Supporting Material

Supermetal: SbF_5-Mediated Methane Oxidation Occurs by C-H Activation and Isobutane Oxidation Occurs by Hydride Transfer

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Alternative ground states

In addition to examining the coordination of HF with $Sb^{V}F_5$, we also examined ground states with CO coordination. The reaction of $Sb^{V}F_5$ + CO → $F_5Sb^{V}(CO)$ has ΔH = -14.0 kcal/mol, and the Gibbs energy ΔG is -3.1 kcal/mol. This suggests that coordination of CO to Sb^{V} is slightly favorable, but reversible. For the dinuclear model, the ΔG for forming the $Sb^{V}_2F_{10}CO$ from Sb_2F_{10} + CO is -5.1 kcal/mol. The lack of strong coordination of CO to the Sb^{V} metal center is likely due to the lack of significant Sb^{V}-to-CO backbonding. $[Sb^{V}F_6]^-[H]^+$ + CO → $F_5Sb(CO)$ + HF is exergonic by 2.2 kcal/mol, and exothermic by 2.7 kcal/mol. For the dinuclear case, the energies are ΔG = -3.1 kcal/mol and ΔH = -2.6 kcal/mol. Methane also weakly associates with $Sb^{V}F_5$, but is endergonic relative to separated methane and $Sb^{V}F_5$. For $Sb^{V}F_5$ + CH_4 → $F_5Sb^{V}(CH_4)$ ΔG = 6.9 kcal/mol and ΔH = -2.4 kcal/mol).

Note about protonation vs hydrogen exchange transition-state structures

Using $[Sb^{V}F_6]^-[H]^+$, Mota[1] previously located both a methane protonation and a one-step hydrogen/hydrogen exchange transition-state structure. Using M06/6-31+G(d,p)/LANL2DZdp with a DMSO SMD solvent model, we were only able to locate a protonation transition state. In the absence of a solvent model, we located the one-step H/H exchange transition-state structure, but we were unable to locate the protonation transition state.

H_2 dissociation

We also located a transition state similar to **TS2**, but with $[Sb^{V}F_6]^-$ instead of CO displacing H_2 (Figure S1). The $\Delta G^{‡}$ for this process is 52.9 kcal/mol.

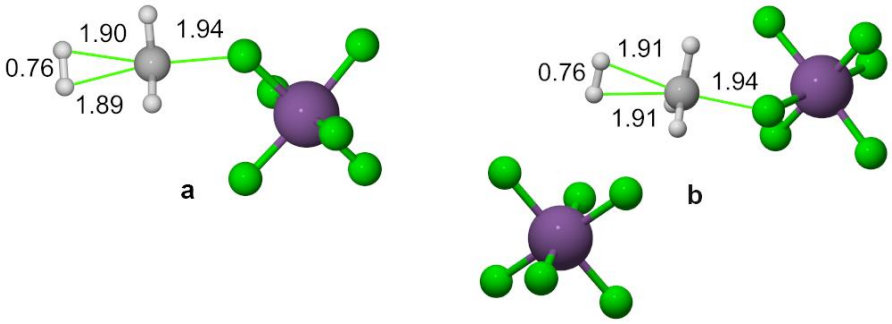
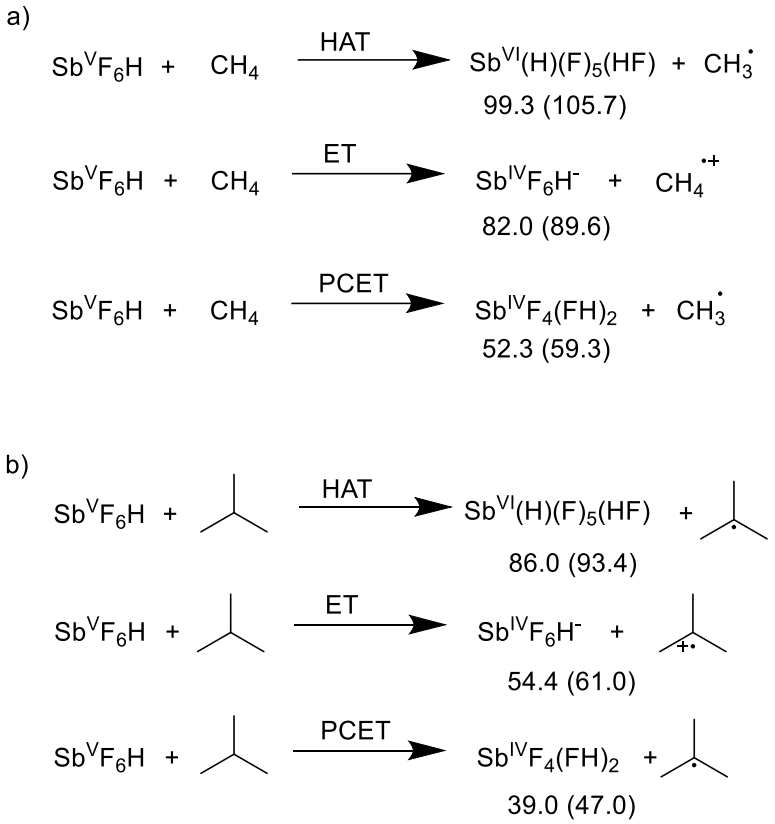


Figure S1. Transition states for H_2 dissociation without CO.

Outline of HAT, ET, and PCET pathways

Hydrogen atom transfer (HAT), electron transfer (ET), and proton-coupled electron transfer (PCET) pathways are less viable than hydride transfer and C-H activation pathways. Scheme S1 outlines calculated energies for these pathways.



Scheme S1. HAT, ET, and PCET reactions for a) methane and b) isobutane with $[Sb^{V}F_6]^-[H]^+$. Energies are given as ΔG (ΔH) in kcal/mol.

Alternative pathways for reduction of $Sb^{V}F_5$

We also explored $Sb^{V}F_5$ reduction by H_2. The exchange reaction thermodynamics for SbF_5 + H_2 → F_4SbH + HF are favorable, with ΔG = -12.9 kcal/mol and ΔH = -10.4 kcal/mol. The subsequent reductive elimination to form $Sb^{III}F_3$ and HF has a barrier with $\Delta G^{‡}$ = 23.1 kcal/mol and $\Delta H^{‡}$ = 22.1 kcal/mol). This moderate barrier suggests that while H_2 reduction of $Sb^{V}F_5$ is feasible, it is not instantaneous, which is consistent with the de Rege's observation.[2]

Comments on solvent model

The methane and isobutane reactions modeled were experimentally performed in either neat $Sb^{V}F_5$ (for methane) or $Sb^{V}F_5/SO_2FCl$ (for isobutane). In $Sb^{V}F_5$, there are known to be small detectable amounts of impurities.[2,3] However, as stated in the main manuscript, Sommer used acetone as a Brønsted base to demonstrate that the small quantity of protons in $Sb^{V}F_5$ are unlikely to be involved with the Sb^{V} to Sb^{III} reduction.[4] Complete accounting for the solvent effect of either neat $Sb^{V}F_5$ or $Sb^{V}F_5/SO_2FCl$ is not possible with continuum models. In condensed phase, SbF_5 forms oligomeric chains that can be modeled as tetramers.[5] While SbF_5 is relatively nonpolar with a low dielectric as a liquid, it does exhibit electrical charge conduction.[6] Because gas phase calculations likely underestimate the stability of charged structures, for example, in the hydride transfer pathway, we modeled the methane and isobutane oxidation reactions in both the gas phase and with the implicit continuum model for DMSO. We did this because many SbF_5 experiments have used SO_2FCl as a co-solvent,[7] and while DMSO is a crude model for this sulfone, it likely captures key electrostatic stabilization effects. This is critical for reliable estimation of carbocation

formation. Importantly, our qualitative conclusions about reaction pathways do not change when comparing gas phase with DMSO continuum results.

Note on isobutane reaction experiments and H/D exchange calculations

Experimentally, Sommer[8] observed that at low concentrations of $Sb^{V}F_5$ in HF (<20 mol %), H/D exchange of the tertiary hydrogen is faster than ionization. They further noted that between 20 and 25 mol % $Sb^{V}F_5$ in HF, protolytic ionization and H/D exchange are competitive, and that at concentration greater than 25 mol % $Sb^{V}F_5$, H/D exchange becomes negligible and ionization occurs with simultaneous reduction of $Sb^{V}F_5$ to $Sb^{III}F_3$. Our calculations using a continuum solvation model are only qualitatively consistent with these observations. Our calculations suggest that hydride abstraction of the tertiary hydrogen of isobutane has more than a 5 kcal/mol lower barrier than protonation. However, in the gas phase, we found an H/H exchange transition state for the tertiary hydrogen of isobutane, similar to the one reported by the Mota group.[1] This transition state has a barrier ~2 kcal/mol lower in energy than hydride abstraction. The close protonation and hydride abstraction barriers are qualitatively consistent with Sommer's observations.

Absolute and relative energies

Table S1. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.49138739	-40.44700302	-40.44318502	-40.46432902
SbF_5	-739.6927504	-739.6822696	-739.6737796	-739.7158196
HF	-100.4653924	-100.4561085	-100.4528035	-100.4725265
SbF_6H	-840.1780808	-840.1549256	-840.1445196	-840.1897096
SbF_6H-methane protonation TS (TS1m)	-880.6554238	-880.5786822	-880.5786822	-880.6296102
$SbF_6H + CH_4 \rightarrow$ TS1m	8.8	14.6	5.7	15.3
$[SbF_6]^-[CH_5]^+$ complex	-880.656476	-880.5744892	-880.5744892	-880.6258172
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	8.2	17.2	8.3	17.7
$[SbF_6]^-[CH_3]^+$ complex	-879.4538986	-879.4023249	-879.3903259	-879.4393989
H_2	-1.169826986	-1.156409749	-1.156409749	-1.171201749
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_3]^+ + H_2$	28.7	27.1	25.7	27.3
$[SbF_6]^-[CH_5]^+[CO]$ substitution TS (TS2m)	-993.9137183	-993.825662	-993.825662	-993.885865
CO	-113.2963149	-113.2912751	-113.2879701	-113.3104121
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	32.7	42.4	31.4	49.3
SbF_6H-methane-CO hydride abstraction TS (TS3m)	-993.9146661	-993.8252835	-993.8252835	-993.8864745
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	32.1	42.6	31.6	48.9

SbF_5-methane-CO hydride abstraction TS	-893.4449581	-893.370165	-893.370165	-893.426659
$SbF_6H \rightarrow SbF_5 + HF$	12.5	10.4	11.3	0.9
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	34.8	42.0	33.1	41.0
SbF_6H-methane CHTS (TS4m)	-880.6228348	-880.5457527	-880.5457527	-880.5980507
$SbF_6H + CH_4 \rightarrow$ TS4m	29.3	35.3	26.3	35.1
HF-SbF_4CH_3	-780.2146812	-780.1459524	-780.1459524	-780.1939344
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	-6.7	-0.1	-6.9	-7.8
HF-SbF_4CH_3-CO TS (TS5m)	-893.481168	-893.403254	-893.403254	-893.463030
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	12.1	21.2	12.3	18.1
CH_3CO^+	-153.0085626	-152.9647342	-152.9602072	-152.9887882
SbF_4^-	-640.0659517	-640.0518989	-640.0518989	-640.0907359
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\,HF + CH_3CO^+$	-24.8	-22.4	-26.4	-37.7
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-994.0308538	-993.954423	-993.93682	-994.003905
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-40.8	-38.4	-38.4	-24.8

