	0.00	0.23	0.01	0.01	0.01	0.00	0.00	0.00	0.17	97.79	1.47	0.29
109 (V)	-2.74	0.00	2.61	20.84	0.05	2.99	0.03	0.01	3.49	0.34	2.86	54.33	12.26
110 (V)	-2.55	0.00	0.72	0.00	28.90	0.40	5.12	6.42	0.16	0.15	3.44	41.25	13.43
111 (V)	-2.41	0.00	0.01	0.00	0.46	0.04	0.45	0.00	0.02	0.00	98.71	0.13	0.17
112 (V)	-2.20	1.87	13.44	9.44	0.31	29.40	2.49	0.00	0.04	2.17	21.05	15.21	4.57
113 (V)	-1.65	0.09	0.04	0.40	0.78	0.06	2.22	12.59	0.00	0.20	9.71	70.23	3.68

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one phosphorus (P) atom, three carbon, and nine hydrogen atoms present in the trimethylphosphine (PMe_3) ligand.

Table S7-A. Optimized geometry of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2(PEt)_3]^+$ (7) in the singlet ground state with E(B3LYP) = – 1627.2272 au.

Re	2.55807732	2.87946704	-3.05142158
N	2.63137618	4.97806800	-3.07529484
C	2.46860357	5.65241303	-1.91125022
C	2.84182543	5.61201236	-4.25418034
C	2.52185283	7.04941361	-1.90359342
C	2.23477896	4.78022501	-0.74192270
C	2.90219736	7.00784033	-4.29207854
C	2.97849660	4.69973261	-5.40787276
C	2.74042501	7.72301762	-3.10535291
H	2.39423285	7.60792791	-0.98401600
C	1.99603706	5.27663345	0.54163410
N	2.24230016	3.42812601	-0.99136316
H	3.06974374	7.53432269	-5.22406037
C	3.15291872	5.15103299	-6.71815283
N	2.90117512	3.35682598	-5.12273376
H	2.78240331	8.80724391	-3.11747411
C	1.74758479	4.39989752	1.59373840
H	1.99406954	6.34634252	0.71625960
C	1.99159931	2.58913009	0.03743063
C	3.24053223	4.23811477	-7.76522411
H	3.21022258	6.21425385	-6.92077983
C	2.98061835	2.48184673	-6.14977630
C	1.74064461	3.03046556	1.33147010
H	1.55577100	4.77937552	2.59201342
H	1.98999837	1.53511493	-0.21030794
C	3.14699534	2.87821160	-7.47196778
H	3.37070277	4.58276234	-8.78580821
H	2.89770545	1.43674592	-5.87862403
H	1.54133394	2.30456578	2.11239458
H	3.19814899	2.12526602	-8.25105068
C	2.61951878	0.96091793	-3.00101016
O	2.70086391	-0.20479792	-2.95256969
C	0.64713417	2.76488314	-3.35756841
O	-0.49365632	2.65219746	-3.53904253
P	5.07926492	2.68797831	-2.62811236
C	5.90045576	1.68026342	-3.96730308
C	7.41743548	1.78377176	-4.18098704
H	5.38692052	1.95991047	-4.89397512
H	5.60575616	0.64181048	-3.76925844
H	7.71389264	1.12672745	-5.00624618
H	7.71921262	2.80069903	-4.45167210
H	7.98846727	1.48226725	-3.29981027
C	5.98487901	4.32246828	-2.54608119
C	7.34282202	4.40602785	-1.83346589

H	5.28800300	5.02015801	-2.06676242
H	6.07670174	4.66184746	-3.58640960
H	7.71857343	5.43448366	-1.88002300
H	7.25828558	4.13833927	-0.77575562
H	8.09579849	3.75878014	-2.28856487
C	5.40918348	1.80414786	-1.01605636
C	6.75396861	1.09570795	-0.79632030
H	4.60129137	1.06907418	-0.92954380
H	5.22970571	2.54460408	-0.22570614
H	6.75880767	0.62601019	0.19361108
H	6.91289408	0.30079551	-1.53116826
H	7.60525991	1.77910721	-0.84141946

Table S7-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PEt$_3$)]$^+$ (7) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	606.7	16.5	2.04	0.0172	115 →116(+99%)
2	559.9	17.9	2.21	0.0117	114 →116(+99%)
3	500.2	20	2.48	0.0054	115 →117(+89%) 113 →116(+7%)
4	472.5	21.2	2.62	0.0011	114 →117(+87%) 113 →116(+12%)
5	428.7	23.3	2.89	0.0935	113 →116(+75%) 115 →117(9%) 114 →117(9%)
6	408.4	24.5	3.04	0.0203	113 →117(+98%)
7	363.3	27.5	3.41	0.0362	115 →118(+89%) 114 →118(5%)
8	358.1	27.9	3.46	0.0079	115 →119(+63%) 114 →119(33%)
9	348.0	28.7	3.56	0.0170	114 →118(+88%) 112 →116(+6%)
10	335.9	29.8	3.69	0.0354	114 →119(+62%) 115 →119(+29%)
11	314.0	31.8	3.95	0.3969	112 →116(+73%) 113 →119(+14%)
12	309.0	32.4	4.01	0.0545	113 →118(+85%) 113 →119(7%)
13	307.9	32.5	4.03	0.1195	113 →119(+77%) 113 →118(+10%) 112 →116(8%)
14	301.6	33.2	4.11	0.0163	115 →121(+90%)
15	296.9	33.7	4.18	0.0000	114 →121(+71%) 115 →120(23%)
16	293.4	34.1	4.23	0.0371	115 →120(+67%) 114 →121(+24%)
17	292.9	34.1	4.23	0.0326	111 →116(+96%)
18	283.9	35.2	4.37	0.0331	115 →122(+83%) 113 →121(+9%)
19	283.6	35.3	4.37	0.0069	114 →120(+91%)
20	278.4	35.9	4.45	0.1285	112 →117(+88%)
21	275.1	36.4	4.51	0.0009	115 →123(+83%)
22	273.7	36.5	4.53	0.0013	111 →117(+94%)
23	270.3	37	4.59	0.0004	114 →122(+65%) 113 →121(+23%)
24	268.8	37.2	4.61	0.0065	114 →123(+86%)

25	258.4	38.7	4.80	0.0103	110 ⟶116(+69%) 113 ⟶ 120(+24%)
26	255.7	39.1	4.85	0.0018	113 ⟶122(+92%)
27	251.9	39.7	4.92	0.2163	113 ⟶120(+64%) 110 ⟶116(18%)
28	247.8	40.3	5.00	0.2345	110 ⟶117(+92%)
29	242.4	41.3	5.12	0.0119	115 ⟶124(+31%) 112 ⟶119(25%) 114 ⟶125(12%) 113 ⟶121(+9%) 115 ⟶125(5%)
30	241.5	41.4	5.13	0.0386	114 ⟶125(+22%) 115 ⟶ 124(+19%) 113 ⟶121(16%) 112 ⟶119(11%) 115 ⟶125(+10%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# ⟶MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S7-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PEt$_3$)]$^+$ (7) in acetonitrile.

	E_{VER} [b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	650.4	15.4	1.91	0.0000	115 →116(+94%)
2	581.4	17.2	2.13	0.0000	114 →116(+95%)
3	553.5	18.1	2.24	0.0000	115 →117(+81%) 114 →117(+9%)
4	512.8	19.5	2.42	0.0000	113 →116(+94%)
5	486.8	20.5	2.55	0.0000	114 →117(+86%) 115 →117(11%)
6	427.5	23.4	2.90	0.0000	113 →117(+95%)
7	397.2	25.2	3.12	0.0000	115 →119(+39%) 112 →117(24%) 114 →119(+6%) 115 →117(6%)
8	388.7	25.7	3.19	0.0000	115 →118(+71%) 114 →118(+8%)
9	385.8	25.9	3.21	0.0000	112 →117(+44%) 115 → 119(+40%)
10	376.8	26.5	3.29	0.0000	112 →116(+77%) 115 →118(9%) 110 →117(6%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S7-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PEt$_3$)]$^+$ (7) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	PEt$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
109 (O)													
110 (O)	-10.68	0.00	0.09	-0.01	0.00	0.00	0.00	0.02	0.04	0.89	97.59	0.33	1.04
111 (O)	-10.12	1.79	4.48	0.00	0.12	1.26	0.53	0.05	6.19	2.12	5.26	13.22	64.99
112 (O)	-9.91	0.00	0.00	0.00	0.01	0.06	0.76	0.02	0.03	0.00	98.13	0.18	0.81
113 (O)	-8.72	0.01	-0.05	0.21	0.00	0.01	0.03	1.42	0.08	54.67	16.79	22.90	3.94
114 (O)	-8.24	0.00	0.07	0.00	3.04	1.98	31.81	28.01	1.11	0.47	12.19	20.80	0.52
115 (O)	-8.13	0.00	0.04	0.00	1.66	2.82	25.88	36.03	0.49	1.25	14.06	16.03	1.73
HOMO-LUMO gap: 2.594 eV (20920.4 cm^{-1})													
116 (V)	-5.54	0.01	0.96	0.05	0.02	0.05	0.02	0.09	0.05	2.99	88.29	4.65	2.81
117 (V)	-5.22	0.00	0.00	0.00	0.00	0.03	0.22	2.57	0.06	0.02	95.72	1.12	0.20
118 (V)	-4.13	0.00	0.52	0.00	0.02	0.01	0.04	0.00	0.00	0.03	98.77	0.07	0.54
119 (V)	-4.06	0.00	0.01	0.00	0.32	0.21	2.03	0.11	0.06	0.01	92.94	3.77	0.55
120 (V)	-3.43	0.00	0.20	0.01	0.01	0.01	0.00	0.01	0.00	0.18	97.74	1.46	0.40
121 (V)	-2.76	0.01	2.38	20.35	0.27	2.63	0.00	0.00	3.47	0.29	2.60	52.66	15.33
122 (V)	-2.56	0.00	0.66	0.09	27.78	0.26	5.02	5.99	0.20	0.12	3.07	40.12	16.70
123 (V)	-2.39	0.00	0.03	0.00	0.38	0.03	0.41	0.00	0.03	0.00	98.53	0.13	0.47
124 (V)	-2.20	1.33	15.75	8.63	0.29	29.87	2.50	0.00	0.21	2.12	20.44	13.59	5.27
125 (V)	-1.63	0.28	1.21	0.15	0.40	0.02	1.42	12.82	0.25	0.12	10.04	65.90	7.39

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one phosphorus (P) atom, six carbon, and fifteen hydrogen atoms present in the triethylphosphine (PEt_3) ligand.

