Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information of

Transition metal carbon quadruple bond: Viability through single electron transmutation

Computational Details

Geometry optimization has been performed using M06-2X,[1] PBE[2] and B3LYP[3] levels of theory using Def2-TZVP basis set. Harmonic vibrational frequency calculations were also performed at the same level of theory to understand the nature of stationary point. All these structures were found to be at their local minimum geometry. It should be noted that the C_{3v} structure in singlet ground state, $^1A_1$, has also been previously found to be the global minima for $AFe(CO)_3^-$ (A = B, C, Si, Ge, Sn, Pb, Sc, Y, La).[4-6] M06-2X produced a shorter C-Fe distance (1.481 Å) compared to 1.514 Å at PBE and 1.525 Å at B3LYP and hence, we adopted all the analyses at M06-2X geometries.

Single point multi-configurational complete-active-space-self-consistent-field (CASSCF) calculations were further performed on the M06-2X optimized geometries to verify the electronic configurations. The calculations used 12 electrons in 12 orbitals, i. e., CASSCF(12e,12o). All these calculations were performed using GAUSSIAN16 suite of program.[7] The relaxed force constant calculations were performed using Compliance 3.0.2 program.[8,9] Adaptive natural density partitioning (AdNDP)[10] analyses were performed using Multiwfn[11] on the M06-2X optimized geometries.

References

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Table S1. Calculated relative energies (kcal/mol) of different isomers and for different spin multiplicities at M06-2X/Def2-TZVP level of theory.

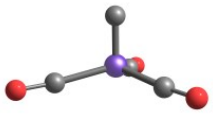
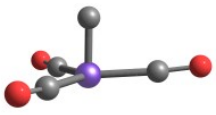
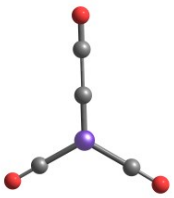
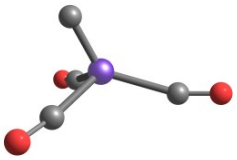
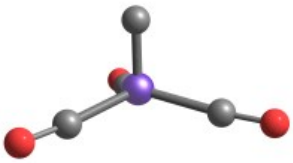
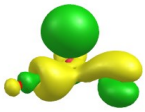
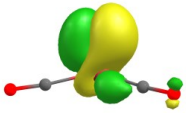
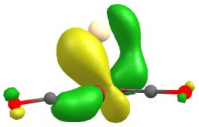
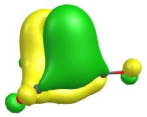
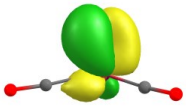
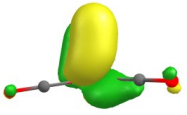
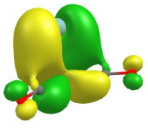
Spin state			
Singlet	 C_{3v}, $^1A_1$ ΔE = 0.0	 C_1 ΔE = 7.4	 Cs ΔE = 43.4
Triplet	 C_1 ΔE = 12.0	 *C3v* ΔE = 28.1	

Table S2. Natural valence orbitals of $AFe(CO)_3$ (A = C, Si, Ge) from CASSCF(12e,12o), their occupation numbers (NOON), coefficient c^2 of the ground state wave function and effective bond order (EBO).

Type	$CFe(CO)_3$	$SiFe(CO)_3$	$GeFe(CO)_3$
5c-bonding	 NOON (1.98)		
π-bonding	 NOON (1.90)	 NOON (1.90)	 NOON (1.89)
π-bonding	 NOON (1.89)	 NOON (1.90)	 NOON (1.89)

