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

SUPPORTING INFORMATION

Two σ- and two π-dative quadruple bonds between the s-block element and transition metal in [BeM(CO)$_4$; M = Fe - Os]

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Computational Methodology

The geometries were optimized using the exchange functional of Becke in conjunction with the correlation functional of Perdew (BP86) at Gaussian 09 program package.[1-2] Single point calculations were performed by meta-GGA exchange correlation functional (M06).[3] The basis set used for optimization as well as single point calculations have triple ζ -quality augmented with two set of valence polarization functions (def2-TZVPP) introduced by Weigend and Ahlrichs.[4] Natural Bond Orbital analysis was computed at M06/def2-TZVPP//BP86/def2-TZVPP level of theory.[5] The bonding possibilities between metal fragment and beryllium were explored by energy decomposition analysis and the natural orbitals for chemical valence (EDA-NOCV).[6] This method quantitatively describes the nature of chemical bond as well as the charge deformation and the associated stabilization energy of the orbital interactions in a chemical bond. Molecules were optimized using ADF 2016.107 programme package at the BP86 level of theory with triple- ζ quality basis set consisting of two sets of polarization (TZ2P).[7] Incorporation of relativistic effects is done by Zeroth Order Regular Approximation (ZORA). [8]

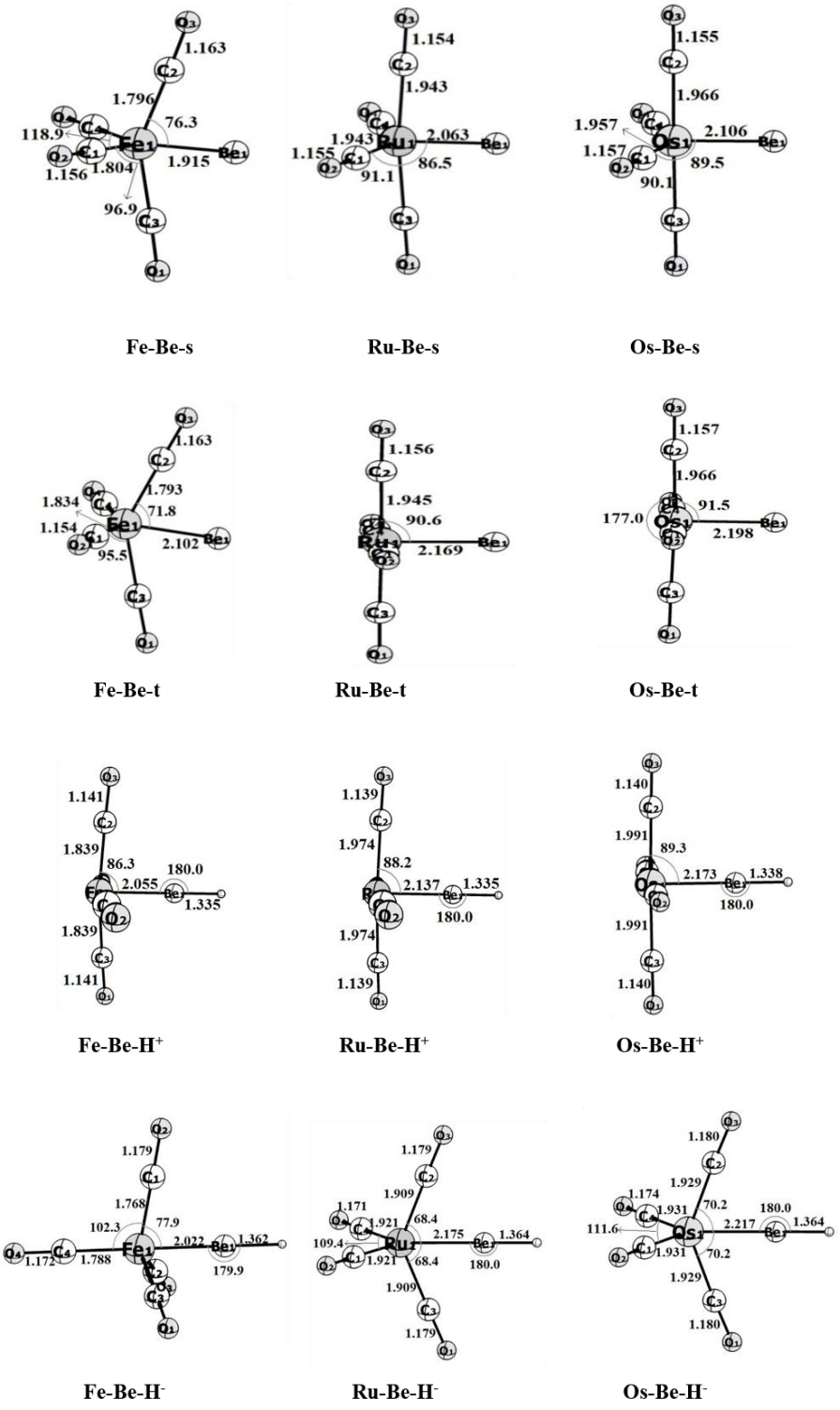


Figure S1. Optimized singlet state (**M-Be-s**) and triplet state (**M-Be-t**) geometries of **M-Be**, **M-Be-H**$^{+}$ and **M-Be-H**$^{-}$ (M = Fe – Os) at the BP86/Def2-TZVPP level of theory (M = Fe – Os).

