Electronic Supporting Information (ESI)

Arylamino radical complexes of ruthenium and osmium: dual radical counter in a molecule

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Table S1 Crystallographic data for **1**, **2**·5/4toluene, **3** and $\mathbf{2}^{+}I_5^{-}\cdot\frac{1}{2}I_2$

complexes	**1**	**2**·5/4 toluene	**3**	$\mathbf{2}^{+}I_5^{-}\cdot\frac{1}{2}I_2$	$\mathbf{2}^{+}I_5^{-}\cdot\frac{1}{2}I_2$
T (K)	100(2)	100(2)	296(2)	135(2)	295(2)
formula	$C_{51}H_{38}ClNO_3P_2Ru$	$C_{59.75}H_{48.5}BrNO_3P_2Os$	$C_{50}H_{38}Cl_2NO_2P_2Ru$	$C_{51}H_{38}BrI_6NO_3P_2Os$	$C_{51}H_{38}BrI_6NO_3P_2Os$
fw	911.28	1160.54	918.72	1806.27	1806.27
crystal colour	Dark green	green	red	green	green
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	*P*-1	*P*-1
a (Å)	9.475(2)	15.239(3)	9.6319(5)	12.0307(4)	12.1385(8)
b (Å)	17.056(2)	24.074(5)	17.1986(9)	15.1139(5)	15.2266(10)
c (Å)	25.674(4)	26.860(6)	25.4291(13)	15.5317(5)	15.6850(10)
α ( )	90.00	90.00	90	73.6450(10)	73.594(3)
β ( )	98.548(13)	90.596(4)	98.221(2)	80.7900(10)	80.258(3)
γ ( )	90.00	90.00	90	77.2910(10)	77.265(3)
V (Å^3)	4103.0(12)	9853(4)	4169.2(4)	2628.91(15)	2694.8(3)
Z	4	8	4	2	2
2θ	69.98	62.26	55.32	51.52	53.03
calcd (g cm^{-3})	1.475	1.565	1.464	2.282	2.226
reflections collected	95037	287604	51063	28896	36736
unique reflections	18036	31509	9777	10031	11115
refection (I>2σ(I))	16336	23776	7824	9278	8479
λ (Å) /μ (mm^{-1})	0.71073/0.572	0.71073/3.512	0.71073/0.624	0.71073/6.811	0.71073/6.644
F(000)	1864	4632	1876	1668	1668
R1[a][I>2σ(I))]/GOF[b]	0.0311/1.084	0.0333/1.029	0.0310/1.010	0.0393/1.038	0.0706/1.046
R1[a] (all data)	0.0356	0.0595	0.0458	0.0430	0.0974
*w*R2[c] (I>2σ (I))	0.0798	0.0599	0.0739	0.1011	0.1890
no. of parameters/restr.	535/1	1257/162	526/0	596/9	587/0
residual density (eÅ^{-3})	1.116	1.655	0.480	2.556	3.306

Observation criterion: [a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$,
[c]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3$.

Table S2 The experimental bond parameters of **1**, **2**·5/4 toluene, $\mathbf{2}^{+}I_5^{-}\cdot\frac{1}{2}I_2$, **3** and calculated bond parameters of $\mathbf{1}^{Me}$, $\mathbf{1}^{Me+}$, $\mathbf{1}^{Me-}$, $\mathbf{2}^{Me}$, $\mathbf{2}^{Me+}$ and $\mathbf{2}^{Me-}$

bonds	**1**	$\mathbf{1}^{Me}$	$\mathbf{1}^{Me+}$	$\mathbf{1}^{Me-}$	**2**·5/4 toluene	$\mathbf{2}^{Me}$	$\mathbf{2}^{+}I_5^{-}\cdot\frac{1}{2}I_2$	$\mathbf{2}^{Me+}$	$\mathbf{2}^{Me-}$	**3**	$\mathbf{3}^{Me}$	$\mathbf{3}^{Me+}$
M-NH	2.031(2)	2.073	1.989	2.072	2.037(2)	2.066	1.978(5)	1.992	2.077	1.972(2)	1.993	1.899
M-O	2.090 (2)	2.136	2.128	2.110	2.094(2)	2.128	2.096(4)	2.127	2.109	2.015(2)	2.064	2.060
M-CO	1.833(2)	1.852	1.873	1.852	1.844(3)	1.851	1.915(6)	1.864	1.848			
M-PPh_3	2.405(1) 2.423(1)	2.424 2.425	2.475 2.474	2.403 2.400	2.383(1) 2.408(1)	2.419 2.421	2.426(2) 2.439(2)	2.477 2.477	2.395 2.397	2.444(1) 2.424(1)	2.433 2.454	2.414 2.413
M-X	2.423(1)	2.500	2.453	2.551	2.583(1)	2.642	2.527(1)	2.590	2.684	2.343(1)/ 2.389(1)	2.454 2.432	2.551 2.447
C2-NH	1.323(2)	1.331	1.365	1.350	1.328(3)	1.333	1.365(8)	1.368	1.350	1.329(3)	1.341	1.377
C2-C3	1.443(2)	1.446	1.425	1.425	1.447(4)	1.444	1.416(9)	1.424	1.425	1.429(3)	1.436	1.419
C3-C4	1.362(2)	1.368	1.381	1.391	1.355(4)	1.368	1.377(10)	1.381	1.391	1.362(4)	1.374	1.384
C4-C5	1.416(2)	1.416	1.403	1.393	1.419(4)	1.417	1.392(11)	1.404	1.393	1.390(4)	1.412	1.402
C5-C6	1.378(2)	1.379	1.392	1.404	1.372(4)	1.378	1.383(10)	1.389	1.403	1.368(3)	1.383	1.392
C6-C15	1.442(2)	1.444	1.422	1.449	1.454(4)	1.446	1.419(9)	1.426	1.449	1.436(3)	1.437	1.421
C2-C15	1.449(2)	1.457	1.439	1.461	1.455(4)	1.457	1.425(9)	1.438	1.461	1.438(3)	1.448	1.433
C14-C15	1.419(2)	1.434	1.462	1.436	1.418(4)	1.429	1.442(9)	1.454	1.432	1.420(3)	1.441	1.458
C14-O16	1.274(2)	1.270	1.258	1.304	1.286(3)	1.277	1.263(7)	1.265	1.309	1.272(2)	1.269	1.264
C7-O17	1.228(2)	1.231	1.224	1.259	1.235(3)	1.231	1.213(9)	1.224	1.259	1.224(3)	1.230	1.224

