Supporting Information

Stabilizing Halogen-Bonded Complex between Metallic Anion and Iodide

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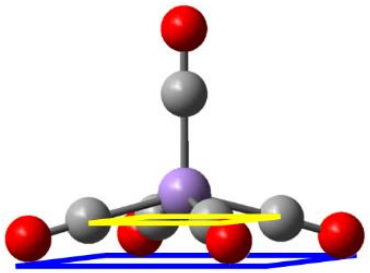


Figure S1. Optimized structure of $Mn(CO)_5^-$ anion. Color code: C, grey; O, red; Mn, purple.

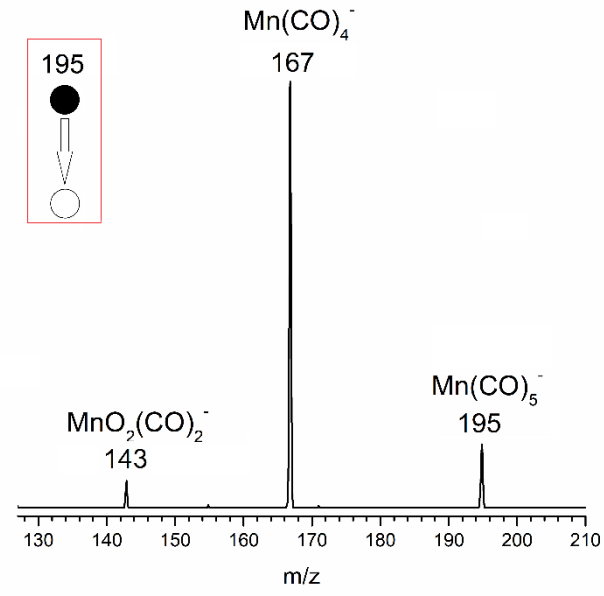
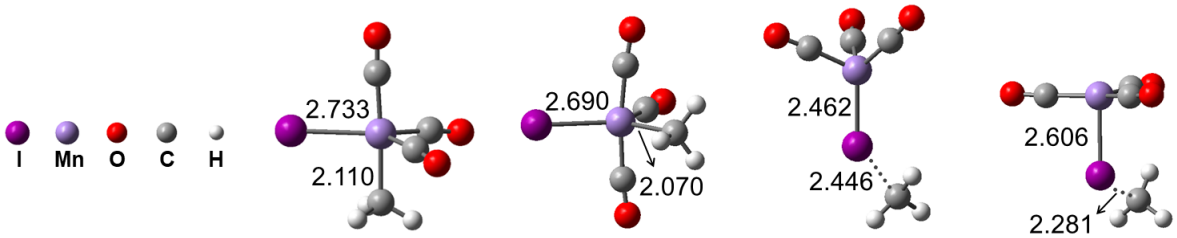


Figure S2. CID fragments of the $Mn(CO)_5^-$ anion.



relative energetics (kcal/mol)				
$\Delta(E_{elec}+ZPE)$	0.0	4.7	54.5	77.0
ΔE_{elec}	0.0	4.8	55.7	78.0
$\Delta H_{298.15K}$	0.0	4.8	55.1	77.6
$\Delta G_{298.15K}$	0.0	4.5	52.8	75.7

Figure S3. Optimized structures of $CH_3I{-}Mn(CO)_3^-$. Relative energetic values are reported.

