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Electronic Supplementary Information for

Electronic structures and properties of dianionic pentacarbonyls $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W)

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Table S1. The singlet-triplet splitting energy E_{S-T} for $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W) given in kcal/mol.

$[TM(CO)_5]^{2-}$	Singlet	Triplet	E_{S-T}
Cr	-2017.650	-1975.030	42.6
Mo	-2036.600	-1994.480	42.1
W	-2042.880	-2002.490	40.4

To determine the spin state of the $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W) dianions, the singlet and triplet states were calculated. As shown in Table S1, the single and triplet bond energies of these three carbonyls are all positive. The singlet state is more stable than the triplet state by more than 40 kcal/mol at the BP86/TZ2P/ZORA level of theory. Therefore, the electron singlet ground state of the pentacarbonyl 18-electron system compounds $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W) with D_{3h} equilibrium configuration are confirmed.

Table S2. Calculated NBO partial charges q in $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W).

TM	TM	C(axial)	C(planar)	O(axial)	O(planar)
Cr	-2.934	+0.814	+0.804	-0.613	-0.627
Mo	-2.237	+0.669	+0.640	-0.593	-0.612
W	-1.983	+0.618	+0.586	-0.594	-0.608

The atomic charges and bonding situations of the optimized $[TM(CO)_5]^{2-}$ were analyzed with the natural bond orbital analysis (NBO 3.1) using the optimized molecules at BP86/def2-QZVPPD. The NBO results are presented in Table S2 here because we found that NBO calculation maybe not suitable for compounds containing transition metals according to the charge distribution between TM and O atoms.

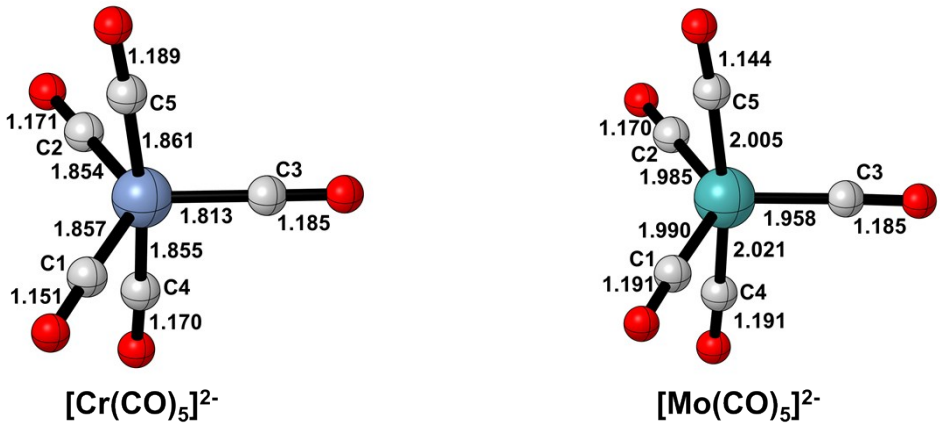

Fig. S1. Experimental geometries of $[TM(CO)_5]^{2-}$ (TM = Cr, Mo) and the selected bond lengths are given in Å, respectively.

