SUPPORTING INFORMATION

Proton Affinities of Pertechnetate (TcO_4^-) and Perrhenate (ReO_4^-)

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Table S1. Bond distances (Å) and NBO bond orders of species in reactions (1) and (2) at the B3LYP/SDD/6-31++G** level of theory.

Species	Bond	Distance	Order
TcO_4^-	Tc—O	1.733	1.596
$HTcO_4$	Tc—O	1.696	1.787
	Tc—OH	1.882	0.907
	TcO—H	0.971	0.707
ReO_4^-	Re—O	1.754	1.584
$HReO_4$	Re—O	1.719	1.770
	Re—OH	1.891	0.907
	ReO—H	0.970	0.696
$(TcO_4^-)(H^+)(ReO_4^-)$	Tc—O	1.708	1.708
	Tc—OH	1.806	1.157
	TcO—H	1.117	0.430
	Re—O	1.738	1.659
	Re—OH	1.796	1.266
	ReO—H	1.291	0.269

Table S2. NPA charges of species in reactions (1) and (2) at the B3LYP/SDD/6-31++G** level of theory.

$(TcO_4^-)(H^+)(ReO_4^-)$		**TcO_4^-**		**ReO_4^-**		**$HTcO_4$**		**$HReO_4$**	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
Tc	1.348	Tc	1.266	Re	1.688	Tc	1.370	Re	1.786
O	-0.448	O	-0.566	O	-0.672	O	-0.378	O	-0.486
O	-0.455	O	-0.566	O	-0.672	O	-0.378	O	-0.500
O	-0.458	O	-0.566	O	-0.672	O	-0.362	O	-0.500
O	-0.702	O	-0.566	O	-0.672	O	-0.777	O	-0.836
H	0.533					H	0.526	H	0.536
Re	1.753								
O	-0.601								
O	-0.594								
O	-0.601								
O	-0.772								

Table S3. Calculated frequencies (cm^{-1}) for Tc-O and Re-O vibrational modes at the B3LYP/SDD/6-31++G** level of theory.

Species	**Mode**	$\boldsymbol{\nu}_{symm}$	$\boldsymbol{\nu}_{asymm}$	$\boldsymbol{\nu}_{sci}$	$\boldsymbol{\nu}_{roc}$
TcO_4^-	Tc-O	915	906	321	338
$HTcO_4$	Tc-O	986	978, 982	343, 351	
ReO_4^-	Re-O	943	891	323,317	316
$HReO_4$	Re-O	963, 966	1001	334, 344	245
$(TcO_4^-)(H^+)(ReO_4^-)$	Tc-O	966	954	339	290
	Re-O	962	917, 919	326	298
$(ReO_4^-)(H^+)(ReO_4^-)$	Re-O	968, 975	920, 922, 937, 940	337	297
$(TcO_4^-)(H^+)(TcO_4^-)$	Tc-O	941, 962	934, 954	334, 338, 340	307
$(L)[(TcO_4^-)(H^+)(ReO_4^-)]$	Tc-O	976	963	347, 340	347
	Re-O	967	909, 925	322	304

Table S4. Calculated absolute PA of TcO_4^- and ReO_4^- ions with different functionals (kcal/mol).[a]

	B3LYP	B3LYP-D3	PBE0	PBE	CAM-B3LYP	M06-2X
PA[$TcO4^-$]	306.75	306.72	308.93	306.11	306.67	308.56
PA[$ReO4^-$]	303.62	303.60	304.64	303.15	302.12	304.06
ΔPA	3.13	3.12	4.29	2.96	4.55	4.50

[a]Using the ADF code (scalar ZORA) with the indicated functional and ZORA-TZP basis sets.

Table S5. Calculated absolute PA of TcO_4^- and ReO_4^- ions with different basis sets (kcal/mol).