Table S2. M06/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.49130474	-40.44692037	-40.44310237	-40.46424637
SbF_5	-739.6419137	-739.63143290	-739.62294290	-739.66498290
HF	-100.4575348	-100.44825094	-100.44494594	-100.46466894
SbF_6H	-840.1206937	-840.09753851	-840.08713251	-840.13232251
SbF_6H-methane protonation TS (TS1m)	-880.5994115	-880.52266990	-880.52266990	-880.57359790
$SbF_6H + CH_4 \rightarrow$ TS1m	7.9	13.7	4.7	14.4
$[SbF_6]^-[CH_5]^+$ complex	-880.6007508	-880.51876400	-880.51876400	-880.57009200
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	7.1	16.1	7.2	16.6
H_2	-1.170446848	-1.15702961	-1.15702961	-1.17182161
$[SbF_6]^-[CH_5]^+[CO]$ substitution TS (TS2m)	-993.8513204	-993.76326413	-993.76326413	-993.82346713
CO	-113.2894388	-113.28439898	-113.28109398	-113.30353598
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	31.4	41.2	30.2	48.1
SbF_6H-methane-CO hydride abstraction TS (TS3m)	-893.3922083	-893.30282565	-893.30282565	-893.36401665

$SbF_6H + CH_4 + CO \rightarrow$ TS3m	32.4	48.8	39.9	44.8
SbF_5-methane-CO hydride abstraction TS	-893.3922083	-893.31741523	-893.31741523	-893.37390923
$SbF_6H \rightarrow SbF_5 + HF$	13.3	11.2	12.1	1.7
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	32.4	39.7	30.7	38.6
SbF_6H-methane CHTS (TS4m)	-880.5689222	-880.49184007	-880.49184007	-880.54413807
$SbF_6H + CH_4 \rightarrow$ TS4m	27.0	33.0	24.1	32.9
HF-SbF_4CH_3	-780.1683796	-780.09965079	-780.09965079	-780.14763279
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	-8.7	-2.2	-9.0	-9.9
HF-SbF_4CH_3-CO TS (TS5m)	-893.4313012	-893.35338672	-893.35338672	-893.41316272
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	7.9	17.1	8.2	14.0
CH_3CO^+	-153.0027136	-152.95888518	-152.95435818	-152.98293918
SbF_4^-	-640.0300487	-640.01599593	-640.01599593	-640.05483293
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\ HF + CH_3CO^+$	-29.1	-26.7	-30.7	-42.0
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-993.9744056	-993.89797479	-993.88037179	-993.94745679
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-45.8	-43.4	-43.3	-29.7

Table S3. M06-2X/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.49872138	-40.45433701	-40.45051901	-40.47166301
SbF_5	-739.5594764	-739.54899557	-739.54050557	-739.58254557
HF	-100.4617798	-100.45249588	-100.44919088	-100.46891388
SbF_6H	-840.0445908	-840.02143561	-840.01102961	-840.05621961
SbF_6H-methane protonation TS (TS1m)	-880.533125	-880.45638342	-880.45638342	-880.50731142
$SbF_6H + CH_4 \rightarrow$ TS1m	6.4	12.2	3.2	12.9
$[SbF_6]^-[CH_5]^+$ complex	-880.5314385	-880.44945169	-880.44945169	-880.50077969
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	7.5	16.5	7.6	17.0
H_2	-1.167658262	-1.15424102	-1.15424102	-1.16903302
$[SbF_6]^-[CH_5]^+[CO]$ substitution TS (TS2m)	-993.8105926	-993.72253638	-993.72253638	-993.78273938
CO	-113.3167101	-113.31167030	-113.30836530	-113.33080730
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	31.0	40.7	29.7	47.7

SbF_6H-methane-CO hydride abstraction TS (TS3m)	-993.8011836	-993.71180103	-993.71180103	-993.77299203
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	36.9	47.5	36.5	53.8
SbF_5-methane-CO hydride abstraction TS	-893.3340616	-893.25926861	-893.25926861	-893.31576261
$SbF_6H \rightarrow SbF_5 + HF$	14.6	12.5	13.4	3.0
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	40.3	47.5	38.6	46.4
SbF_6H-methane CHTS (TS4m)	-880.4919203	-880.41483822	-880.41483822	-880.46713622
$SbF_6H + CH_4 \rightarrow$ TS4m	32.2	38.2	29.3	38.1
HF-SbF_4CH_3	-780.0854503	-780.01672149	-780.01672149	-780.06470349
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	-2.5	4.1	-2.7	-3.6
HF-SbF_4CH_3-CO TS (TS5m)	-893.3567864	-893.27887194	-893.27887194	-893.33864794
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	26.0	35.2	26.3	32.1
CH_3CO^+	-153.0312615	-152.98743305	-152.98290605	-153.01148705
SbF_4^-	-639.9132787	-639.89922591	-639.89922591	-639.93806291
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\ HF + CH_3CO^+$	-5.1	-2.6	-6.7	-18.0
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-993.8957419	-993.81931113	-993.80170813	-993.86879313
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-22.4	-20.0	-20.0	-6.3

Table S4. M06-2X/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.49999158	-40.45560721	-40.45178921	-40.47293321
SbF_5	-739.5472579	-739.53677706	-739.52828706	-739.57032706
HF	-100.4614057	-100.45212184	-100.44881684	-100.46853984
SbF_6H	-840.0341845	-840.01102935	-840.00062335	-840.04581335
SbF_6H-methane protonation TS (TS1m)	-880.5245728	-880.44783116	-880.44783116	-880.49875916
$SbF_6H + CH_4 \rightarrow$ TS1m	6.0	11.8	2.9	12.5
$[SbF_6]^-[CH_5]^+$ complex	-880.5228996	-880.44091283	-880.44091283	-880.49224083
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	7.1	16.1	7.2	16.6
H_2	-1.168046603	-1.15462937	-1.15462937	-1.16942137
$[SbF_6]^-[CH_5]^+$[CO] substitution TS (TS2m)	-993.7997744	-993.71171816	-993.71171816	-993.77192116
CO	-113.3145165	-113.30947674	-113.30617174	-113.32861374

$SbF_6H + CH_4 + CO \rightarrow$ TS2m	30.7	40.4	29.4	47.3
SbF_6H-methane-CO hydride abstraction TS (TS3m)	-993.7922001	-993.70281748	-993.70281748	-993.76400848
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	35.4	46.0	35.0	52.3
SbF_5-methane-CO hydride abstraction TS	-893.3251601	-893.25036707	-893.25036707	-893.30686107
$SbF_6H \rightarrow SbF_5 + HF$	16.0	13.9	14.8	4.4
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	39.0	46.2	37.3	45.2
SbF_6H-methane CHTS (TS4m)	-880.4854545	-880.40837237	-880.40837237	-880.46067037
$SbF_6H + CH_4 \rightarrow$ TS4m	30.6	36.6	27.6	36.4
$HF\text{-}SbF_4CH_3$	-780.0791449	-780.01041605	-780.01041605	-780.05839805
$SbF_6H + CH_4 \rightarrow HF\text{-}SbF_4CH_3 + HF$	-4.0	2.6	-4.3	-5.1
$HF\text{-}SbF_4CH_3$-CO TS (TS5m)	-893.3494034	-893.27148889	-893.27148889	-893.33126489
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	23.8	32.9	24.0	29.8
CH_3CO^+	-153.0295395	-152.98571111	-152.98118411	-153.00976511
SbF_4^-	-639.9070543	-639.89300148	-639.89300148	-639.93183848
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\ HF + CH_3CO^+$	-6.7	-4.3	-8.3	-19.7
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-993.8879607	-993.81152990	-993.79392690	-993.86101190
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-24.6	-22.2	-22.2	-8.6

Table S5. ωB97X-D/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.51776887	-40.47338450	-40.46956650	-40.49071050
SbF_5	-739.7227122	-739.71223144	-739.70374144	-739.74578144
HF	-100.4735997	-100.46431575	-100.46101075	-100.48073375
SbF_6H	-840.2125278	-840.18937256	-840.17896656	-840.22415656
SbF_6H-methane protonation TS (TS1m)	-880.7202557	-880.64351405	-880.64351405	-880.69444205
$SbF_6H + CH_4 \rightarrow$ TS1m	6.3	12.1	3.1	12.8
$[SbF_6]^-[CH_5]^+$ complex	-880.71937	-880.63738322	-880.63738322	-880.68871122
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	6.9	15.9	7.0	16.4
H_2	-1.175359346	-1.16194211	-1.16194211	-1.17673411

$[SbF_6]^-[CH_5]^+[CO]$ substitution TS (TS2m)	-993.9953396	-993.90728332	-993.90728332	-993.96748632
CO	-113.3164146	-113.31137485	-113.30806985	-113.33051185
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	32.2	41.9	30.9	48.9
SbF_6H-methane-CO hydride abstraction TS (TS3m)	-993.995173	-993.90579037	-993.90579037	-993.96698137
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	32.3	42.9	31.9	49.2
SbF_5-methane-CO hydride abstraction TS	-893.5162977	-893.44150465	-893.44150465	-893.49799865
$SbF_6H \rightarrow SbF_5 + HF$	10.2	8.0	8.9	-1.5
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	35.7	42.9	33.9	41.8
SbF_6H-methane CHTS (TS4m)	-880.6851766	-880.60809448	-880.60809448	-880.66039248
$SbF_6H + CH_4 \rightarrow$ TS4m	28.3	34.3	25.4	34.2
$HF\text{-}SbF_4CH_3$-CO TS (TS5m)	-893.5491402	-893.47122567	-893.47122567	-893.53100167
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	15.0	24.2	15.3	21.1
CH_3CO^+	-153.049767	-153.00593856	-153.00141156	-153.02999256
SbF_4^-	-640.0832002	-640.06914743	-640.06914743	-640.10798443
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\ HF + CH_3CO^+$	-21.0	-18.6	-22.6	-33.9
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-994.1072637	-994.03083292	-994.01322992	-994.08031492
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-38.0	-35.6	-35.5	-21.9

Table S6. ωB97X-D/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.51833367	-40.47394930	-40.47013130	-40.49127530
SbF_5	-739.6893999	-739.67891908	-739.67042908	-739.71246908
HF	-100.4693224	-100.46003854	-100.45673354	-100.47645654
SbF_6H	-840.1767144	-840.15355918	-840.14315318	-840.18834318
SbF_6H-methane protonation TS (TS1m)	-880.6854167	-880.60867514	-880.60867514	-880.65960314
$SbF_6H + CH_4 \rightarrow$ TS1m	6.0	11.8	2.9	12.6
$[SbF_6]^-[CH_5]^+$ complex	-880.6842655	-880.60227866	-880.60227866	-880.65360666
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	6.8	15.8	6.9	16.3
H_2	-1.175834565	-1.16241733	-1.16241733	-1.17720933