Table S1. Relative energy and atomic orbital occupancies, Wiberg Bond Index (WBI) and bond occupancy (BO) of M-Be bond of **M-Be** (M = Fe - Os) from NBO analysis at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Complexes	Relative energy (kcal/mol)		Charge		Occupancies on Be				WBI	BO
	Singlet	Triplet	M	Be	2s	$2p_x$	$2p_y$	$2p_z$		
Fe-Be	0	20.42	-2.5	0.97	0.78	0.05	0.12	0.06	0.82	1.56
Ru-Be	0	24.78	-2.1	0.72	1.1	0.03	0.06	0.07	0.77	1.64
Os-Be	0	23.14	-1.7	0.70	1.1	0.03	0.5	0.1	0.78	1.60

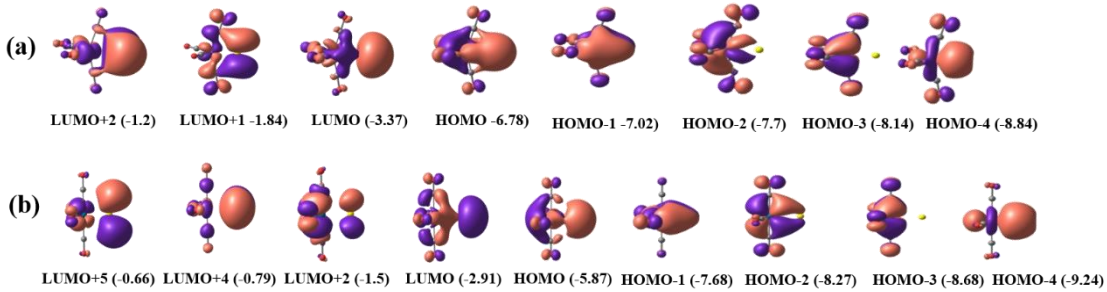
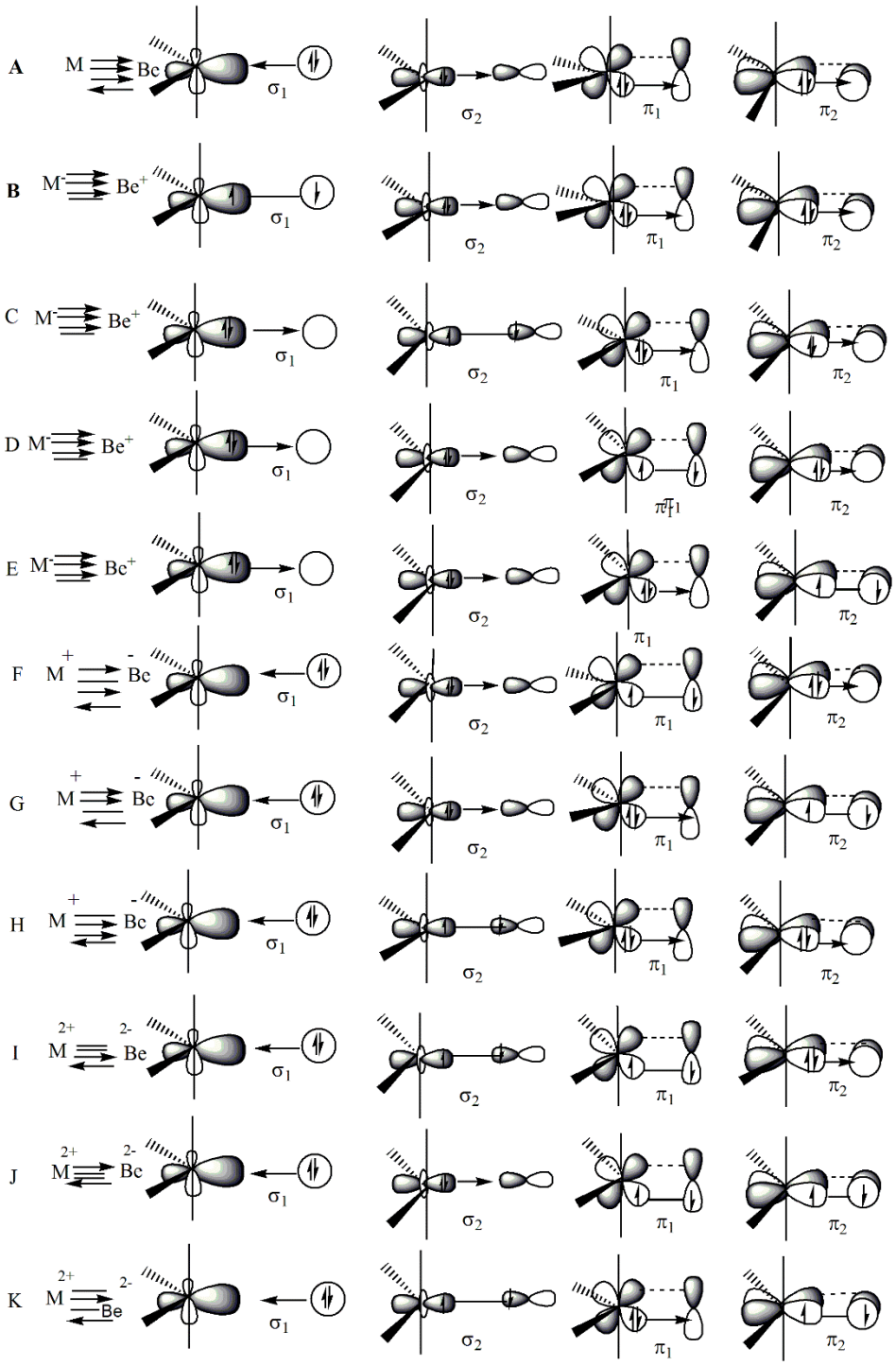