	B3LYP/TZP	B3LYP/TZ2P
PA[$TcO4^-$]	306.75	307.41
PA[$ReO4^-$]	303.62	304.59
ΔPA	3.13	2.82

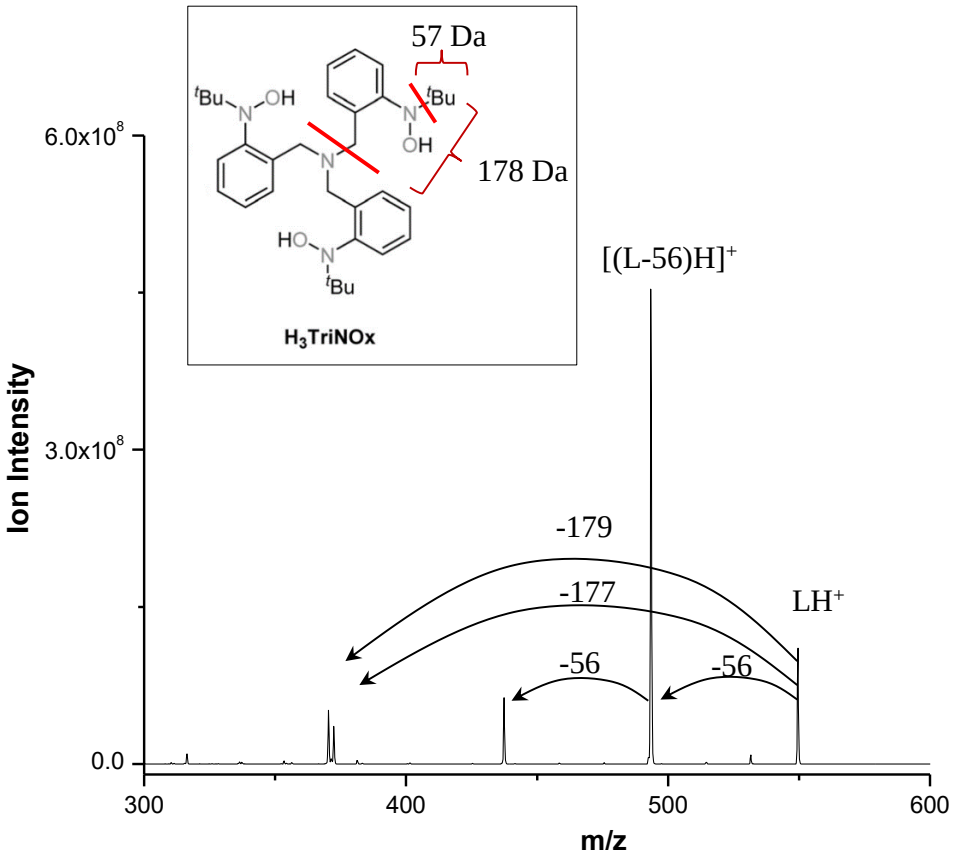


Figure S1. CID mass spectrum of $H_4TriNOx^+$ (LH^+) at a nominal CID voltage of 0.55V. Dominant CID pathways, indicated by arrows, correspond to the ligand bond cleavages indicated in the inset.