$[SbF_6]^-[CH_5]^+[CO]$ substitution TS (TS2m)	-993.9560151	-993.86795887	-993.86795887	-993.92816187
CO	-113.312321	-113.30728119	-113.30397619	-113.32641819
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	32.2	41.9	30.9	48.9
SbF_6H-methane-CO hydride abstraction TS (TS3m)	-993.9584303	-993.86904768	-993.86904768	-993.93023868
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	30.7	41.3	30.3	47.6
SbF_5-methane-CO hydride abstraction TS	-893.4833369	-893.40854391	-893.40854391	-893.46503791
$SbF_6H \rightarrow SbF_5 + HF$	11.3	9.2	10.0	-0.4
$SbF_6H + CH_4 + CO \rightarrow$ TS3m + HF	34.3	41.5	32.6	40.5
SbF_6H-methane CHTS (TS4m)	-880.6528624	-880.57578032	-880.57578032	-880.62807832
$SbF_6H + CH_4 \rightarrow$ TS4m	26.5	32.5	23.5	32.3
$HF\text{-}SbF_4CH_3$	-780.2375704	-780.16884159	-780.16884159	-780.21682359
$SbF_6H + CH_4 \rightarrow HF\text{-}SbF_4CH_3 + HF$	-7.4	-0.9	-7.7	-8.6
$HF\text{-}SbF_4CH_3$-CO TS (TS5m)	-893.5182912	-893.44037674	-893.44037674	-893.50015274
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	12.4	21.6	12.6	18.5
$[CH_3CO]^+$	-153.0460899	-153.00226151	-152.99773451	-153.02631551
$[SbF_4]^-$	-640.0594759	-640.04542307	-640.04542307	-640.08426007
$SbF_6H + CH_4 + CO \rightarrow SbF_4^- + 2\ HF + CH_3CO^+$	-23.1	-20.7	-24.7	-36.1
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-994.0724506	-993.99601981	-993.97841681	-994.04550181
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-40.8	-38.4	-38.4	-24.8

Table S7. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.3787433	-158.2489496	-158.2422956	-158.2765306
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.543493	-998.392849	-998.377220	-998.434342
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	8.4	6.9	6.0	20.0
$[SbF_6]^-$	-839.8054495	-839.7925741	-839.7832271	-839.8230461
$[H_2C_4H_9]^+$	-158.731309	-158.592930	-158.585576	-158.621238
$SbF_6H + C_4H_{10} \rightarrow SbF_6^- + [H_2C_4H_9]^+$	12.6	11.5	11.3	13.8
$[H_2C_4H_9]^+\ [SbF_6]^-$ complex	-998.536937	-998.389963	-998.373075	-998.434172

$SbF_6H + C_4H_{10} \rightarrow [H_2C_4H_9]^+ [SbF_6]^-$	12.5	8.7	8.6	20.1
$[H_2C_4H_9]^+ [SbF_6]^-$ H_2 release TS (TS7m)	-998.540829	-998.387478	-998.370321	-998.431693
$SbF_6H + C_4H_{10} \rightarrow$ TS7m	10.0	10.3	10.4	21.7
$[C_4H_9]^+$	-157.5738561	-157.4579026	-157.4507026	-157.4867796
$[H_2C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-7.8	-13.4	-13.5	-23.1
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	4.8	-1.9	-2.2	-9.3
SbF_6H-C_4H_{10} hydride abstraction TS (TS8m)	-998.547378	-998.399350	-998.381850	-998.443672
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	5.9	2.8	3.1	14.2
$[HF\text{-}F_5SbH]^-$	-840.979366	-840.9493833	-840.9381593	-840.9875333
$SbF_6H + C_4H_{10} \rightarrow [HF\text{-}F_5SbH]^- + [C_4H_9]^+$	2.3	-2.1	-1.3	-5.1
$[F_5SbH]^-$	-740.5066950	-740.4886108	-740.4799968	-740.5198868
$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	6.8	0.8	2.1	-8.1
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1480.221379	-1480.190839	-1480.174482	-1480.234443
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow [F_5SbH]^-[SbF_5]$ TS + HF + $[C_4H_9]^+$	-6.9	-11.7	-10.9	-7.3
F_4SbH	-640.4171052	-640.4017258	-640.3939228	-640.4351278
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	-7.7	-13.9	-12.6	-22.2
HF-F_4SbH-C_4H_{10} protonation TS (TS9m)	-899.262510	-899.109337	-899.091971	-899.155174
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m + $[SbF_6]^- + [C_4H_9]^+$	-8.5	-15.5	-14.4	-4.0
F_4SbH-C_4H_{10} protonation TS	-798.7909755	-798.6498222	-798.6346552	-798.6942562
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above + $[SbF_6]^- + [C_4H_9]^+ + HF$	-4.6	-13.4	-11.6	-11.3
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-8.6	-10.2	-13.4	-22.4
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-16.3	-23.7	-26.9	-45.5

Table S8. M06/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G

C_4H_{10} (isobutane)	-158.376442	-158.24664832	-158.23999432	-158.27422932
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.485503	-998.33485920	-998.31923020	-998.37635220
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	7.3	5.9	5.0	19.0
$[SbF_6]^-$	-839.7478329	-839.73495748	-839.72561048	-839.76542948
$[H_2C_4H_9]^+$	-158.7306985	-158.59232034	-158.58496634	-158.62062834
$SbF_6H + C_4H_{10} \rightarrow SbF_6^- + [H_2C_4H_9]^+$	11.7	10.6	10.4	12.9
$[C_4H_9]^+$	-157.5727051	-157.45675158	-157.44955158	-157.48562858
$[H_2C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-7.8	-13.5	-13.6	-23.1
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	3.9	-2.9	-3.2	-10.2
SbF_6H-C_4H_{10} hydride abstraction TS (TS8m)	-998.4910756	-998.34304736	-998.32554736	-998.38736936
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	3.8	0.7	1.0	12.0
$[HF\text{-}F_5SbH]^-$	-840.9257109	-840.89572824	-840.88450424	-840.93387824
$SbF_6H + C_4H_{10} \rightarrow [HF\text{-}F_5SbH]^- + [C_4H_9]^+$	-0.8	-5.2	-4.3	-8.1
$[F_5SbH]^-$	-740.4603343	-740.44225012	-740.43363612	-740.47352612
$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	4.1	-1.9	-0.6	-10.8
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1480.126435	-1480.095895	-1480.079538	-1480.139499
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow [F_5SbH]^-[SbF_5]$ TS + HF + $[C_4H_9]^+$	-11.1	-15.9	-15.0	-11.5
F_4SbH	-640.3774999	-640.36212052	-640.35431752	-640.39552252
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	-10.4	-16.6	-15.3	-24.9
HF-F_4SbH-C_4H_{10} protonation TS (TS9m)	-899.2625096	-899.10933670	-899.09197070	-899.15517370
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m + $[SbF_6]^- + [C_4H_9]^+$	-42.4	-49.4	-48.4	-37.9
F_4SbH-C_4H_{10} protonation TS	-798.7531057	-798.61195241	-798.59678541	-798.65638641
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above + $[SbF_6]^- + [C_4H_9]^+ + HF$	-9.8	-18.6	-16.8	-16.5
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-14.6	-16.3	-19.5	-28.5
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-22.5	-29.8	-33.0	-51.6

Table S9. M062x/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.4223445	-158.29255081	-158.28589681	-158.32013181
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.4582239	-998.30758010	-998.29195110	-998.34907310
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	5.5	4.0	3.1	17.1
$[SbF_6]^-$	-839.6774603	-839.66458493	-839.65523793	-839.69505693
$[H_2C_4H_9]^+$	-158.7731539	-158.63477573	-158.62742173	-158.66308373
$SbF_6H + C_4H_{10} \rightarrow SbF_6^- + [H_2C_4H_9]^+$	10.2	9.2	9.0	11.4
$[C_4H_9]^+$	-157.6131312	-157.49717768	-157.48997768	-157.52605468
$[H_2C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-4.8	-10.4	-10.5	-20.1
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	5.5	-1.3	-1.6	-8.7
SbF_6H-C_4H_{10} hydride abstraction TS (TS8m)	-998.4481861	-998.30015780	-998.28265780	-998.34447980
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	11.8	8.7	9.0	20.0
$[HF\text{-}F_5SbH]^-$	-840.8377805	-840.80779783	-840.79657383	-840.84594783
$SbF_6H + C_4H_{10} \rightarrow [HF\text{-}F_5SbH]^- + [C_4H_9]^+$	10.1	5.7	6.5	2.7
$[F_5SbH]^-$	-740.3676542	-740.34956998	-740.34095598	-740.38084598
$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	15.3	9.3	10.5	0.3
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1479.953032	-1479.922492	-1479.906135	-1479.966096
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow [F_5SbH]^-[SbF_5]$ TS + HF + $[C_4H_9]^+$	-1.0	-5.8	-4.9	-1.4
F_4SbH	-640.2728442	-640.25746482	-640.24966182	-640.29086682
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	0.8	-5.5	-4.2	-13.8
HF-F_4SbH-C_4H_{10} protonation TS (TS9m)	-899.151785	-898.99861210	-898.98124610	-899.04444910
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m + $[SbF_6]^- + [C_4H_9]^+$	4.0	-3.0	-2.0	8.5
F_4SbH-C_4H_{10} protonation TS	-798.682386	-798.54123273	-798.52606573	-798.58566673
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above + $[SbF_6]^- + [C_4H_9]^+ + HF$	8.8	0.0	1.8	2.1
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	6.2	4.6	1.4	-7.6

SbF_6H + 2 C_4H_{10} + SbF_5 → $[SbF_4]^-$ + $[SbF_6]^-$ + 2 $[C_4H_9]^+$ + HF + H_2	1.5	-5.9	-9.1	-27.7

Table S10. M06-2X/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.4241769	-158.29438319	-158.28772919	-158.32196419
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.4505499	-998.29990606	-998.28427706	-998.34139906
SbF_6H + C_4H_{10} → TS6m	4.9	3.5	2.6	16.6
$[SbF_6]^-$	-839.6669645	-839.65408910	-839.64474210	-839.68456110
$[H_2C_4H_9]^+$	-158.7753166	-158.63693839	-158.62958439	-158.66524639
SbF_6H + C_4H_{10} → SbF_6^- + $[H_2C_4H_9]^+$	10.1	9.0	8.8	11.3
$[C_4H_9]^+$	-157.6145115	-157.49855795	-157.49135795	-157.52743495
$[H_2C_4H_9]^+$ → H_2 + $[C_4H_9]^+$	-4.5	-10.2	-10.3	-19.8
SbF_6H + C_4H_{10} → $[SbF_6]^-$ + $[C_4H_9]^+$ + H_2	5.5	-1.2	-1.5	-8.6
SbF_6H-C_4H_{10} hydride abstraction TS (TS8m)	-998.4419084	-998.29388008	-998.27638008	-998.33820208
SbF_6H + C_4H_{10} → TS8m	10.3	7.2	7.5	18.6
$[HF\text{-}F_5SbH]^-$	-840.8305909	-840.80060817	-840.78938417	-840.83875817
SbF_6H + C_4H_{10} → $[HF\text{-}F_5SbH]^-$ + $[C_4H_9]^+$	8.3	3.9	4.8	1.0
$[F_5SbH]^-$	-740.3604234	-740.34233924	-740.33372524	-740.37361524
SbF_6H + C_4H_{10} → $[F_5SbH]^-$ + $[C_4H_9]^+$ + HF	13.8	7.8	9.1	-1.1
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1479.936584	-1479.906043	-1479.889686	-1479.949647
SbF_6H + C_4H_{10} + SbF_5 → $[F_5SbH]^-[SbF_5]$ TS + HF + $[C_4H_9]^+$	-4.3	-9.1	-8.3	-4.7
F_4SbH	-640.2642332	-640.24885382	-640.24105082	-640.28225582
SbF_6H + C_4H_{10} + SbF_5 → F_4SbH + $[SbF_6]^-$ + $[C_4H_9]^+$ + HF	-0.9	-7.2	-5.9	-15.5
HF-F_4SbH-C_4H_{10} protonation TS (TS9m)	-899.1479346	-898.99476176	-898.97739576	-899.04059876
SbF_6H + 2 C_4H_{10} + SbF_5 → TS9m + $[SbF_6]^-$ + $[C_4H_9]^+$	0.2	-6.8	-5.7	4.7
F_4SbH-C_4H_{10} protonation TS	-798.6786501	-798.53749676	-798.52232976	-798.58193076