Table S8-A. Optimized geometry of *mer*,*cis*-[Re(tpy-κ^3*N*)$(CO)_2(PPh_3)]^+$ (8) in the singlet ground state with E(B3LYP) = – 2084.4196 au.

Re	0.17309688	-0.10467847	-0.02318131
N	-1.94717145	-0.29405216	0.38393341
C	-2.93013561	-0.50719729	-0.51622391
C	-2.30401278	-0.10021682	1.69621252
C	-4.27608047	-0.56428843	-0.17315072
H	-2.60643846	-0.62455315	-1.54494715
C	-3.64002952	-0.15919827	2.09833900
C	-4.64101765	-0.39792915	1.16144284
H	-5.01851723	-0.73609603	-0.94910557
H	-3.89828721	-0.00856999	3.14317802
H	-5.68434390	-0.44113371	1.46756108
N	0.01681921	0.26551481	2.04404262
C	-1.20202424	0.21721686	2.62818302
C	1.13555922	0.58066747	2.73651464
C	-1.33317405	0.49717908	3.99089938
C	1.05105656	0.88008814	4.09883854
C	-0.19480911	0.83315413	4.72263083
H	-2.30345735	0.46492448	4.47834480
H	1.93637128	1.14771270	4.66904598
H	-0.28003210	1.06348703	5.78277516
C	0.37471036	-0.45586480	-1.89750777
O	0.52957895	-0.65561486	-3.04030102
C	-0.05784675	1.75411668	-0.48758088
O	-0.19788927	2.86300436	-0.80223497
C	2.36624893	0.58423046	1.91972001
C	3.62226241	0.89926717	2.44159526
N	2.20512339	0.27585469	0.59034105
C	4.73814049	0.91991624	1.60931773
H	3.72679276	1.13753345	3.49692851
C	3.29409249	0.30620631	-0.20617147
C	4.56551876	0.62336059	0.25909517
H	5.71919435	1.16969132	2.00825946
H	3.11811464	0.07297637	-1.25092385
H	5.40109464	0.63432400	-0.43694450
P	0.46915700	-2.65139551	0.41587278
C	2.15576525	-3.33881676	0.08440573
C	2.77377054	-4.29735655	0.90290604
C	2.79118836	-2.95834911	-1.10979021
C	4.00928642	-4.84166574	0.54630131
H	2.29514901	-4.63082352	1.82086658
C	4.02062196	-3.51242860	-1.46817906
H	2.31353142	-2.24816882	-1.78223050
C	4.63699143	-4.44962226	-0.63688721
H	4.47635892	-5.58274018	1.19383467

H	4.49329344	-3.21513054	-2.40355408
H	5.59763064	-4.88064945	-0.91538916
C	-0.59137521	-3.83421910	-0.53056036
C	-0.63369407	-5.19118192	-0.16107845
C	-1.28904754	-3.42366777	-1.67372994
C	-1.37522064	-6.10465569	-0.90694259
H	-0.08384578	-5.53905152	0.71189889
C	-2.02654126	-4.34283531	-2.42528744
H	-1.23781053	-2.38920375	-1.99909970
C	-2.07567554	-5.68182539	-2.04078484
H	-1.40000192	-7.15154699	-0.60742487
H	-2.55554902	-4.00882672	-3.31694944
H	-2.64963230	-6.39874933	-2.62626441
C	0.10616322	-3.05413369	2.18137374
C	-1.16832335	-3.50210381	2.56742676
C	1.05900040	-2.79735095	3.18346258
C	-1.47074736	-3.71487944	3.91438419
H	-1.92493063	-3.70889912	1.81303864
C	0.75595275	-3.01619916	4.52796489
H	2.05433823	-2.44699728	2.91327026
C	-0.50933642	-3.47814268	4.89783242
H	-2.45894980	-4.07998264	4.19194283
H	1.51507704	-2.83473616	5.28810790
H	-0.74147346	-3.65861835	5.94656081

Table S8-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PPh$_3$)]$^+$ (8) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	579.5	17.3	2.14	0.0134	151 →152(+99%)
2	530.3	18.9	2.34	0.0128	150 →152(+99%)
3	481.1	20.8	2.58	0.0053	151 →153(+93%)
4	450.2	22.2	2.75	0.0017	150 →153(+85%) 149 →152(14%)
5	415.2	24.1	2.99	0.0813	149 →152(+76%) 150 →153(+11%) 151 →153(+6%)
6	391.1	25.6	3.17	0.0173	149 →153(+97%)
7	355.2	28.2	3.49	0.0179	151 →154(+90%)
8	351.0	28.5	3.53	0.0059	151 →155(+76%) 150 →155(19%)
9	340.3	29.4	3.64	0.0131	148 →152(+60%) 150 →154(23%) 147 →152(+11%)
10	337.2	29.7	3.68	0.0082	150 →154(+59%) 148 →152(+13%) 146 →152(8%) 147 →152(+8%) 150 →155(+5%)
11	326.8	30.4	3.77	0.0151	147 →152(+69%) 148 →152(16%)
12	327.6	30.5	3.78	0.0017	151 →156(+72%) 151 →157(+6%) 147 →152(+6%)
13	326.8	30.6	3.79	0.0271	150 →155(+65%) 151 →155(+17%)
14	319.1	31.3	3.89	0.0207	145 →152(+74%) 146 →152(+11%) 143 →152(6%)
15	316.7	31.6	3.92	0.2654	146 →152(+63%) 148 →153(9%) 150 →154(+8%)
16	313.0	32.0	3.96	0.0277	148 →153(+53%) 147 →153(+19%) 150 →156(+10%) 146 →152(+5%)
17	312.1	32.0	3.97	0.0218	150 →156(+59%) 150 →157(+9%) 148 →153(6%) 150 →162(5%)
18	305.5	32.7	4.06	0.1144	144 →152(+48%) 143 →152(29%)
19	304.6	32.8	4.07	0.0913	151 →157(+71%) 151 →156(9%) 151 →158(+7%)
20	303.1	33.0	4.09	0.0130	147 →153(+57%) 143 →152(15%) 148 →153(14%) 145 →153(+6%)
21	302.8	33.0	4.09	0.0165	144 →152(+43%) 143 →152(+36%) 147 →153(+6%)
22	301.2	33.2	4.12	0.0176	151 →158(+61%) 149 →154(+6%) 151 →157(6%)
23	300.4	33.3	4.13	0.0477	149 →155(+68%) 149 →154(22%)
24	299.2	33.4	4.14	0.0219	149 →154(+63%) 149 →155(+18%) 151 →158(9%)