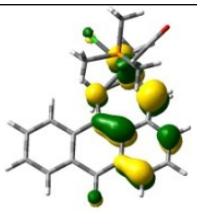
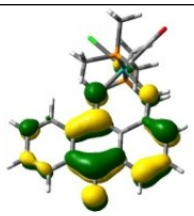
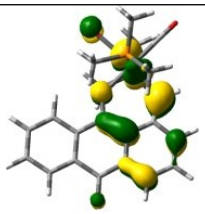
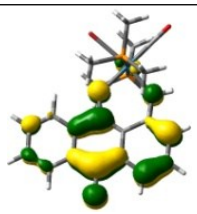
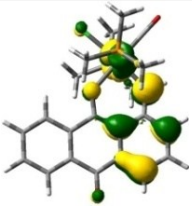
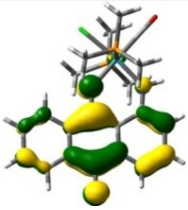
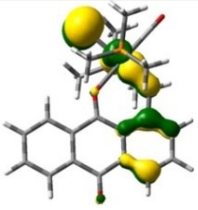
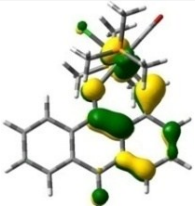
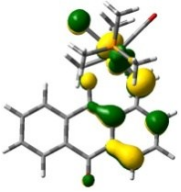
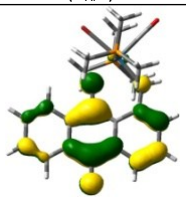
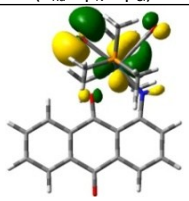
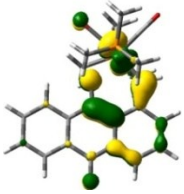
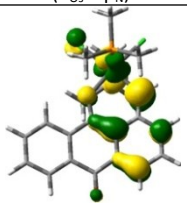
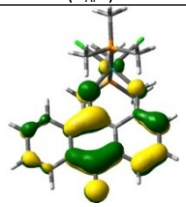
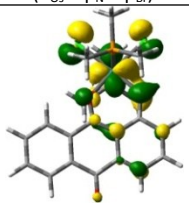
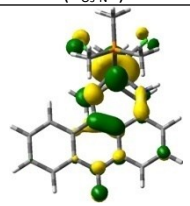
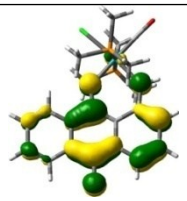
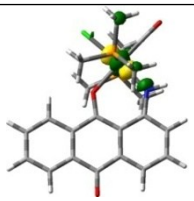
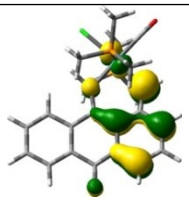
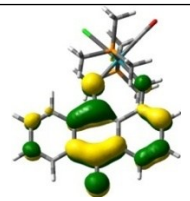
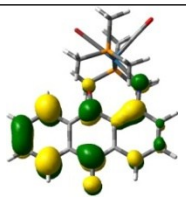
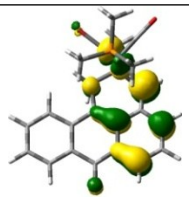
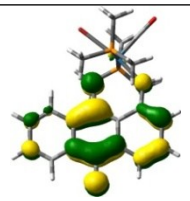
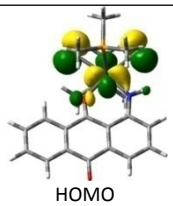
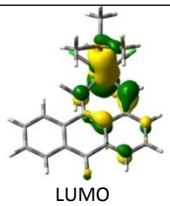
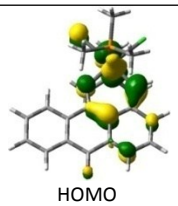
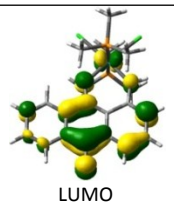
	 HOMO ($p_N + d_{Ru}$)	 LUMO (π_{Ar}*)	 HOMO ($p_N + d_{Os}$)	 LUMO (π_{Ar}*)
	1^{Me}		**2**^{Me}	
1^{Me+}	 α-HOMO ($d_{Ru} + p_N$)	 α-LUMO (π_{Ar}*)	 β-HOMO ($d_{Ru} + p_N + p_{Cl}$)	 β-LUMO (π_{Ru-N}*)
2^{Me+}	 α-HOMO ($d_{Os} + p_N$)	 α-LUMO (π_{Ar}*)	 β-HOMO ($d_{Os} + p_N + p_{Br}$)	 β-LUMO (π_{Os-N}*)
3^{Me}	 α-HOMO	 α-LUMO	 β-HOMO	 β-LUMO
1^{Me-}	 α-HOMO	 α-LUMO	 β-HOMO	 β-LUMO
2^{Me-}	 α-HOMO	 α-LUMO	 β-HOMO	 β-LUMO
	 HOMO	 LUMO	 HOMO	 LUMO
	3^{Me+}		**3**$^{Me-}$	