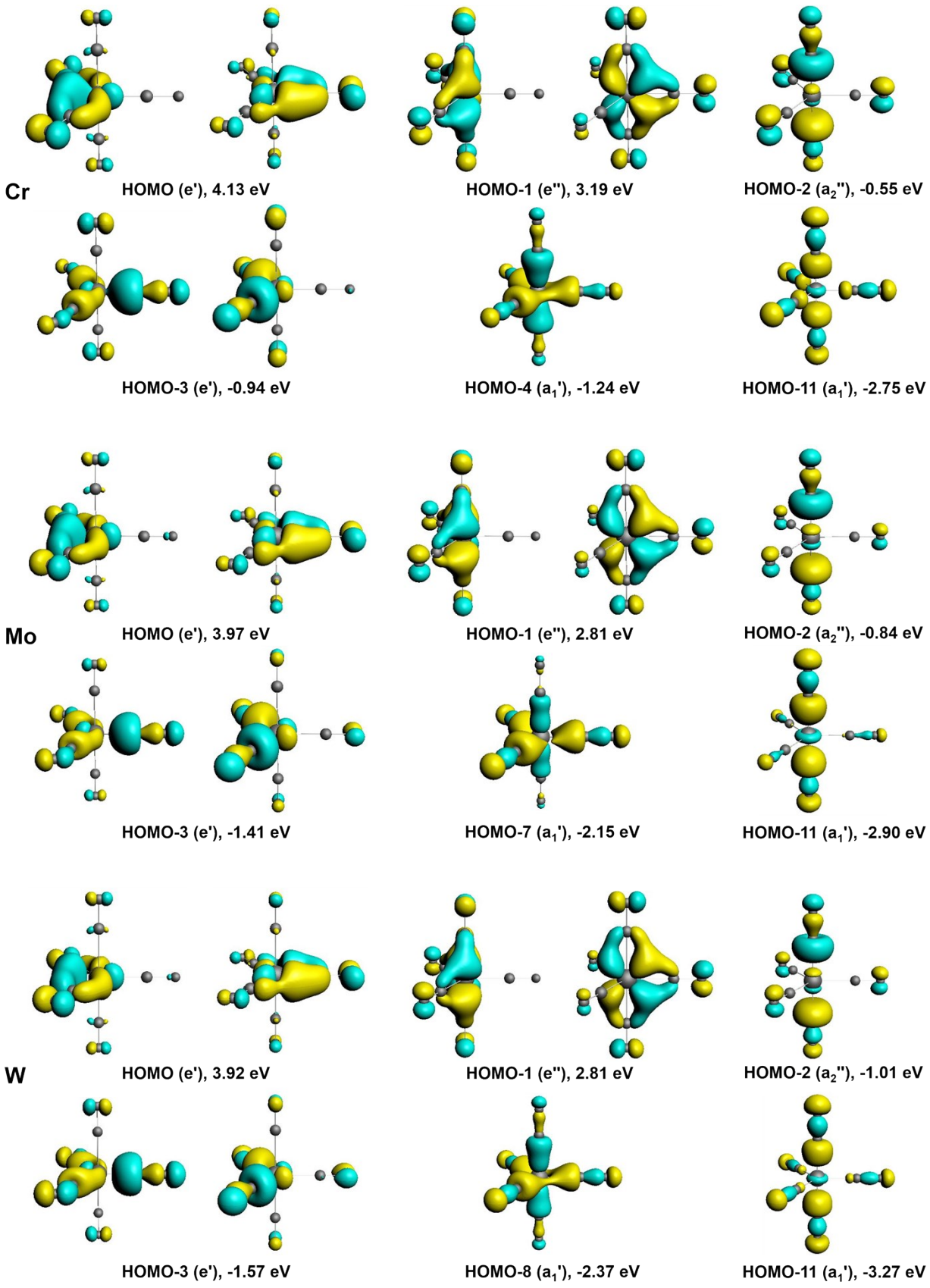

Fig. S2. Selected molecular orbitals (isovalue = 0.05) of $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W) with energy eigenvalues given in eV.