25	295.0	33.9	4.20	0.0023	145 →153(+58%) 146 →153(+16%) 143 →153(11%) 148 →153(+6%)
26	292.2	34.2	4.24	0.0003	151 →162(+33%) 151 →159(17%) 151 →163(11%) 151 →165(6%) 150 →157(+5%) 151 →157(+5%)
27	289.8	34.5	4.28	0.0071	150 →157(+53%) 150 →156(17%) 150 →162(8%) 151 →162(5%)
28	289.2	34.6	4.29	0.0147	151 →159(+69%) 151 →165(8%) 151 →160(6%) 151 →162(+5%) 150 →157(+5%)
29	287.3	34.8	4.32	0.0171	146 →153(+61%) 142 →152(13%) 143 →153(+8%)
30	286.3	34.9	4.33	0.0026	150 →158(+51%) 150 →162(+8%) 150 →157(+6%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S8-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PPh$_3$)]$^+$ (8) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	616.6	16.2	2.01	0.0000	151 →152(+93%)
2	552.6	18.1	2.24	0.0000	150 →152(+94%)
3	528.2	18.9	2.35	0.0000	151 →153(+75%) 150 → 153(+12%)
4	485.2	20.6	2.56	0.0000	149 →152(+88%)
5	466.2	21.4	2.66	0.0000	150 →153(+80%) 151 →153(15%)
6	408.9	24.5	3.03	0.0000	149 →153(+86%)
7	391.1	25.6	3.17	0.0000	145 →153(+21%) 146 →153(19%) 143 →153(+9%) 150 →153(+6%) 151 →155(6%) 141 →152(+6%) 151 →153(+5%)
8	379.4	26.4	3.27	0.0000	145 →152(+22%) 146 →152(22%) 143 →152(+10%) 149 →153(9%) 151 →155(+8%) 141 →153(+6%)
9	379.1	26.4	3.27	0.0000	151 →155(+54%) 151 →154(10%) 150 →155(+9%) 145 →153(+6%)
10	373.4	26.8	3.32	0.0000	151 →154(+63%) 150 →154(+7%) 151 →155(+7%) 145 →152(5%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S8-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PPh$_3$)]$^+$ (8) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	PPh$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
143 (O)	-9.71	0.00	0.01	0.39	0.15	0.06	0.01	0.23	0.06	0.00	8.51	0.46	90.12
144 (O)	-9.47	0.00	0.05	0.00	0.00	0.02	0.09	0.00	0.03	0.25	9.08	0.12	90.35
145 (O)	-9.44	0.04	0.00	-0.02	0.03	0.05	0.01	0.48	0.02	0.02	2.28	0.50	96.60
146 (O)	-9.34	0.00	0.12	0.00	0.00	0.01	0.18	0.03	0.02	0.27	2.32	0.52	96.52
147 (O)	-9.27	0.00	0.03	0.01	0.00	0.01	0.06	0.00	0.07	0.44	37.06	0.17	62.15
148 (O)	-9.05	0.38	0.02	2.80	0.30	0.33	0.04	1.61	2.16	0.07	2.54	6.63	83.11
149 (O)	-8.70	0.03	0.00	0.03	0.03	7.21	0.40	44.77	2.38	1.67	12.29	25.03	6.17
150 (O)	-8.15	0.00	1.06	0.02	0.02	0.79	17.77	0.02	2.08	41.33	15.87	18.30	2.74
151 (O)	-7.98	0.00	2.78	0.06	0.05	2.08	42.25	2.19	4.29	15.73	7.91	19.46	3.20
HOMO-LUMO gap: 2.769 eV (22329.4 cm^{-1})													
152 (V)	-5.21	0.03	0.01	0.42	0.14	0.09	0.03	2.10	0.00	0.03	87.27	4.05	5.83
153 (V)	-5.11	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.14	1.55	90.26	0.66	7.37
154 (V)	-4.04	0.00	0.01	0.51	0.12	0.01	0.00	-0.02	0.04	0.00	92.20	0.06	7.07
155 (V)	-3.97	0.00	0.48	0.01	0.01	0.00	0.00	0.04	0.23	2.29	89.84	4.68	2.43
156 (V)	-3.62	-0.27	0.08	2.94	0.13	0.29	0.01	0.76	0.58	0.03	41.16	3.06	51.22
157 (V)	-3.29	-0.14	0.08	1.98	0.05	0.30	0.00	0.46	0.97	0.07	24.95	5.21	66.07
158 (V)	-3.17	0.00	0.60	0.11	0.10	0.03	0.09	0.01	0.00	-0.02	17.08	0.67	81.34
159 (V)	-2.95	-0.11	0.02	0.74	4.38	0.93	0.02	0.06	0.88	0.13	14.49	8.49	69.98
161 (V)	-2.82	0.20	0.11	0.09	0.37	0.21	0.04	0.07	0.09	0.02	26.73	0.47	71.59
162 (V)	-2.56	0.00	0.15	0.12	0.13	0.00	0.45	0.02	0.02	0.23	13.91	1.31	83.76
163 (V)	-2.37	-0.48	0.00	0.12	10.59	4.65	0.06	0.14	2.16	0.32	4.41	43.11	34.91
164 (V)	-2.20	-0.01	10.63	0.25	0.02	0.06	3.86	0.04	0.08	1.68	51.10	14.32	17.99

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one phosphorus (P) atom, eighteen carbon, and fifteen hydrogen atoms present in the triphenylphosphine (PPh_3) ligand.

Table S9-A. Optimized geometry of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2(P(OMe)_3)]^+$ (9) in the singlet ground state with E(B3LYP) = – 1734.9320 au.

Re	0.32835803	-0.08430962	-0.15601948
N	-1.80048115	-0.29253322	0.14059302
C	-2.72843818	-0.49782491	-0.81743196
C	-2.22623861	-0.13257189	1.43518860
C	-4.09113496	-0.56568803	-0.54891223
H	-2.34353933	-0.60137867	-1.82779762
C	-3.58209398	-0.19801484	1.76221740
C	-4.52900575	-0.41876296	0.76615688
H	-4.78991283	-0.72856261	-1.36634453
H	-3.89851242	-0.06659747	2.79365581
H	-5.58769793	-0.46636109	1.01308737
N	0.07131068	0.23997460	1.90975787
C	-1.17089552	0.13777026	2.43476500
C	1.16020803	0.48942755	2.67058688
C	-1.35898811	0.29372835	3.81059463
C	1.02028398	0.65614185	4.05081234
C	-0.25066432	0.55537553	4.61584443
H	-2.34751887	0.21189451	4.25388137
H	1.88193495	0.85776785	4.68112339
H	-0.37822534	0.68064347	5.68929213
C	0.56942078	-0.50443767	-2.01600786
O	0.71945960	-0.77676941	-3.14248349
C	0.09184247	1.77690376	-0.67782354
O	-0.04079667	2.87303762	-1.02826328
C	2.42327137	0.56930235	1.90672590
C	3.64747747	0.88964771	2.49665891
N	2.32668231	0.33414527	0.55847878
C	4.79474004	0.98447471	1.71406709
H	3.70257945	1.07421281	3.56629496
C	3.44364102	0.43884656	-0.19139406
C	4.68660878	0.75986691	0.34270283
H	5.75130647	1.23766755	2.16679631
H	3.31212566	0.26142953	-1.25460441
H	5.54922061	0.83356096	-0.31568824
P	0.63678296	-2.48568508	0.35943994
O	1.42921711	-3.47122365	-0.67085602
O	-0.69070498	-3.40083607	0.57998617
O	1.36578544	-2.66871181	1.79592262
C	1.55562952	-3.97239509	2.40006170
H	2.22985290	-3.81834334	3.24706612
H	0.59428995	-4.36577831	2.74558584
H	2.00745694	-4.66723747	1.68333936
C	2.69431955	-3.12078703	-1.26260551
H	2.56307952	-2.33356870	-2.01302924

H	3.41354296	-2.80420084	-0.49607418
H	3.06135242	-4.02897798	-1.74939690
C	-1.41176806	-3.97649216	-0.52687573
H	-0.79826884	-4.73096144	-1.02954561
H	-2.30413299	-4.44138956	-0.09818359
H	-1.71025460	-3.20387022	-1.24760684

Table S9-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OMe)$_3$)]$^+$ (9) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	557.4	17.9	2.22	0.0095	115 →116(+99%)
2	520.8	19.2	2.38	0.0189	114 →116(+99%)
3	465.0	21.5	2.67	0.0044	115 →117(+93%)
4	439.9	22.7	2.82	0.0046	114 →117(+85%) 113 → 116(+13%)
5	399.0	25.1	3.11	0.0861	113 →116(+79%) 114 →117(10%)
6	375.7	26.6	3.30	0.0152	113 →117(+97%)
7	346.8	28.8	3.57	0.0085	115 →118(+91%)
8	344.7	29.0	3.60	0.0044	115 →119(+82%) 114 → 119(+14%)
9	334.2	29.9	3.71	0.0001	114 →118(+74%) 112 → 116(+20%)
10	321.3	31.1	3.86	0.0383	114 →119(+73%) 115 →119(12%) 114 →118(5%)
11	311.1	32.1	3.98	0.4941	112 →116(+61%) 114 →118(13%) 115 →121(7%)
12	306.0	32.7	4.05	0.1218	115 →121(+59%) 115 →122(10%) 112 →116(+9%) 115 →120(+8%)
13	301.8	33.1	4.11	0.0041	114 →121(+58%) 114 →122(15%) 114 →120(+14%) 115 →121(6%)
14	294.8	33.9	4.21	0.0214	115 →122(+68%) 115 → 121(+19%) 115 →120(6%)
15	291.6	34.3	4.25	0.0174	113 →118(+52%) 113 →119(43%)
16	290.8	34.4	4.26	0.0092	113 →119(+52%) 113 → 118(+39%) 112 →117(6%)
17	283.8	35.2	4.37	0.0118	115 →120(+69%) 115 → 122(+13%) 115 →123(6%)
18	281.1	35.6	4.41	0.0039	114 →122(+42%) 114 → 121(+19%) 113 →121(15%)
19	276.8	36.1	4.48	0.1389	112 →117(+77%) 111 → 116(+12%) 113 →118(+6%)
20	275.0	36.4	4.51	0.0349	111 →116(+78%) 112 →117(7%) 110 →116(5%)
21	273.5	36.6	4.53	0.0166	114 →120(+65%) 114 → 122(+16%) 114 →121(5%)
22	267.0	37.5	4.64	0.000	115 →123(+84%) 115 →120(+7%)
23	263.1	38.0	4.71	0.0016	114 →123(+46%) 113 →122(32%) 113 →121(11%)
24	260.7	38.9	4.76	0.0061	114 →123(+37%) 113 → 122(+35%) 113 →121(+15%)

