Supporting Information

Dynamic factors in the reactions between the magic cluster Al_{13}^- and HCl/HI

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Table S1: Charge numbers for the (o-bridge) $Al_{13}HCl^-$ intermediate calculated by B3LYP/6- 31++G** using Mulliken, Natural Bond Order (NBO) and Atomic Polar Tensors(APT) analysis.

	Charge Population		
atom	Mulliken Charge	NBO Charge	APT Charge
Al(central atom)	0.29	-1.72	-0.58
Al(bonded with H and Cl)	0.18	0.54	0.68
Al	-0.09	-0.03	-0.07
Al	0.01	0.10	-0.03
Al	0.08	0.14	0.02
Al(bonded with H)	-0.06	0.25	0.02
Al	0.03	0.09	-0.05
Al	-0.37	0.10	0.03
Al	-0.22	0.12	0.04
Al	-0.15	0.06	0.01
Al	0.19	0.13	-0.04
Al	-0.14	0.02	-0.05
Al	-0.15	0.09	-0.01
H	-0.10	-0.36	-0.18
Cl	-0.51	-0.56	-0.79

Based on B3LYP results, the natural population produced a surprisingly negative charge of -1.68 on the central Al atom in $Al_{13}HCl^-$, which meant that not only the

single charge of $Al_{13}HCl^-$ was on it, but it also draw further charges away from the other 12 Al atoms. Similar results were obtained for $Al_{13}HX^-$ and reported before for other $Al_{13}HCl^-$ derivatives.[1] Results of natural bonding orbital analysis (NBO) indicated that the natural population was an artifact. Four lone pairs were identified on the central Al of $Al_{13}HCl^-$, occupying one s and three p orbitals in the NBO results, but the occupation number was only 1.3 for each of the p orbitals and 0.9 for the s orbital, significantly lower than the number of 2 expected for a lone pair. Furthermore, out of a total of 85 valence orbitals, 8 non-Lewis orbitals were identified, which clearly indicated that the delocalized metal-metal interactions could not be adequately described by localized natural orbitals.

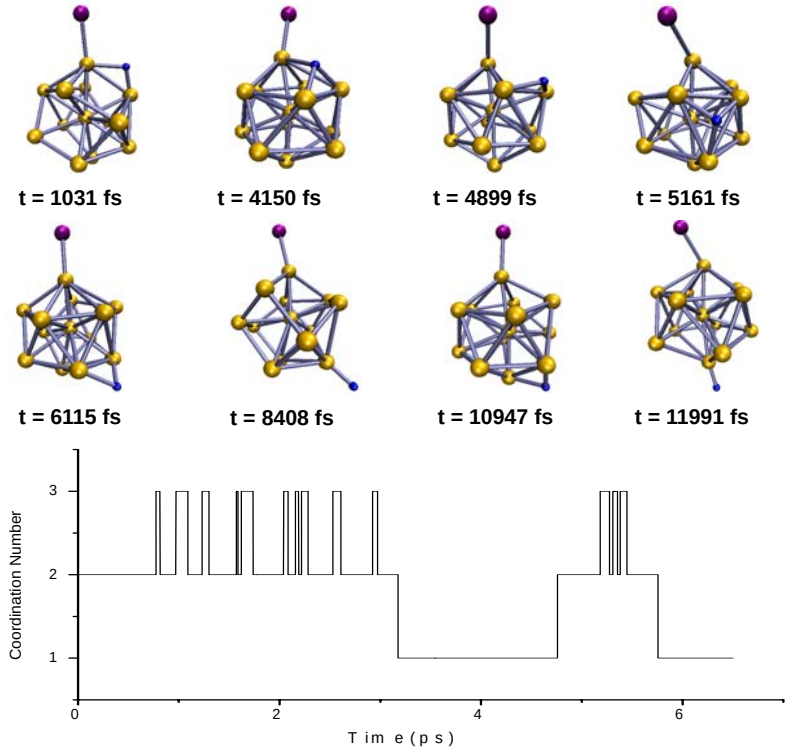
In contrast, the Mulliken charge on the central Al, as listed in Table S1 for the product (o-bridge) $Al_{13}HCl^-$ was +0.29. However, a small change in the $Al_{13}HCl^-$ geometry induced a big change in the charge number. For the isomeric structures discussed later, the Mulliken analysis produced charges on the central Al ranging from -0.34 to +2.9. It was well known that the Mulliken population numbers were sensitive to the basis functions, and the numerical instability was likely due to the fact that the central Al in $Al_{13}HCl^-$ was bonded to 12 Al atoms and a shift in the positions of the basis functions due to even small geometrical changes could induce dramatic change in the calculated population numbers. Only the APT method[2] produced reasonable results, with a charge between -0.4 to -0.6 on the central Al atom for $Al_{13}HCl^-$ and various $Al_{13}HCl^-$ isomers. On the other hand, all population analysis methods were in agreement regarding the transfer of charge to H and Cl in $Al_{13}HCl^-$, with both being negatively charged, as listed in Table S1.