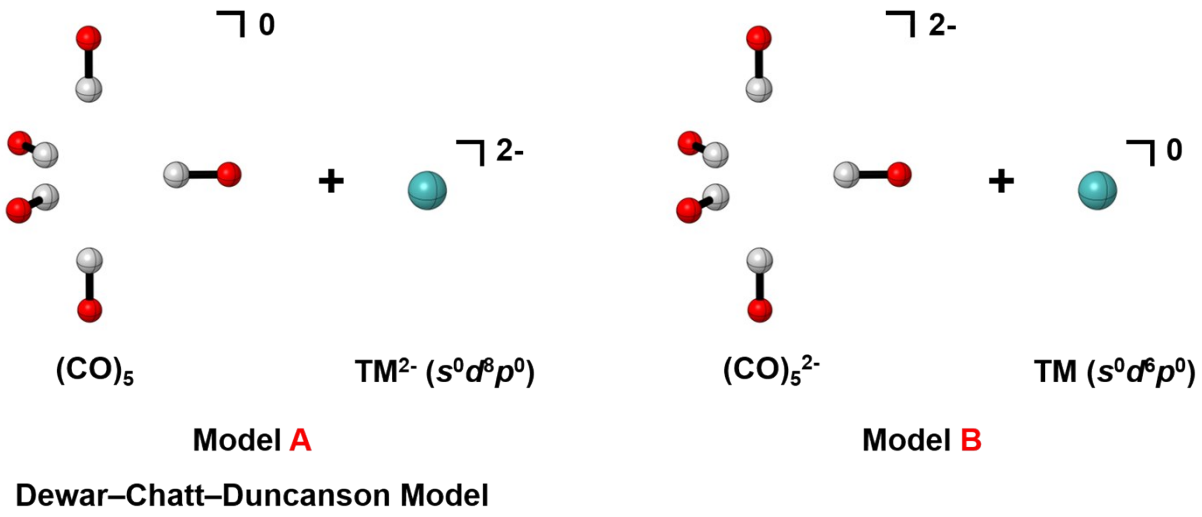

Fig. S3. Two different models for EDA-NOCV analysis of the TM–$(CO)_5$ interactions bond in $[TM(CO)_5]^{2-}$ (TM = Cr, Mo, W).

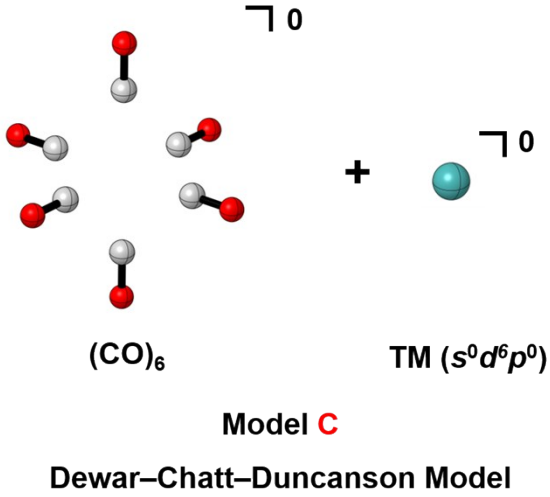

Fig. S4. The model for EDA-NOCV analysis of the TM–$(CO)_6$ interactions in $TM(CO)_6$ (TM = Cr, Mo, W).

Table S3. EDA-NOCV results of the TM─$[(CO)_5]^{2-}$ interactions in $[TM(CO)_5]^{2-}$ dianions (TM = Cr, Mo, W) at the BP86-D3(BJ)/TZ2P+ level using TM($s^0d^6p^0$) (triplet) and $[(CO)_5]^{2-}$ (triplet) fragments. All values are in kcal/mol.

	Orbital interaction	Cr($s^0d^6p^0$) + $[(CO)_5]^{2-}$	Mo($s^0d^6p^0$) + $[(CO)_5]^{2-}$	W($s^0d^6p^0$) + $[(CO)_5]^{2-}$
ΔE_{int}		-447.51	-437.9	-507.9
ΔE_{Pauli}		+480.8	+533.2	+567.3
ΔE_{disp}		-5.6	-7.9	-7.3
ΔE_{elstat}[a]		-379.9 (41.2%)	-418.4 (43.4%)	-481.9 (45.1%)
ΔE_{orb}[a]		-542.7 (58.8%)	-544.8 (56.6%)	-585.8 (54.9%)
$\Delta E_{orb(1)}$[b] (e_g)	TM(d)─$[(CO)_5]^{2-}$ electron-sharing bonding	-89.3 (16.5%)	-102.5 (18.8%)	-109.4 (18.7%)
$\Delta E_{orb(2)}$[b] (t_{2g})		-89.3 (16.5%)	-102.5 (18.8%)	-109.4 (18.7%)
$\Delta E_{orb(3)}$[b] (a_{2u})	TM(d) → $[(CO)_5]^{2-}$ π backdonation	-138.4 (25.5%)	-114.1 (20.9%)	-117.7 (20.1%)
$\Delta E_{orb(4)}$[b] (a_{1g})		-138.4 (25.5%)	-114.1 (20.9%)	-117.7 (20.1%)
$\Delta E_{orb(5)}$[b] (t_{2g})	TM(d) ← $[(CO)_5]^{2-}$ σ donation	-61.6 (11.3%)	-76.1 (14.0%)	-79.8 (13.6%)
$\Delta E_{orb(6)}$[b] (a_{2u})	TM(p) ← $[(CO)_5]^{2-}$ σ donation	-5.9 (1.1%)	-7.0 (1.3%)	-14.6 (2.5%)
$\Delta E_{orb(7)}$[b] (t_{2g})	TM(p) ← $[(CO)_5]^{2-}$ σ donation	-5.9 (1.1%)	-7.0 (1.3%)	-9.0 (1.5%)
$\Delta E_{orb(8)}$[b] (a_{2u})	TM(s) ← $[(CO)_5]^{2-}$ σ donation	-4.7 (0.9%)	-6.3 (1.2%)	-9.0 (1.5%)
$\Delta E_{orb(9)}$[b] (a_{2u})	TM(p) ← $[(CO)_5]^{2-}$ σ donation	-3.5 (0.6%)	-5.9 (1.1%)	-7.2 (1.2%)
$\Delta E_{orb(rest)}$[b]		-5.7 (1.0%)	-9.3 (1.7%)	-12.0 (2.1%)