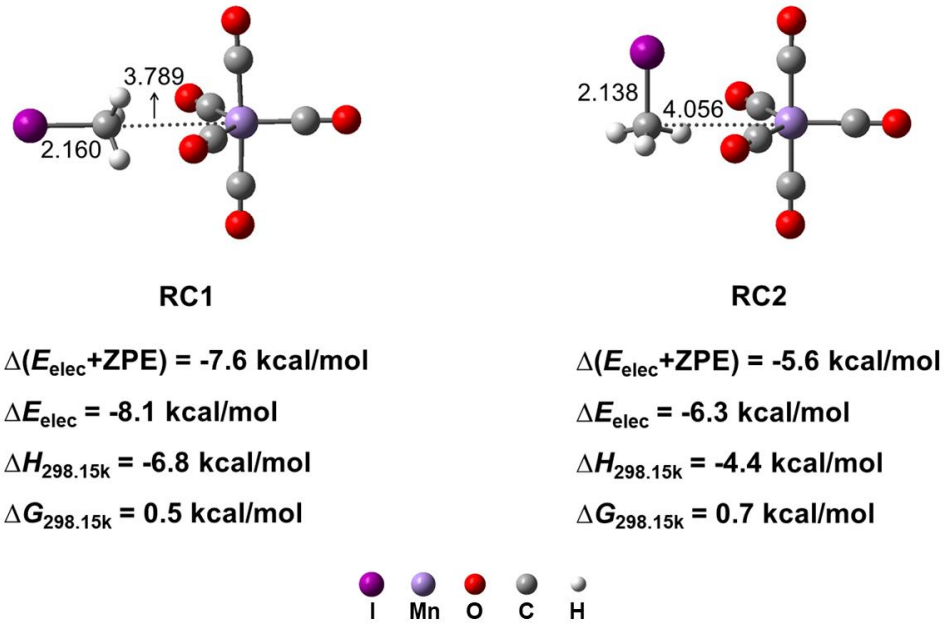


Figure S4. Additional conformers of the pre-reaction complex (RC) of CH_3I reacting with $Mn(CO)_5^-$. Energetic values are given in relative to the total energy of isolated $Mn(CO)_5^-$ and CH_3I.

Cartesian coordinates (Å) of all calculated structures for $Mn(CO)_5^-$ + CR_3I reactions (R = H, F).

$Mn(CO)_5^-$

Mn	0.00000000	0.00000000	-0.01271400
C	0.00000000	1.77338200	0.43836200
C	-1.77338200	0.00000000	0.43836200
C	0.00000000	-1.77338200	0.43836200
C	1.77338200	0.00000000	0.43836200
C	0.00000000	0.00000000	-1.78591700
O	-2.88192900	0.00000000	0.75057700
O	0.00000000	2.88192900	0.75057700
O	0.00000000	0.00000000	-2.93822600
O	2.88192900	0.00000000	0.75057700
O	0.00000000	-2.88192900	0.75057700

XC

Mn	1.57003600	-0.00048900	0.00044000
C	1.14385200	1.75225500	0.34711600
C	1.14040700	0.34712300	-1.75117200
C	1.13917500	-1.75152200	-0.34951800
C	1.13973500	-0.34957600	1.75166200
C	3.34562600	-0.00106800	0.00123200
O	0.84083400	0.56245000	-2.83940800
O	0.84696400	2.84134900	0.56155400
O	4.49626500	-0.00117000	0.00159700
O	0.84029400	-0.56714800	2.83946100
O	0.83803500	-2.83870700	-0.56775200
I	-2.08191700	0.00075000	0.00043600
C	-4.24928500	0.00161800	0.00069200
H	-4.58802200	1.01354100	0.19309000
H	-4.58874400	-0.33756000	-0.97166500
H	-4.58869900	-0.67067900	0.78079500

XC'

Mn	-1.99192500	0.00006700	0.00007400
C	-1.62118400	-0.17552800	1.80610800
C	-1.62483200	-1.80685400	-0.17552200
C	-1.62295200	0.17552200	-1.80628900
C	-1.62493300	1.80701600	0.17561900
C	-3.77608300	0.00001300	0.00084200
O	-1.36761500	-2.91597400	-0.28373500
O	-1.36079000	-0.28362700	2.91453500

O	-4.92235400	-0.00046600	0.00131400
O	-1.36656400	2.91591800	0.28332200
O	-1.36366500	0.28371600	-2.91498000
I	1.23201700	0.00025100	-0.00011200
C	3.48684800	-0.00024900	-0.00012700
F	4.00910800	-0.12826600	1.23598100
F	4.00895900	-1.00699200	-0.72883800
F	4.00948300	1.13403200	-0.50751700
RC			
Mn	2.22667400	0.03446600	-0.00038600
C	1.45198200	-0.22056400	1.60336500
C	1.58500400	1.76073100	0.00027400
C	1.40019400	-0.23572700	-1.57631100
C	2.75238000	-1.73532100	-0.00044700
C	3.93313900	0.59802800	-0.03012600
O	1.15551300	2.82361500	-0.00103100
O	0.92699000	-0.38480200	2.62004100
O	5.02610500	0.96192700	-0.04885700
O	3.06655800	-2.83644900	-0.00009600
O	0.84269000	-0.41095800	-2.57334700
C	-1.56579100	-0.06424300	0.00606300
H	-1.24116400	0.93231300	-0.26223200
H	-1.25124200	-0.79325700	-0.72775300
H	-1.25424500	-0.33266800	1.00609200
I	-3.72461300	-0.04739900	0.00005500
RC1			
Mn	-2.22195200	0.00308600	-0.00195700
C	-1.44042200	-0.01381300	1.61801000
C	-2.20219800	-1.84165900	-0.01027400
C	-1.32352800	-0.01210200	-1.56198400
C	-2.13127100	1.84544700	-0.00658200
C	-4.01769100	0.03696400	-0.05853900
O	-2.17594200	-2.98673600	-0.01895500
O	-0.91317300	-0.02536800	2.64677600
O	-5.16901400	0.05879000	-0.09513100
O	-2.05972300	2.98866000	-0.01307400
O	-0.71821700	-0.02205700	-2.54632400
C	1.56585300	-0.02438900	0.06599000
H	1.23829600	-0.88934100	-0.49408100
H	1.22095800	0.89170100	-0.39357700