Figure S2. Important molecular orbitals of (a) **Fe-Be** and (b) **Os-Be** at the M06/Def2TZVPP//BP86/Def2-TZVPP level of theory. Eigenvalues are given in eV.

EDA-NOCV analysis

The best bonding strategy of M and beryllium is analyzed using EDA-NOCV analysis at the BP86/TZ2P level of theory by fragmenting M-Be complex as $M(CO)_4$ and beryllium. Different bonding possibilities (A-K) are shown in scheme S1. In possibility A, both the fragments are in neutral state with four donor-acceptor interactions in which three donor acceptor interactions are from transition metal fragment to beryllium fragment and a reverse donation from the beryllium fragment to the vacant orbital on transition metal fragment. One electron sharing and three donor acceptor interactions are considered in B-E. In these possibilities transition metal fragment carries one negative charge and beryllium has one positive charge. Next three representations (F – H) correspond to one electron sharing and three donor acceptor interactions in which transition metal fragment carries one positive charge and beryllium has one negative charge. Two donor acceptor interaction and two electron sharing interactions are considered in the bonding patterns from I-K. Here, transition metal fragment is in $M(CO)_4^{2+}$ and beryllium is in Be^{2-} states.



Scheme S1. Schematic representation of the electronic configurations of the interacting M (M = Fe, Ru, Os) and Be fragments, which are used in the EDA-NOVC calculations.

Table S2. EDA-NOCV results of different bonding situations for **M-Be** (M = Fe, Ru, Os) bonds in Scheme S1 at the BP86/TZ2P level of theory. Energies are given in kcal/mol.

Complexes		ΔE_{int}	ΔE_{Pauli}	ΔE_{Elstat}	ΔE_{Orb}
	A	-60.50	193.47	-123.36	-130.60
	B	-207.06	92.07	-162.12	-137.01
	C	-497.05	168.31	-284.57	-380.78
	D	-321.12	87.29	-177.72	-230.69
	E	-299.71	40.30	-158.25	-181.76
Fe-Be	**F**	-267.98	250.95	-255.35	-263.57
	G	-280.06	415.62	-409.21	-286.47
	H	-290.55	328.15	-314.90	-303.80
	I	-752.59	556.06	-762.93	-545.71
	J	-727.22	383.61	-613.93	-496.91
	K	-726.89	472.47	-697.66	-501.69
	A	-49.02	169.36	-127.64	-90.74
	B	-216.18	87.72	-172.28	-131.61
	C	-519.13	204.17	-314.68	-408.61
	D	-358.55	49.34	-161.19	-246.70
Ru-Be	**E**	-340.71	36.18	-162.78	-214.10
	F	-258.86	214.55	-260.19	-213.22
	G	-282.12	257.90	-284.20	-255.82
	H	-256.49	388.76	-435.49	-209.76
	I	-728.87	496.26	-759.11	-466.02
	J	-733.01	327.28	-582.49	-477.80
	K	-704.89	448.60	-730.40	-423.10
	A	-55.40	190.51	-148.92	-96.99
	B	-222.28	103.21	-185.83	-139.66
	C	-522.43	231.64	-339.58	-414.49
Os-Be	**D**	-363.13	49.59	-166.23	-246.49
	E	-350.22	41.33	-169.72	-221.83
	F	-288.38	270.35	-302.50	-256.23
	G	-270.71	240.65	-286.42	-224.93
	H	-260.87	441.46	-492.76	-209.57
	I	-730.35	542.51	-809.21	-463.66
	J	-732.44	337.87	-602.60	-467.71
	K	-712.23	509.21	-790.36	-431.08