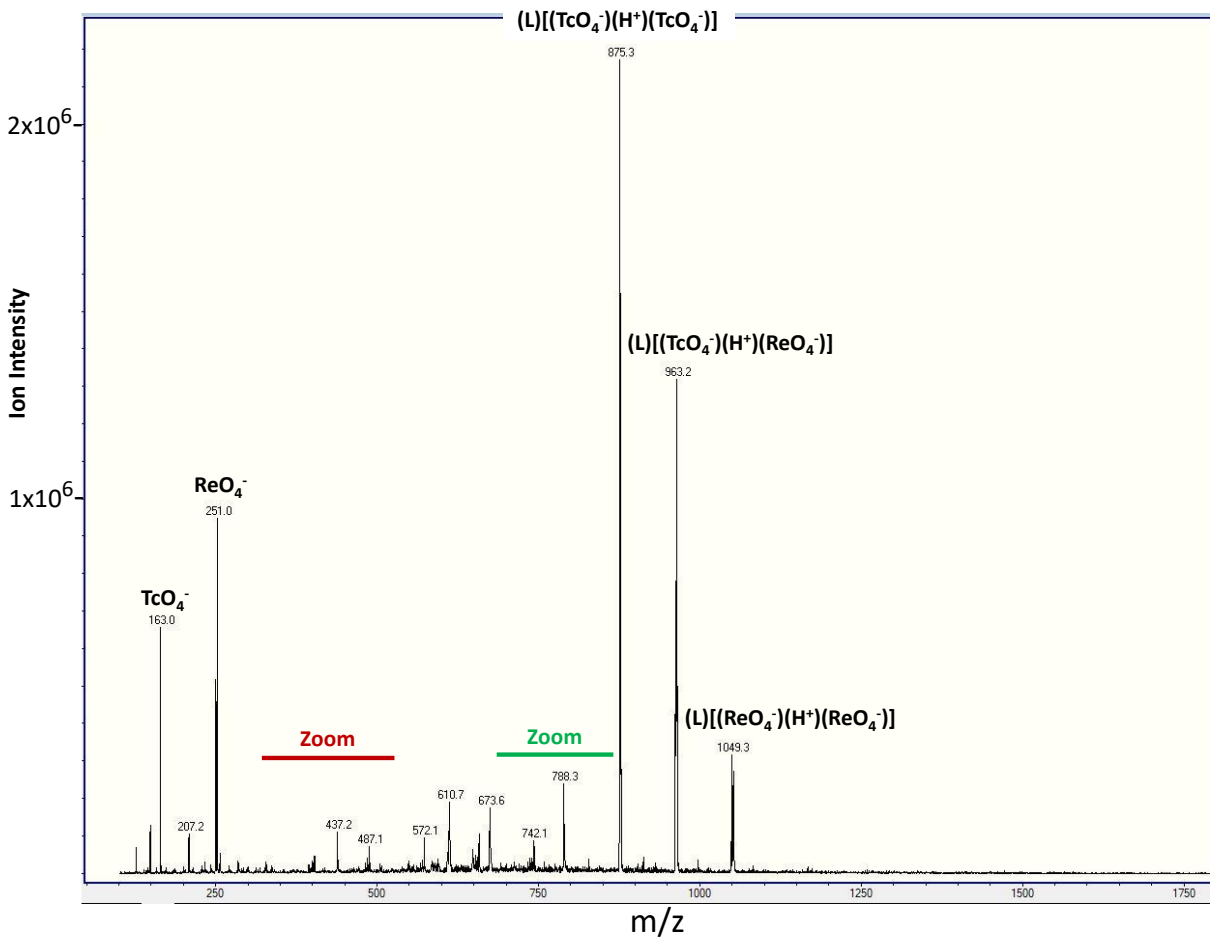


Figure S2a. Negative mode ESI mass spectrum of solution of $H_3TriNOx$, NH_4TcO_4 and NH_4ReO_4 (concentration ratio 1:5:5). This is the same solution and conditions as for the separately acquired spectrum in Figure 4. The main peaks are assigned as labeled. Two m/z segments of this spectrum indicated by the red and green bars are shown in Figure S2b with the z-axis magnified ("Zoomed").