H	1.28501800	-0.08439800	1.10848000
I	3.72431400	-0.00083200	-0.00449000
RC2			
Mn	1.75056800	-0.08417000	-0.00153100
C	0.92108400	-1.73710000	-0.04762200
C	1.04539200	0.22382200	1.62244200
C	2.56378700	1.56751300	0.04344300
C	0.84656100	0.40464900	-1.47286700
C	3.35913500	-0.88382400	-0.14671100
O	0.56917300	0.44462100	2.65154800
O	0.41552000	-2.76290300	-0.07768700
O	4.39021800	-1.39195800	-0.24074700
O	0.23723800	0.74171600	-2.39610100
O	3.06451000	2.59846900	0.07168200
C	-1.86783000	1.74597300	-0.07446600
H	-2.44914600	2.42292000	0.53875000
H	-1.85370400	2.04154700	-1.11580800
H	-0.86124800	1.59659600	0.30050900
I	-2.81551200	-0.16835100	0.01320600
RC'			
Mn	-2.53040500	0.04105100	-0.00001300
C	-1.75061600	-0.41040400	1.55544400
C	-3.43749800	-1.56322900	-0.00035200
C	-1.75137800	-0.40822700	-1.55640400
C	-1.62655200	1.64690900	0.00138900
C	-4.09820000	0.92481000	0.00021700
O	-4.00252800	-2.56037400	-0.00034100
O	-1.24438600	-0.71065400	2.54922200
O	-5.10335900	1.49236200	0.00043800
O	-1.06113900	2.64434800	0.00244300
O	-1.24558100	-0.70705300	-2.55081000
C	1.59252600	-0.01306500	-0.00017700
F	1.13296900	-1.24450800	-0.00043300
F	1.17468300	0.61948500	-1.07521800
F	1.17456900	0.61909200	1.07505600
I	3.76615900	-0.06231500	-0.00005000
TS1			
Mn	-1.97858700	0.00000300	-0.00513600
C	-1.69605100	0.00186400	1.82449000
C	-1.61654300	-1.81677400	0.01300600

C	-1.52616000	-0.00188800	-1.80242900
C	-1.61611200	1.81673400	0.00926900
C	-3.76400000	0.00011400	-0.08228800
O	-1.34795300	-2.92826700	0.02324500
O	-1.47689800	0.00302100	2.94700300
O	-4.90777900	0.00018700	-0.13332700
O	-1.34724400	2.92817800	0.01722700
O	-1.19814400	-0.00301700	-2.89784600
C	0.89224300	-0.00000200	0.00202300
H	0.85808700	-0.92893300	-0.53265800
H	0.85813900	0.92683500	-0.53628500
H	0.84762300	0.00209600	1.07335300
I	3.49216400	-0.00002200	0.01300300

TS1'

Mn	2.27901400	0.00026400	-0.00712300
C	1.89472200	1.80426400	-0.10762000
C	1.73372900	-0.13587400	-1.76588800
C	1.91966600	-1.80360100	0.16196300
C	2.04938800	0.13500800	1.81936000
C	4.06677000	0.00125900	-0.15427900
O	1.33720600	-0.21908400	-2.83613600
O	1.60232300	2.90796600	-0.16996300
O	5.20666300	0.00184800	-0.25320300
O	1.84299700	0.21768700	2.94059700
O	1.64151000	-2.90793600	0.26403200
C	-0.81260200	-0.00114300	-0.01163000
F	-0.81673100	-1.16717400	-0.53611700
F	-0.79788000	0.13032700	1.25956500
F	-0.82010600	1.03314800	-0.76314600
I	-3.64563300	0.00044100	0.02493100