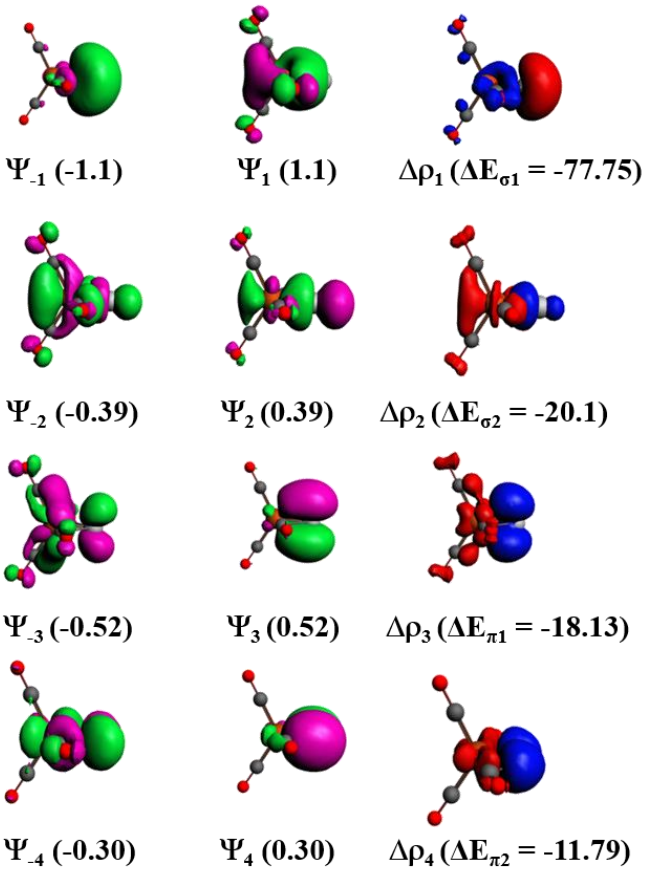


Figure S3. Plots of important NOCV pair of orbitals Ψ_{-n}/ Ψ_n of **Fe-Be** with best bonding possibility A with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.003 for $\Delta\rho_1$ and 0.001 for $\Delta\rho_2$, $\Delta\rho_3$ and $\Delta\rho_4$ respectively.

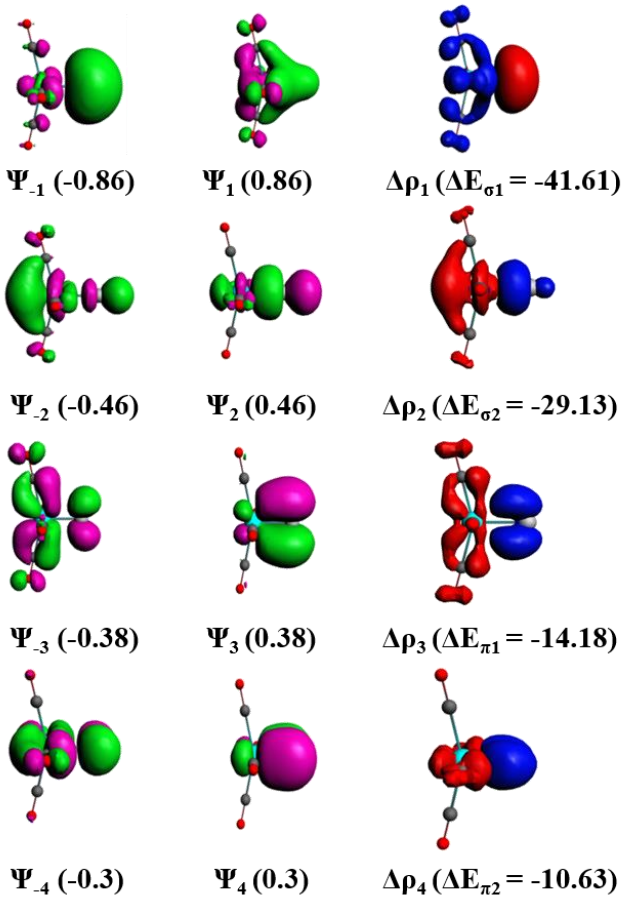


Figure S4. Plots of important NOCV pair of orbitals Ψ_{-n}/ Ψ_n of **Os-Be** with best bonding possibility A with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.001 respectively.

