Electronic Supplementary Material (ESI) for Dalton Transactions.

Multicenter electron-sharing σ bonding in the $AgFe(CO)_4^-$ complex

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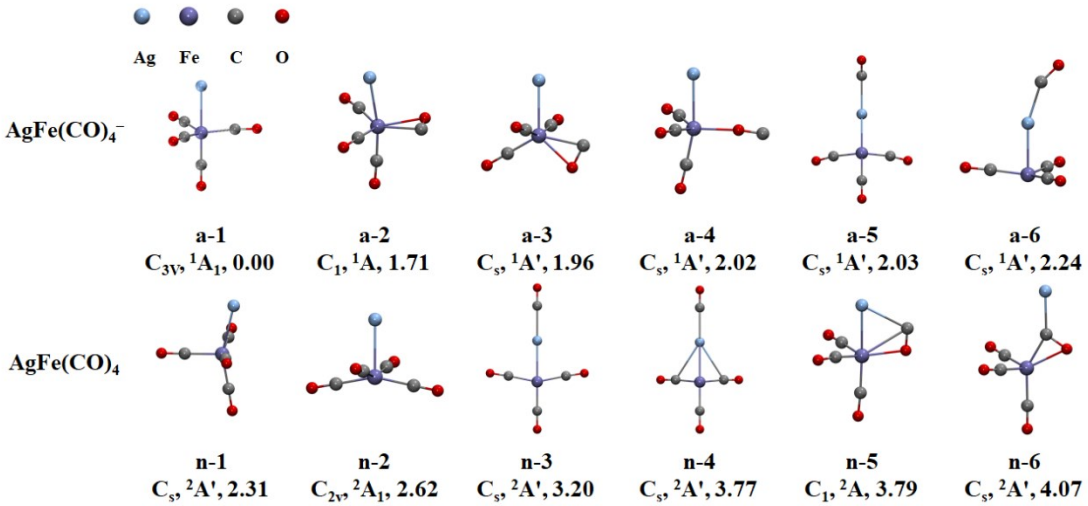


Fig. S1 Optimized ground-state and low-lying geometries of $AgFe(CO)_4^{-1/0}$ complexes at the B3LYP/def2-TZVPP level. The symmetry, electronic states, and the energies (in eV) relative to the ground-state anion are indicated.

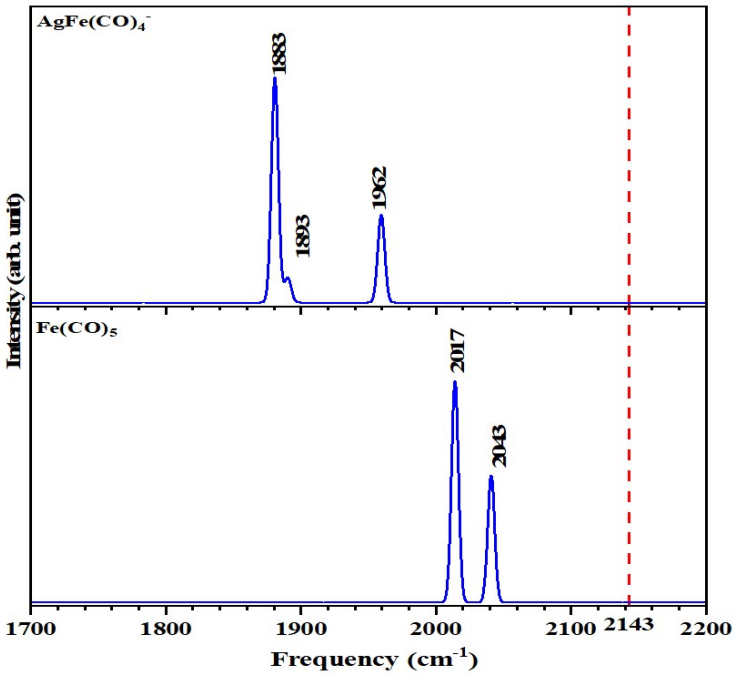


Fig. S2 Simulated IR spectra of $AgFe(CO)_4^-$ and $Fe(CO)_5$ complexes.