[a] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.

[b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

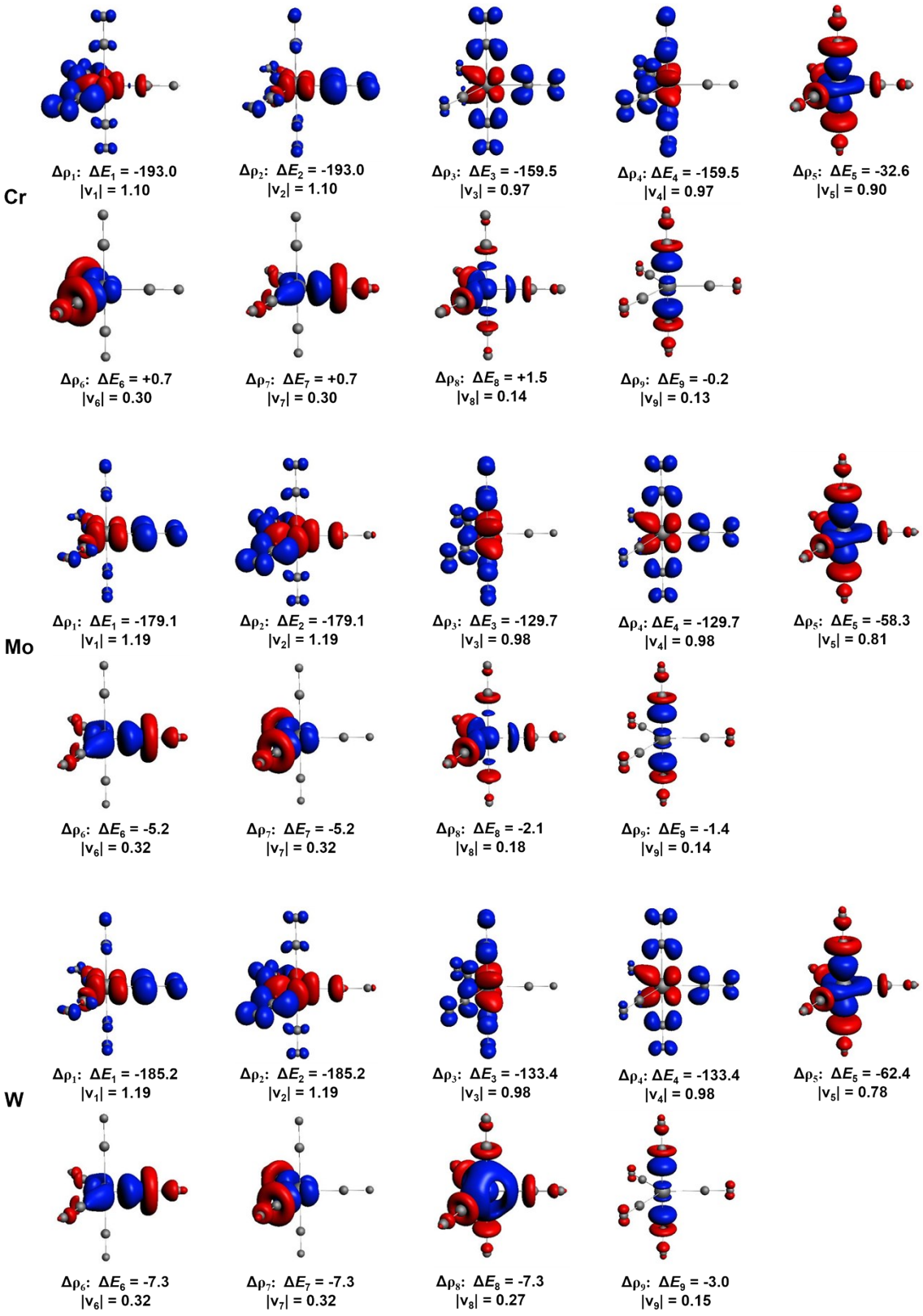

Fig. S5. Deformation densities $\Delta\rho_{1-5}$ (isovalue = 0.005) and $\Delta\rho_{6-9}$ (isovalue = 0.002) of the pairwise orbital interaction between TM^{2-} and $(CO)_5$ using $[TM(s^0d^8p^0)]^{2-}$ (singlet) and $(CO)_5$ (singlet) ligand as interacting fragments (Model A) with the association interaction energies ΔE (in kcal/mol) and their energy eigenvalues ν (in e) which indicates the amount of donated and accepted charge. The direction of the charge flow is red → blue.