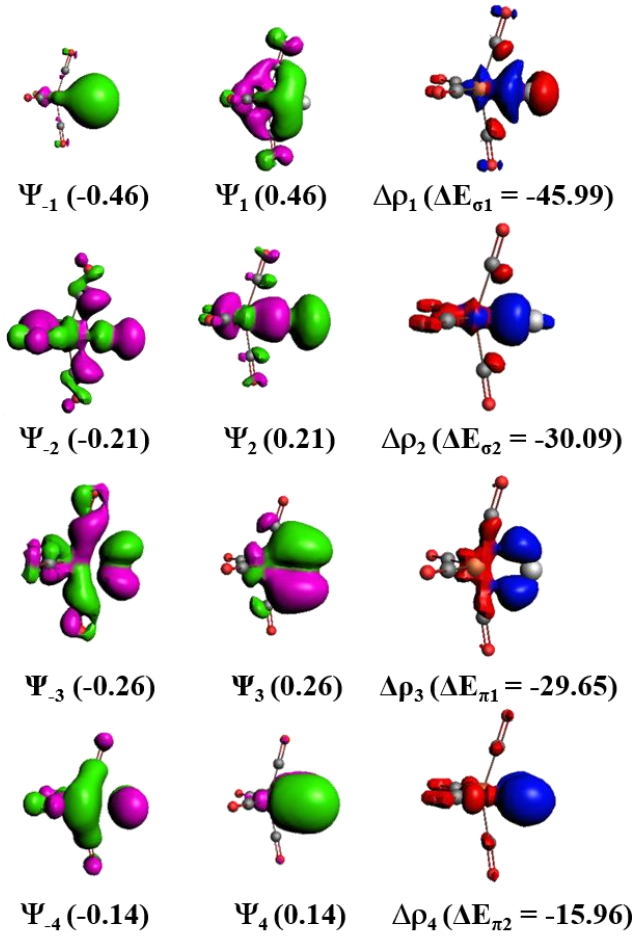


Figure S5. Plots of important NOCV pair of orbitals Ψ_{-n}/ Ψ_n of **Fe-Be** with bonding possibility B with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.001 respectively.

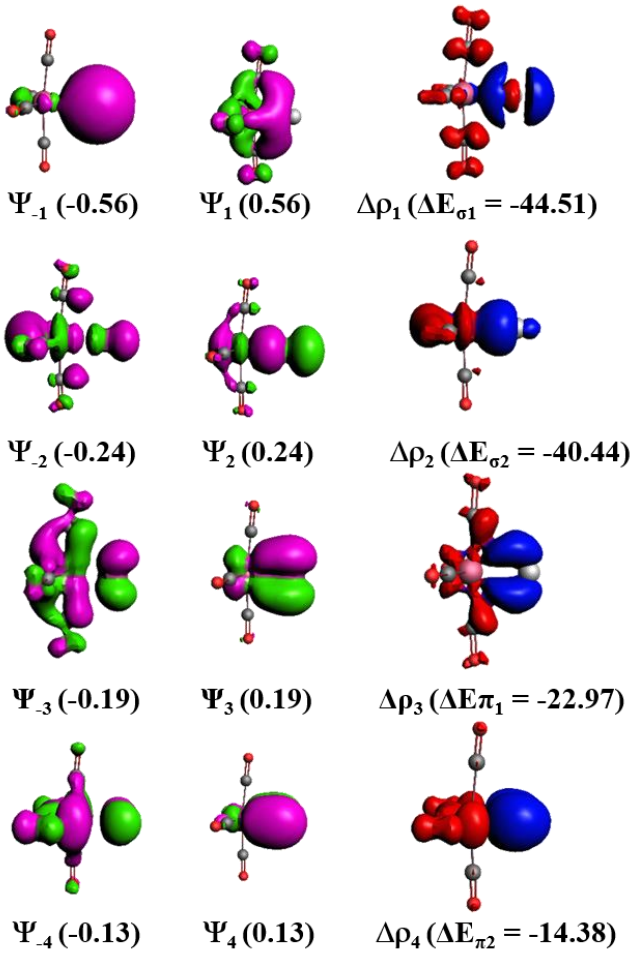


Figure S6. Plots of important NOCV pair of orbitals Ψ_{-n}/ Ψ_n of **Ru-Be** with bonding possibility B with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.001 respectively.