TS2

Mn	1.51253500	-0.11239600	-0.06103700
C	0.57522500	-1.69030500	0.37730700
C	1.75760200	0.15630300	1.75682300
C	1.92914600	1.68066200	-0.27956600
C	0.57528900	0.03737700	-1.68038600
C	3.02842900	-0.91930900	-0.55602100
O	1.87650500	0.36958900	2.87527400
O	0.06335000	-2.65702800	0.67873800
O	4.01796300	-1.40187700	-0.86977900

O	0.01703300	0.18106500	-2.66238000
O	2.03640100	2.81948700	-0.34286800
C	-0.83258700	2.01387800	0.53702200
H	-1.81797200	2.26030200	0.88439600
H	-0.58347000	2.35130000	-0.45626700
H	-0.05661800	2.06788000	1.28078800
I	-2.67252800	-0.11379500	0.02743500

TS2'

Mn	-1.70940000	-0.27342400	0.00012000
C	-0.56399900	-0.93888300	-1.36536800
C	-2.49165600	0.81936900	-1.30686200
C	-2.49121200	0.82142200	1.30566400
C	-0.56373400	-0.93705600	1.36629000
C	-2.94608100	-1.56131800	0.00120500
O	-2.98084100	1.47843800	-2.09665000
O	0.06505900	-1.29593300	-2.23875600
O	-3.73663300	-2.38675200	0.00191000
O	0.06551900	-1.29293100	2.24001100
O	-2.98017500	1.48176500	2.09452700
C	0.99719200	1.53650100	-0.00058100
I	2.70424100	-0.58791900	0.00008000
F	0.31203100	1.92275100	1.09624700
F	2.07742400	2.34137700	-0.00129600
F	0.31095800	1.92236200	-1.09691100

PC1

Mn	1.37321600	-0.00012600	0.00297200
C	2.60597700	-1.31111400	0.48656000
C	0.30671600	-1.37753500	-0.87976600
C	0.30942400	1.38375200	-0.87290100
C	2.60960400	1.30558800	0.49129100
C	0.41962400	-0.00269100	1.64853000
O	-0.12901600	-2.21718500	-1.49111400
O	3.41317300	-2.08614200	0.68468700
O	-0.01687500	-0.00380800	2.69013600
O	3.41945700	2.07733000	0.69148700
O	-0.12561400	2.22690700	-1.47986800
C	2.44885900	0.00448100	-1.90166600
H	1.74072400	-0.00192400	-2.73239500
H	3.07868400	0.88777800	-2.02578100
H	3.09188200	-0.86960500	-2.02280700

I	-2.77230000	-0.00009100	0.07758100
PC1'			
Mn	0.93951700	0.38451400	-0.00063800
C	1.96691500	1.22400800	1.33763500
C	0.00253000	-0.65919800	1.40665000
C	0.00398100	-0.66721400	-1.40247600
C	1.96898000	1.21572800	-1.34225500
C	-0.36381100	1.82517000	-0.00533500
O	-0.37183400	-1.27348200	2.26830500
O	2.61460200	1.70055400	2.13386400
O	-0.94799300	2.78902600	-0.00851900
O	2.61846800	1.68670600	-2.14034800
O	-0.37026500	-1.28663900	-2.26050400
C	2.44300100	-1.09024600	0.00275200
F	2.44559900	-1.94520400	1.07516700
F	2.45958000	-1.93387500	-1.07872500
F	3.72495800	-0.57707400	0.01355900
I	-3.12514300	-0.17974100	0.00003300
TS3			
Mn	-1.35623300	-0.06512000	0.04624100
C	-1.97686800	1.61106500	-0.40080000
C	-0.20868200	0.78022100	1.40423500
C	-0.21965800	-1.64900400	-0.09610400
C	-2.53888600	-0.75851700	-1.23077400
C	-2.43223300	-0.68251200	1.37763600
O	0.27754600	1.31021500	2.26941500
O	-2.53437700	2.62775500	-0.55252200
O	-3.16276000	-0.99450100	2.19567800
O	-3.29266400	-1.15000800	-1.98308200
O	0.25601000	-2.66778300	-0.18039300
C	-0.51412200	1.38418500	-1.53153100
H	0.00076600	2.29511900	-1.24148500
H	0.24953300	0.61102900	-1.61573300
H	-1.02704200	1.51821600	-2.48011300
I	2.82406100	0.00161400	-0.13108400
TS3'			
Mn	-1.08516600	-0.61386400	0.04485900
C	-1.97055200	0.77301700	0.96997800
C	0.17110800	-0.69953100	1.59311500
C	0.15548200	-1.53203900	-1.19871700