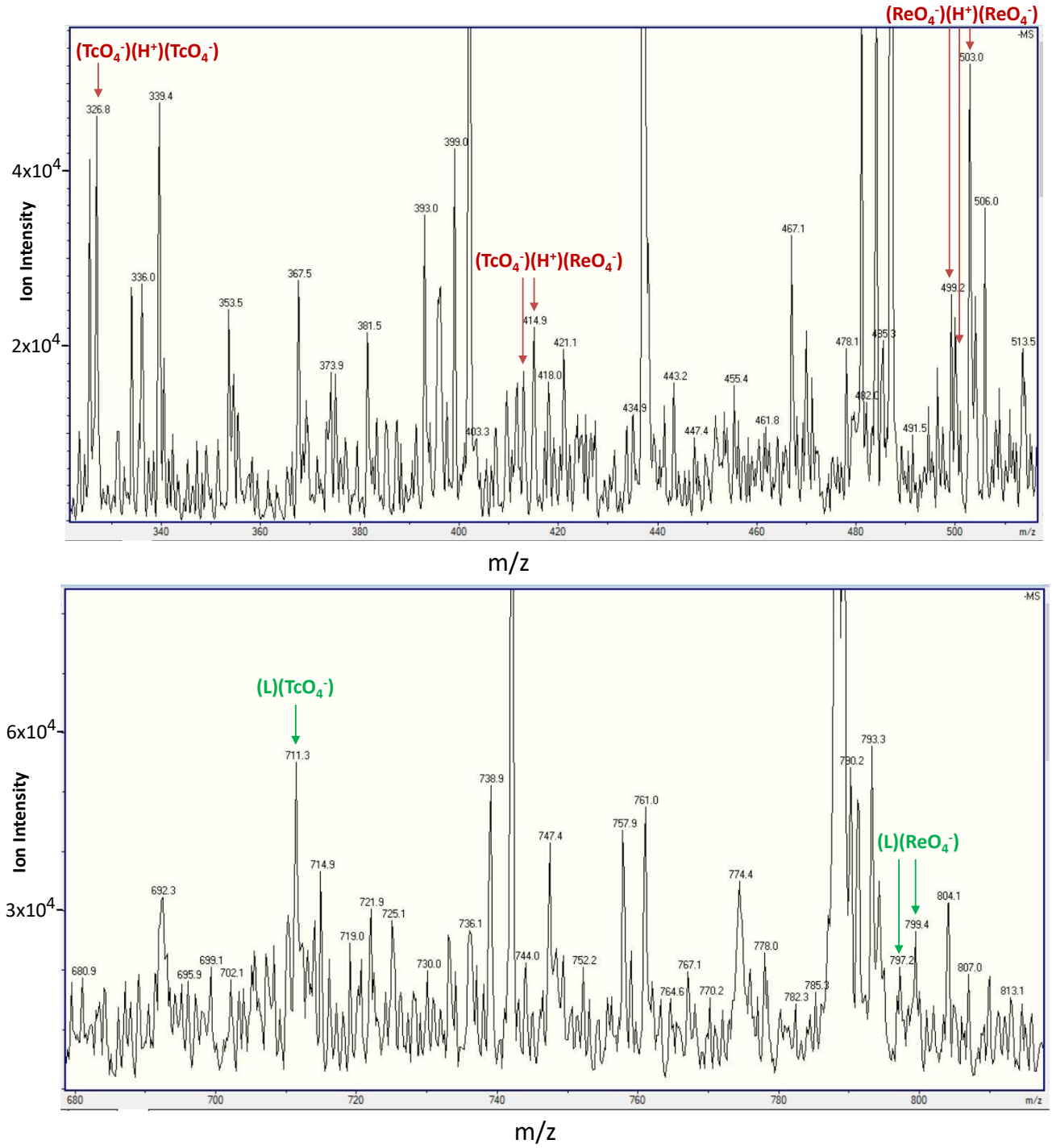


Figure S2b. Two m/z segments of the ESI mass spectrum in Figure S2a with the y-axis magnified ("Zoomed"). Peaks corresponding to selected species are identified. The peak at 414.9 m/z corresponds to ($^{99}TcO_4^-$)(H^+)($^{187}ReO_4^-$) that was isolated for CID.