25	257.0	38.9	4.82	0.0449	111 →117(+94%)
26	255.4	39.2	4.85	0.0877	110 →116(+84%)
27	244.5	40.9	5.07	0.2037	110 →117(+94%)
28	242.6	41.2	5.11	0.1022	113 →120(+48%) 112 → 119(+19%)
29	240.8	41.5	5.15	0.0039	115 →126(+28%) 112 → 119(+24%) 109 →116(+18%) 113 →120(5%) 108 →116(+5%)
30	240.6	41.6	5.15	0.0065	115 →126(+51%) 109 →116(16%) 112 →119(7%) 113 →120(+6%)

[a] # is the state. [b] E_{VER} is the energy of the vertical transition. [c] f is the oscillator strength. [d] Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S9-C. Calculated triplet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OMe)$_3$)]$^+$ (9) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	588.0	17.0	2.11	0.0000	115 →116(+86%) 114 →116(12%)
2	545.5	18.3	2.27	0.0000	114 →116(+86%) 115 →116(+13%)
3	508.0	19.7	2.44	0.0000	115 →117(+58%) 114 →117(25%) 112 →117(+8%)
4	468.4	21.3	2.65	0.0000	113 →116(+76%) 115 →117(+14%)
5	459.6	21.8	2.70	0.0000	114 →117(+63%) 115 →117(+23%) 113 →116(12%)
6	395.7	25.3	3.13	0.0000	113 →117(+70%) 112 →116(25%)
7	384.5	26.0	3.22	0.0000	112 →117(+58%) 114 →117(+8%) 113 →116(+7%) 110 →116(6%)
8	374.3	26.7	3.31	0.0000	112 →116(+56%) 113 →117(+28%)
9	368.1	27.2	3.37	0.0000	115 →119(+43%) 114 →119(20%) 115 →118(14%) 112 →117(8%) 114 →118(+6%)
10	364.1	27.5	3.41	0.0000	115 →118(+48%) 114 →118(16%) 115 →119(+13%) 112 →116(+6%) 114 →119(6%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S9-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OMe)$_3$)]$^+$ (9) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	P(OMe)$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
108 (O)	-11.23	0.00	0.07	0.02	0.01	0.01	0.00	0.04	0.02	0.23	26.34	0.37	72.91
109 (O)	-10.94	0.00	-0.04	0.00	0.03	0.03	-0.01	0.03	0.00	0.06	8.48	0.04	91.37
110 (O)	-10.70	0.06	0.01	0.29	0.09	-0.04	0.02	1.38	0.04	0.06	76.94	0.80	20.35
111 (O)	-10.14	0.85	0.04	1.83	0.38	1.67	0.03	0.16	2.54	0.05	18.39	4.16	69.90
112 (O)	-9.90	0.14	0.03	0.26	0.04	0.20	0.00	0.02	0.11	1.09	85.98	0.57	11.56
113 (O)	-9.03	0.01	0.00	-0.01	0.12	8.61	0.28	44.34	3.09	0.55	16.32	23.58	3.11
114 (O)	-8.54	0.01	1.86	0.05	0.00	0.02	33.21	0.09	1.01	29.58	14.44	18.79	0.96
115 (O)	-8.39	-0.01	2.95	-0.02	0.00	0.00	31.23	0.63	1.20	32.66	12.22	17.48	1.65
HOMO-LUMO gap: 2.727 eV (21995.8 cm^{-1})													
116 (V)	-5.66	0.01	0.04	1.36	0.19	0.55	0.02	1.20	0.72	0.03	89.41	4.18	2.29
117 (V)	-5.26	0.00	0.01	0.02	0.00	0.01	0.02	0.01	0.08	2.29	96.48	0.92	0.18
118 (V)	-4.25	0.02	0.26	0.24	0.08	0.00	0.01	-0.01	0.15	0.72	95.53	1.26	1.73
119 (V)	-4.09	0.00	0.30	0.30	0.00	0.00	0.01	0.00	0.01	1.23	95.30	2.65	0.20
120 (V)	-3.48	0.00	0.20	0.22	0.01	0.05	0.05	0.11	0.09	0.00	96.09	2.29	0.89
121 (V)	-3.21	0.08	0.39	4.74	15.84	4.61	0.12	0.60	-0.13	-0.01	2.24	41.25	30.28
122 (V)	-3.08	-0.07	21.88	0.23	0.87	0.26	5.97	0.00	0.14	1.26	2.54	30.41	36.51
126 (V)	-1.81	7.33	-0.01	2.67	1.78	9.19	0.35	5.09	7.82	0.13	16.66	20.06	28.93

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one phosphorus (P) atom, three oxygen, three carbon, and nine hydrogen atoms present in the trimethylphosphite ($POMe_3$) ligand.

Table S10-A. Optimized geometry of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2(P(OEt)_3)]^+$ (10) in the singlet ground state with E(B3LYP) = – 1852.8749 au.

Re	0.41284227	-0.13412476	-0.21022674
N	-1.72377568	-0.42889321	-0.18271138
C	-2.52069965	-0.62863281	-1.25341638
C	-2.30847076	-0.34018905	1.05566658
C	-3.90164999	-0.75920618	-1.15518463
H	-2.01341453	-0.67499992	-2.21258448
C	-3.68995240	-0.46923330	1.21270964
C	-4.50041745	-0.68340492	0.10152374
H	-4.48967921	-0.91360802	-2.05707053
H	-4.13296384	-0.39284071	2.20224465
H	-5.57823720	-0.78011077	0.21573427
N	-0.10153206	0.09205768	1.81902670
C	-1.39270862	-0.07578445	2.18550081
C	0.87784810	0.34461144	2.71556948
C	-1.75018423	0.01403227	3.53331281
C	0.56725992	0.44621538	4.07421550
C	-0.75735652	0.27824054	4.47664264
H	-2.78079008	-0.12041510	3.84987985
H	1.33882973	0.64987661	4.81153493
H	-1.01751122	0.35309041	5.53068496
C	0.88877393	-0.47415159	-2.04096037
O	1.17992326	-0.70005409	-3.14996273
C	0.17047114	1.73704481	-0.68943016
O	0.03917961	2.84166496	-1.01420830
C	2.21888441	0.50049512	2.11394317
C	3.34988062	0.83896883	2.85941453
N	2.29344694	0.31920784	0.75592858
C	4.57770643	1.00725577	2.22571137
H	3.26886047	0.98069466	3.93393823
C	3.48731274	0.49391215	0.15156144
C	4.64344562	0.83607086	0.84391019
H	5.46220302	1.27551189	2.80000707
H	3.49121155	0.35588138	-0.92555993
H	5.57500170	0.96757645	0.29808286
P	0.74626543	-2.54923107	0.25085350
O	1.70422128	-3.45685038	-0.70563414
O	-0.56754450	-3.50845842	0.25613907
O	1.28609050	-2.76281292	1.76406198
C	1.44920796	-4.08796331	2.35780817
H	0.45193371	-4.52007854	2.50053331
H	2.00719882	-4.72167799	1.65688625
C	3.04312447	-3.05281709	-1.09552111
H	2.97272033	-2.15955054	-1.72849976
H	3.61965115	-2.80627123	-0.19226740

C	-1.12723509	-4.05917075	-0.96687335
H	-0.40548812	-4.76802581	-1.38874348
H	-1.27809259	-3.24817711	-1.69431661
C	3.67273636	-4.20822530	-1.85147080
H	4.68762428	-3.93480773	-2.16920310
H	3.73607799	-5.10307578	-1.22002511
H	3.08516502	-4.45007969	-2.74548377
C	2.18717441	-3.92169670	3.67216256
H	1.62478721	-3.27357679	4.35644322
H	2.31298502	-4.90106515	4.15251435
H	3.18182451	-3.48610474	3.51328668
C	-2.43890063	-4.73511526	-0.61561084
H	-2.87676465	-5.18440070	-1.51681548
H	-2.28011685	-5.53054891	0.12293527
H	-3.15562741	-4.01366366	-0.20288007

Table S10-B. Calculated singlet excited states of for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OEt)$_3$)]$^+$ (10) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	561.1	17.8	2.21	0.01	127 →128(+99%)
2	524.5	19.1	2.36	0.0183	126 →128(+99%)
3	467.9	21.4	2.65	0.0046	127 →129(+93%)
4	443.1	22.6	2.8	0.0042	126 →129(+85%) 125 →128(13%)
5	401.7	24.9	3.09	0.0851	125 →128(+78%) 126 → 129(+10%)
6	378.5	26.4	3.28	0.0158	125 →129(+97%)
7	348.6	28.7	3.56	0.0098	127 →130(+90%)
8	346.2	28.9	3.58	0.005	127 →131(+80%) 126 →131(15%)
9	335.5	29.8	3.7	0.0008	126 →130(+74%) 124 →128(18%) 126 →131(+7%)
10	322.9	31	3.84	0.0373	126 →131(+70%) 127 → 131(+13%) 126 →130(7%)
11	311.3	32.1	3.98	0.5205	124 →128(+67%) 126 → 130(+11%)
12	305.3	32.8	4.06	0.0803	127 →133(+68%) 127 →134(7%) 127 →132(6%) 126 →133(6%) 124 →128(5%)
13	301.2	33.2	4.12	0.0028	126 →133(+65%) 126 →134(11%) 126 →132(10%) 127 →133(+7%)
14	293.7	34.1	4.22	0.0193	127 →134(+66%) 127 → 133(+11%) 125 →130(+9%) 127 →132(+7%)
15	293.4	34.1	4.23	0.0203	125 →130(+51%) 125 →131(39%)
16	292.2	34.2	4.24	0.012	125 →131(+56%) 125 → 130(+33%)
17	284.7	35.1	4.36	0.0112	127 →132(+73%) 127 →134(12%) 127 →135(5%)
18	281.3	35.6	4.41	0.0127	123 →128(+67%) 126 →134(16%)
19	279.5	35.8	4.44	0.0186	126 →134(+29%) 123 → 128(+27%) 125 →133(+14%) 126 → 133(+11%) 126 →132(+7%)
20	276.8	36.1	4.48	0.1502	124 →129(+83%) 125 →130(+6%)
21	274.5	36.4	4.52	0.0155	126 →132(+68%) 126 →134(15%)