C	-2.40995700	-0.50648000	-1.30015700
C	-1.87699700	-2.13431900	0.67142100
O	0.63344300	-0.83375100	2.61026000
O	-2.62022900	1.40820200	1.70504500
O	-2.42054800	-3.03916300	1.09480300
O	-3.25242900	-0.48102200	-2.05529300
O	0.66947900	-2.16266900	-1.97724200
C	-1.03941300	1.97440600	-0.15411600
F	-0.34483800	2.79532800	0.63597300
F	-0.25205800	1.68555900	-1.21795400
F	-2.06328900	2.69979100	-0.66469400
I	2.80783100	0.08183800	-0.08322900
PC2			
Mn	-0.72000100	0.35574700	-0.00001500
C	-0.67608000	0.05406100	1.85394900
C	-2.51381600	0.77366900	-0.00002200
C	-0.67609400	0.05425300	-1.85398700
C	-0.19844500	2.15584300	0.00006700
O	-0.66499700	-0.22373600	2.95603600
O	0.09126900	3.25519800	0.00012900
O	-0.66502600	-0.22341100	-2.95611200
O	-3.61622500	1.04987000	-0.00005100
C	-1.31610000	-1.68152100	-0.00004300
O	-2.49373800	-1.99823200	0.00042200
C	-0.28906500	-2.80478500	-0.00047000
H	-0.79411600	-3.77210600	-0.00063000
H	0.36382200	-2.70504100	0.86818300
H	0.36366300	-2.70462900	-0.86918800
I	2.09196200	-0.11129300	0.00003100
PC2'			
Mn	-0.25966900	0.99272800	0.00001500
C	-0.12334500	0.79455500	-1.88169400
C	0.30359900	2.75153800	0.00009000
C	-0.12314300	0.79435300	1.88168500
C	-2.07346300	1.49466500	0.00015400
O	0.00997500	0.64700400	-2.99693300
O	-3.15884800	1.82687400	0.00023500
O	0.01027600	0.64670300	2.99689900
O	0.61467800	3.84364800	0.00015100
C	1.79303200	0.50189900	-0.00020700

O	2.68309100	1.32577800	-0.00064000
C	2.32311400	-0.97235100	0.00013900
F	3.66209300	-1.05656400	-0.00011200
F	1.89797900	-1.63337100	-1.08493300
F	1.89844200	-1.63273400	1.08578000
I	-1.40579300	-1.59287200	-0.00010800

$Mn(CO)_4I^-$

Mn	-0.74464500	-0.00012200	-0.00009000
C	-0.78121400	1.91151600	0.00016800
C	-1.91372600	0.00059200	-1.52011600
C	-1.91166500	-0.00087200	1.52191800
C	-0.78057900	-1.91179500	-0.00118400
O	-0.87446100	3.04780200	0.00014400
O	-0.87338900	-3.04811200	-0.00186100
O	-2.64071600	-0.00141200	2.40948300
O	-2.64398700	0.00123800	-2.40674000
I	2.02263500	0.00019400	-0.00020100

$CH_3I–Mn(CO)_3^-$

Mn	0.76115600	-0.02265000	-0.00039900
C	2.04281400	-0.12234100	-1.26699400
C	2.04095400	-0.12287000	1.26787200
C	0.58970000	1.83067500	-0.00001800
O	2.84272300	-0.30513200	2.06446000
O	2.84578300	-0.30417200	-2.06245400
O	0.54742800	2.96966800	0.00047700
C	0.83725900	-2.13091300	-0.00062900
H	1.82159800	-2.60958300	-0.00053100
H	0.28790400	-2.48379400	0.87726400
H	0.28802000	-2.48370000	-0.87862600
I	-1.96940100	-0.14088500	-0.00017700

$CF_3I–Mn(CO)_3^-$

Mn	0.48445500	0.50213200	0.00002700
C	1.72046200	0.83677800	-1.30780400
C	1.72163900	0.83578400	1.30690500
C	-0.18826400	2.26177200	0.00083600
O	2.48625800	1.00172000	2.13421600
O	2.48427600	1.00348000	-2.13569300
O	-0.56063500	3.33477500	0.00142700
C	1.14412800	-1.47440100	-0.00012000
I	-2.07891900	-0.28907000	-0.00003000

F	0.76251200	-2.22403000	1.08138100
F	2.52584000	-1.62813400	-0.00373300
F	0.75657900	-2.22694500	-1.07738200