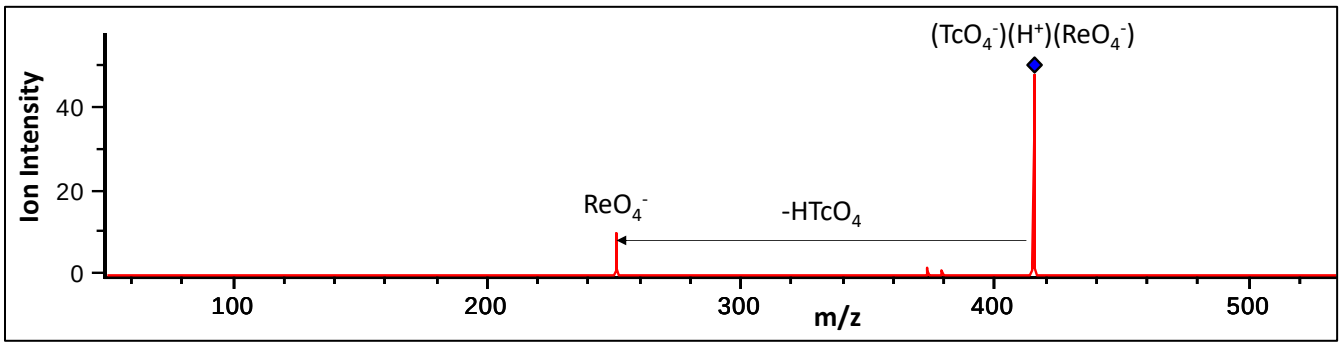
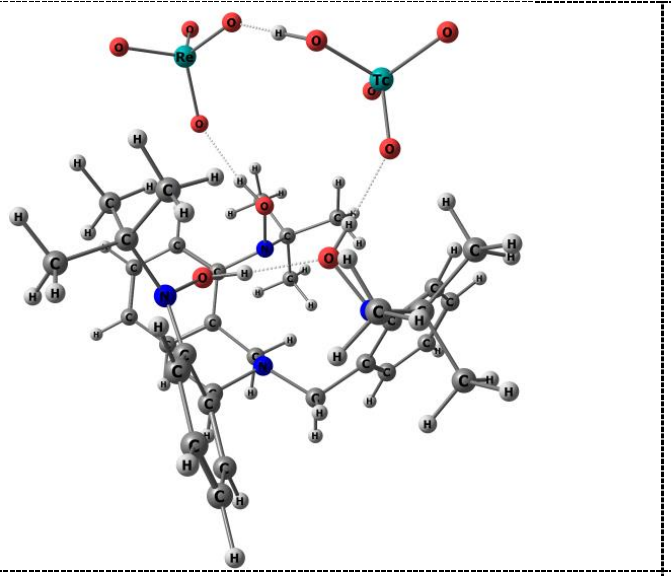
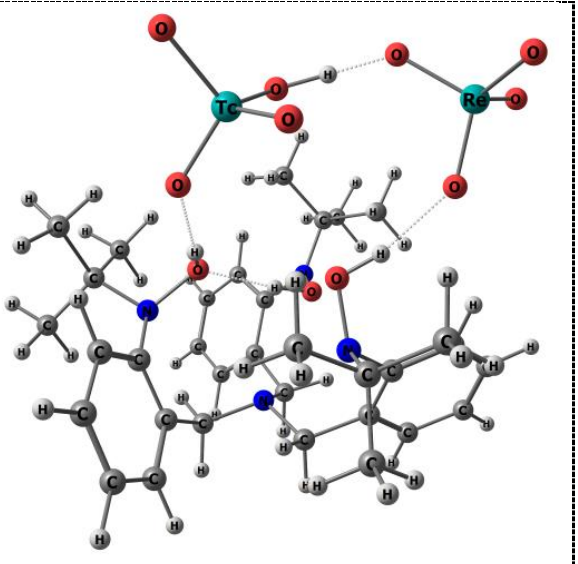


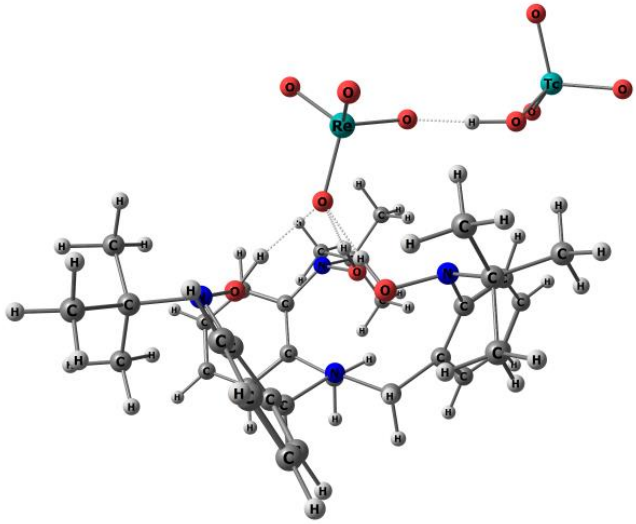
Figure S3. CID mass spectrum of $(TcO_4^-)(H^+)(ReO_4^-)$ showing loss of $HTcO_4$ to yield ReO_4^-, which is the same result as in Figure 4. For this CID experiment the $(TcO_4^-)(H^+)(ReO_4^-)$ dimer was produced by ESI of a solution of 500 µM each of NH_4TcO_4 and NH_4ReO_4 in ethanol (<10% water) with no TriNOx ligand added. The nominal CID voltage was 0.30 V, which is slightly higher than the 0.25 V employed for the result in Figure 4, demonstrating the qualitative nature of this CID parameter.



1 / 3.4 kcal/mol



2/ 0.00 kcal/mol



3 / 0.30 kcal/mol

Figure S4. Optimized structures and relative energies of (H_3TriNOx)[(TcO_4^-)(H^+)(ReO_4^-)] conformers at the B3LYP/SDD/6-31G* level of theory.