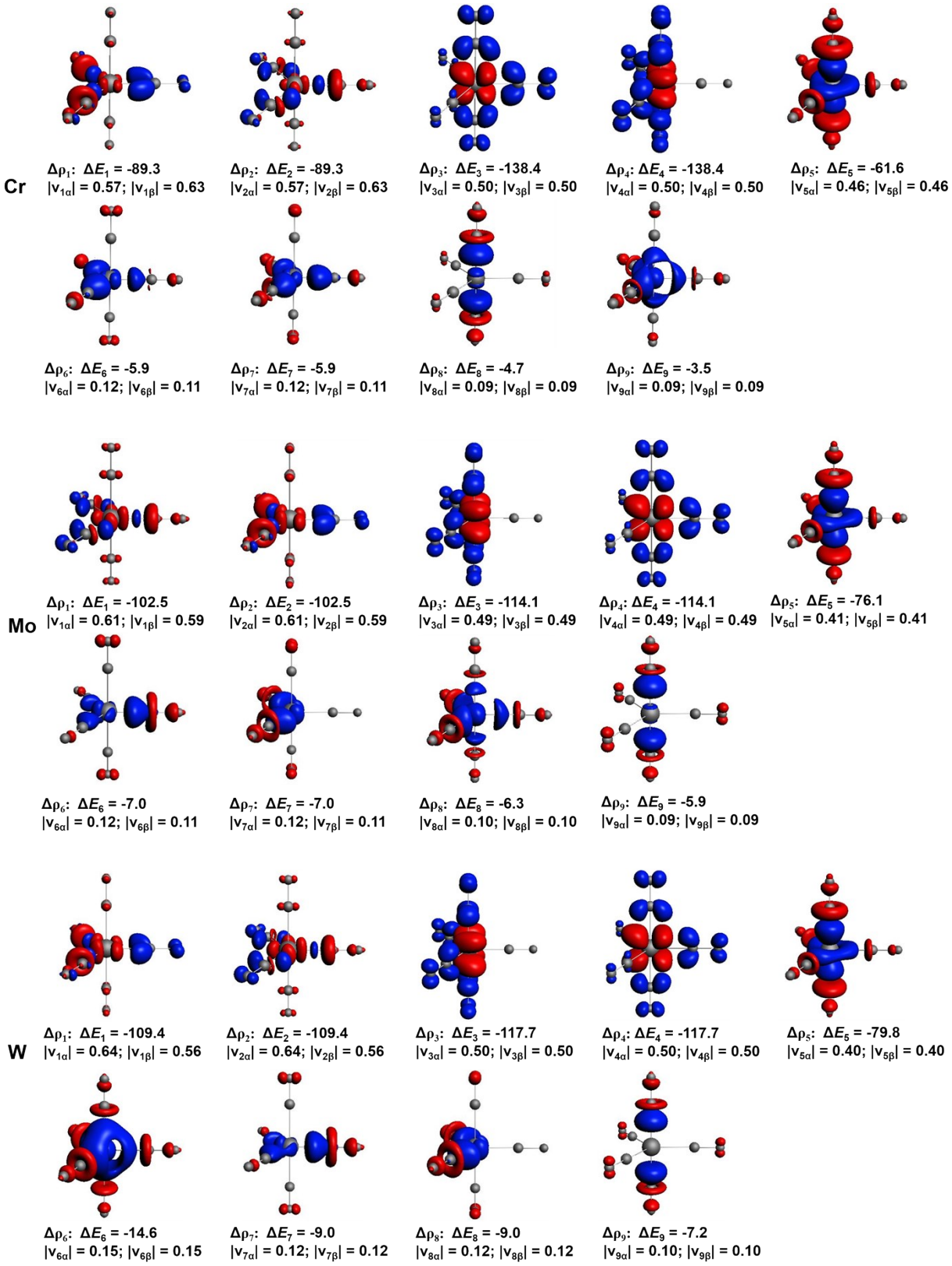

Fig. S6. Deformation densities $\Delta\rho_{1-5}$ (isovalue = 0.005) and $\Delta\rho_{6-9}$ (isovalue = 0.002) of the pairwise orbital interaction between TM^{2-} and $(CO)_5$ using $[TM(s^0d^6p^0)]$ (triplet) and $[(CO)_5]^{2-}$ (triplet) ligand as interacting fragments (Model B) with the association interaction energies ΔE (in kcal/mol) and their energy eigenvalues ν (in e) which indicates the amount of donated and accepted charge. The direction of the charge flow is red → blue.