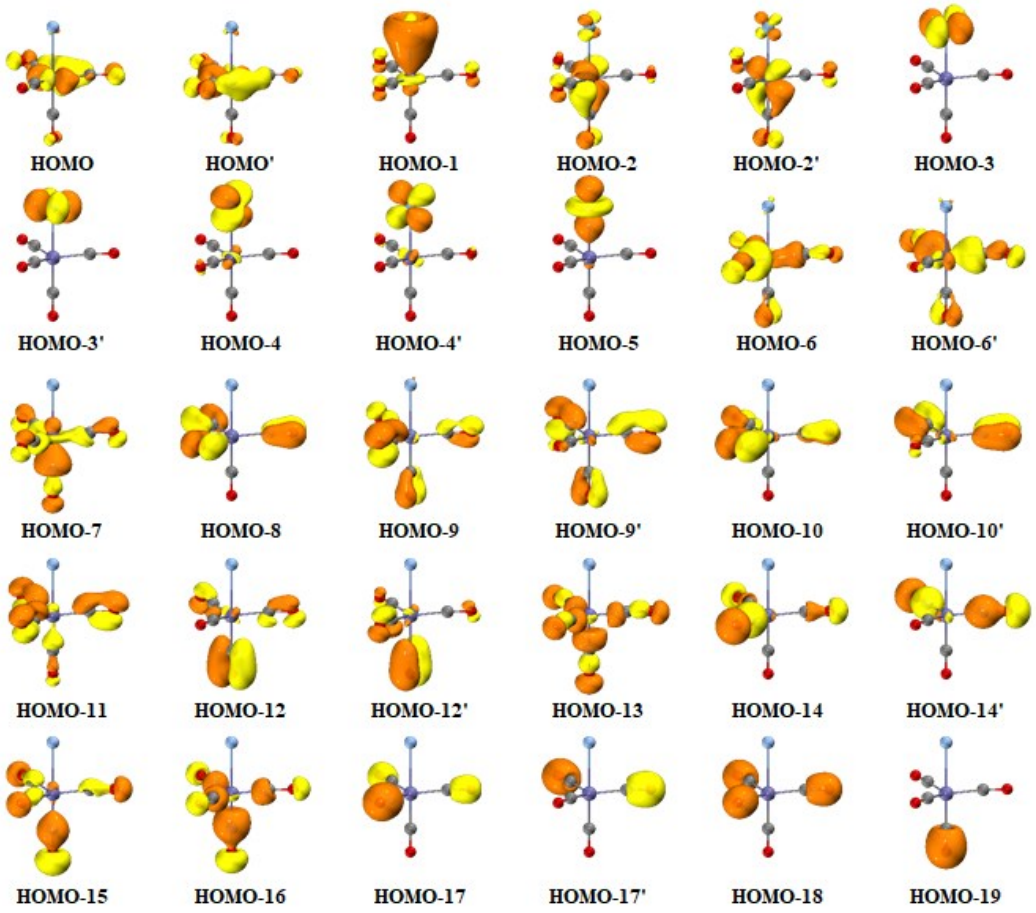


Fig. S3 Valence canonical molecular orbitals of $AgFe(CO)_4^-$ anion at the B3LYP-D3(BJ)/def2-TZVPP level. (isosurface = 0.06 au)