Table S2. Charge population for different adsorption intermediates (Ads. IM) of Al_{13}^-+HCl. Different charge population methods such as Mulliken, NBO and APT are used. All the calculations are carried out with B3LYP/6-31++G**.

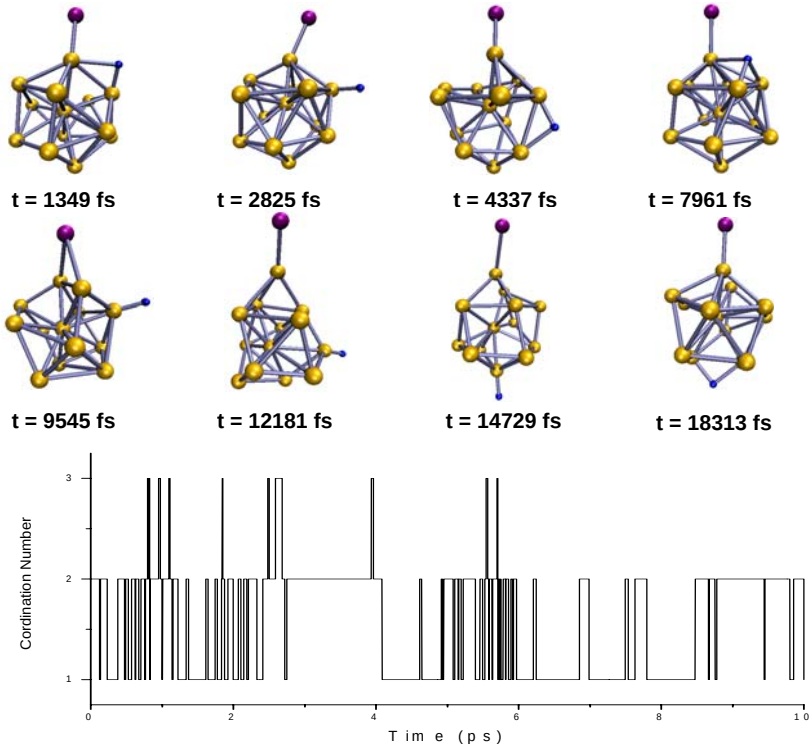
Ads. IM	**Charge population**				**Ads. IM**	**Charge population**			
	atom	**Mulliken**	**NBO**	**APT**		**atom**	**Mulliken**	**NBO**	**APT**
m-bridge	Al	2.89	-1.67	-0.58	**p-bridge**	Al	2.67	-1.69	-0.59
	Al	0.07	0.37	0.71		Al	0.02	0.28	0.69
	Al	-0.58	-0.10	-0.09		Al	-0.23	0.20	-0.07
	Al	-0.08	0.07	0.05		Al	0.01	0.15	-0.01
	Al	-0.19	0.06	0.02		Al	-0.06	0.06	0.03
	Al	-0.20	0.23	0.01		Al	-0.22	0.06	-0.04
	Al	-0.51	0.09	-0.07		Al	-0.60	0.09	-0.01
	Al	-0.47	0.10	-0.03		Al	0.25	0.27	0.01
	Al	-0.03	0.06	-0.02		Al	-0.69	0.20	-0.07
	Al	-0.78	0.21	0.00		Al	-0.03	0.08	0.01
	Al	-0.31	0.27	0.01		Al	-0.36	-0.10	-0.08
	Al	-0.29	0.08	-0.05		Al	0.05	0.27	0.06
	Al	-0.05	0.10	0.01		Al	-0.72	0.02	0.01
	H	-0.06	-0.34	-0.14		H	-0.17	-0.36	-0.07