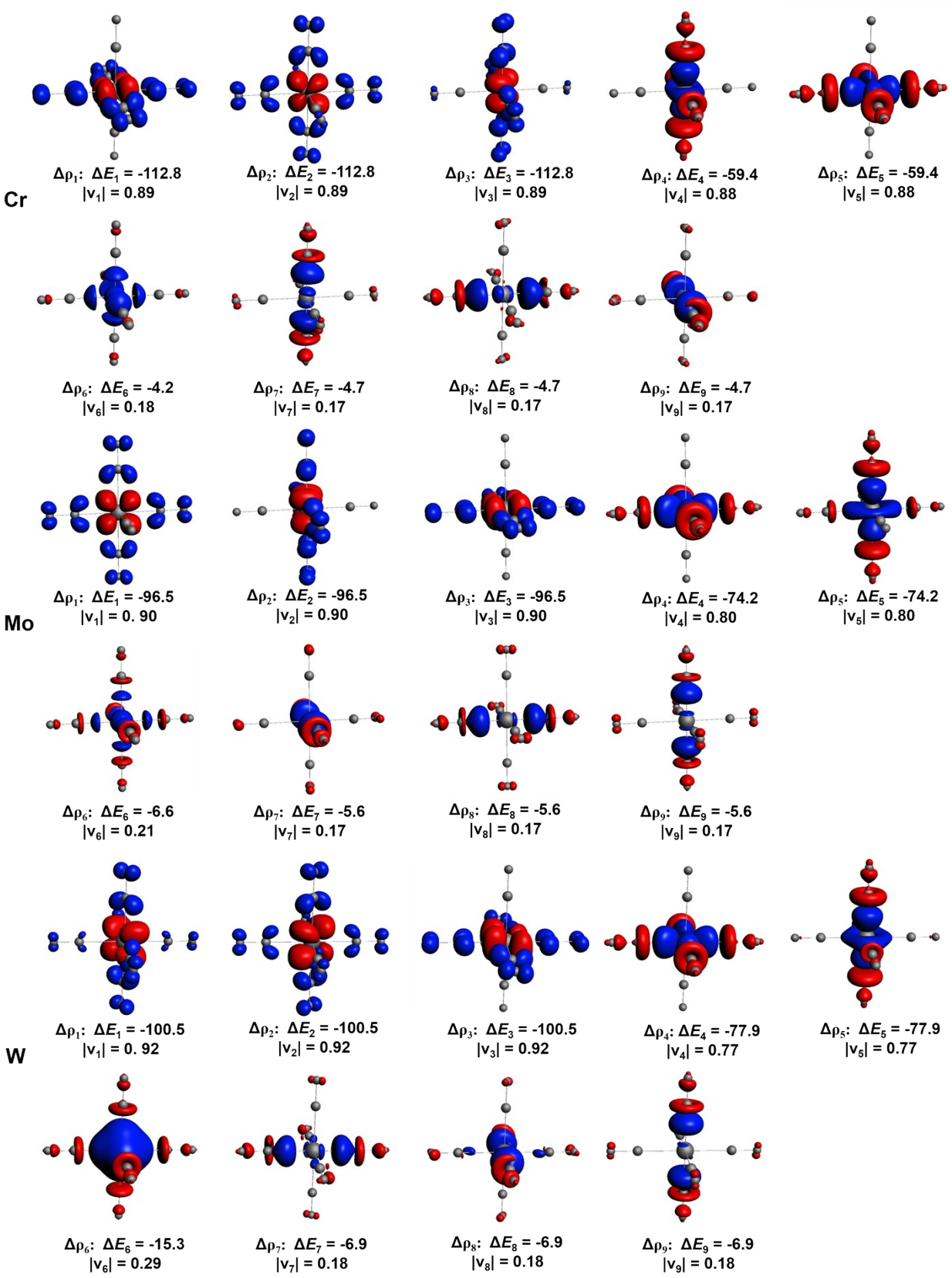

Fig. S7. Deformation densities $\Delta\rho_{1-5}$ (isovalue = 0.005) and $\Delta\rho_{6-9}$ (isovalue = 0.002) of the pairwise orbital interaction between TM and $(CO)_6$ using TM($s^0d^6p^0$) (singlet) and $(CO)_6$ (singlet) ligand as interacting fragments (Model C) with the association interaction energies ΔE (in kcal/mol) and their energy eigenvalues ν (in e) which indicates the amount of donated and accepted charge. The direction of the charge flow is red → blue.

(1) $[Cr(CO)_5]^{2-}$, (D_{3h})
BP86/def-QZVPPD, Singlet
Energy = -1611.722 a.u.
Gibbs free energy = -1611.724 a.u.

Cr	0.000013	-0.000256	0.000006
C	1.870984	0.000878	0.000045
C	-0.000386	1.844014	0.000036
C	0.000244	-0.922841	-1.597034
C	0.000118	-0.922892	1.597017
C	-1.870959	0.000312	-0.000064
O	3.061865	0.002188	0.000070
O	-0.000646	3.041517	0.000055
O	0.000394	-1.521859	-2.633954
O	0.000186	-1.521943	2.633918
O	-3.061840	0.001261	-0.000109