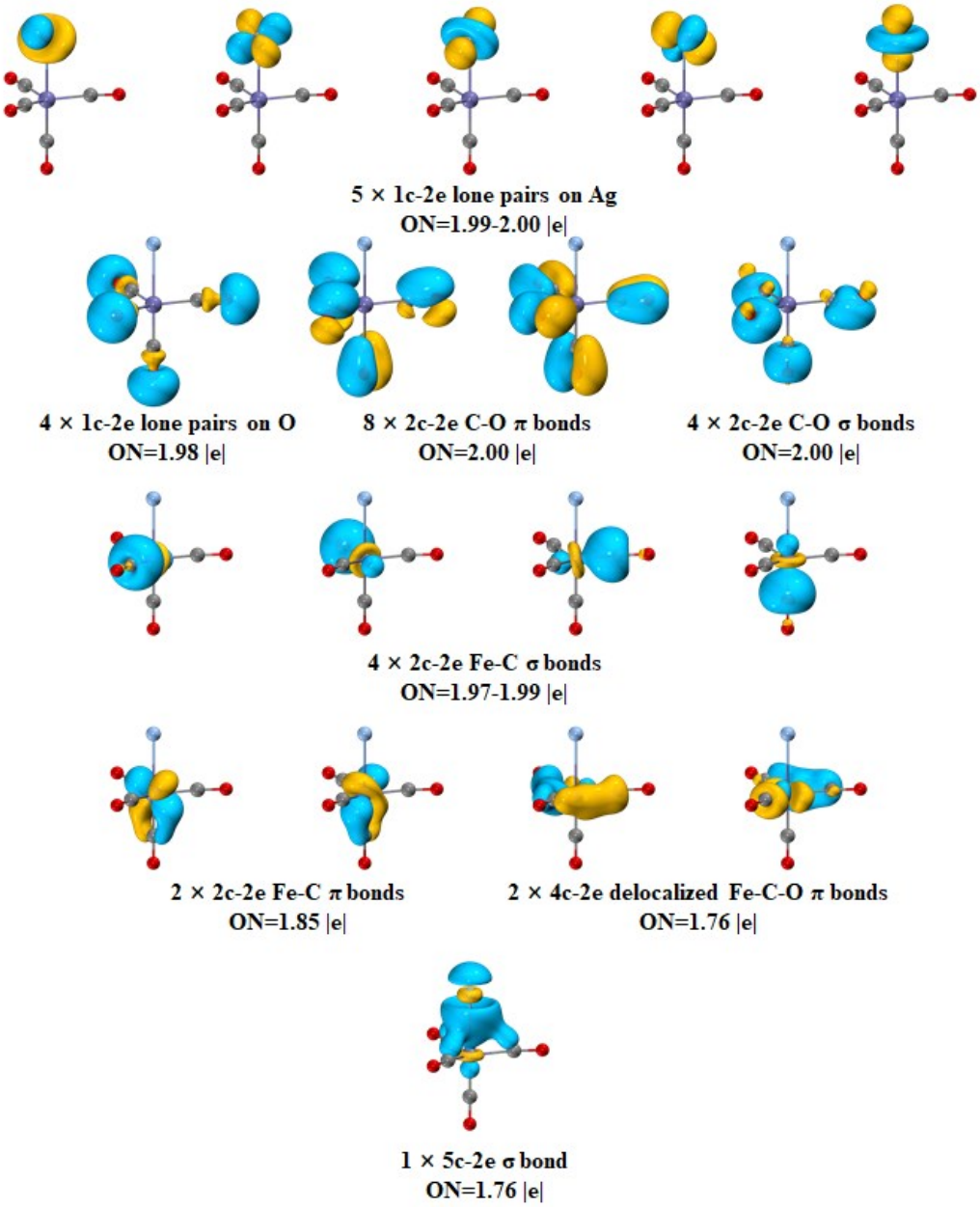


Fig.S4 The AdNDP analysis for $AgFe(CO)_4^-$ anion at the B3LYP-D3(BJ)/def2-TZVPP level. Occupation numbers (ONs) are shown. (isosurface = 0.06 au)