Fig. S1 Photo active orbitals of **1**^{Me}, **1**$^{Me+}$, **1**$^{Me-}$, **2**^{Me}, **2**$^{Me+}$, **2**$^{Me-}$, **3**^{Me}, **3**$^{Me+}$ and **3**$^{Me-}$

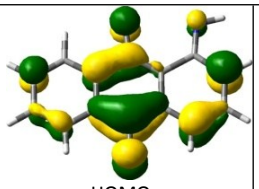
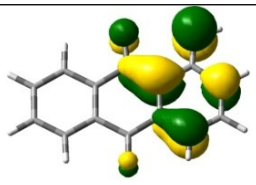
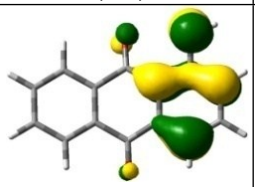
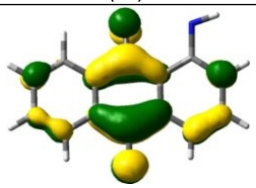
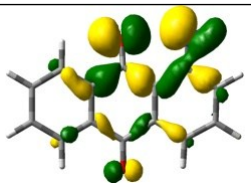
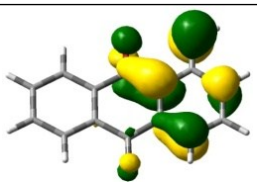
$AqNH^-$	 HOMO (π_{Ar}*)	 LUMO (π*)		
$AqNH^{\bullet}$	 α-HOMO (p_N)	 α-LUMO (π_{Ar}*)	 β-HOMO (π)	 β-LUMO (π*)

Fig. S2 Photo active orbitals of $AqNH^-$ and $AqNH^{\bullet}$.

Table S3 UV-vis-NIR absorption spectral data and calculated excitation energies (λ/nm), oscillation strengths (f) and transition types of $AqNH^-$, $\mathbf{1}^{Me}$ and $\mathbf{2}^{Me}$ obtained from TD DFT calculations in CH_2Cl_2

λ_{exp}/nm	λ_{calc}/nm	f	significant contributions	transition types
$AqNH^-$				
	699.37	0.12	HOMO → LUMO (77%)	$p_N(95) \rightarrow \pi_{Ar}$*(98)
$\mathbf{1}^{Me}$				
800 (0.25), 728 (0.35), 667 (0.3)	732.22	0.07	HOMO → LUMO (80%)	$p_N + d_{Ru} \rightarrow \pi_{Ar}$*
$\mathbf{2}^{Me}$				
845 (0.30), 758 (0.36), 680 (0.3)	804.52	0.07	HOMO → LUMO (79%)	$p_N + d_{Os} \rightarrow \pi_{Ar}$*

Table S4 Gas phase optimized coordinates of $AqNH^{\bullet}$

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.153213	-0.299754	-1.991395
2	C	0	1.110058	-0.680295	-2.202933
3	C	0	1.558214	-1.170692	-3.479077
4	C	0	2.896505	-1.391084	-3.748808
5	C	0	3.856666	-1.137936	-2.760174
6	C	0	3.464965	-0.702943	-1.481637
7	C	0	4.556724	-0.418139	-0.490753
8	C	0	4.162879	0.117230	0.836309
9	C	0	5.153790	0.506799	1.749335
10	C	0	4.791561	1.008717	2.997436
11	C	0	3.437280	1.111254	3.346150
12	C	0	2.448210	0.709474	2.449216
13	C	0	2.803425	0.218961	1.185883
14	C	0	1.721168	-0.234935	0.253639
15	C	0	2.109618	-0.521228	-1.160942
16	O	0	0.581602	-0.398592	0.669663
17	O	0	5.733813	-0.596970	-0.791003
18	H	0	-0.711789	-0.525181	-2.823734
19	H	0	0.808360	-1.329696	-4.251172
20	H	0	3.206275	-1.745439	-4.728305
21	H	0	4.915200	-1.277870	-2.952234
22	H	0	6.195541	0.408548	1.460746
23	H	0	5.559540	1.317469	3.701580
24	H	0	3.156032	1.501798	4.320627
25	H	0	1.395672	0.766730	2.707576

Table S5 Gas phase optimized coordinates of $AqNH^-$

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.249578	-0.627069	-1.966075
2	C	0	1.045256	-0.754250	-2.176852
3	C	0	1.567717	-1.213849	-3.463013

4	C	0	2.902515	-1.361713	-3.735196
5	C	0	3.870412	-1.065638	-2.748302
6	C	0	3.458679	-0.622703	-1.495552
7	C	0	4.556193	-0.337196	-0.527206
8	C	0	4.171945	0.139991	0.826090
9	C	0	5.167212	0.425333	1.776131
10	C	0	4.817276	0.873111	3.046812
11	C	0	3.460698	1.037898	3.372977
12	C	0	2.472847	0.755606	2.432657
13	C	0	2.813753	0.303271	1.146596
14	C	0	1.699613	0.011993	0.163683
15	C	0	2.071984	-0.451334	-1.158345
16	O	0	0.536926	0.193927	0.567380
17	O	0	5.752107	-0.483984	-0.815493
18	H	0	-0.731497	-0.900645	-2.832127
19	H	0	0.828071	-1.444452	-4.230980
20	H	0	3.222594	-1.709242	-4.717797
21	H	0	4.931394	-1.174911	-2.943720
22	1	0	6.205608	0.286793	1.489081
23	H	0	5.588922	1.093827	3.781947
24	H	0	3.180091	1.387675	4.365269
25	H	0	1.417365	0.873787	2.658031