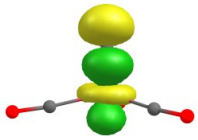
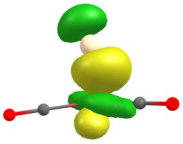
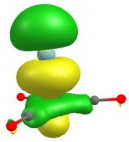
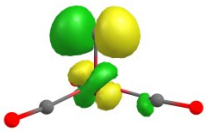
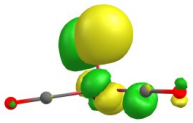
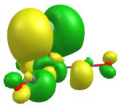
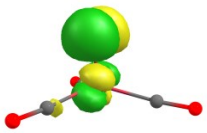
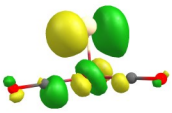
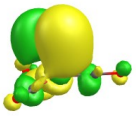
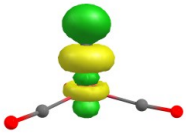
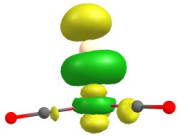
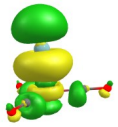
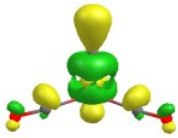
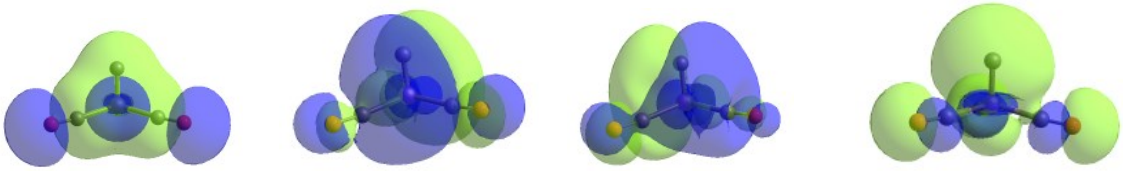
σ-bonding	 NOON (1.91)	 NOON (1.90)	 NOON (1.89)
π*-anti-bonding	 NOON (0.11)	 NOON (0.10)	 NOON (0.11)
π*-anti-bonding	 NOON (0.11)	 NOON (0.10)	 NOON (0.11)
σ*-bonding	 NOON (0.09)	 NOON (0.10)	 NOON (0.12)
5c-anti-bonding	 NOON (0.01)		
Coefficient, c^2	0.953	0.941	0.944
EBO	3.68	2.70	2.66

Table S3. Fe-CO bond lengths (Å) and CO stretching frequencies (cm^{-1}) of the complexes.

Complex	**Fe-CO bond length (Å)**	**CO stretching frequency (cm^{-1})**
$CFe(CO)_3$	1.884	2191.2
$SiFe(CO)_3$	1.825	2114.8
$GeFe(CO)_3$	1.817	2100.1



O. N = 1.99 O. N = 1.97 O. N = 1.96 O. N = 1.96

Fig S1. AdNDP orbitals showing 5c-2e bonds with their corresponding occupation number (O.N).