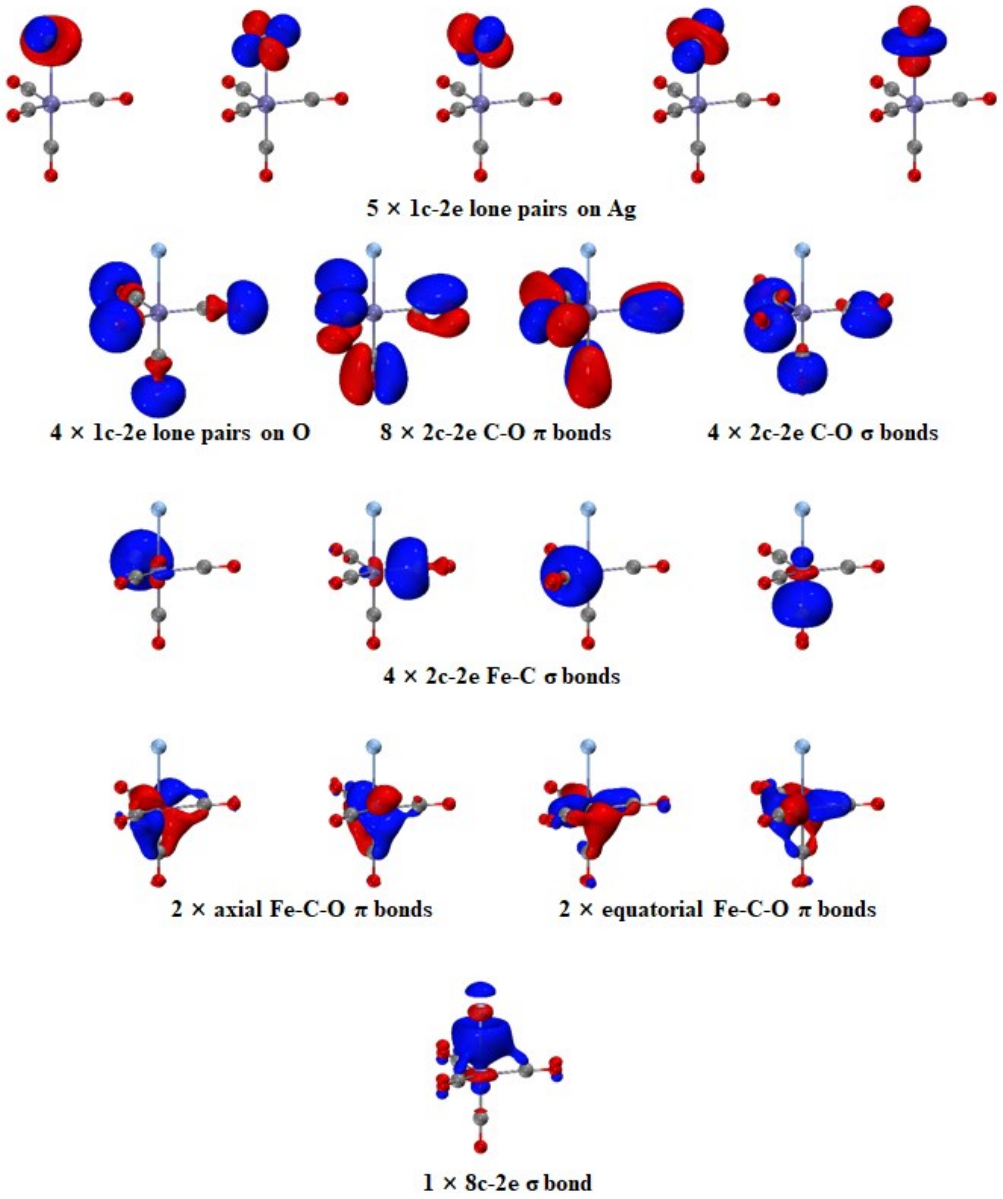


Fig. S5 The natural localized molecular orbital (NLMO) analysis for $AgFe(CO)_4^-$ anion at the B3LYP-D3(BJ)/def2-TZVPP level. (isosurface = 0.06 au)