Table S6 Gas phase optimized coordinates of **1**^{Me}

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.201705	-0.512960	-2.039674
2	C	0	1.112715	-0.634815	-2.213828
3	C	0	1.592627	-1.026209	-3.520545
4	C	0	2.922376	-1.190855	-3.798195
5	C	0	3.897160	-0.974830	-2.793646
6	C	0	3.506940	-0.592376	-1.527157
7	C	0	4.600913	-0.379023	-0.530027
8	C	0	4.207763	0.050032	0.834199
9	C	0	5.195744	0.272675	1.803867
10	C	0	4.838365	0.676861	3.087873
11	C	0	3.485913	0.859529	3.409838
12	C	0	2.497693	0.638757	2.452324
13	C	0	2.848948	0.232583	1.153435
14	C	0	1.773976	0.000784	0.148328
15	C	0	2.116891	-0.405676	-1.183151
16	O	0	0.595325	0.194450	0.579897
17	O	0	5.783925	-0.549942	-0.824765
18	C	0	-2.956165	-0.189197	-1.193268
19	O	0	-3.974872	-0.304823	-1.744357
20	P	0	-1.236756	2.363440	-0.825833
21	P	0	-1.387960	-2.303841	0.434621
22	H	0	-0.715678	-0.719043	-2.890449
23	H	0	0.848126	-1.194101	-4.297001
24	H	0	3.233039	-1.489421	-4.796483
25	H	0	4.954218	-1.101631	-2.998815
26	H	0	6.234125	0.122682	1.525529
27	H	0	5.605964	0.849508	3.837685
28	H	0	3.203058	1.174202	4.411094
29	H	0	1.448282	0.774435	2.690718
30	C	0	-2.876722	3.202486	-0.768892
31	H	0	-2.769522	4.288675	-0.871313
32	H	0	-3.518233	2.829658	-1.574099
33	H	0	-3.351783	2.967046	0.188183
34	C	0	-0.251169	3.304701	0.413939
35	H	0	-0.316892	4.383128	0.227340
36	H	0	-0.642282	3.074534	1.409200

37	H	0	0.796756	2.994445	0.376242
38	C	0	-0.534214	2.920164	-2.442948
39	H	0	0.488942	2.547401	-2.552003
40	H	0	-1.132202	2.516426	-3.266741
41	H	0	-0.525728	4.014341	-2.514542
42	C	0	-0.760035	-3.639298	-0.679444
43	H	0	0.279989	-3.437265	-0.953507
44	H	0	-0.817833	-4.619303	-0.191146
45	H	0	-1.354140	-3.667109	-1.598966
46	C	0	-3.076929	-2.891937	0.881189
47	H	0	-3.043069	-3.894742	1.322803
48	H	0	-3.510534	-2.187605	1.597398
49	H	0	-3.713853	-2.914972	-0.009095
50	C	0	-0.438314	-2.567457	1.991638
51	H	0	-0.591046	-3.583867	2.373361
52	H	0	0.628943	-2.405943	1.815848
53	H	0	-0.780685	-1.837739	2.731070
54	Ru	0	-1.310970	-0.015210	-0.360750
55	Cl	0	-2.373120	0.605390	1.815763

Table S7 Gas phase optimized coordinates of $\mathbf{1}^{Me+}$ used to calculate the ground state energy in CH_2Cl_2

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.159659	-0.523114	-2.034287
2	C	0	1.185523	-0.645153	-2.232621
3	C	0	1.625807	-1.030676	-3.532628
4	C	0	2.964876	-1.188072	-3.832644
5	C	0	3.935736	-0.966123	-2.844730
6	C	0	3.551270	-0.584680	-1.562642
7	C	0	4.649922	-0.362774	-0.561609
8	C	0	4.261035	0.052631	0.807223
9	C	0	5.251545	0.273060	1.770524
10	C	0	4.895079	0.664830	3.061428
11	C	0	3.545429	0.837668	3.395997
12	C	0	2.551604	0.619379	2.443136
13	C	0	2.900947	0.225347	1.139901
14	C	0	1.836686	-0.005912	0.141091
15	6	0	2.181370	-0.413146	-1.219936
16	O	0	0.652153	0.166451	0.528497
17	O	0	5.821211	-0.522954	-0.879831
18	C	0	-2.884716	-0.218333	-1.302831
19	O	0	-3.887080	-0.333231	-1.861701
20	P	0	-1.262704	2.404947	-0.806797
21	P	0	-1.430223	-2.334463	0.477600
22	H	0	-0.664183	-0.736027	-2.892142
23	H	0	0.875004	-1.203908	-4.300548
24	H	0	3.263924	-1.483898	-4.833960
25	H	0	4.993294	-1.083608	-3.055008
26	H	0	6.290699	0.133428	1.490452
27	H	0	5.666123	0.835409	3.807179
28	H	0	3.269476	1.142268	4.401374
29	H	0	1.504717	0.749560	2.695240
30	C	0	-2.941466	3.148693	-0.765778
31	H	0	-2.873678	4.239914	-0.836706
32	H	0	-3.543822	2.777282	-1.600753
33	H	0	-3.432017	2.873909	0.172049
34	C	0	-0.322412	3.318286	0.480206
35	H	0	-0.414244	4.398015	0.317353
36	H	0	-0.724602	3.059747	1.463328
37	H	0	0.734752	3.040349	0.448806
38	C	0	-0.545931	2.984233	-2.404074
39	H	0	0.493096	2.653521	-2.496315
40	H	0	-1.116785	2.574329	-3.243290
41	H	0	-0.574453	4.078327	-2.461492
42	C	0	-0.790925	-3.689239	-0.598117