	Cl	-0.40	-0.55	-0.82		Cl	-0.40	-0.55	-0.81
Ads. IM	**Charge population**				**Ads. IM**	**Charge population**			
	atom	**Mulliken**	**NBO**	**APT**		**atom**	**Mulliken**	**NBO**	**APT**
o-top	Al	1.19	-1.56	-0.53	**m-top**	Al	2.59	-1.45	-0.55
	Al	0.05	0.37	0.71		Al	-0.26	0.38	0.73
	Al	-0.22	0.02	0.01		Al	-0.08	0.08	0.04
	Al	0.58	0.12	0.10		Al	0.05	0.08	0.04
	Al	-0.19	-0.01	-0.07		Al	-0.31	0.13	-0.04
	Al	-0.76	0.02	-0.01		Al	-0.29	0.01	-0.09
	Al	-0.19	-0.01	-0.07		Al	-0.32	0.15	-0.01
	Al	0.02	0.09	-0.06		Al	-0.30	0.12	-0.04
	Al	0.07	0.26	0.03		Al	-0.57	0.10	-0.05
	Al	-0.22	0.02	0.01		Al	0.25	-0.01	0.16
	Al	-0.33	0.15	-0.01		Al	-0.29	0.00	-0.09
	Al	0.02	0.09	-0.06		Al	-0.33	0.15	-0.01
	Al	0.07	0.26	0.03		Al	-0.09	0.08	0.04
	H	-0.68	-0.29	-0.25		H	-0.65	-0.29	-0.29
	Cl	-0.42	-0.55	-0.82		Cl	-0.38	-0.55	-0.82
Ads. IM	**Charge population**				**Ads. IM**	**Charge population**			
	atom	**Mulliken**	**NBO**	**APT**		**atom**	**Mulliken**	**NBO**	**APT**
p-top	Al	-0.27	-1.44	-0.43	**o-hollow**	Al	0.87	-1.72	-0.60
	Al	0.27	0.32	0.62		Al	-0.05	0.46	0.65
	Al	-0.04	0.07	-0.05		Al	-0.11	0.02	-0.06
	Al	-0.06	0.08	-0.05		Al	-0.13	0.10	0.00
	Al	-0.06	0.08	-0.05		Al	-0.08	0.11	0.02
	Al	-0.04	0.07	-0.06		Al	-0.22	0.22	-0.01
	Al	-0.04	0.07	-0.05		Al	-0.03	0.08	-0.08
	Al	-0.06	0.08	-0.05		Al	-0.08	0.11	0.02
	Al	0.61	0.19	0.25		Al	0.02	0.14	0.07
	Al	-0.06	0.08	-0.05		Al	-0.08	0.04	0.00
	Al	-0.03	0.06	-0.06		Al	-0.22	0.22	-0.01
	Al	-0.04	0.07	-0.06		Al	-0.11	0.02	-0.06
	Al	-0.06	0.08	-0.05		Al	-0.13	0.10	0.00
	H	-0.68	-0.29	-0.68		H	-0.11	-0.37	-0.15
	Cl	-0.47	-0.53	-0.23		Cl	-0.52	-0.55	-0.77
Ads. IM	**Charge population**				**Ads. IM**	**Charge population**			
	atom	**Mulliken**	**NBO**	**APT**		**atom**	**Mulliken**	**NBO**	**APT**
	Al	-0.33	-1.70	-0.59		Al	-0.34	-1.67	-0.58
	Al	0.14	0.25	0.62		Al	0.26	0.29	0.64

m-hollow	Al	-0.05	0.10	-0.05	**p-hollow**	Al	-0.01	0.11	-0.01
	Al	-0.03	0.11	0.02		Al	-0.06	0.11	-0.01
	Al	-0.10	0.04	-0.01		Al	-0.09	0.04	0.00
	Al	0.08	0.18	-0.06		Al	-0.02	0.12	-0.06
	Al	0.01	0.10	-0.02		Al	-0.01	0.10	-0.01
	Al	-0.10	0.04	-0.02		Al	0.07	0.22	-0.03
	Al	-0.01	0.15	0.05		Al	0.04	0.20	0.02
	Al	0.05	0.22	0.02		Al	0.07	0.22	-0.03
	Al	0.08	0.18	-0.06		Al	-0.10	0.02	-0.06
	Al	-0.05	0.10	-0.05		Al	-0.03	0.12	-0.05
	Al	-0.03	0.11	0.02		Al	-0.09	0.04	-0.00
	H	-0.13	-0.34	-0.07		H	-0.14	-0.34	-0.01
	Cl	-0.52	-0.57	-0.79		Cl	-0.54	-0.57	-0.79



(a)



(b)

Figure S1. Snapshots for hydrogen migration and time evolution coordination numbers in $Al_{13}HI^-$ at 500K(a) and 1000K(b). The coordination is defined as the number of Al atom connected with H atom.

