Unveiling the Quantum Secrets of Triel Metal Triangles: A Tale of Stability, Aromaticity, and Relativistic Effects

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1   Supporting Information

Table S1 Different properties of the lowest lying energy spin-states of the X_3^- (X= Al, Ga, In and Tl) triangles. ΔE is ZPE corrected MCQDP/MCSCF (10,12) relative energy with respect to the singlet in kcal/mol. R corresponds to the equilibrium bond lengths in Å. MCI is the total multicenter index, MCI_π is the π contribution to MCI.

M	ΔE	$R_{1,3}^{1,2}$	$R_{2,3}$	MCI	MCI_π
Al_3^-					
$^1A_1'$	0.0	2.558		0.49	0.23
$^3B_2$	7.36	2.543	2.762	0.35	0.22
$^3A_1^\dagger$	7.57	2.651	2.536	0.37	0.23
$^3A_2$	12.41	2.619	2.951	0.25	0.03
$^3B_1$	13.39	2.800	2.561	0.27	0.03
$^5A_2''$	12.18	2.758		0.12	0.03
Ga_3^-					
$^1A_1'$	0.0	2.576		0.48	0.24
$^3B_2$	7.04	2.552	2.835	0.35	0.23
$^3A_1^\dagger$	7.41	2.684	2.504	0.35	0.23
$^3A_2$	11.64	2.615	3.075	0.27	0.03
$^3B_1^\dagger$	12.80	3.075	2.558	0.27	0.03
$^5A_2''$	11.93	2.777		0.11	0.03
In_3^-					
$^1A_1'$	0.0	2.979		0.47	0.22
$^3B_2$	2.54	2.931	3.326	0.32	0.22
$^3A_1^\dagger$	3.05	3.085	2.914	0.32	0.22
$^3A_2$	5.59	2.988	3.485	0.26	0.03
$^3B_1^\dagger$	6.74	3.236	2.925	0.26	0.03
$^5A_2''$	3.20	3.147		0.10	0.03
Tl_3^-					
$^1A_1'$	0.0	3.129		0.47	0.22
$^3B_2$	-0.71	3.049	3.441	0.29	0.22
$^3A_1^\dagger$	0.09	3.237	3.023	0.29	0.22
$^3A_2$	0.57	3.079	3.711	0.25	0.03
$^3B_1^\dagger$	2.58	3.387	3.026	0.26	0.03
$^5A_2''$	-2.94	3.263		0.08	0.03

† Transition state.

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Table S2 Contribution of the different MO sets (see Figure ??) to the atom-pair DIs for the Ga_3^- and In^- different electronic states. The first values of the triplet correspond to the symmetric atom-pair corresponding to the two short bonds while the second corresponds the atoms pairs forming the largest bond.

MO sets	Ga_3^-			In_3^-		
	$^1A_1'$	$^3B_2$	$^5A_2''$	$^1A_1'$	$^3B_2$	$^5A_2''$
Ψ_σ	0.42	0.47/0.31	0.34	0.35	0.40/0.25	0.30
Ψ_π	0.32	0.36/0.30	0.16	0.32	0.32/0.35	0.16
Ψ_r	0.26	0.10/0.09	0.07	0.26	0.08/0.09	0.07
Ψ_t	-0.03	0.12/0.03	0.21	-0.02	0.14/0.03	0.22

Table S3 Configuration interaction coefficients (CIC) of the main configurations of the MCSCF wavefunctions of the different triangles studied in the present work (CIC's of 0.09 or larger are shown). Note that the orbitals of the Ψ_σ system $((a_1')^2(e')^2(e')^2$ in D_{3h}, and $(a_1)^2(a_1)^2(b_2)^2)$ are common in all the configurations, and omitted for simplicity.

State		$(a_2'')^2(a_1')^2$	$(a_2'')^2(e')^2$	$(a_1')^2(e')^2$
$^1A_1'$	Al_3^-	0.88	-0.11	-0.09
	Ga_3^-	0.88	-0.11	-0.09
	In_3^-	0.88	-	-
	Tl_3^-	0.90	-0.09	-0.11
		$(b_1)^2(a_1)^1(b_2)^1$	$(b_1)^2(b_2)^1(2a_1)^1$	$(a_1)^2(b_2)^1(b_1)^1$
$^3B_2$	Al_3^-	0.88	-0.13	-0.11
	Ga_3^-	0.89	-0.12	-0.12
	In_3^-	0.90	-	-0.13
	Tl_3^-	0.91	-	-0.15
		$(a_2'')^1(a_1')^1(e')^1(e')^1$		
$^5A_2''$	Al_3^-	0.91		
	Ga_3^-	0.92		
	In_3^-	0.92		
	Tl_3^-	0.93		