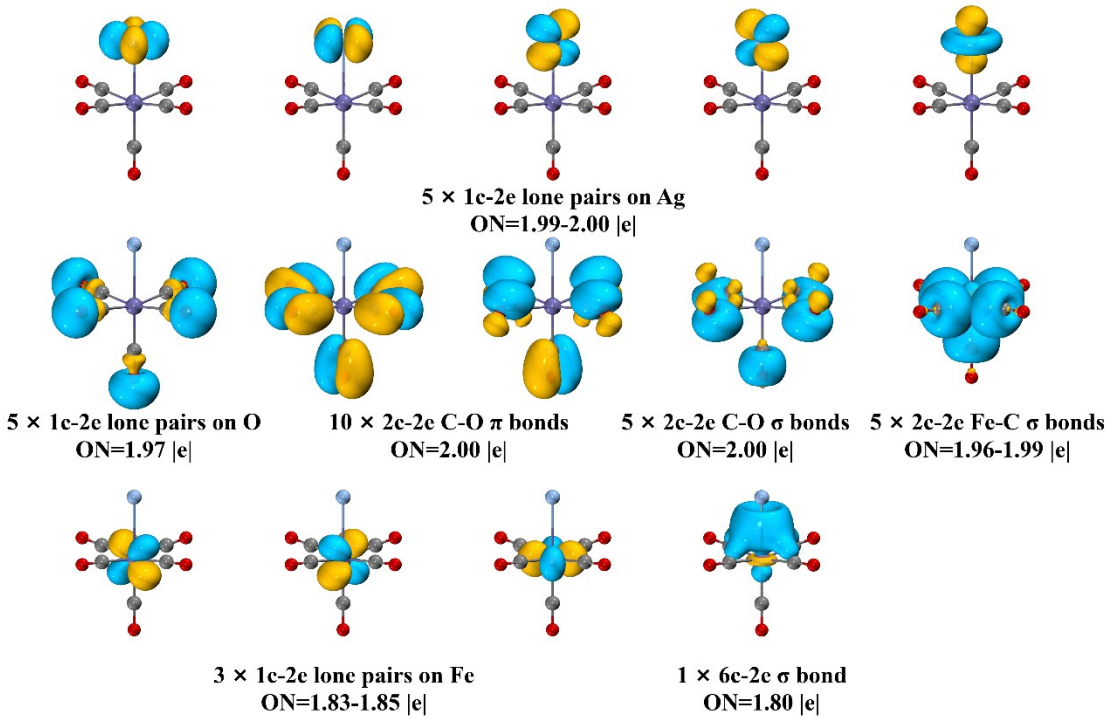
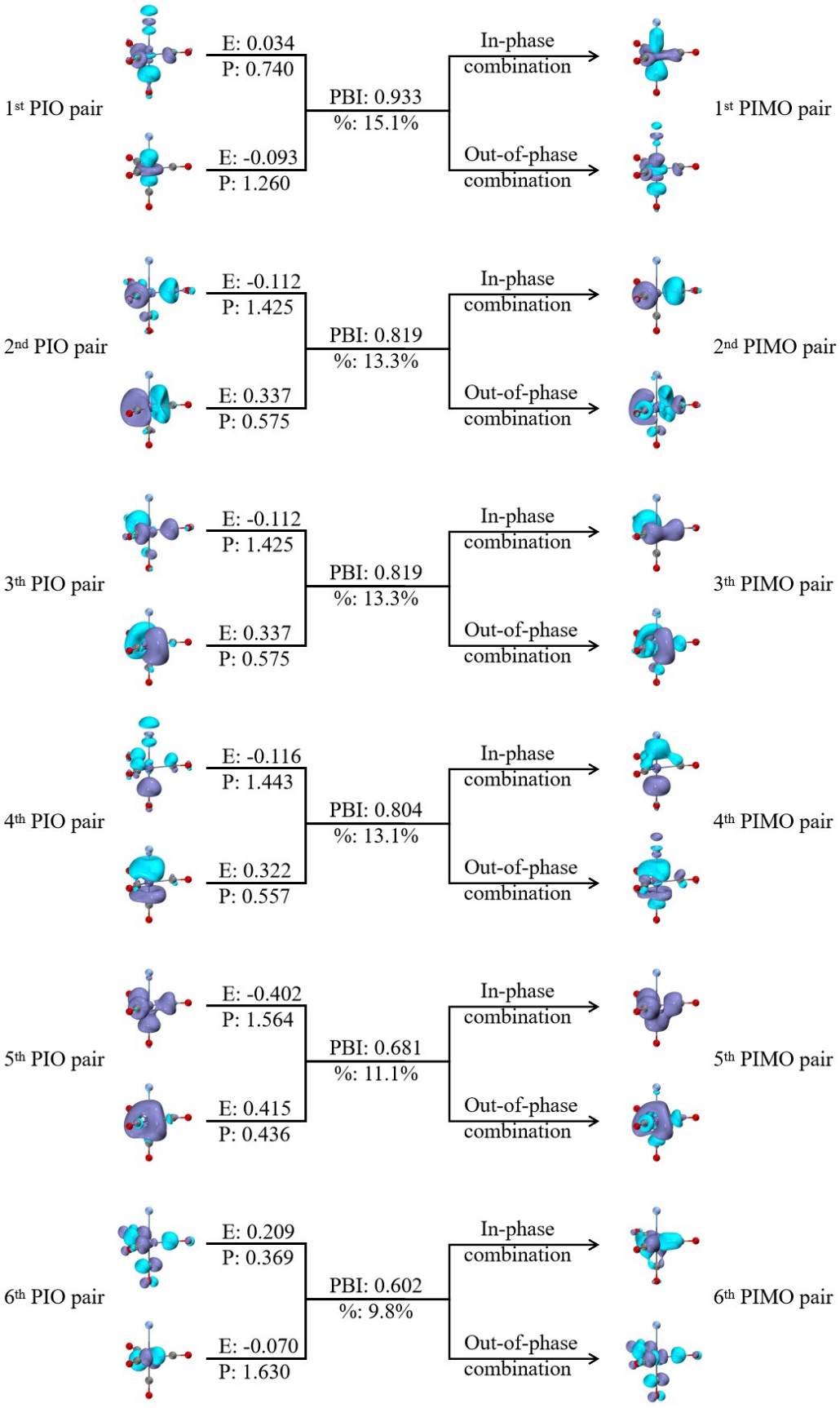