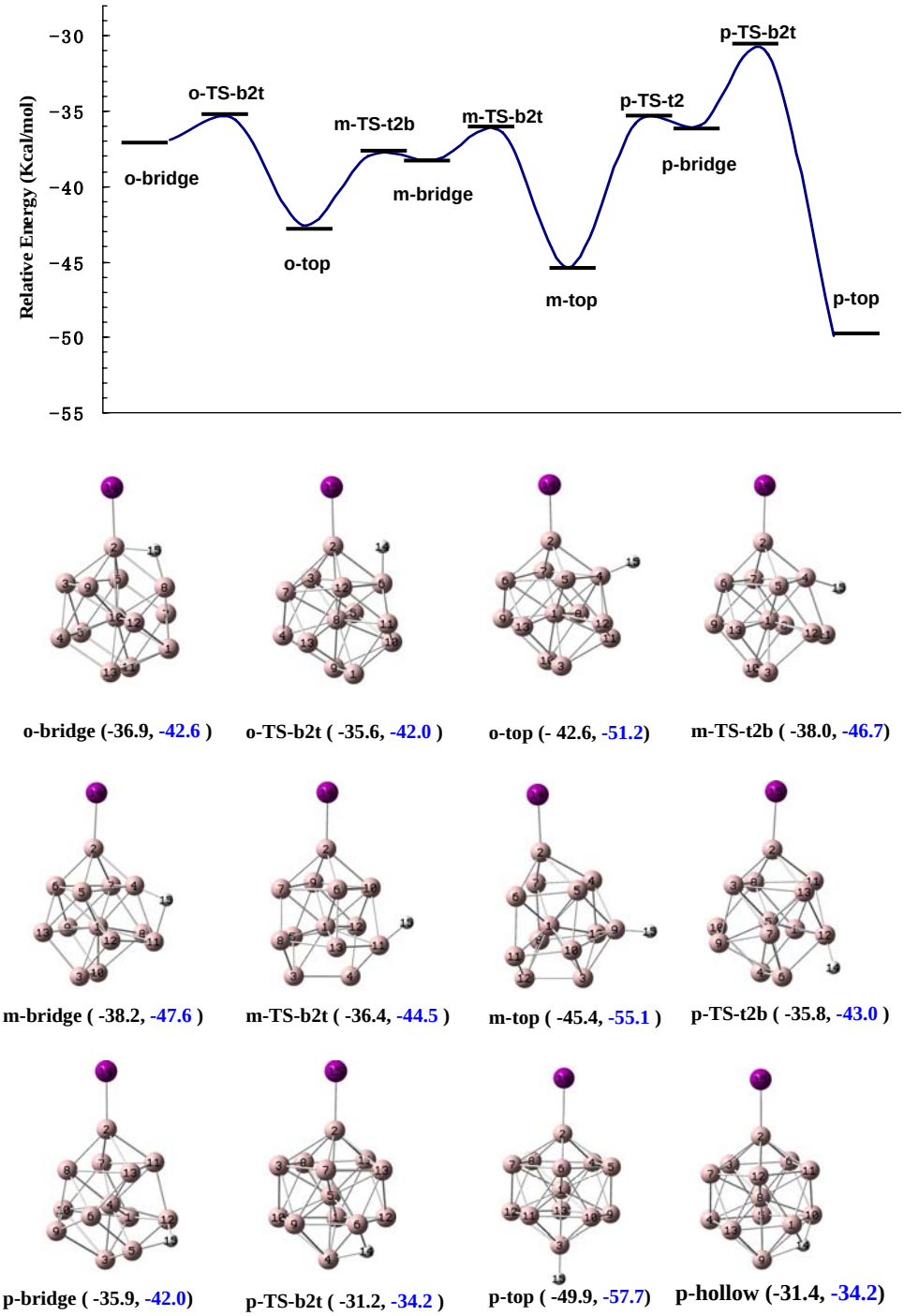


Figure S2. Potential energy surface (PES) curve and corresponding geometries for H migration started from o-bridge structure. The given energy in bracket labeled as black is the relative energy to separated reactants calculated by B3LYP/6-311++G(3df,2p)//B3LYP/6-31++G**, the energy labeled as blue is calculated by BHandHLYP/6-311++G(3df,2p)//BHandHLYP/6-31++G**. The unit of the energy is kcal/mol. The largest barrier for the H migration from o-bridge structure to the most stable o-top is 14.3 kcal/mol.

Reference:

1 B. K. Rao, S. N. Khanna and P. Jena, Phys. Rev. B: Condens. Matter, 2000, 62, 4666–4671.

2 J. Cioslowski, Phys. Rev. Lett., 1989, 62, 1469–1471.