43	H	0	0.265667	-3.524268	-0.829769
44	H	0	-0.894528	-4.657289	-0.094993
45	H	0	-1.351836	-3.721661	-1.537580
46	C	0	-3.155806	-2.836473	0.858249
47	H	0	-3.166408	-3.817841	1.345279
48	H	0	-3.607101	-2.094623	1.522770
49	H	0	-3.747176	-2.891633	-0.061135
50	C	0	-0.528502	-2.542108	2.064761
51	H	0	-0.711777	-3.543059	2.471226
52	H	0	0.546493	-2.410227	1.913593
53	H	0	-0.879364	-1.787960	2.774139
54	Ru	0	-1.235858	-0.040322	-0.432254
55	Cl	0	-2.329872	0.568337	1.677505

Table S8 Gas phase optimized coordinates of **1**$^{Me-}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.159659	-0.523114	-2.034287
2	6	0	1.185523	-0.645153	-2.232621
3	6	0	1.625807	-1.030676	-3.532628
4	6	0	2.964876	-1.188072	-3.832644
5	6	0	3.935736	-0.966123	-2.844730
6	6	0	3.551270	-0.584680	-1.562642
7	6	0	4.649922	-0.362774	-0.561609
8	6	0	4.261035	0.052631	0.807223
9	6	0	5.251545	0.273060	1.770524
10	6	0	4.895079	0.664830	3.061428
11	6	0	3.545429	0.837668	3.395997
12	6	0	2.551604	0.619379	2.443136
13	6	0	2.900947	0.225347	1.139901
14	6	0	1.836686	-0.005912	0.141091
15	6	0	2.181370	-0.413146	-1.219936
16	8	0	0.652153	0.166451	0.528497
17	8	0	5.821211	-0.522954	-0.879831
18	6	0	-2.884716	-0.218333	-1.302831
19	8	0	-3.887080	-0.333231	-1.861701
20	15	0	-1.262704	2.404947	-0.806797
21	15	0	-1.430223	-2.334463	0.477600
22	1	0	-0.664183	-0.736027	-2.892142
23	1	0	0.875004	-1.203908	-4.300548
24	1	0	3.263924	-1.483898	-4.833960
25	1	0	4.993294	-1.083608	-3.055008
26	1	0	6.290699	0.133428	1.490452
27	1	0	5.666123	0.835409	3.807179
28	1	0	3.269476	1.142268	4.401374
29	1	0	1.504717	0.749560	2.695240
30	6	0	-2.941466	3.148693	-0.765778
31	1	0	-2.873678	4.239914	-0.836706
32	1	0	-3.543822	2.777282	-1.600753
33	1	0	-3.432017	2.873909	0.172049
34	6	0	-0.322412	3.318286	0.480206
35	1	0	-0.414244	4.398015	0.317353
36	1	0	-0.724602	3.059747	1.463328
37	1	0	0.734752	3.040349	0.448806
38	6	0	-0.545931	2.984233	-2.404074
39	1	0	0.493096	2.653521	-2.496315
40	1	0	-1.116785	2.574329	-3.243290
41	1	0	-0.574453	4.078327	-2.461492
42	6	0	-0.790925	-3.689239	-0.598117
43	1	0	0.265667	-3.524268	-0.829769
44	1	0	-0.894528	-4.657289	-0.094993
45	1	0	-1.351836	-3.721661	-1.537580
46	6	0	-3.155806	-2.836473	0.858249
47	1	0	-3.166408	-3.817841	1.345279
48	1	0	-3.607101	-2.094623	1.522770
49	1	0	-3.747176	-2.891633	-0.061135
50	6	0	-0.528502	-2.542108	2.064761

51	1	0	-0.711777	-3.543059	2.471226
52	1	0	0.546493	-2.410227	1.913593
53	1	0	-0.879364	-1.787960	2.774139
54	44	0	-1.235858	-0.040322	-0.432254
55	17	0	-2.329872	0.568337	1.677505

Table S9 Gas phase optimized coordinates of **2**^{Me}

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.209369	-0.509643	-2.012203
2	C	0	1.107231	-0.629095	-2.185847
3	C	0	1.584879	-1.020471	-3.490769
4	C	0	2.915107	-1.182486	-3.767421
5	C	0	3.888247	-0.962633	-2.760687
6	C	0	3.498930	-0.580311	-1.494897
7	C	0	4.590550	-0.363601	-0.496430
8	C	0	4.192133	0.063021	0.866372
9	C	0	5.176613	0.288148	1.839121
10	C	0	4.814710	0.689933	3.122478
11	C	0	3.460645	0.867667	3.441364
12	C	0	2.475247	0.644907	2.481905
13	C	0	2.831079	0.241134	1.182686
14	C	0	1.764390	0.007552	0.175732
15	C	0	2.106570	-0.396232	-1.151431
16	O	0	0.578645	0.199928	0.609955
17	O	0	5.774770	-0.530443	-0.790166
18	C	0	-2.972887	-0.175965	-1.144617
19	O	0	-4.010477	-0.286022	-1.678397
20	P	0	-1.219808	2.355991	-0.840625
21	P	0	-1.376410	-2.307173	0.419089
22	H	0	-0.725978	-0.717295	-2.860570
23	H	0	0.840679	-1.190621	-4.267059
24	H	0	3.227984	-1.481406	-4.764709
25	H	0	4.945835	-1.087244	-2.965246
26	H	0	6.216195	0.141842	1.563325
27	H	0	5.579809	0.864449	3.874383
28	H	0	3.174347	1.180299	4.442260
29	H	0	1.425103	0.777099	2.718937
30	C	0	-2.852607	3.204900	-0.772577
31	H	0	-2.741689	4.284229	-0.927559
32	H	0	-3.517974	2.798158	-1.540859
33	H	0	-3.302332	3.016648	0.206682
34	C	0	-0.194669	3.338792	0.333360
35	H	0	-0.251040	4.407551	0.096216
36	H	0	-0.565387	3.164135	1.347483
37	H	0	0.848670	3.014012	0.287590
38	C	0	-0.559571	2.855092	-2.494194
39	H	0	0.460987	2.479907	-2.617761
40	H	0	-1.179888	2.424941	-3.287490
41	H	0	-0.554092	3.946064	-2.601524
42	C	0	-0.814777	-3.608139	-0.768515
43	H	0	0.218226	-3.415174	-1.073630
44	H	0	-0.873891	-4.604512	-0.315486
45	H	0	-1.444647	-3.588740	-1.664140
46	C	0	-3.053037	-2.893272	0.908091
47	H	0	-3.014299	-3.920667	1.288060
48	H	0	-3.445825	-2.227829	1.682411
49	H	0	-3.727525	-2.853687	0.046768
50	C	0	-0.366123	-2.647268	1.922457
51	H	0	-0.518060	-3.677073	2.265928