22	267.3	37.4	4.64	0.0000	127 →135(+85%) 127 →132(+6%)
23	263.1	38	4.71	0.0041	126 →135(+61%) 125 →134(22%)
24	261.4	38.3	4.74	0.0232	123 →129(+95%)
25	260.4	38.4	4.76	0.004	125 →134(+51%) 126 → 135(+23%) 125 →133(+15%)
26	255.9	39.1	4.85	0.0802	122 →128(+86%)
27	245.4	40.8	5.05	0.2152	122 →129(+93%)
28	244.3	40.9	5.08	0.0023	121 →128(+87%) 125 →132(6%)
29	243.3	41.1	5.1	0.1087	125 →132(+51%) 124 → 131(+17%)
30	240.8	41.5	5.15	0.0209	124 →131(+25%) 124 →130(21%) 125 →132(11%) 120 →128(+10%) 127 →138(7%) 119 →128(5%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]f is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S10-C. Calculated triplet excited states of for *mer*,*cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OEt)$_3$)]$^+$ (10) in acetonitrile.

	E_{VER}[b]				
#[a]	nm	1000 cm^{-1}	eV	*f*[c]	Assignment; MO# →MO#[d]
1	592.9	16.9	2.09	0.0000	127 →128(+86%) 126 → 128(+11%)
2	548.9	18.2	2.26	0.0000	126 →128(+87%) 127 →128(12%)
3	511.8	19.5	2.42	0.0000	127 →129(+60%) 126 → 129(+23%) 124 →129(+8%)
4	471.9	21.2	2.63	0.0000	125 →128(+79%) 127 → 129(+12%)
5	462.5	21.6	2.68	0.0000	126 →129(+66%) 127 →129(23%) 125 →128(+9%)
6	398.0	25.1	3.12	0.0000	125 →129(+76%) 124 →128(20%)
7	385.4	25.9	3.22	0.0000	124 →129(+57%) 126 →129(8%) 122 →128(6%) 125 →128(+6%)
8	375.0	26.7	3.31	0.0000	124 →128(+58%) 125 → 129(+22%) 122 →129(6%)
9	370.4	27.0	3.35	0.0000	127 →131(+38%) 127 →130(19%) 126 →131(+16%) 124 →129(10%) 126 →130(7%)
10	366.0	27.3	3.39	0.0000	127 →130(+43%) 127 → 131(+19%) 126 →130(+13%) 124 → 128(+8%) 126 →131(+7%)

[a] # is the state. [b]E_{VER} is the energy of the vertical transition. [c]*f* is the oscillator strength. [d]Assignment; MO# →MO# is the occupied and the virtual orbitals that define the transition. The value and phase (+/–) of the transition coefficient for each transition is given in parentheses.

Table S10-D. The Fragment Analysis Based on Mullikan Populations for *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OEt)$_3$)]$^+$ (10) in the Singlet Ground State.[a]

molecular orbital	*E*, eV	Re									tpy[b]	CO[c]	P(OEt)$_3$[d]
		s	p_x	p_y	p_z	d_{x^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	$\sum_{s,p,d}$	$\sum_{s,p,d}$	$\sum_{s,p,d}$
119 (O)	-10.47	0.00	1.97	-0.02	0.13	0.03	0.02	0.19	0.03	1.84	82.51	2.70	10.59
120 (O)	-10.30	-0.02	0.00	0.01	1.11	0.20	0.02	2.34	-0.09	0.01	93.36	0.88	2.18
121 (O)	-9.65	-0.04	0.08	0.08	0.47	1.11	0.10	8.87	0.20	0.59	71.59	10.55	6.40
122 (O)	-9.22	-0.05	0.06	0.12	0.05	2.69	0.07	23.32	0.68	0.42	54.52	2.71	15.42
123 (O)	-8.85	0.01	0.36	0.03	0.11	0.07	0.25	0.37	2.15	22.34	51.53	1.39	21.38
124 (O)	-8.50	0.01	0.15	0.00	0.11	0.09	0.00	0.70	1.67	14.45	62.63	5.62	14.57
125 (O)	-8.25	0.00	3.36	0.18	0.88	9.91	50.68	1.22	2.16	0.86	28.26	0.68	1.81
126 (O)	-5.40	0.42	2.48	0.95	18.22	1.44	0.14	0.00	4.15	1.44	44.54	1.04	25.17
127 (O)	-5.16	0.45	8.96	2.84	7.31	-0.26	0.79	0.34	0.10	1.93	47.80	1.90	27.87
HOMO-LUMO gap: 1.069 eV (8618.8 cm^{-1})													
128 (V)	-4.09	0.72	3.26	1.51	6.82	0.35	0.74	0.13	3.46	-0.32	61.69	4.93	17.66
129 (V)	-3.98	0.16	3.80	0.26	8.70	-0.23	0.61	0.15	5.10	1.37	35.31	2.50	42.27
130 (V)	-3.60	1.54	5.44	0.22	0.24	0.00	1.14	0.99	1.11	1.72	23.30	0.48	63.84
131 (V)	-3.58	4.03	3.18	15.21	0.99	0.22	0.31	3.22	0.66	0.53	16.63	0.52	54.50
132 (V)	-3.14	0.00	0.48	0.02	0.00	0.03	0.16	0.00	0.50	0.60	90.73	2.15	5.33
133 (V)	-3.09	0.00	0.67	0.06	0.70	-0.14	0.09	-0.20	0.00	0.37	90.57	1.32	6.55
134 (V)	-2.62	3.77	0.52	2.99	0.26	-2.95	0.54	0.55	5.95	1.31	39.83	1.31	45.91
135 (V)	-2.52	2.72	0.16	-1.01	5.56	2.10	0.20	4.45	6.52	0.39	52.98	2.05	23.87
138 (V)	-2.16	-0.08	0.43	1.56	3.84	1.99	0.48	0.52	1.82	0.30	55.28	2.95	30.92

[a]The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). [b]Sum of the percent population for the three nitrogen, fifteen carbon, and eleven hydrogen atoms present in the terpyridine (2,2';6',2''-terpyridine (tpy); $C_{15}H_{11}N_3$) ligand. [c]Sum of the percent population for the two carbon and two oxygen atoms present in the two carbonyl (CO) ligands. [d]Sum of the percent population for the one phosphorus (P) atom, three oxygen, six carbon, and fifteen hydrogen atoms present in the triethylphosphite ($POMe_3$) ligand.

2. Electrochemical Parameterization

Table S11. Calculated values *E* and $\sum E_L(L)$.

vs. NHE	$\sum E_L(L)$	E_{CALC}	E_{OBS}	E_{DIFF}
Re(tpy-κ^3*N*)Cl_3 (Harman)	0.03	-0.92	-1.51	0.59
[Re(tpy-κ^3*N*)$(PPh_3)Cl_2$]$^+$ (Harman)	0.66	-0.45	-1.32	0.87
[Re(tpy-κ^3*N*)$(PPh_3)_2Cl$]$^+$ (Harman)	1.29	0.03	-0.99	1.02
[Re(tpy-κ^3*N*)(PPh_3)(bpy)]$^+$ (Harman)	1.66	0.31	-0.14	0.45
[Re(tpy-κ^3*N*)(PPh_3)(η^2-cyclohexenone)]$^+$ (Harman)	1.66	0.31	0.04	0.27
mer,*cis*-Re(tpy-κ^3N)$(CO)_2Cl$	1.99	0.56	0.239	0.32
mer,*cis*-[Re(tpy-κ^3N)$(CO)_2(PMe^3)$]$^+$	2.56	0.995	0.599	0.40
mer,*cis*-[Re(tpy-κ^3N)$(CO)_2(PEt_3)$]$^+$	2.57	1.003	0.609	0.39
mer,*cis*-[Re(tpy-κ^3N)$(CO)_2(P(OMe)_3)$]$^+$	2.65	1.064	0.679	0.39
mer,*cis*-[Re(tpy-κ^3N)$(CO)_2(PPh_3)$]$^+$	2.62	1.041	0.699	0.34