SbF_6H + 2 C_4H_{10} + SbF_5 → TS above + $[SbF_6]^-$ + $[C_4H_9]^+$ + HF	5.2	-3.6	-1.8	-1.5
SbF_6H + 2 C_4H_{10} + SbF_5 → $[SbF_4]^-$ + $[H_2C_4H_9]^+$ + $[SbF_6]^-$ + $[C_4H_9]^+$ + HF	2.9	1.2	-2.0	-11.0
SbF_6H + 2 C_4H_{10} + SbF_5 → $[SbF_4]^-$ + $[SbF_6]^-$ + 2 $[C_4H_9]^+$ + HF + H_2	-1.7	-9.0	-12.3	-30.8

Table S11. ωB97X-D/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.4684528	-158.33865914	-158.33200514	-158.36624014
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.6729064	-998.52226256	-998.50663356	-998.56375556
SbF_6H + C_4H_{10} → TS6m	5.1	3.6	2.7	16.7
$[SbF_6]^-$	-839.839091	-839.82621558	-839.81686858	-839.85668758
$[H_2C_4H_9]^+$	-158.825002	-158.68662385	-158.67926985	-158.71493185
SbF_6H + C_4H_{10} → SbF_6^- + $[H_2C_4H_9]^+$	10.6	9.5	9.3	11.8
$[C_4H_9]^+$	-157.6584118	-157.54245830	-157.53525830	-157.57133530
$[H_2C_4H_9]^+$ → H_2 + $[C_4H_9]^+$	-5.5	-11.2	-11.3	-20.8
SbF_6H + C_4H_{10} → $[SbF_6]^-$ + $[C_4H_9]^+$ + H_2	5.1	-1.6	-1.9	-9.0
SbF_6H-C_4H_{10} hydride abstraction TS (TS8m)	-998.6721052	-998.52407697	-998.50657697	-998.56839897
SbF_6H + C_4H_{10} → TS8m	5.6	2.5	2.8	13.8
$[HF\text{-}F_5SbH]^-$	-841.0170484	-840.98706566	-840.97584166	-841.02521566
SbF_6H + C_4H_{10} → $[HF\text{-}F_5SbH]^-$ + $[C_4H_9]^+$	3.5	-0.9	-0.1	-3.9
$[F_5SbH]^-$	-740.535256	-740.51717182	-740.50855782	-740.54844782
SbF_6H + C_4H_{10} → $[F_5SbH]^-$ + $[C_4H_9]^+$ + HF	8.6	2.6	3.9	-6.4
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1480.272741	-1480.242200	-1480.225843	-1480.285804
SbF_6H + C_4H_{10} + SbF_5 → $[F_5SbH]^-[SbF_5]$ TS + HF + $[C_4H_9]^+$	-0.7	-5.5	-4.6	-1.1
F_4SbH	-640.4409571	-640.42557773	-640.41777473	-640.45897973

$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	-5.3	-11.5	-10.2	-19.8
$HF\text{-}F_4SbH\text{-}C_4H_{10}$ protonation TS (TS9m)	-899.383296	-899.23012313	-899.21275713	-899.27596013
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m $+ [SbF_6]^- + [C_4H_9]^+$	-5.4	-12.5	-11.4	-1.0
$F_4SbH\text{-}C_4H_{10}$ protonation TS	-798.9033515	-798.76219824	-798.74703124	-798.80663224
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [SbF_6]^- + [C_4H_9]^+ + HF$	-1.4	-10.2	-8.4	-8.1
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-4.5	-6.2	-9.3	-18.4
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-10.0	-17.3	-20.6	-39.2

Table S12. ωB97X-D/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.4678506	-158.33805685	-158.33140285	-158.36563785
$SbF_6H\text{-}C_4H_{10}$ protonation TS (TS6m)	-998.6372006	-998.48655682	-998.47092782	-998.52804982
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	4.6	3.2	2.3	16.3
$[SbF_6]^-$	-839.8021054	-839.78923002	-839.77988302	-839.81970202
$[H_2C_4H_9]^+$	-158.8252706	-158.68689239	-158.67953839	-158.71520039
$SbF_6H + C_4H_{10} \rightarrow SbF_6^- + [H_2C_4H_9]^+$	10.8	9.7	9.5	12.0
$[C_4H_9]^+$	-157.6580728	-157.54211934	-157.53491934	-157.57099634
$[H_2C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-5.4	-11.1	-11.2	-20.7
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	5.4	-1.3	-1.7	-8.7
$SbF_6H\text{-}C_4H_{10}$ hydride abstraction TS (TS8m)	-998.6384912	-998.49046297	-998.47296297	-998.53478497
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	3.8	0.7	1.0	12.0
$[HF\text{-}F_5SbH]^-$	-840.9838116	-840.95382887	-840.94260487	-840.99197887
$SbF_6H + C_4H_{10} \rightarrow [HF\text{-}F_5SbH]^- + [C_4H_9]^+$	1.7	-2.7	-1.9	-5.6
$[F_5SbH]^-$	-740.5056985	-740.48761434	-740.47900034	-740.51889034

$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	7.2	1.2	2.4	-7.8
$[F_5SbH]^-[SbF_5]$ fluoride transfer TS	-1480.213090	-1480.182549	-1480.166192	-1480.226153
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow [F_5SbH]^-[SbF_5]$ TS + $HF + [C_4H_9]^+$	-4.1	-8.9	-8.1	-4.5
F_4SbH	-640.4150963	-640.39971690	-640.39191390	-640.43311890
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	-6.7	-12.9	-11.6	-21.2
$HF\text{-}F_4SbH\text{-}C_4H_{10}$ protonation TS (TS9m)	-899.356045	-899.20287209	-899.18550609	-899.24870909
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m + $[SbF_6]^- + [C_4H_9]^+$	-9.0	-16.1	-15.0	-4.6
$F_4SbH\text{-}C_4H_{10}$ protonation TS	-798.880049	-798.73889569	-798.72372869	-798.78332969
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above + $[SbF_6]^- + [C_4H_9]^+ + HF$	-4.9	-13.6	-11.8	-11.5
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-7.8	-9.5	-12.6	-21.7
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-13.2	-20.6	-23.8	-42.4

Table S13. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.402266	-1479.379134	-1479.362187	-1479.423997
$Sb_2F_{10} \rightarrow 2\ SbF_5$	10.5	9.2	9.2	-4.8
$Sb_2F_{11}H$	-1579.88731	-1579.852433	-1579.833155	-1579.899726
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.366560	-1680.319458	-1680.298290	-1680.368858
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	12.3	10.8	11.4	2.0
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H + HF$	8.7	6.8	7.7	-2.1
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.373116	-1620.29614	-1620.274715	-1620.345527
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	3.5	2.1	1.0	11.6
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.378169	-1620.297474	-1620.275290	-1620.348246

$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	0.3	1.2	0.7	9.9
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.637638	-1733.553235	-1733.528372	-1733.608724
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	23.5	23.5	22.6	41.3
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-21.3	-22.6	-24.9	-23.4
Sb_2F_{10}-methane-CO hydride abstraction TS	-1633.169055	-1633.095675	-1633.073305	-1633.148102
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	25.5	24.4	24.0	33.8
$Sb_2F_{11}H$-methane-CO hydride abstraction TS (TS3d)	-1733.636602	-1733.552158	-1733.526809	-1733.609648
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS3d	24.1	24.2	23.5	40.7
Sb_2F_{10}-methane complex	-1519.901260	-1519.832921	-1519.813042	-1519.880072
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	7.6	6.5	6.6	7.2
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.339954	-1620.263541	-1620.241763	-1620.314633
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	24.3	22.5	21.7	31.0
$HF\text{-}F_9Sb_2CH_3$	-1519.938213	-1519.867871	-1519.847928	-1519.915207
$Sb_2F_{11}H + CH_4 \rightarrow HF\text{-}F_9Sb_2CH_3$ + HF	-15.6	-15.4	-15.3	-14.9
$HF\text{-}F_9Sb_2CH_3$-CO TS (TS5d)	-1633.230185	-1633.155105	-1633.131328	-1633.210547
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS5d + HF	-12.9	-12.9	-12.4	-5.4
$[Sb_2F_9]^-$	-1379.836680	-1379.81785220	-1379.801413	-1379.864203
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\ HF + [CH_3CO]^+$	-63.4	-65.3	-64.6	-77.5
$[Sb_2F_9]^-(HF)_2[CH_3CO]^+$	-1733.788609	-1733.699536	-1733.672995	-1733.760337
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^-(HF)_2[CH_3CO]^+$	-71.3	-68.3	-68.2	-53.9

Table S14. M06/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.302747	-1479.279615	-1479.262668	-1479.324478
$Sb_2F_{10} \rightarrow 2\ SbF_5$	11.9	10.5	10.5	-3.4
$Sb_2F_{11}H$	-1579.781426	-1579.746549	-1579.727271	-1579.793842
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.252823	-1680.205720	-1680.184552	-1680.255120
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	13.3	11.7	12.3	2.9
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H + HF$	8.7	6.9	7.7	-2.1

$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.268502	-1620.191526	-1620.170101	-1620.240913
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	2.7	1.2	0.2	10.8
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.273539	-1620.192844	-1620.170660	-1620.243616
$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-0.5	0.4	-0.2	9.1
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.526313	-1733.441910	-1733.417047	-1733.497399
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	22.5	22.6	21.6	40.3
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-22.0	-23.3	-25.6	-24.1
Sb_2F_{10}-methane-CO hydride abstraction TS	-1633.067506	-1632.994126	-1632.971756	-1633.046553
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	23.3	22.3	21.8	31.6
Sb_2F_{10}-methane complex	-1519.805399	-1519.737061	-1519.717182	-1519.784212
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	6.1	5.1	5.2	5.8
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.237711	-1620.161298	-1620.139520	-1620.212390
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	22.0	20.2	19.4	28.7
HF-$F_9Sb_2CH_3$	-1519.843953	-1519.773611	-1519.753668	-1519.820947
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-18.0	-17.8	-17.7	-17.3
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1633.13096	-1633.055880	-1633.032103	-1633.111322
$Sb_2F_11H + CH_4 + CO \rightarrow$ TS5d + HF	-16.5	-16.5	-16.1	-9.0
$[Sb_2F_9]^-$	-1379.750664	-1379.731837	-1379.715398	-1379.778188
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\ HF + [CH_3CO]^+$	-66.7	-68.6	-67.9	-80.8

Table S15. M06-2X/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.139571	-1479.116439	-1479.099492	-1479.161302
$Sb_2F_{10} \rightarrow 2\ SbF_5$	12.9	11.6	11.6	-2.4
$Sb_2F_{11}H$	-1579.624029	-1579.589152	-1579.569874	-1579.636445
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.102901	-1680.055798	-1680.034630	-1680.105198
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	14.2	12.7	13.3	3.9
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H + HF$	10.7	8.9	9.8	-0.1
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.121920	-1620.044944	-1620.023519	-1620.094331