(2) $[Cr(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Singlet
Bond Energy = -3.215 a.u. = -2017.65 kcal/mol.

Cr	0.000000	0.000000	0.049742
C	-1.264039	1.263987	-0.441028
C	1.264039	1.263987	-0.4410280
C	0.000000	0.000000	1.869998
C	-1.264039	-1.263987	-0.441028
C	1.264039	-1.263987	-0.441028
O	-2.068500	2.068236	-0.806111
O	2.068500	2.068236	-0.806111
O	0.000000	0.000000	3.068814
O	-2.068500	-2.068236	-0.806111
O	2.068500	-2.068236	-0.806111

(3) $[Cr(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Triplet
Bond Energy = -3.147 a.u. = -1975.03 kcal/mol.

Cr	0.000000	0.000000	-0.229423
C	-1.156248	1.486026	-0.448246
C	1.156248	1.486026	-0.448246
C	0.000000	0.000000	1.569531
C	-1.156248	-1.486026	-0.448246
C	1.156248	-1.486026	-0.448246
O	-1.729479	2.535379	-0.578025
O	1.729479	2.535379	-0.578025
O	0.000000	0.000000	2.764975
O	-1.729479	-2.535379	-0.578025
O	1.729479	-2.535379	-0.578025

(4) $[Mo(CO)_5]^{2-}$, (D_{3h})
BP86/def-QZVPPD, Singlet
Energy = -635.386 a.u.
Gibbs free energy = -635.391 a.u.