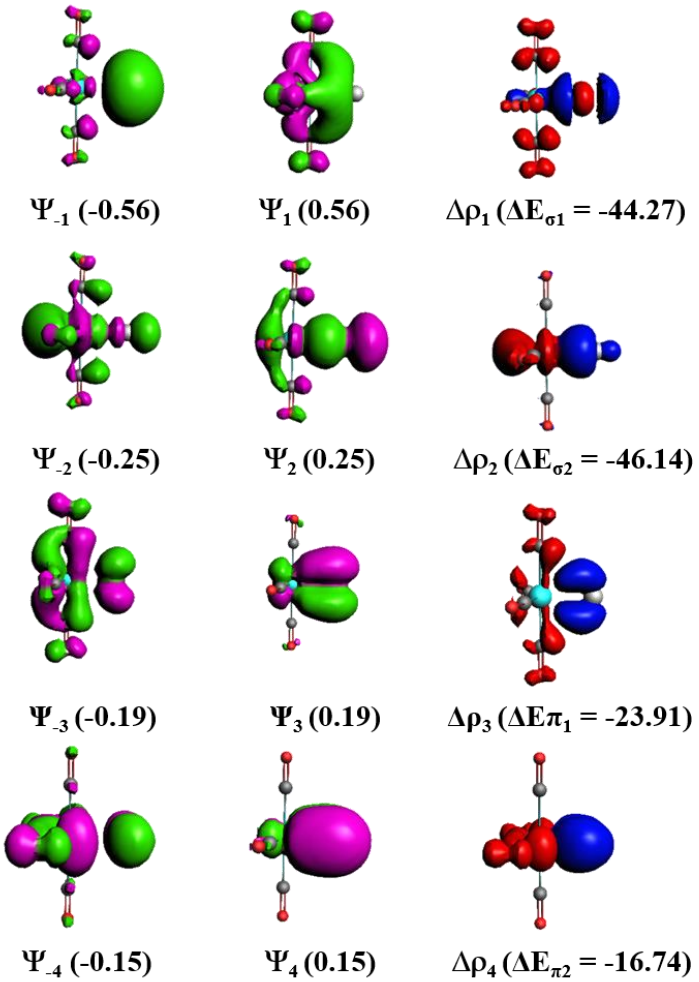


Figure S7. Plots of important NOCV pair of orbitals Ψ_{-n}/ Ψ_n of **Os-Be** with bonding possibility B with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.001 respectively.

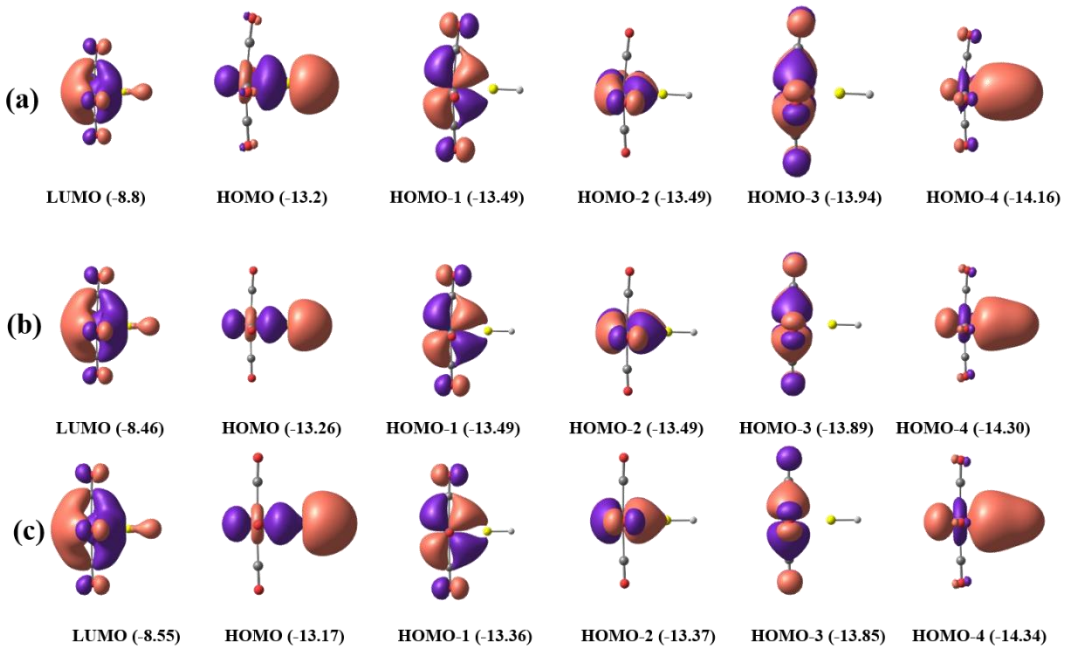


Figure S8. Important molecular orbitals of (a) **Fe-Be-H**$^{+}$ (b) **Ru-Be-H**$^{+}$ and (c) **Os-Be-H**$^{+}$ at the M06/Def2-TZVPP//BP86/Def2-TZVPP level of theory. Eigenvalues are given in eV.