$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	0.5	-0.9	-2.0	8.6
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.124187	-1620.043492	-1620.021308	-1620.094264
$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-0.9	0.0	-0.6	8.7
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.405321	-1733.320918	-1733.296055	-1733.376407
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	21.4	21.5	20.5	39.2
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-20.7	-22.0	-24.3	-22.8
Sb_2F_{10}-methane-CO hydride abstraction TS	-1632.929377	-1632.855997	-1632.833627	-1632.908424
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	30.3	29.3	28.8	38.6
Sb_2F_{10}-methane complex	-1519.644464	-1519.576125	-1519.556246	-1519.623276
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	10.4	9.3	9.4	10.0
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.080291	-1620.003878	-1619.982100	-1620.054970
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	26.6	24.9	24.0	33.3
HF-$F_9Sb_2CH_3$	-1519.679244	-1519.608902	-1519.588959	-1519.656238
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-11.5	-11.2	-11.1	-10.7
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1632.978599	-1632.903519	-1632.879742	-1632.958961
$Sb_2F_11H + CH_4 + CO \rightarrow$ TS5d + HF	-0.6	-0.5	-0.1	6.9
$[Sb_2F_9]^-$	-1379.555400	-1379.536573	-1379.520134	-1379.582924
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2$ HF + $[CH_3CO]^+$	-44.4	-46.3	-45.6	-58.6

Table S16. M06-2X/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.117913	-1479.094781	-1479.077834	-1479.139644
$Sb_2F_{10} \rightarrow 2\ SbF_5$	14.7	13.3	13.3	-0.6
$Sb_2F_{11}H$	-1579.604722	-1579.569846	-1579.550568	-1579.617139
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.083151	-1680.036048	-1680.014880	-1680.085448
$Sb_2F_{11}H \rightarrow Sb_2F_{10}$ + HF	15.9	14.4	15.0	5.6
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H$ + HF	10.7	8.8	9.7	-0.1
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.104295	-1620.027319	-1620.005894	-1620.076706
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	0.3	-1.2	-2.2	8.4
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.106415	-1620.025720	-1620.003536	-1620.076492

$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-1.1	-0.2	-0.7	8.5
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.385284	-1733.300881	-1733.276018	-1733.356370
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	21.3	21.4	20.4	39.1
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-20.1	-21.4	-23.7	-22.2
Sb_2F_{10}-methane-CO hydride abstraction TS	-1632.911611	-1632.838231	-1632.815861	-1632.890658
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	29.0	28.0	27.5	37.3
Sb_2F_{10}-methane complex	-1519.628605	-1519.560267	-1519.540388	-1519.607418
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	9.2	8.2	8.3	8.9
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.065046	-1619.988633	-1619.966855	-1620.039725
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	24.9	23.1	22.3	31.6
HF-$F_9Sb_2CH_3$	-1519.664285	-1519.593943	-1519.574000	-1519.641279
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-13.2	-12.9	-12.8	-12.4
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1632.961764	-1632.886684	-1632.862907	-1632.942126
$Sb_2F_11H + CH_4 + CO \rightarrow$ TS5d + HF	-2.5	-2.4	-2.0	5.0
$[Sb_2F_9]^-$	-1379.538923	-1379.520096	-1379.503657	-1379.566447
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\ HF + [CH_3CO]^+$	-45.2	-47.1	-46.4	-59.4

Table S17. ωB97X-D/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.458914	-1479.435782	-1479.418835	-1479.480645
$Sb_2F_{10} \rightarrow 2\ SbF_5$	8.5	7.1	7.1	-6.9
$Sb_2F_{11}H$	-1579.94964	-1579.914763	-1579.895485	-1579.962056
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.438353	-1680.391250	-1680.370082	-1680.440650
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	10.7	9.2	9.8	0.4
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H + HF$	9.5	7.6	8.5	-1.3
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.465347	-1620.388371	-1620.366946	-1620.437758
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	1.3	-0.1	-1.2	9.4
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.468972	-1620.388277	-1620.366093	-1620.439049
$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-1.0	-0.1	-0.7	8.6

$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.747326	-1733.662923	-1733.638060	-1733.718412
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	22.9	23.0	22.0	40.7
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-20.5	-21.8	-24.1	-22.6
Sb_2F_{10}-methane-CO hydride abstraction TS	-1633.267247	-1633.193867	-1633.171497	-1633.246294
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	27.0	25.9	25.5	35.3
Sb_2F_{10}-methane complex	-1519.978979	-1519.910641	-1519.890762	-1519.957792
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	9.3	8.3	8.3	8.9
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.430053	-1620.353640	-1620.331862	-1620.404732
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	23.4	21.7	20.8	30.1
HF-$F_9Sb_2CH_3$	-1520.016197	-1519.945855	-1519.925912	-1519.993191
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-14.0	-13.8	-13.7	-13.3
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1633.325996	-1633.250916	-1633.227139	-1633.306358
$Sb_2F_11H + CH_4 + CO \rightarrow$ TS5d + HF	-9.9	-9.9	-9.4	-2.4
$[Sb_2F_9]^-$	-1379.880488	-1379.861661	-1379.845222	-1379.908012
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2$ HF + $[CH_3CO]^+$	-58.8	-60.7	-59.9	-72.9

Table S18. ωB97X-D/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.395029	-1479.371897	-1479.354950	-1479.416760
$Sb_2F_{10} \rightarrow 2\ SbF_5$	10.2	8.8	8.8	-5.1
$Sb_2F_{11}H$	-1579.883550	-1579.848673	-1579.829395	-1579.895966
$[Sb_2F_{11}]^-[H_2F]^+$	-1680.368108	-1680.321005	-1680.299837	-1680.370405
$Sb_2F_{11}H \rightarrow Sb_2F_{10}$ + HF	12.0	10.5	11.1	1.7
$[Sb_2F_{11}]^-[H_2F]^+ \rightarrow Sb_2F_{11}H$ + HF	9.6	7.7	8.6	-1.3
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.400197	-1620.323221	-1620.301796	-1620.372608
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	1.1	-0.4	-1.4	9.2
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.403207	-1620.322512	-1620.300328	-1620.373284

$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-0.8	0.1	-0.5	8.8
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.677366	-1733.592963	-1733.568100	-1733.648452
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	23.1	23.2	22.2	40.9
$Sb_2F_{11}H + CH_4 + CO \rightarrow Sb_2F_{11}^- + CH_3CO^+ + H_2$	-19.8	-21.1	-23.4	-21.9
Sb_2F_{10}-methane-CO hydride abstraction TS	-1633.203905	-1633.130525	-1633.108155	-1633.182952
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	25.7	24.7	24.2	34.0
Sb_2F_{10}-methane complex	-1519.919224	-1519.850886	-1519.831007	-1519.898037
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ complex + HF	8.4	7.3	7.4	8.0
$Sb_2F_{11}H$-methane CHTS (TS4d)	-1620.367398	-1620.290985	-1620.269207	-1620.342077
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	21.6	19.9	19.0	28.3
HF-$F_9Sb_2CH_3$	-1519.957812	-1519.887470	-1519.867527	-1519.934806
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-15.8	-15.6	-15.5	-15.1
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1633.263958	-1633.188878	-1633.165101	-1633.244320
$Sb_2F_11H + CH_4 + CO \rightarrow$ TS5d + HF	-12.0	-11.9	-11.5	-4.5
$[Sb_2F_9]^-$	-1379.824807	-1379.805979	-1379.789540	-1379.852330
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2$ HF + $[CH_3CO]^+$	-59.8	-61.8	-61.0	-74.0

Table S19. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.259966	-1738.097185	-1738.072001	-1738.152002
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	3.8	2.6	2.2	15.2
$[Sb_2F_{11}]^-$	-1579.530514	-1579.505520	-1579.487300	-1579.551691
$[H_2][C_4H_9]^+[Sb_2F_{11}]^-$ H2 release TS (TS7d)	-1738.261883	-1738.101272	-1738.075304	-1738.157786
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS7d	2.6	0.1	0.1	11.6
$[H_2][C_4H_9]^+[Sb_2F_{11}]^-$ complex	-1738.267875	-1738.101202	-1738.075766	-1738.156090
$Sb_2F_{11}H + C_4H_{10} \rightarrow [H_2][C_4H_9]^+[Sb_2F_{11}]^-$	-1.1	0.1	-0.2	12.7

$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	2.7	1.8	1.6	2.1
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-5.1	-11.6	-11.9	-21.0
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.266641	-1738.106469	-1738.08016	-1738.163868
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	-0.4	-3.2	-3.0	7.8
$[HF][F_{10}Sb_2H]^-$	-1580.715456	-1580.673011	-1580.653156	-1580.721631
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-14.6	-18.5	-17.8	-20.2
$Sb_2F_{11}H$-isobutane tertiary carbon CHTS (TS9d)	-1738.213984	-1738.056372	-1738.030403	-1738.112038
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS9d	32.7	28.2	28.3	40.3
$[F_{10}Sb_2H]^-$	-1480.24541	-1480.214574	-1480.197462	-1480.259048
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ + HF$	-11.7	-17.1	-16.0	-26.4
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2320.419267	-2320.362382	-2320.335233	-2320.419385
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	-21.5	-23.0	-23.0	-8.8
HF-F_9Sb_2H	-1480.61927	-1480.577202	-1480.55898	-1480.623504
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-$F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	-25.0	-27.6	-27.4	-25.9
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1639.001871	-1638.833344	-1638.808273	-1638.888083
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d + $[SbF6]^- + [C_4H_9]^+$	-27.4	-32.1	-31.8	-18.4
$[HF][F_9Sb_2]^-[H_2][C_4H_9]^+$ complex	-1639.044175	-1638.872582	-1638.846201	-1638.930877
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [HF][F_9Sb_2]^-[H_2][C_4H_9]^+ + [C_4H_9]^+ + [SbF_6]^-$	-53.9	-56.8	-55.6	-45.2
SbF_3	-540.0235154	-540.018393	-540.012381	-540.048168
$Sb_2F_{11}H + 2\ C_4H_{10} + 2\ SbF_5 \rightarrow$ TS7d $+ [C_4H_9]^+ + [SbF_6]^- + SbF_3 + HF$	-62.6	-69.9	-68.5	-65.2
F_9Sb_2H-isobutane protonation TS	-1538.534675	-1538.378981	-1538.356311	-1538.430656
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ above TS $+ [SbF_6]^- + [C_4H_9]^+ + HF$	-26.2	-33.2	-32.3	-27.9
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-47.2	-53.2	-51.6	-62.2
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-54.9	-66.6	-65.1	-85.3

Table S20. M06/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.153381	-1737.990600	-1737.965416	-1738.045417
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	2.8	1.6	1.2	14.2
$[Sb_2F_{11}]^-$	-1579.424097	-1579.39910185	-1579.38088185	-1579.44527285
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	1.9	1.1	0.9	1.4
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-5.9	-12.4	-12.7	-21.7
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.162193	-1738.002021	-1737.975712	-1738.059420
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	-2.7	-5.5	-5.3	5.4
$[HF][F_{10}Sb_2H]^-$	-1580.612816	-1580.570371	-1580.550516	-1580.618991
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-17.4	-21.3	-20.6	-22.9
$[F_{10}Sb_2H]^-$	-1480.150277	-1480.119441	-1480.102329	-1480.163915
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ + HF$	-14.2	-19.6	-18.5	-29.0
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2320.267330	-2320.210445	-2320.183296	-2320.267448
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above + $[C_4H_9]^+$	-25.3	-26.7	-26.8	-12.6
HF-F_9Sb_2H	-1480.524458	-1480.482390	-1480.464168	-1480.528692
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-F_9Sb_2H + $[SbF_6]^-$ + $[C_4H_9]^+$	-28.4	-31.0	-30.8	-29.3
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1638.906460	-1638.737933	-1638.712862	-1638.792672
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d + $[SbF6]^-$ + $[C_4H_9]^+$	-31.9	-36.6	-36.3	-22.9
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-52.2	-58.3	-56.6	-67.3
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-60.0	-71.7	-70.2	-90.4