3. UV/vis Spectra

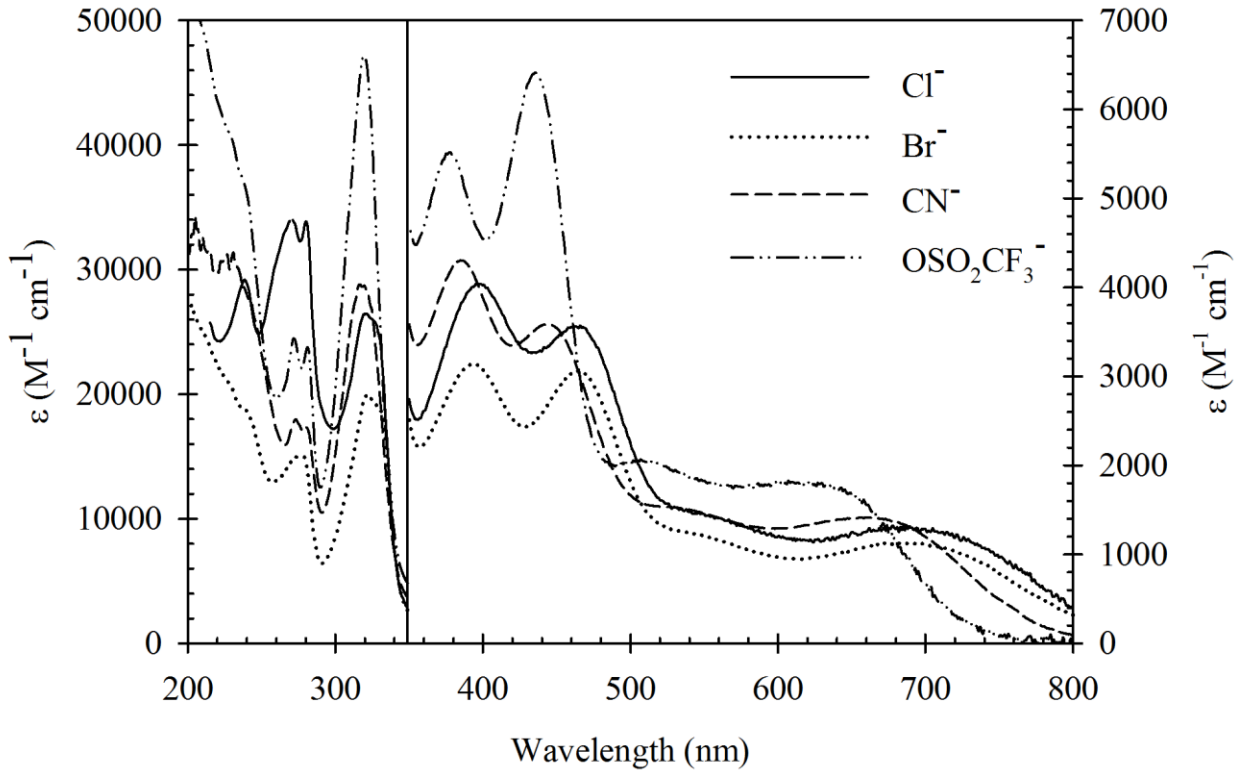


Figure S1. UV/vis spectra of *mer*,*cis*-Re(tpy-κ^3*N*)(CO)$_2$L (where L = Cl^-, Br^-, $OSO_2CF_3^-$ and CN^-) complexes.

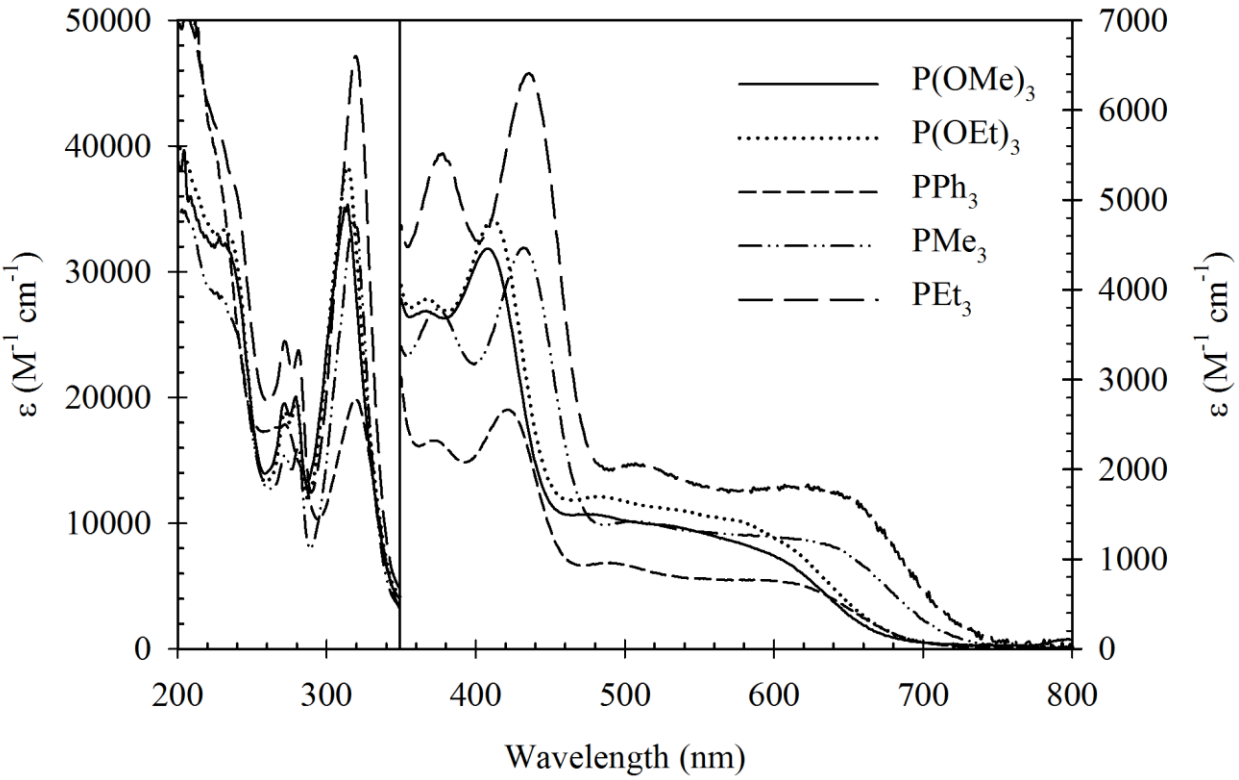


Figure S2. UV/vis spectra of *mer,cis*-[Re(tpy-κ^3*N*)$(CO)_2$(L)]$^+$ (where L = $P(OMe)_3$, $P(OEt)_3$, PPh_3, PMe_3 and PEt_3) complexes.