52	H	0	0.695457	-2.494134	1.708127
53	H	0	-0.664225	-1.947765	2.708658
54	Os	0	-1.314452	-0.010912	-0.339690
55	Br	0	-2.343165	0.655710	2.000654

Table S10 Gas phase optimized coordinates of $\mathbf{2}^{Me+}$ used to calculate the ground state energy in CH_2Cl_2

Center Number	Atom	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.179697	-0.513691	-2.002600
2	C	0	1.169117	-0.638623	-2.197882
3	C	0	1.607808	-1.027655	-3.495706
4	C	0	2.946053	-1.189593	-3.794189
5	C	0	3.919952	-0.968495	-2.806815
6	C	0	3.537682	-0.583617	-1.528426
7	C	0	4.633624	-0.361172	-0.525994
8	C	0	4.241054	0.060088	0.840687
9	C	0	5.228572	0.282487	1.806315
10	C	0	4.868724	0.679425	3.094791
11	C	0	3.518312	0.855183	3.424929
12	C	0	2.526974	0.634971	2.470229
13	C	0	2.879903	0.236099	1.168872
14	C	0	1.822787	0.002272	0.167093
15	C	0	2.164093	-0.407226	-1.186212
16	O	0	0.633257	0.179052	0.558562
17	O	0	5.806229	-0.524739	-0.838314
18	C	0	-2.902289	-0.203432	-1.253707
19	O	0	-3.912190	-0.319450	-1.814200
20	P	0	-1.248024	2.412776	-0.820199
21	P	0	-1.412467	-2.344889	0.465585
22	H	0	-0.684291	-0.726842	-2.859468
23	H	0	0.857226	-1.200584	-4.264006
24	H	0	3.243923	-1.488734	-4.794904
25	H	0	4.976717	-1.090175	-3.018548
26	H	0	6.268344	0.140266	1.529861
27	H	0	5.637786	0.851614	3.842227
28	H	0	3.239906	1.163579	4.428466
29	H	0	1.479684	0.767265	2.719409
30	C	0	-2.916810	3.174969	-0.761116
31	H	0	-2.841045	4.260313	-0.887991
32	H	0	-3.547960	2.767502	-1.556935
33	1	0	-3.381639	2.951943	0.203108
34	C	0	-0.257521	3.372331	0.393482
35	H	0	-0.340568	4.443841	0.180913
36	H	0	-0.630498	3.170188	1.400982
37	H	0	0.795042	3.079451	0.344074
38	C	0	-0.575545	2.914607	-2.461299
39	H	0	0.457222	2.569961	-2.569937
40	H	0	-1.175883	2.474901	-3.263965
41	H	0	-0.596497	4.005189	-2.564164
42	C	0	-0.819683	-3.645004	-0.698902
43	H	0	0.228173	-3.471842	-0.961856
44	H	0	-0.910047	-4.635974	-0.240614
45	1	0	-1.416762	-3.627146	-1.616146
46	C	0	-3.125217	-2.861318	0.879655
47	H	0	-3.122936	-3.872712	1.300401
48	H	0	-3.549298	-2.164854	1.607999
49	H	0	-3.750272	-2.851571	-0.018683
50	C	0	-0.454939	-2.637572	2.005910
51	H	0	-0.625780	-3.658771	2.363869
52	H	0	0.614581	-2.499178	1.823824
53	H	0	-0.776127	-1.925083	2.770247
54	Os	0	-1.254978	-0.028174	-0.397969
55	Br	0	-2.314944	0.620138	1.874849

Table S11 Gas phase optimized coordinates of $\mathbf{2}^{Me-}$

Center	Atom	Atomic	Coordinates (Angstroms)