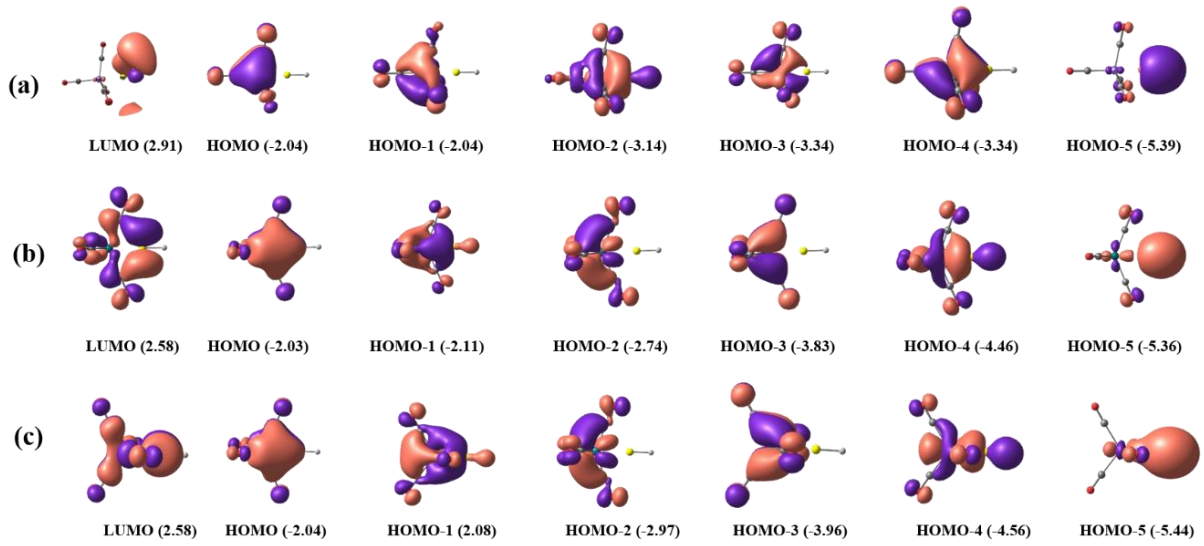


Figure S9. Important molecular orbitals of (a) **Fe-Be-H**$^{-}$ (b) **Ru-Be-H**$^{-}$ and (c) **Os-Be-H**$^{-}$ at the M06/Def2-TZVPP//BP86/Def2-TZVPP level of theory. Eigenvalues are given in eV.

Table S3. The proton affinity (PA) and hydride affinity values (HA) of **M-Be** at the M06/Def2-TZVPP//BP86/Def2-TZVPP level of theory.

Molecules	PA (kcal/mol)	HA (kcal/mol)
Fe-Be	215.0	141.6
Ru-Be	229.6	129.8
Os-Be	228.9	130.3

Cartesian coordinates of Molecules

Fe-Be

Electronic energy (BP86) = -1732.250841
Zero-point correction (BP86) = 0.034698
Electronic energy(M06) = -1731.7060387

26	0.000000000	0.000000000	0.138260000
4	0.000000000	0.000000000	2.052851000
6	0.000000000	1.552884000	-0.779122000
6	1.745153000	0.000000000	0.562150000
6	-1.745153000	0.000000000	0.562150000
6	0.000000000	-1.552884000	-0.779122000
8	-2.881244000	0.000000000	0.810828000
8	0.000000000	2.536273000	-1.385984000
8	2.881244000	0.000000000	0.810828000
8	0.000000000	-2.536273000	-1.385984000

Ru-Be

Electronic energy (BP86) = -563.365661
Zero-point correction (BP86) = 0.033686
Electronic energy (M06) = -562.9923996

44	0.000000000	0.000000000	0.107125000
4	0.000000000	0.000000000	2.170000000
6	0.000000000	1.840069000	-0.515892000
6	1.939388000	0.000000000	0.225781000
6	-1.939388000	0.000000000	0.225781000
6	0.000000000	-1.840069000	-0.515892000
8	-3.091206000	0.000000000	0.296933000
8	0.000000000	2.923477000	-0.916444000
8	3.091206000	0.000000000	0.296933000

8	0.000000000	-2.923477000	-0.916444000

Os-Be

Electronic energy (BP86) = -559.184122
Zero-point correction (BP86) = 0.034044
Electronic energy (M06) = -558.7895092