Table S21. M06-2X/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure

geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.045430	-1737.882649	-1737.857465	-1737.937466
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	0.6	-0.6	-1.1	12.0
$[Sb_2F_{11}]^-$	-1579.273492	-1579.248497	-1579.230277	-1579.294668
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	-0.2	-1.0	-1.2	-0.7
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-5.0	-11.4	-11.7	-20.8
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.038498	-1737.878326	-1737.852017	-1737.935725
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	4.9	2.1	2.4	13.1
$[HF][F_{10}Sb_2H]^-$	-1580.44447	-1580.402024	-1580.382169	-1580.450644
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-7.0	-11.0	-10.3	-12.6
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2320.018671	-2319.961786	-2319.934637	-2320.018789
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above + $[C_4H_9]^+$	-16.3	-17.7	-17.8	-3.6
HF-F_9Sb_2H	-1480.345649	-1480.303581	-1480.285359	-1480.349883
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-F_9Sb_2H + $[SbF_6]^-$ + $[C_4H_9]^+$	-19.1	-21.7	-21.5	-20.0
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1638.767098	-1638.598571	-1638.573500	-1638.653310
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d + [SbF6]$^-$ + $[C_4H_9]^+$	-18.5	-23.3	-22.9	-9.5
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	-33.1	-39.1	-37.5	-48.2
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	-37.9	-49.6	-48.1	-68.3

Table S22. M06-2X/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$[Sb_2F_{11}]^-$	-1579.253753	-1579.228758	-1579.210538	-1579.274929
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	-0.1	-0.9	-1.1	-0.7
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-4.7	-11.1	-11.4	-20.5

$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.023606	-1737.863434	-1737.837125	-1737.920833
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	3.3	0.5	0.7	11.5
$[HF][F_{10}Sb_2H]^-$	-1580.428014	-1580.385569	-1580.365714	-1580.434189
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-8.6	-12.5	-11.8	-14.1
$[F_{10}Sb_2H]^-$	-1479.960696	-1479.929860	-1479.912748	-1479.974334
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ +$ HF	-4.8	-10.2	-9.2	-19.6
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2319.991963	-2319.935078	-2319.907929	-2319.992081
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	-19.0	-20.5	-20.5	-6.3
HF-F_9Sb_2H	-1480.328696	-1480.286628	-1480.268406	-1480.332930
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-$F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	-21.3	-24.0	-23.8	-22.3
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1638.753681	-1638.585154	-1638.560083	-1638.639893
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d $+ [SbF6]^- + [C_4H_9]^+$	-21.9	-26.6	-26.3	-12.9
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ +$ HF	-35.6	-41.7	-40.1	-50.7
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ +$ HF $+ H_2$	-40.2	-51.9	-50.4	-70.6

Table S23. ωB97X-D/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.417209	-1738.254428	-1738.229244	-1738.309245
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	0.6	-0.6	-1.1	12.0
$[Sb_2F_{11}]^-$	-1579.591375	-1579.566380	-1579.548160	-1579.612551
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	1.1	0.3	0.0	0.5
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-4.4	-10.9	-11.2	-20.3
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.418878	-1738.258706	-1738.232397	-1738.316105

$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	-0.5	-3.3	-3.1	7.7
$[HF][F_{10}Sb_2H]^-$	-1580.779721	-1580.737276	-1580.717421	-1580.785896
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-12.6	-16.5	-15.8	-18.2
$[F_{10}Sb_2H]^-$	-1480.300867	-1480.270031	-1480.252919	-1480.314505
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ +$ HF	-9.3	-14.7	-13.6	-24.0
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2320.509466	-2320.452581	-2320.425432	-2320.509584
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	-17.0	-18.4	-18.5	-4.3
HF-F_9Sb_2H	-1480.678099	-1480.636031	-1480.617809	-1480.682333
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-$F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	-21.8	-24.5	-24.3	-22.8
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1639.151717	-1638.983190	-1638.958119	-1639.037929
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d + [SbF6]$^-$ + $[C_4H_9]^+$	-25.1	-29.8	-29.5	-16.1
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ +$ HF	-42.3	-48.3	-46.7	-57.3
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ +$ HF + H_2	-47.8	-59.4	-57.9	-78.1

Table S24. ωB97X-D/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)].

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.351249	-1738.188468	-1738.163284	-1738.243285
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	0.1	-1.1	-1.6	11.5
$[Sb_2F_{11}]^-$	-1579.523805	-1579.498810	-1579.480590	-1579.544981
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	1.5	0.6	0.4	0.9
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	-4.0	-10.4	-10.7	-19.8
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.355093	-1738.194921	-1738.168612	-1738.252320
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	-2.3	-5.1	-4.9	5.8
$[HF][F_{10}Sb_2H]^-$	-1580.715623	-1580.673177	-1580.653322	-1580.721797

$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	-14.0	-17.9	-17.2	-19.6
$[F_{10}Sb_2H]^-$	-1480.240601	-1480.209765	-1480.192653	-1480.254239
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ +$ HF	-10.4	-15.8	-14.8	-25.2
$[HF][F_{10}Sb_2H]^-$-SbF_5 fluoride transfer TS	-2320.414268	-2320.357382	-2320.330234	-2320.414386
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	-19.8	-21.2	-21.3	-7.1
HF-F_9Sb_2H	-1480.618553	-1480.576485	-1480.558263	-1480.622787
$Sb_2F_11H + C_4H_{10} + SbF_5 \rightarrow$ HF-$F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	-23.8	-26.5	-26.3	-24.7
HF-F_9Sb_2H-isobutane protonation TS (TS10d)	-1639.093201	-1638.924674	-1638.899603	-1638.979413
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS10d + $[SbF6]^- + [C_4H_9]^+$	-28.1	-32.8	-32.5	-19.1
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ +$ HF	-44.5	-50.5	-48.9	-59.6
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ +$ HF + H_2	-49.9	-61.6	-60.1	-80.3

Table S25. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.4931564	-40.44877203	-40.44495403	-40.46609803
SbF_5	-739.6863876	-739.6759069	-739.6674169	-739.7094569
HF	-100.4570883	-100.4478044	-100.4444994	-100.4642224
SbF_6H	-840.1587855	-840.1356303	-840.1252243	-840.1704143
SbF_6H-methane protonation TS (TS1m)	-880.6182616	-880.554454	-880.54152	-880.592448
$SbF_6H + CH_4 \rightarrow$ TS1m	21.1	18.8	18.0	27.7
$[SbF_6]^-[CH_5]^+$ complex	-880.5938512	-880.5250155	-880.5118645	-880.5631925
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$ complex	36.5	37.3	36.6	46.0
$[SbF_6]^-[CH_5]^+$[CO] substitution TS (TS2m)	-993.8535173	-993.781607	-993.765461	-993.825664
CO	-113.3014373	-113.2963975	-113.2930925	-113.3155345

$SbF_6H + CH_4 + CO \rightarrow$ TS2m	62.7	62.2	61.4	79.3
SbF_6H-methane-CO hydride abstraction TS (TS3)	-993.8669724	-993.7775898	-993.7775898	-993.8387808
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	54.2	64.8	53.8	71.1
SbF_5-methane-CO hydride abstraction TS	-893.4015075	-893.3407235	-893.3267145	-893.3832085
$SbF_6H \rightarrow SbF_5 + HF$	9.6	7.5	8.4	-2.0
$SbF_6H + CH_4 + CO \rightarrow$ TS above + HF	59.5	57.9	57.8	65.6
SbF_6H-methane CHTS (TS4m)	-880.5877359	-880.5237848	-880.5106538	-880.5629518
$SbF_6H + CH_4 \rightarrow$ TS4m	40.3	38.0	37.4	46.2
HF-SbF_4CH_3	-780.1907453	-780.1338075	-780.1220165	-780.1699985
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	2.6	1.8	2.3	1.4
HF-SbF_4CH_3-CO TS (TS5m)	-893.4218898	-893.3592273	-893.3439753	-893.4037513
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	46.7	46.3	46.9	52.8
$[CH_3CO]^+$	-152.8932751	-152.8932751	-152.8932751	-152.8932751
$[SbF_4]^-$	-639.9707653	-639.9643725	-639.9567125	-639.9955495
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^- + 2\ HF + [CH_3CO]^+$	109.9	80.0	78.0	84.6
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-993.9110039	-993.8345731	-993.8169701	-993.8840551
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$	26.6	29.0	29.1	42.7

Table S26. ωB97X-D/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
CH_4	-40.51998454	-40.47560017	-40.47178217	-40.49292617
SbF_5	-739.6824768	-739.67199604	-739.66350604	-739.70554604
HF	-100.4612354	-100.45195154	-100.44864654	-100.46836954
SbF_6H	-840.1572439	-840.13408872	-840.12368272	-840.16887272
SbF_6H-methane protonation TS (TS1m)	-880.6478447	-880.57110311	-880.57110311	-880.62203111
$SbF_6H + CH_4 \rightarrow$ TS1m	18.4	24.2	15.3	25.0
$[SbF_6]^-[CH_5]^+$ complex	-880.6214994	-880.53951256	-880.53951256	-880.59084056
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$ complex	35.0	44.0	35.1	44.5
$[SbF_6]^-[CH_5]^+$[CO] substitution TS (TS2m)	-993.8956598	-993.80760350	-993.80760350	-993.86780650

CO	-113.3174644	-113.31242455	-113.30911955	-113.33156155
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	62.1	71.9	60.9	78.8
SbF_6H-methane-CO hydride abstraction TS (TS3)	-993.9104411	-993.82105845	-993.82105845	-993.88224945
$SbF_6H + CH_4 + CO \rightarrow$ TS3m	52.9	63.4	52.4	69.7
SbF_5-methane-CO hydride abstraction TS	-893.4395296	-893.36473655	-893.36473655	-893.42123055
$SbF_6H \rightarrow SbF_5 + HF$	8.5	6.4	7.2	-3.2
$SbF_6H + CH_4 + CO \rightarrow$ TS above + HF	58.9	66.2	57.2	65.1
SbF_6H-methane CHTS (TS4m)	-880.6171855	-880.54010337	-880.54010337	-880.59240137
$SbF_6H + CH_4 \rightarrow$ TS4m	37.7	43.7	34.7	43.5
HF-SbF_4CH_3	-780.2137863	-780.14505751	-780.14505751	-780.19303951
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	1.4	8.0	1.1	0.2
HF-SbF_4CH_3-CO TS (TS5m)	-893.4592955	-893.38138098	-893.38138098	-893.44115698
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	46.5	55.7	46.8	52.6
$[CH_3CO]^+$	-152.9309349	-152.88710650	-152.88257950	-152.91116050
$[SbF_4]^-$	-639.9657859	-639.95173313	-639.95173313	-639.99057013
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^- + 2\ HF + [CH_3CO]^+$	110.1	112.6	108.5	97.2
$[SbF_4]^-(HF)_2[CH_3CO]^+$ complex	-993.9543312	-993.87790044	-993.86029744	-993.92738244
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^-(HF)_2[CH_3CO]^+$	25.3	27.7	27.8	41.4

Table S27. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.3777656	-158.2479719	-158.2413179	-158.2755529
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.5153798	-998.364736	-998.349107	-998.406229
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	13.3	11.8	10.9	24.9
$[SbF_6]^-$	-839.7293914	-839.716516	-839.707169	-839.746988
$[H_2][C_4H_9]^+$	-158.6194993	-158.4811212	-158.4737672	-158.5094292
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [H_2][C_4H_9]^+$	117.8	116.7	116.5	118.9
H_2	-1.170723437	-1.1573062	-1.1573062	-1.1720982
$[C_4H_9]^+$	-157.4729345	-157.356981	-157.349781	-157.385858
$[H_2][C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-15.2	-20.8	-20.9	-30.5