Number		Type	X	Y	Z
1	N	0	-0.253818	-0.492074	-2.006680
2	C	0	1.076627	-0.629541	-2.191295
3	C	0	1.541136	-1.024968	-3.478945
4	C	0	2.892384	-1.194748	-3.763462
5	C	0	3.856783	-0.978409	-2.781152
6	C	0	3.471766	-0.583663	-1.490754
7	C	0	4.548115	-0.367510	-0.512274
8	C	0	4.146406	0.054481	0.829545
9	C	0	5.131065	0.286418	1.815916
10	C	0	4.781434	0.687520	3.094816
11	C	0	3.417420	0.867569	3.424554
12	C	0	2.435243	0.645158	2.474328
13	C	0	2.773354	0.236182	1.157410
14	C	0	1.723327	0.010447	0.176676
15	C	0	2.075119	-0.396819	-1.150858
16	O	0	0.506637	0.210831	0.616241
17	O	0	5.760141	-0.533801	-0.809062
18	C	0	-3.009932	-0.178797	-1.156332
19	O	0	-4.034971	-0.300633	-1.727806
20	P	0	-1.210195	2.336085	-0.821713
21	P	0	-1.358930	-2.280375	0.418393
22	H	0	-0.774622	-0.702495	-2.849926
23	H	0	0.795525	-1.197197	-4.255525
24	H	0	3.191774	-1.499985	-4.765442
25	H	0	4.915754	-1.102996	-2.978686
26	H	0	6.168486	0.138576	1.529931
27	H	0	5.551293	0.863257	3.844147
28	H	0	3.137099	1.181606	4.428417
29	H	0	1.385407	0.777998	2.714427
30	C	0	-2.809384	3.259139	-0.794712
31	H	0	-2.655341	4.331266	-0.969517
32	H	0	-3.480668	2.860388	-1.562650
33	H	0	-3.278715	3.107071	0.182172
34	C	0	-0.179223	3.287769	0.373043
35	H	0	-0.187875	4.358382	0.133417
36	H	0	-0.580490	3.124356	1.377596
37	H	0	0.847870	2.913688	0.355447
38	C	0	-0.493883	2.812540	-2.459762
39	H	0	0.501968	2.371845	-2.564050
40	H	0	-1.122006	2.417886	-3.265456
41	H	0	-0.423433	3.902819	-2.558880
42	C	0	-0.741105	-3.560609	-0.766232
43	H	0	0.279908	-3.314083	-1.071963
44	H	0	-0.755271	-4.559053	-0.311859
45	H	0	-1.369109	-3.565058	-1.663508
46	C	0	-3.007853	-2.949995	0.910276
47	H	0	-2.924601	-3.975521	1.291048
48	H	0	-3.427658	-2.299574	1.683845
49	H	0	-3.683836	-2.937462	0.048838
50	C	0	-0.338725	-2.584749	1.923006
51	H	0	-0.426070	-3.627969	2.251295
52	H	0	0.709065	-2.351815	1.714375
53	H	0	-0.683157	-1.913150	2.714828
54	Os	0	-1.368999	-0.003757	-0.323948
55	Br	0	-2.462399	0.665821	2.034054

Table S12. Gas phase optimized coordinates of **3**^{Me}

Center	Atoms	Atomic	Coordinates (Angstroms)

Number		Type	X	Y	Z
1	N	0	-0.085697	-0.284466	-1.994691
2	C	0	1.217226	-0.562880	-2.149967
3	C	0	1.690492	-0.949405	-3.449329
4	C	0	3.002252	-1.290197	-3.673465
5	C	0	3.942658	-1.240862	-2.621479
6	C	0	3.549884	-0.833215	-1.359130
7	C	0	4.614714	-0.752127	-0.311904
8	C	0	4.234616	-0.186403	1.005693
9	C	0	5.207119	-0.044898	2.005586
10	C	0	4.863892	0.488473	3.245539
11	C	0	3.540323	0.878179	3.495935
12	C	0	2.565225	0.734892	2.511116
13	C	0	2.904106	0.204418	1.254412
14	C	0	1.847972	0.034743	0.225444
15	C	0	2.185767	-0.481813	-1.076445
16	O	0	0.684428	0.393297	0.585049
17	O	0	5.763989	-1.127610	-0.538107
18	P	0	-1.417831	2.467640	-0.868591
19	P	0	-1.222458	-2.234706	0.378954
20	H	0	-0.619281	-0.285375	-2.862428
21	H	0	0.966737	-0.987310	-4.260563
22	H	0	3.318460	-1.597792	-4.666858
23	H	0	4.982376	-1.503247	-2.783253
24	H	0	6.222658	-0.358527	1.785587
25	H	0	5.620232	0.599386	4.017934
26	H	0	3.268922	1.290791	4.464027
27	H	0	1.536320	1.022013	2.699387
28	C	0	-3.117546	3.112508	-0.597999
29	H	0	-3.169780	4.180158	-0.842404
30	H	0	-3.815304	2.549714	-1.223699
31	H	0	-3.392394	2.952251	0.447696
32	C	0	-0.356719	3.597539	0.131000
33	H	0	-0.561719	4.648498	-0.104793
34	H	0	-0.558000	3.416404	1.191163
35	H	0	0.700404	3.386910	-0.060011
36	C	0	-1.048255	2.953097	-2.611391
37	H	0	-0.010101	2.706757	-2.856560
38	H	0	-1.707934	2.395523	-3.284267
39	H	0	-1.206996	4.026736	-2.766263
40	C	0	-0.807739	-3.502547	-0.897344
41	H	0	0.218375	-3.363999	-1.251748
42	H	0	-0.912997	-4.517119	-0.495192
43	H	0	-1.486563	-3.381326	-1.747496
44	C	0	-2.892990	-2.750064	0.951209
45	H	0	-2.890369	-3.803213	1.256366
46	H	0	-3.190312	-2.117409	1.791833
47	H	0	-3.609656	-2.597505	0.139540
48	C	0	-0.135444	-2.661704	1.807587
49	H	0	-0.306309	-3.693203	2.137650
50	H	0	0.918512	-2.546660	1.536244
51	H	0	-0.357813	-1.974749	2.629867
52	Ru	0	-1.135613	0.108246	-0.345962
53	Cl	0	-2.224760	0.655811	1.784521
54	Cl	0	-3.151659	-0.277194	-1.650807

Table S13. Gas phase optimized coordinates of **3**$^{Me+}$ (CSS)

Center Number	Atoms	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	0.182844	-0.540464	-2.040670