76	0.000000000	0.000000000	0.082388000
4	0.000000000	0.000000000	2.188254000
6	0.000000000	1.888049000	-0.430856000
6	1.966351000	0.000000000	0.098945000
6	-1.966351000	0.000000000	0.098945000
6	0.000000000	-1.888049000	-0.430856000
8	-3.121007000	0.000000000	0.104282000
8	0.000000000	2.986904000	-0.793755000
8	3.121007000	0.000000000	0.104282000
8	0.000000000	-2.986904000	-0.793755000

Fe-Be-H$^+$

Electronic energy (BP86) = -1732.572844
Zero-point correction (BP86) = 0.041506
Electronic energy (M06) = - 1732.0554788

26	0.000000000	0.000000000	0.246305000
4	0.000000000	0.000000000	-1.808864000
6	0.000000000	1.835744000	0.129155000
6	-1.835638000	0.000000000	0.128007000
6	1.835638000	0.000000000	0.128007000
6	0.000000000	-1.835744000	0.129155000
8	2.972325000	0.000000000	0.026507000
8	0.000000000	2.972550000	0.029086000
8	-2.972325000	0.000000000	0.026507000
8	0.000000000	-2.972550000	0.029086000
1	0.000000000	0.000000000	-3.143898000

Ru-Be-H$^+$

Electronic energy (BP86) = -563.714387
Zero-point correction (BP86) = 0.040985
Electronic energy (M06) = -563.3656331

44	0.000000000	0.000000000	0.162198000
4	0.000000000	0.000000000	-1.974716000
6	0.000000000	1.973097000	0.104590000

6	-1.972875000	0.000000000	0.100496000
6	1.972875000	0.000000000	0.100496000
6	0.000000000	-1.973097000	0.104590000
8	3.110618000	0.000000000	0.045893000
8	0.000000000	3.111054000	0.054794000
8	-3.110618000	0.000000000	0.045893000
8	0.000000000	-3.111054000	0.054794000
1	0.000000000	0.000000000	-3.309912000

Os-Be-H^{+}

Electronic energy (BP86) = -559.531954
Zero-point correction (BP86) = 0.041194
Electronic energy (M06) = -559.1615592

76	0.000000000	0.000000000	0.107455000
4	0.000000000	0.000000000	-2.065249000
6	0.000000000	1.990555000	0.077222000
6	-1.990757000	0.000000000	0.081626000
6	1.990757000	0.000000000	0.081626000
6	0.000000000	-1.990555000	0.077222000
8	3.130749000	0.000000000	0.054091000
8	0.000000000	3.130564000	0.045378000
8	-3.130749000	0.000000000	0.054091000
8	0.000000000	-3.130564000	0.045378000
1	0.000000000	0.000000000	-3.403244000

Fe-Be-H^{-}

Electronic energy (BP86) = -1732.988952
Zero-point correction (BP86) = 0.041096
Electronic energy (M06) = -1732.4404327

26	-0.016640000	-0.005519000	0.000000000
4	-1.885056000	-0.778142000	0.000000000
6	-1.019193000	1.450812000	0.000000000
6	-0.033943000	-0.946623000	1.496021000
6	-0.033943000	-0.946623000	-1.496021000
6	1.638218000	0.671430000	0.000000000
8	-0.033943000	-1.571665000	-2.495655000
8	-1.679508000	2.427381000	0.000000000
8	-0.033943000	-1.571665000	2.495655000
8	2.723494000	1.113664000	0.000000000
1	-3.142767000	-1.299634000	0.000000000

Ru-Be-H^{-}

Electronic energy (BP86) = -564.085219
Zero-point correction (BP86) = 0.039153
Electronic energy (M06) = -563.7069641

44	0.000000000	0.000000000	0.019840000
4	0.000000000	0.000000000	2.194473000
6	0.000000000	1.567889000	-1.089836000
6	1.774072000	0.000000000	0.723860000
6	-1.774072000	0.000000000	0.723860000
6	0.000000000	-1.567889000	-1.089836000
8	-2.861929000	0.000000000	1.178660000
8	0.000000000	2.548602000	-1.729754000
8	2.861929000	0.000000000	1.178660000
8	0.000000000	-2.548602000	-1.729754000
1	0.000000000	0.000000000	3.558366000

Os-Be-H$^-$

Electronic energy (BP86) = -559.902558
Zero-point correction (BP86) = 0.039311
Electronic energy (M06) = -559.5047423

76	0.000000000	0.000000000	0.018764000
4	0.000000000	0.000000000	2.235599000
6	0.000000000	1.597115000	-1.067013000
6	1.815236000	0.000000000	0.670789000
6	-1.815236000	0.000000000	0.670789000
6	0.000000000	-1.597115000	-1.067013000
8	-2.906853000	0.000000000	1.117962000
8	0.000000000	2.589349000	-1.693813000
8	2.906853000	0.000000000	1.117962000
8	0.000000000	-2.589349000	-1.693813000
1	0.000000000	0.000000000	3.599828000

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