Fig.S6 The AdNDP analysis for $AgFe(CO)_5^+$ cation at the B3LYP-D3(BJ)/def2-TZVPP level. Occupation numbers (ONs) are shown. (isosurface = 0.06 au)


1st PIO pair
E: 0.034
P: 0.740
E: -0.093
P: 1.260
PBI: 0.933
%: 15.1%
In-phase combination
Out-of-phase combination
1st PIMO pair
2nd PIO pair
E: -0.112
P: 1.425
E: 0.337
P: 0.575
PBI: 0.819
%: 13.3%
In-phase combination
Out-of-phase combination
2nd PIMO pair
3th PIO pair
E: -0.112
P: 1.425
E: 0.337
P: 0.575
PBI: 0.819
%: 13.3%
In-phase combination
Out-of-phase combination
3th PIMO pair
4th PIO pair
E: -0.116
P: 1.443
E: 0.322
P: 0.557
PBI: 0.804
%: 13.1%
In-phase combination
Out-of-phase combination
4th PIMO pair
5th PIO pair
E: -0.402
P: 1.564
E: 0.415
P: 0.436
PBI: 0.681
%: 11.1%
In-phase combination
Out-of-phase combination
5th PIMO pair
6th PIO pair
E: 0.209
P: 0.369
E: -0.070
P: 1.630
PBI: 0.602
%: 9.8%
In-phase combination
Out-of-phase combination
6th PIMO pair