$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	102.6	95.9	95.6	88.5
SbF_6H-isobutane hydride abstraction TS (TS8m)	-998.5134895	-998.3654612	-998.3479612	-998.4097832
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	14.5	11.4	11.7	22.7
$[HF][F_5SbH]^-$	-840.90188	-840.8718973	-840.8606733	-840.9100473
$SbF_6H + C_4H_{10} \rightarrow [HF][F_5SbH]^- + [C_4H_9]^+$	101.5	97.1	97.9	94.2
$[F_5SbH]^-$	-740.4216458	-740.4035616	-740.3949476	-740.4348376
$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	116.0	110.0	111.3	101.1
$[F_5SbH]^-SbF_5$ fluoride transfer TS	-1480.145822	-1480.115281	-1480.098924	-1480.158885
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ HF + [C_4H_9]^+$	92.3	87.5	88.3	91.9
F_4SbH	-640.4011961	-640.3858167	-640.3780137	-640.4192187
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	101.9	95.6	96.9	87.3
HF-F_4SbH-isobutane protonation TS (TS9m)	-899.2107004	-899.0575275	-899.0401615	-899.1033645
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m $+ [SbF_6]^- + [C_4H_9]^+$	117.8	110.7	111.8	122.2
F_4SbH-isobutane protonation TS	-798.7408221	-798.5996688	-798.5845018	-798.6441028
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [SbF_6]^- + [C_4H_9]^+ + HF$	125.8	117.0	118.8	119.1
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	220.3	213.8	215.5	206.4
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	205.1	193.0	194.5	176.0

Table S28. ωB97X-D/aug-cc-PVTZ energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.4666709	-158.33687716	-158.33022316	-158.36445816
SbF_6H-C_4H_{10} protonation TS (TS6m)	-998.6086734	-998.45802959	-998.44240059	-998.49952259
$SbF_6H + C_4H_{10} \rightarrow$ TS6m	9.6	8.1	7.2	21.2
$[SbF_6]^-$	-839.7263018	-839.71342639	-839.70407939	-839.74389839
$[H_2][C_4H_9]^+$	-158.7133156	-158.57493744	-158.56758344	-158.60324544

$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [H_2][C_4H_9]^+$	115.6	114.6	114.4	116.8
H_2	-1.176667787	-1.16325055	-1.16325055	-1.17804255
$[C_4H_9]^+$	-157.5571526	-157.44119913	-157.43399913	-157.47007613
$[H_2][C_4H_9]^+ \rightarrow H_2 + [C_4H_9]^+$	-12.9	-18.5	-18.6	-28.2
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [C_4H_9]^+ + H_2$	102.8	96.1	95.7	88.7
SbF_6H-isobutane hydride abstraction TS (TS8m)	-998.6041987	-998.45617046	-998.43867046	-998.50049246
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	12.4	9.3	9.6	20.6
$[HF][F_5SbH]^-$	-840.9067348	-840.87675213	-840.86552813	-840.91490213
$SbF_6H + C_4H_{10} \rightarrow [HF][F_5SbH]^- + [C_4H_9]^+$	100.4	96.0	96.9	93.1
$[F_5SbH]^-$	-740.421158	-740.40307375	-740.39445975	-740.43434975
$SbF_6H + C_4H_{10} \rightarrow [F_5SbH]^- + [C_4H_9]^+ + HF$	115.7	109.7	110.9	100.7
$[F_5SbH]^-SbF_5$ fluoride transfer TS	-1480.137894	-1480.107353	-1480.090996	-1480.150957
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ HF + [C_4H_9]^+$	94.2	89.4	90.2	93.8
F_4SbH	-640.3991283	-640.38374893	-640.37594593	-640.41715093
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ + HF$	102.0	95.8	97.1	87.5
HF-F_4SbH-isobutane protonation TS (TS9m)	-899.3047635	-899.15159059	-899.13422459	-899.19742759
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m $+ [SbF_6]^- + [C_4H_9]^+$	116.0	109.0	110.0	120.4
F_4SbH-isobutane protonation TS	-798.8304931	-798.68933980	-798.67417280	-798.73377380
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [SbF_6]^- + [C_4H_9]^+ + HF$	124.2	115.4	117.2	117.5
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	219.2	217.5	214.4	205.3
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	206.3	199.0	195.7	177.1

Table S29. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.387446	-1479.364314	-1479.347367	-1479.409177

$Sb_2F_{10} \rightarrow 2\ SbF_5$	9.2	7.8	7.9	-6.1
$Sb_2F_{11}H$	-1579.855874	-1579.820997	-1579.801719	-1579.86829
Sb_2F_{11}-H_2F	-1680.337385	-1680.290282	-1680.269114	-1680.339682
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	7.1	5.6	6.2	-3.2
Sb_2F_{11}-$H_2F \rightarrow Sb_2F_{11}H + HF$	15.3	13.5	14.4	4.5
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.331177	-1620.254201	-1620.232776	-1620.303588
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	11.2	9.8	8.7	19.3
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.300352	-1620.219657	-1620.197473	-1620.270429
Sb2F11H + CH4 $\rightarrow$ $[Sb_2F_{11}]^-[CH_5]^+$	30.5	31.4	30.9	40.1
$[Sb_2F_{11}]^-[CH_5]^+$[CO] substitution TS (TS2d)	-1733.569414	-1733.485011	-1733.460148	-1733.5405
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	50.9	50.9	50.0	68.7
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_{11}]^- + [CH_3CO]^+ + H_2$	72.5	43.7	38.6	58.0
Sb_2F_{10}-methane-CO hydride abstraction TS	-1633.111918	-1633.038538	-1633.016168	-1633.090965
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS above + HF	51.1	50.1	49.6	59.4
Sb_2F_{10}-methane complex	-1519.855884	-1519.787546	-1519.767667	-1519.834697
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ + HF	22.6	21.6	21.7	22.3
Sb2F11H-methane CHTS (TS4d)	-1620.283965	-1620.207552	-1620.185774	-1620.258644
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	40.8	39.0	38.2	47.5
HF-$F_9Sb_2CH_3$	-1519.893399	-1519.823057	-1519.803114	-1519.870393
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-0.9	-0.7	-0.6	-0.1
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1633.151335	-1633.076255	-1633.052478	-1633.131697
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS5d + HF	26.4	26.4	26.8	33.9
$[Sb_2F_9]^-$	-1379.762062	-1379.743235	-1379.726796	-1379.789586
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\ HF + [CH_3CO]^+$	50.8	21.4	19.3	24.2
$[SbF_6]^-[SbF_3](HF)_2[CH_3CO]^+$ complex	-1733.747138	-1733.655293	-1733.630184	-1733.711698
$Sb_2F_{11}H + CH_4 + CO \rightarrow [SbF_6]^-[SbF_3](HF)_2[CH_3CO]^+$	-60.7	-55.9	-56.7	-38.8

Table S30. ωB97X-D/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G

Sb_2F_{10}	-1479.379372	-1479.356240	-1479.339293	-1479.401103
$Sb_2F_{10} \rightarrow 2\ SbF_5$	9.0	7.7	7.7	-6.3
$Sb_2F_{11}H$	-1579.851502	-1579.816625	-1579.797347	-1579.863918
Sb_2F_{11}-H_2F	-1680.338387	-1680.291285	-1680.270117	-1680.340685
$Sb_2F_{11}H \rightarrow Sb_2F_{10} + HF$	6.8	5.3	5.9	-3.5
Sb_2F_{11}-$H_2F \rightarrow Sb_2F_{11}H + HF$	16.1	14.2	15.1	5.3
$Sb_2F_{11}H$-methane protonation TS (TS1d)	-1620.357483	-1620.280507	-1620.259082	-1620.329894
$Sb_2F_{11}H + CH_4 \rightarrow$ TS1d	8.8	7.4	6.3	16.9
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.324925	-1620.244230	-1620.222046	-1620.295002
Sb2F11H + CH4 $\rightarrow$ $[Sb_2F_{11}]^-[CH_5]^+$	29.2	30.1	29.5	38.8
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.608807	-1733.524404	-1733.499541	-1733.579893
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	50.3	50.4	49.4	68.1
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_{11}]^- + [CH_3CO]^+ + H_2$	73.6	72.3	70.0	71.5
Sb_2F_{10}-methane complex	-1519.873333	-1519.804994	-1519.785115	-1519.852145
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4 + HF$	23.2	22.1	22.2	22.8
Sb2F11H-methane CHTS (TS4d)	-1620.310772	-1620.234359	-1620.212581	-1620.285451
$Sb_2F_{11}H + CH_4 \rightarrow$ TS4d	38.1	36.3	35.5	44.8
HF-$F_9Sb_2CH_3$	-1519.913030	-1519.842688	-1519.822745	-1519.890024
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3 + HF$	-1.7	-1.5	-1.4	-1.0
HF-$F_9Sb_2CH_3$-CO TS (TS5d)	-1633.185704	-1633.110624	-1633.086847	-1633.166066
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS5d + HF	26.4	26.4	26.8	33.9
$[Sb_2F_9]^-$	-1379.751196	-1379.732369	-1379.715930	-1379.778720
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\ HF + [CH_3CO]^+$	52.9	51.0	51.7	38.8

Table S31. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.224474	-1738.061693	-1738.036509	-1738.11651
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	5.8	4.6	4.1	17.2
$[Sb_2F_{11}]^-$	-1579.470872	-1579.445877	-1579.427657	-1579.492048
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- +]H_2][C_4H_9]^+$	89.9	89.1	88.9	89.3

$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	74.7	68.3	68.0	58.9
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.209971	-1738.049799	-1738.02349	-1738.107198
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	14.9	12.0	12.3	23.0
$[HF][F_{10}Sb_2H]^-$	-1580.645472	-1580.603026	-1580.583171	-1580.651646
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	72.3	68.4	69.1	66.7
$[F_{10}Sb_2H]^-$	-1480.173445	-1480.142609	-1480.125497	-1480.187083
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ + HF$	81.7	76.3	77.3	66.9
$[HF][F_{10}Sb_2H]^-SbF_5$ fluoride transfer TS	-2320.347199	-2320.290314	-2320.263165	-2320.347317
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	62.7	61.2	61.2	75.37930321
$HF\text{-}F_9Sb_2H$	-1480.572909	-1480.530841	-1480.512619	-1480.577143
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow HF\text{-}F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	90.9	88.2	88.4	89.9
$HF\text{-}F_9Sb_2H$-isobutane protonation TS (TS9d)	-1638.946909	-1638.778382	-1638.753311	-1638.833121
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9d $+ [SbF_6]^- + [C_4H_9]^+$	93.2	88.5	88.8	102.2
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	161.2	155.1	156.7	146.1
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	146.0	134.3	135.8	115.6

Table S32. ωB97X-D/aug-cc-PVTZ energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)] with an implicit solvent model for DMSO. The electronic energies were calculated in the absence of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$Sb_2F_{11}H$-isobutane protonation TS (TS6d)	-1738.314935	-1738.152154	-1738.126970	-1738.20697
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS6d	2.0	0.8	0.4	13.4
$[Sb_2F_{11}]^-$	-1579.464057	-1579.439062	-1579.420842	-1579.485233
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- +]H_2][C_4H_9]^+$	88.4	87.5	87.3	87.8
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	75.5	69.0	68.7	59.6
$Sb_2F_{11}H$-isobutane hydride abstraction TS (TS8d)	-1738.297906	-1738.137734	-1738.111425	-1738.195133
$Sb_2F_{11}H + C_4H_{10} \rightarrow$ TS8d	12.7	9.9	10.1	20.9