2	C	0	1.541346	-0.661311	-2.230899
3	C	0	1.989796	-1.042632	-3.521713
4	C	0	3.337421	-1.190872	-3.799769
5	C	0	4.289672	-0.961590	-2.796888
6	C	0	3.886595	-0.583886	-1.519419
7	C	0	4.961561	-0.351267	-0.496066
8	C	0	4.537279	0.058525	0.864092
9	C	0	5.504868	0.293113	1.847491
10	C	0	5.117331	0.679862	3.130706
11	C	0	3.758831	0.832999	3.438498
12	C	0	2.786940	0.600911	2.466773
13	C	0	3.167969	0.212639	1.170696
14	C	0	2.132768	-0.029072	0.148995
15	C	0	2.510096	-0.424892	-1.202161
16	O	0	0.931574	0.125945	0.512367
17	O	0	6.140463	-0.498170	-0.791568
18	P	0	-1.458373	2.245820	-0.711386
19	P	0	-1.648433	-2.136409	0.463001
20	H	0	-0.356960	-0.746163	-2.886661
21	H	0	1.249918	-1.219512	-4.298469
22	H	0	3.655054	-1.484622	-4.795818
23	H	0	5.351328	-1.070987	-2.991974
24	H	0	6.551337	0.168488	1.588324
25	H	0	5.870882	0.861943	3.891428
26	H	0	3.458836	1.133585	4.438174
27	H	0	1.733575	0.716105	2.698750
28	C	0	-3.215652	2.693864	-0.482555
29	H	0	-3.331958	3.760523	-0.708198
30	H	0	-3.832922	2.101823	-1.161400
31	H	0	-3.516007	2.496923	0.547620
32	C	0	-0.478995	3.353531	0.373353
33	H	0	-0.750363	4.394749	0.162561
34	H	0	-0.689514	3.122972	1.419481
35	H	0	0.589632	3.219549	0.182551
36	C	0	-1.048821	2.778600	-2.425823
37	H	0	0.016503	2.634061	-2.627288
38	H	0	-1.635411	2.190805	-3.136546
39	H	0	-1.291544	3.841239	-2.545518
40	C	0	-1.332547	-3.488098	-0.747911
41	H	0	-0.266099	-3.554123	-0.981537
42	H	0	-1.662038	-4.442866	-0.320747
43	H	0	-1.893464	-3.289744	-1.664928
44	C	0	-3.429100	-2.266896	0.854607
45	H	0	-3.635494	-3.296693	1.169372
46	H	0	-3.684852	-1.573814	1.657182
47	H	0	-4.015074	-2.026988	-0.034844
48	C	0	-0.733376	-2.631124	1.973115
49	H	0	-1.106674	-3.603029	2.316972
50	H	0	0.335036	-2.718100	1.755627
51	H	0	-0.882596	-1.882710	2.753756
52	Ru	0	-0.844627	-0.079839	-0.511046
53	Cl	0	-1.900886	0.564671	1.720312
54	Cl	0	-2.772251	-0.390911	-1.986808

Table S14. Gas phase optimized coordinates of **3**$^{Me+}$ (Triplet)

Center Number	Atoms	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	N	0	-0.044589	-0.498155	-1.923828
2	C	0	1.289094	-0.626934	-2.141690
3	C	0	1.732742	-1.010826	-3.440859
4	C	0	3.076515	-1.162076	-3.725233
5	C	0	4.041154	-0.936912	-2.728904
6	C	0	3.647894	-0.558845	-1.448322
7	C	0	4.724786	-0.330272	-0.426772

8	C	0	4.302663	0.076396	0.936807
9	C	0	5.271556	0.304133	1.919646
10	C	0	4.886635	0.687061	3.205441
11	C	0	3.529477	0.843578	3.516843
12	C	0	2.555497	0.618708	2.545530
13	C	0	2.933994	0.234419	1.247592
14	C	0	1.901832	-0.001043	0.224440
15	C	0	2.275614	-0.395543	-1.123614
16	O	0	0.699322	0.156479	0.580171
17	O	0	5.903001	-0.477639	-0.723134
18	P	0	-1.273210	2.411424	-0.852856
19	P	0	-1.468365	-2.349334	0.431406
20	H	0	-0.607902	-0.701063	-2.748983
21	H	0	0.987096	-1.184810	-4.212915
22	H	0	3.386665	-1.456074	-4.723661
23	H	0	5.100370	-1.050501	-2.933923
24	H	0	6.317443	0.177332	1.659115
25	H	0	5.642096	0.863465	3.965580
26	H	0	3.232368	1.140952	4.518252
27	H	0	1.503124	0.736752	2.780838
28	C	0	-2.946285	3.115907	-0.591563
29	H	0	-2.945403	4.181979	-0.845073
30	H	0	-3.667178	2.589409	-1.222464
31	H	0	-3.238308	2.986045	0.453350
32	C	0	-0.155664	3.452923	0.171248
33	H	0	-0.302933	4.514049	-0.059771
34	H	0	-0.374335	3.282483	1.229389
35	H	0	0.890114	3.191840	-0.017575
36	C	0	-0.863914	2.838683	-2.596132
37	H	0	0.164565	2.546698	-2.829682
38	H	0	-1.544306	2.306851	-3.268357
39	H	0	-0.973251	3.916356	-2.761889
40	C	0	-1.171276	-3.622991	-0.865096
41	H	0	-0.136873	-3.576756	-1.219193
42	H	0	-1.363996	-4.625922	-0.467603
43	H	0	-1.843275	-3.443762	-1.710099
44	C	0	-3.169720	-2.694631	1.023376
45	H	0	-3.248920	-3.741866	1.336117
46	H	0	-3.405132	-2.041009	1.866850
47	H	0	-3.884218	-2.497813	0.219560
48	C	0	-0.373603	-2.825238	1.831150
49	H	0	-0.596786	-3.845252	2.163750
50	H	0	0.677173	-2.773944	1.529468
51	H	0	-0.532831	-2.133489	2.663497
52	Ru	0	-1.139217	-0.011324	-0.333162
53	Cl	0	-2.166892	0.593186	1.725039
54	Cl	0	-3.058981	-0.296622	-1.674908