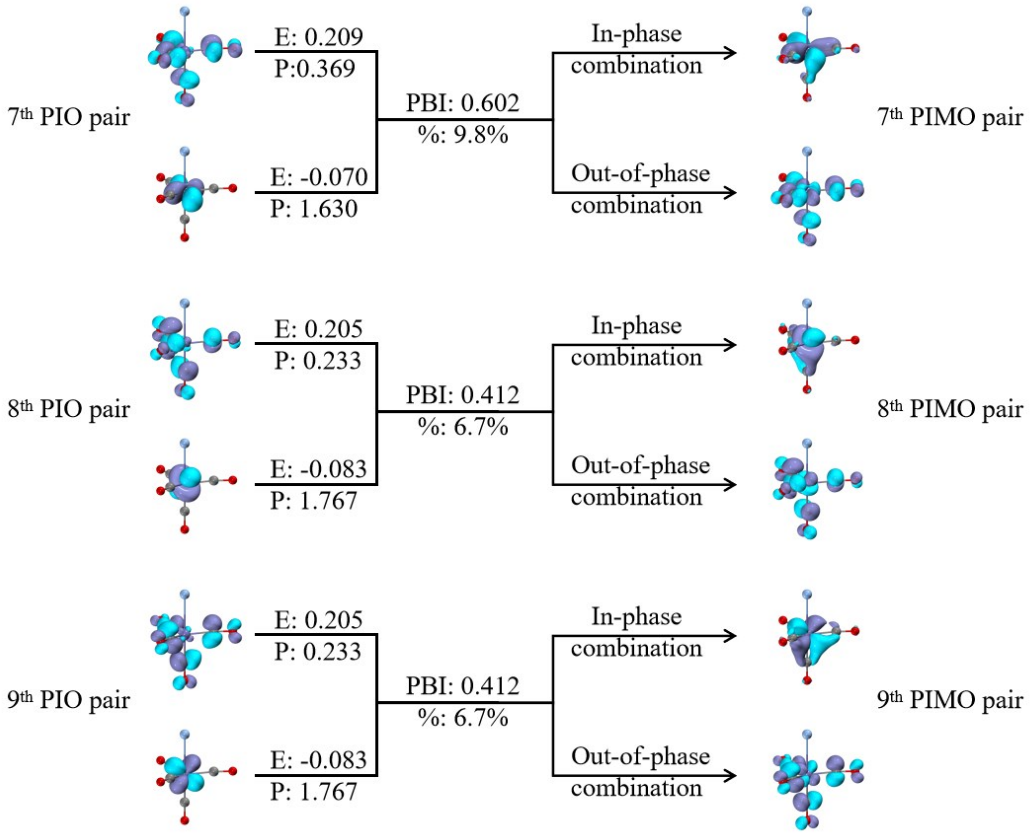


Fig. S7 Results of analysis on $AgFe(CO)_4^-$ anion with the central iron atom as one fragment and the remaining as the other fragment at the B3LYP-D3(BJ)/def2-TZVPP level. (isosurface = 0.06 au)

The cartesian coordinates of $AgFe(CO)_4^{-/0}$, $Fe(CO)_5$ and $AgFe(CO)_5^+$ at B3LYP-D3(BJ)/def2-TZVPP level.

(1) $AgFe(CO)_4^-$

Ag	0.000000000000	0.000000000000	1.804700000000
Fe	0.000000000000	0.000000000000	-0.731457000000
C	0.000000000000	0.000000000000	-2.477211000000
O	0.000000000000	0.000000000000	-3.635520000000
C	0.000000000000	1.776263000000	-0.538385000000
O	0.000000000000	2.935904000000	-0.506860000000
C	1.538289000000	-0.888132000000	-0.538385000000
O	2.542567000000	-1.467952000000	-0.506860000000
C	-1.538289000000	-0.888132000000	-0.538385000000
O	-2.542567000000	-1.467952000000	-0.506860000000

(2) $AgFe(CO)_4$

Ag	-0.825033000000	-1.637729000000	0.000000000000
Fe	0.456806000000	0.554392000000	0.000000000000
C	0.403002000000	0.171929000000	1.786906000000
O	0.403002000000	0.023544000000	2.920162000000
C	-0.861883000000	1.839150000000	0.000000000000
O	-1.683968000000	2.628036000000	0.000000000000
C	1.924470000000	1.615157000000	0.000000000000
O	2.838967000000	2.296136000000	0.000000000000
C	0.403002000000	0.171929000000	-1.786906000000
O	0.403002000000	0.023544000000	-2.920162000000

(3) $Fe(CO)_5$

Fe	0.000000000000	0.000000000000	0.000000000000

C	0.000000000000	1.815686000000	0.000000000000
O	0.000000000000	2.955656000000	0.000000000000
C	1.572430000000	-0.907843000000	0.000000000000
O	2.559673000000	-1.477828000000	0.000000000000
O	-2.559673000000	-1.477828000000	0.000000000000
C	-1.572430000000	-0.907843000000	0.000000000000
O	0.000000000000	0.000000000000	2.958337000000
C	0.000000000000	0.000000000000	1.822121000000
C	0.000000000000	0.000000000000	-1.822121000000
O	0.000000000000	0.000000000000	-2.958337000000

(4) $AgFe(CO)_5^+$

Ag	0.000000000000	0.000000000000	1.873767000000
Fe	0.000000000000	0.000000000000	-0.718782000000
C	0.000000000000	1.842708000000	-0.493918000000
O	0.000000000000	2.966353000000	-0.393264000000
C	-1.842708000000	0.000000000000	-0.493918000000
O	-2.966353000000	0.000000000000	-0.393264000000
C	1.842708000000	0.000000000000	-0.493918000000
O	2.966353000000	0.000000000000	-0.393264000000
C	0.000000000000	0.000000000000	-2.566658000000
O	0.000000000000	0.000000000000	-3.692532000000
C	0.000000000000	-1.842708000000	-0.493918000000
O	0.000000000000	-2.966353000000	-0.393264000000