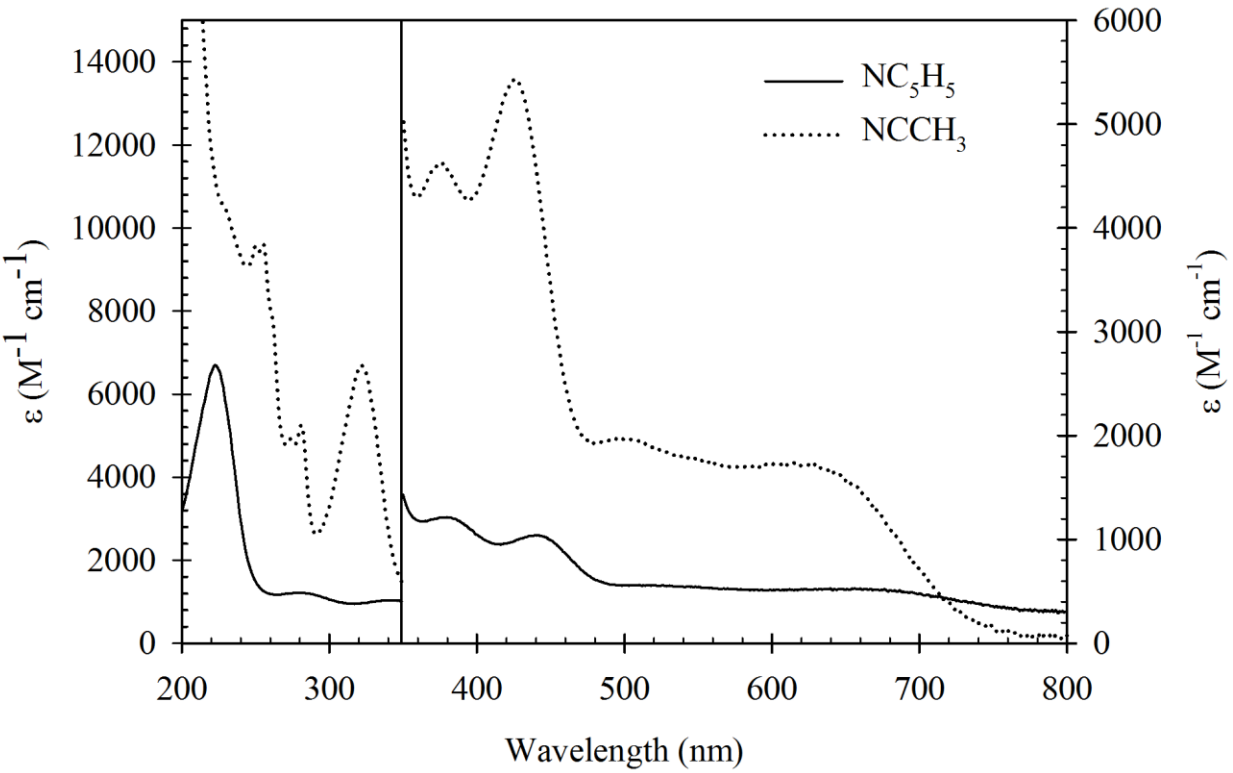
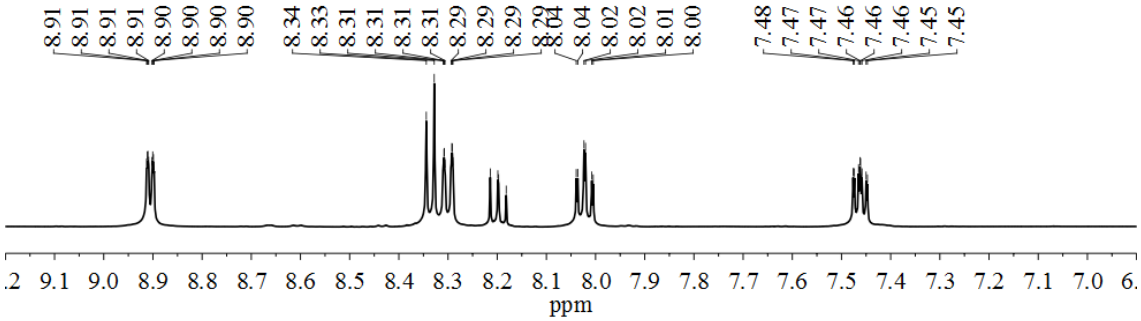
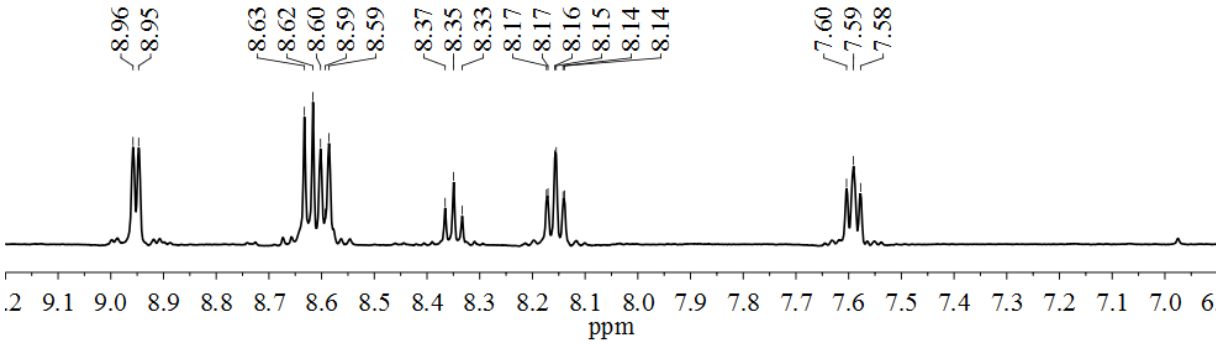


Figure S3. UV/vis spectra of *mer*,*cis*-[Re(tpy-κ^3*N*)(CO)$_2$(L)]$^+$ (where L = NC_5H_5 and $NCCH_3$) complexes.

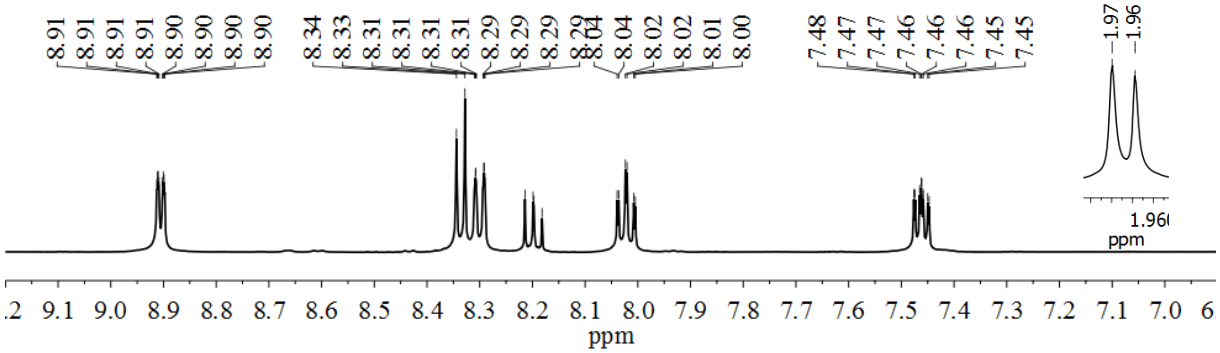
4. Nuclear Magnetic Resonance (NMR) Spectra



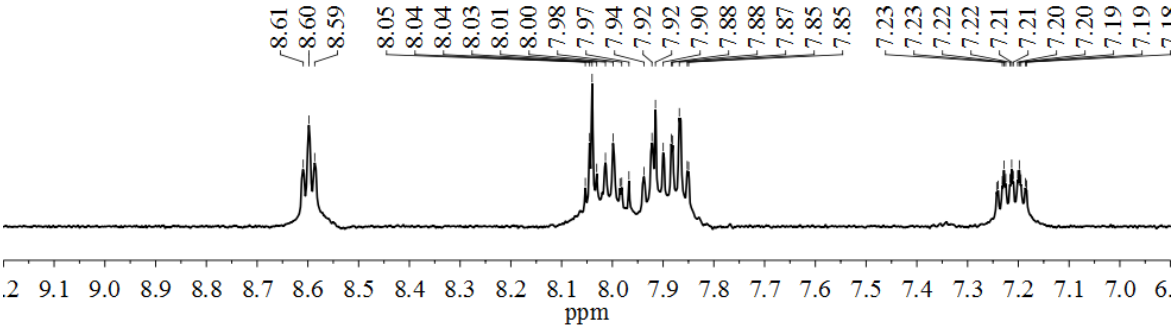
^{1}H NMR of *mer,cis*-Re(tpy-κ^{3}*N*)(CO)$_2$Cl (**1**) in DMSO-d_6.



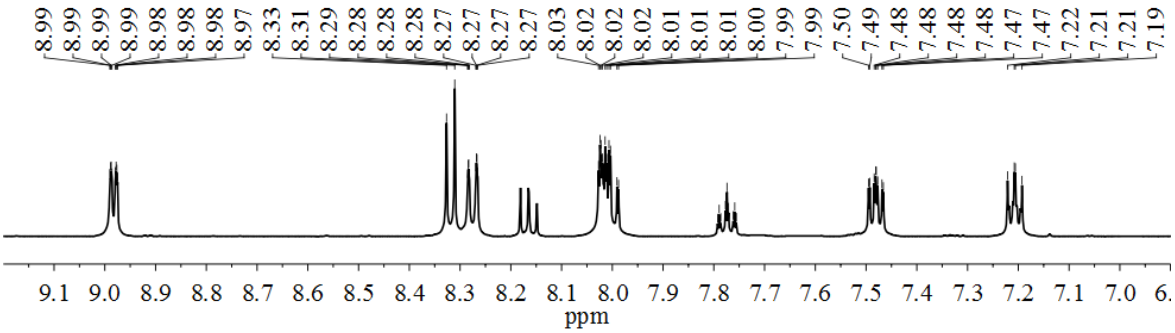
^{1}H NMR of *mer,cis*-Re(tpy-κ^{3}*N*)(CO)$_2$(CF$_3$SO$_3$) (**2**) in DMSO-d_6.



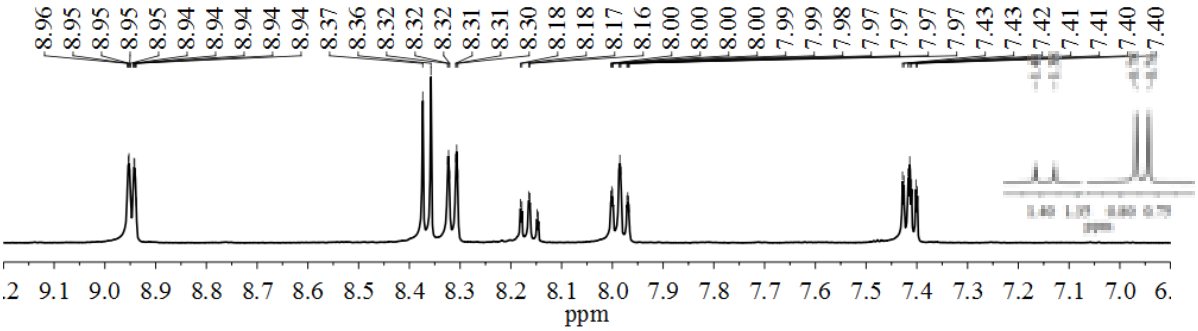
^{1}H NMR of *mer,cis*-[Re(tpy-κ^{3}*N*)(CO)$_2$(CH$_3$CN)]$^{+}$CF$_3$SO$_3^{-}$ (**3**) in acetonitrile-d_3.