$[HF][F_{10}Sb_2H]^-$	-1580.645931	-1580.603485	-1580.583630	-1580.652105
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	72.2	68.3	69.0	66.6
$[F_{10}Sb_2H]^-$	-1480.168862	-1480.138026	-1480.120914	-1480.182500
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ + HF$	82.2	76.8	77.8	67.4
$[HF][F_{10}Sb_2H]^-SbF_5$ fluoride transfer TS	-2320.342342	-2320.285457	-2320.258308	-2320.342460
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow$ TS above $+ [C_4H_9]^+$	63.5	62.0	62.0	76.2
$HF\text{-}F_9Sb_2H$	-1480.572064	-1480.529996	-1480.511774	-1480.576298
$Sb_2F_{11}H + C_4H_{10} + SbF_5 \rightarrow HF\text{-}F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	91.1	88.4	88.6	90.1
$HF\text{-}F_9Sb_2H$-isobutane protonation TS (TS9d)	-1639.038143	-1638.869616	-1638.844545	-1638.924355
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9d $+ [SbF_6]^- + [C_4H_9]^+$	91.4	86.7	87.0	100.4
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	162.0	155.9	157.5	146.9
$Sb_2F_{11}H + 2\ C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\ [C_4H_9]^+ + HF + H_2$	149.1	137.4	138.9	118.7

Table S33. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)]. Structures were optimized and electronic energies were obtained without the use of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
HF	-100.4590288	-100.4494172	-100.4461122	-100.4658172
CH_4	-40.4947069	-40.45021899	-40.44640199	-40.46754199
SbF_5	-739.6860822	-739.674223	-739.666309	-739.706587
SbF_6H	-840.1633817	-840.139814	-840.129373	-840.174708
CO	-113.3014364	-113.2963854	-113.2930804	-113.3155224
H/H exchange TS	-880.6237656	-880.5559439	-880.5440009	-880.5929429
$SbF_6H + CH_4 \rightarrow$ TS above	21.5	21.4	19.9	30.9
$[SbF_6]^-[CH_5]^+$ complex	-880.6645138	-880.5940441	-880.5801061	-880.6339161
$SbF_6H + CH_4 \rightarrow [SbF_6]^-[CH_5]^+$	-4.0	-2.5	-2.7	5.2
TS2m	-993.8776508	-993.8053347	-993.7898797	-993.8472597
$SbF_6H + CH_4 + CO \rightarrow$ TS2m	51.4	50.9	49.6	69.3
SbF_5-CH_4-CO hydride TS	-893.4030573	-893.3411786	-893.3275836	-893.3823036
$SbF_6H \rightarrow SbF_5 + HF$	11.5	10.1	10.6	1.4

$SbF_6H + CH_4 + CO \rightarrow$ TS above + HF	61.1	60.1	59.7	68.8
TS4m	-880.6004253	-880.5352882	-880.5219502	-880.5777372
$SbF_6H + CH_4 \rightarrow$ TS4m	36.2	34.4	33.8	40.5
HF-SbF_4CH_3	-780.1974351	-780.1400068	-780.1282188	-780.1769078
$SbF_6H + CH_4 \rightarrow$ HF-SbF_4CH_3 + HF	1.0	0.4	0.9	-0.3
TS5m	-893.4391605	-893.3756896	-893.3608816	-893.4193526
$SbF_6H + CH_4 + CO \rightarrow$ TS5m + HF	38.5	38.5	38.8	45.6
$[CH_3CO]^+$	-152.8953664	-152.8510562	-152.8465522	-152.8751062
$[SbF_4]^-$	-639.972768	-639.9660113	-639.9584743	-639.9971443
$SbF_6H + CH_4 + CO \rightarrow [SbF_4]^- + 2$ HF + $[CH_3CO]^+$	108.8	107.0	107.7	96.6

Table S34. M06/Def2-TZVPpd energies using a mononuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)]. Structures were optimized and electronic energies were obtained without the use of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
C_4H_{10} (isobutane)	-158.3812243	-158.2507343	-158.2440953	-158.2783133
exchange TS for tertiary H	-998.5193449	-998.3657275	-998.3497635	-998.4085065
$SbF_6H + C_4H_{10} \rightarrow$ TS above	15.9	15.6	14.9	27.9
$[SbF_6]^-$	-839.729766	-839.7164803	-839.7073513	-839.7466903
$[H_2][C_4H_9]^+$	-158.6487316	-158.5215184	-158.5124414	-158.5524284
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- + [H_2][C_4H_9]^+$	104.2	95.7	96.4	96.6
H_2	-1.1711145	-1.16097927	-1.15767427	-1.17246427
$[C_4H_9]^+$	-157.4770122	-157.3615279	-157.3548679	-157.3908689
$SbF_6H + C_4H_{10} \rightarrow [SbF_6]^- [C_4H_9]^+ + H_2$	104.6	95.1	96.4	89.7
TS8m	-998.511048	-998.3612803	-998.3441213	-998.4056753
$SbF_6H + C_4H_{10} \rightarrow$ TS8m	21.1	18.4	18.4	29.7
$[HF][F_5SbH]^-$	-840.9056151	-840.8744253	-840.8634853	-840.9130453
$SbF_6H + C_4H_{10} \rightarrow [HF][F_5SbH]^- + [C_4H_9]^+$	101.6	97.0	97.3	93.6
$[F_5SbH]^-$	-740.4237981	-740.4052324	-740.3968404	-740.4363084
SbF_6H + C4H10 $\rightarrow [F_5SbH]^- + [C_4H_9]^+ +$ HF	115.9	109.4	110.2	100.4
$[F_5SbH]^-SbF_5$ fluoride transfer TS	-1480.150497	-1480.11906	-1480.103128	-1480.16188
$SbF_6H + C_4H_{10} + SbF_5 \rightarrow$ TS above + HF + $[C_4H_9]^+$	90.5	84.6	85.1	88.5
F_4SbH	-640.4029507	-640.3865007	-640.3791247	-640.4174507

$SbF_6H + C_4H_{10} + SbF_5 \rightarrow F_4SbH + [SbF_6]^- + [C_4H_9]^+ +$ HF	101.6	94.7	95.6	87.1
HF-F_4SbH-isobutane protonation TS (TS9m)	-899.2224766	-899.068673	-899.05165	-899.112776
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS9m + $[SbF_6]^- + [C_4H_9]^+$	114.6	105.9	106.7	117.7
F_4SbH-isobutane protonation TS	-798.7432021	-798.6032922	-798.5881662	-798.6453592
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow$ TS above + $[SbF_6]^- + [C_4H_9]^+ +$ HF	127.3	116.0	117.6	118.7
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ +$ HF	203.7	188.6	191.2	178.8
$SbF_6H + 2\ C_4H_{10} + SbF_5 \rightarrow [SbF_4]^- + [SbF_6]^- + 2\ [C_4H_9]^+ +$ HF + H_2	204.1	188.0	191.1	172.0

Table S35. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)]. Structures were optimized and electronic energies were obtained without the use of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
Sb_2F_{10}	-1479.411906	-1479.387914	-1479.371473	-1479.431955
$Sb_2F_{10} \rightarrow 2\ SbF_5$	24.9	24.8	24.4	11.8
$Sb_2F_{11}H$	-1579.863092	-1579.826924	-1579.807819	-1579.874729
Sb_2F_{11}-H_2F	-1680.362613	-1680.312459	-1680.292852	-1680.359474
$Sb_2F_{11}H \rightarrow Sb_2F_{10}$ + HF	-4.9	-6.5	-6.1	-14.5
Sb_2F_{11}-$H_2F \rightarrow Sb_2F_{11}H$ + HF	25.4	22.7	24.4	11.9
$[Sb_2F_{11}]^-[CH_5]^+$ complex	-1620.365799	-1620.282193	-1620.260079	-1620.333249
$Sb_2F_{11}H + CH_4 \rightarrow [Sb_2F_{11}]^-[CH_5]^+$	-5.0	-3.2	-3.7	5.7
$[Sb_2F_{11}]^-[CH_5]^+[CO]$ substitution TS (TS2d)	-1733.602781	-1733.517733	-1733.493633	-1733.57123
$Sb_2F_{11}H + CH_4 + CO \rightarrow$ TS2d	35.4	35.0	33.7	54.3
$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_{11}]^- + [CH_3CO]^+ + H_2$	75.9	72.8	72.2	75.1
Sb_2F_{10}-methane complex	-1519.885318	-1519.815383	-1519.794621	-1519.866084
$Sb_2F_{11}H + CH_4 \rightarrow Sb_2F_{10}$-$CH_4$ + HF	8.4	7.7	8.5	6.5
HF-$F_9Sb_2CH_3$	-1519.924211	-1519.853466	-1519.834053	-1519.901309
$Sb_2F_{11}H + CH_4 \rightarrow$ HF-$F_9Sb_2CH_3$ + HF	-16.0	-16.2	-16.3	-15.6
$[Sb_2F_9]^-$	-1379.765814	-1379.746171	-1379.730134	-1379.791414

$Sb_2F_{11}H + CH_4 + CO \rightarrow [Sb_2F_9]^- + 2\,HF + [CH_3CO]^+$	50.2	48.6	49.2	37.4

Table S36. M06/Def2-TZVPpd energies using a dinuclear model for the antimony center. Absolute energies are given in Hartrees. Reaction energies are given in kcal/mol. Structure geometries and frequency calculations (for thermochemistry corrections) were performed using M06/LANL2DZdp[6-31+G(d,p)]. Structures were optimized and electronic energies were obtained without the use of an implicit solvent model.

structure or reaction	E_{elec}	E_{elec} + ZPE	H	G
$[Sb_2F_{11}]^-$	-1579.471784	-1579.445463	-1579.427967	-1579.490466
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [H_2][C_4H_9]^+$	77.7	69.5	70.0	69.1
$Sb_2F_{11}H + C_4H_{10} \rightarrow [Sb_2F_{11}]^- + [C_4H_9]^+ + H_2$	78.1	68.8	69.9	62.3
$[HF][F_{10}Sb_2H]^-$	-1580.650069	-1580.606319	-1580.586736	-1580.656965
$Sb_2F_{11}H + C_4H_{10} \rightarrow [HF][F_{10}Sb_2H]^- + [C_4H_9]^+$	73.6	68.9	69.2	66.0
$[F_{10}Sb_2H]^-$	-1480.176598	-1480.145091	-1480.128223	-1480.189718
$Sb_2F_{11}H + C_4H_{10} \rightarrow [F_{10}Sb_2H]^- + [C_4H_9]^+ + HF$	82.6	76.3	77.0	66.9
$HF\text{-}F_9Sb_2H$	-1480.605424	-1480.56284	-1480.545785	-1480.607467
$Sb_2F_{11}H + C_4H_{10} + SbF5 \rightarrow HF\text{-}F_9Sb_2H + [SbF_6]^- + [C_4H_9]^+$	74.2	69.7	69.2	71.9
$Sb_2F_{11}H + 2\,C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [H_2][C_4H_9]^+ + [SbF_6]^- + [C_4H_9]^+ + HF$	145.1	130.2	132.7	119.7
$Sb_2F_{11}H + 2\,C_4H_{10} + SbF_5 \rightarrow [Sb_2F_9]^- + [SbF_6]^- + 2\,[C_4H_9]^+ + HF + H_2$	145.5	129.6	132.6	112.8

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