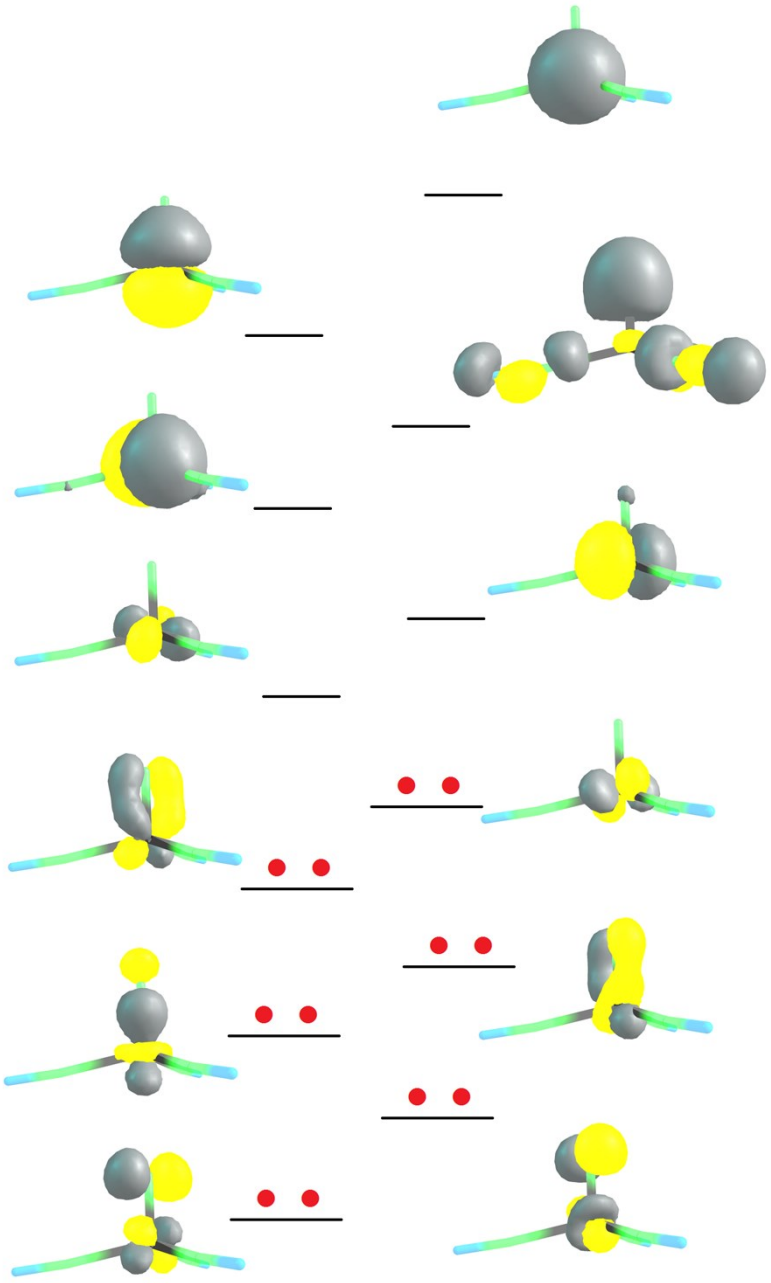


Fig S2. CAS(12,12) active orbitals.

Cartesian coordinates of the optimized geometries, lowest vibrational frequency along with the total energy in a.u.

$CFe(CO)_3$

ν_1 = 67.6 cm^{-1}

Sum of electronic and zero-point Energies= -1641.580445

Sum of electronic and thermal Energies= -1641.571120

Sum of electronic and thermal Enthalpies= -1641.570176

Sum of electronic and thermal Free Energies= -1641.616214

26	0.000060000	-0.000147000	0.144352000
6	1.807886000	-0.361221000	-0.244875000
6	-0.591365000	1.745878000	-0.244690000
6	-1.216535000	-1.385104000	-0.244305000
8	2.904463000	-0.579788000	-0.379423000
8	-0.950061000	2.804925000	-0.379414000
8	-1.954924000	-2.224728000	-0.379336000
6	0.000452000	0.000542000	1.625909000

$SiFe(CO)_3$

$\nu_1 = 43.8\ cm^{-1}$

Sum of electronic and zero-point Energies= -1893.018989

Sum of electronic and thermal Energies= -1893.009358

Sum of electronic and thermal Enthalpies= -1893.008413

Sum of electronic and thermal Free Energies= -1893.056347

26	-0.001375000	0.000176000	-0.246122000
6	0.741264000	-1.662708000	-0.364307000
6	1.079798000	1.465457000	-0.366624000
6	-1.812011000	0.193392000	-0.372213000
8	1.204675000	-2.695990000	-0.440165000
8	1.752573000	2.376191000	-0.445684000
8	-2.937819000	0.311839000	-0.456379000

14	-0.012427000	0.005876000	1.696847000

$GeFe(CO)_3$

$\nu_1 = 34.5\ cm^{-1}$

Sum of electronic and zero-point Energies= -3680.564532

Sum of electronic and thermal Energies= -3680.556314

Sum of electronic and thermal Enthalpies= -3680.555370

Sum of electronic and thermal Free Energies= -3680.599733

26	-0.012109000	0.004982000	-0.626931000
6	-0.746735000	1.667146000	-0.655481000
6	-1.097127000	-1.452423000	-0.670453000
6	1.792655000	-0.194179000	-0.709514000
8	-1.206047000	2.706020000	-0.695500000
8	-1.775369000	-2.363093000	-0.722246000
8	2.919699000	-0.318522000	-0.791830000
32	0.034870000	-0.014001000	1.443422000