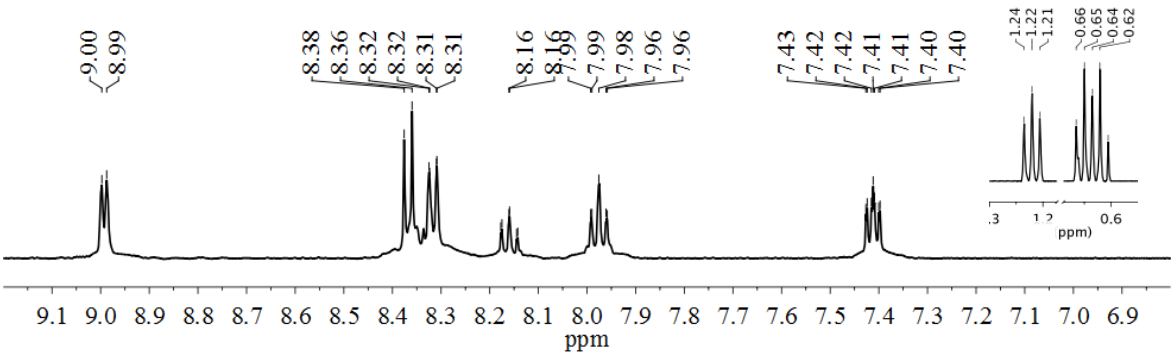
^{1}H NMR of *mer,cis*-Re(tpy-κ^3*N*)(CO)$_2$(CN) (**4**) in acetonitrile-d_3.



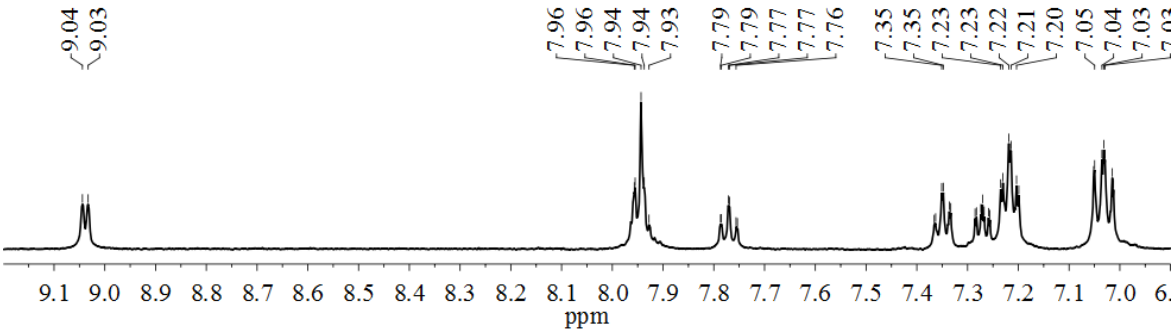
^{1}H NMR of *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(NC$_5$H$_5$)](CF$_3$SO$_3$) (**5**) in acetonitrile-d_3.



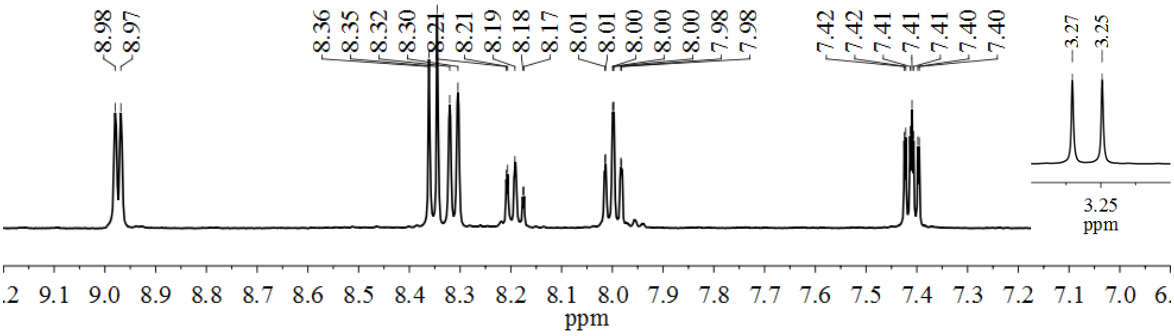
^{1}H NMR of *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PMe$_3$)](CF$_3$SO$_3$) (**6**) in acetonitrile-d_3.



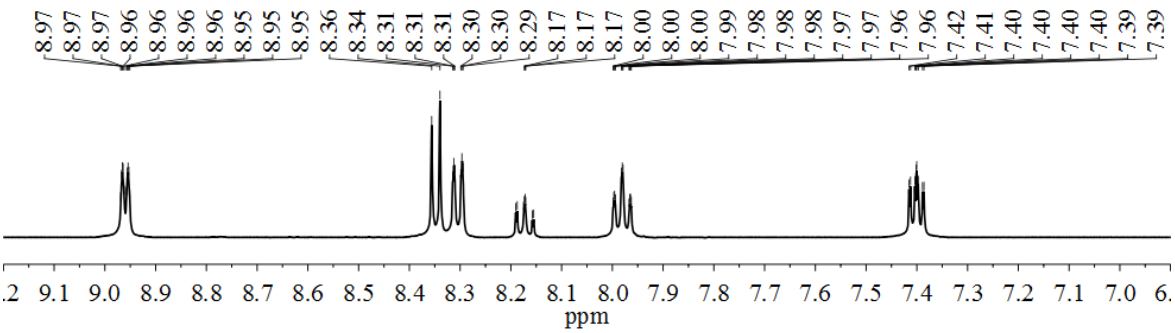
^{1}H NMR of *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PEt$_3$)](CF$_3$SO$_3$) (**7**) in acetonitrile-d_3.



^{1}H NMR of *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(PPh$_3$)](CF$_3$SO$_3$) (**8**) in acetonitrile-d_3.



^{1}H NMR of *mer,cis*-[Re(tpy-κ^3*N*)(CO)$_2$(P(OMe)$_3$)](CF$_3$SO$_3$) (**9**) in acetonitrile-d_3.



^{1}H NMR of *mer,cis*-[Re(tpy-κ^{3}*N*)(CO)$_2$(P(OEt)$_3$)](CF$_3$SO$_3$) (**10**) in acetonitrile-d_3.

Figure S4. Individual nuclear magnetic resonance (NMR) spectra for *mer*,*cis*-[Re(tpy-κ^{3}*N*)(CO)$_2$(L)]^{n} complexes.

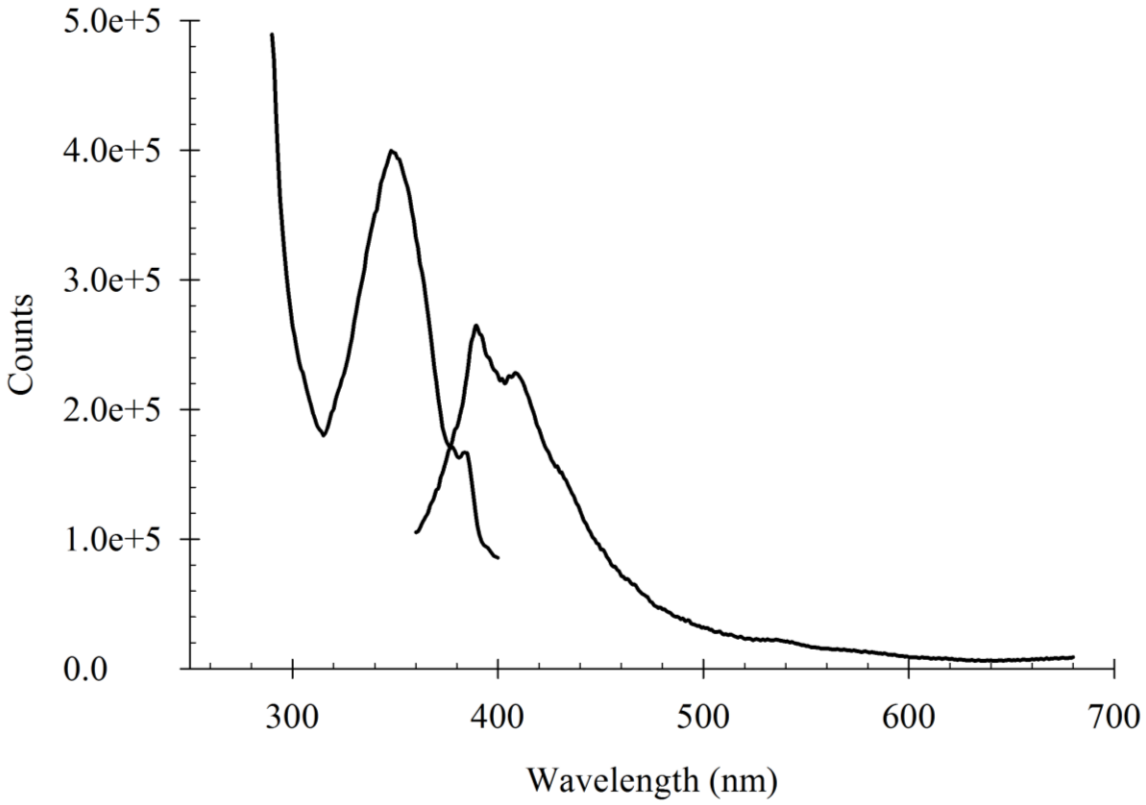


Figure S5. Excitation and emission spectra for *mer,cis*-[Re(tpy-κ^3N)$(CO)_2(P(OEt)_3)]^+$ (**10**) at 77 K. Excitation: λ_{EM}=425 nm, monitored 290–400 nm; Emission: λ_{EX}=389 nm.