Mo	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.030750
C	0.000000	1.995350	0.000000
C	1.728024	-0.997675	0.000000
C	-1.728024	-0.997675	0.000000
C	0.000000	0.000000	-2.030750
O	0.000000	0.000000	3.217455
O	0.000000	3.190642	0.000000
O	2.763177	-1.595321	0.000000
O	-2.763177	-1.595321	0.000000
O	0.000000	0.000000	-3.217455

(5) $[Mo(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Singlet
Bond Energy = -3.246 a.u. = -2036.60 kcal/mol.

Mo	0.000000	0.000000	-0.019583
C	0.000000	-2.030135	-0.019683
C	1.750990	0.000000	-0.980566
C	-1.750990	0.000000	-0.980566
C	0.000000	0.000000	1.971794
C	0.000000	2.030135	-0.019683
O	0.000000	-3.217267	-0.013208
O	2.804555	0.000000	-1.546422
O	-2.804555	0.000000	-1.546422
O	0.000000	0.000000	3.167548
O	0.000000	3.217267	-0.013208

(6) $[Mo(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Triplet
Bond Energy = -3.178 a.u. = -1994.48 kcal/mol.

Mo	0.000000	0.000000	0.285236
C	0.000000	-2.022675	0.040112
C	1.444328	0.000000	-1.057606
C	-1.444328	0.000000	-1.057606
C	0.000000	0.000000	2.402391
C	0.000000	2.022675	0.040112
O	0.000000	-3.164706	-0.274472
O	2.338072	0.000000	-1.861286
O	-2.338072	0.000000	-1.861286
O	0.000000	0.000000	3.618875
O	0.000000	3.164706	-0.274472

(7) $[W(CO)_5]^{2-}$, (D_{3h})
BP86/def-QZVPPD, Singlet
Energy = -634.289 a.u.
Gibbs free energy = -634.294 a.u.

W	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.044250
C	0.000000	2.005420	0.000000
C	1.736745	-1.002710	0.000000
C	-1.736745	-1.002710	0.000000
C	0.000000	0.000000	-2.044250
O	0.000000	0.000000	3.232282
O	0.000000	3.202365	0.000000
O	2.773329	-1.601182	0.000000
O	-2.773329	-1.601182	0.000000
O	0.000000	0.000000	-3.232282

(8) $[W(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Singlet
Bond Energy = -3.256 a.u. = -2042.88 kcal/mol.

W	0.000000	0.000000	-0.116273
C	-1.965599	0.000000	0.348518
C	0.000000	1.948823	0.404585
C	0.000000	-1.948823	0.404585
C	0.000000	0.000000	-2.078330
C	1.965599	0.000000	0.348518
O	-3.110528	0.000000	0.684509
O	0.000000	3.084833	0.772695
O	0.000000	-3.084833	0.772695
O	0.000000	0.000000	-3.277072
O	3.110528	0.000000	0.684509

(9) $[W(CO)_5]^{2-}$, (C_{2v})
BP86/TZ2P/ZORA, Triplet
Bond Energy = -3.191a.u. = -2002.49 kcal/mol.

W	0.000000	0.000000	0.104788
C	-2.046515	0.000000	0.306246
C	0.000000	2.013065	0.411128
C	0.000000	-2.013065	0.411128
C	0.000000	0.000000	-1.835647
C	2.046515	0.000000	0.306246
O	-3.246439	0.000000	0.453153
O	0.000000	3.170271	0.686875
O	0.000000	-3.170271	0.686875
O	0.000000	0.000000	-3.035007
O	3.246439	0.000000	0.453153

(10) $Cr(CO)_6$, (O_h)
BP86/def-QZVPPD, Singlet
Energy = -1725.142 a.u.
Gibbs free energy = -1725.133 a.u.

Cr	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.908254
C	0.000000	0.000000	-1.908254
C	0.000000	1.908254	0.000000
C	-1.908254	0.000000	0.000000
O	0.000000	0.000000	3.060076
O	0.000000	0.000000	-3.060076
O	0.000000	3.060076	0.000000
O	-3.060076	0.000000	0.000000
C	1.908254	0.000000	0.000000
C	0.000000	-1.908254	0.000000
O	3.060076	0.000000	0.000000
O	0.000000	-3.060076	0.000000

(11) $Mo(CO)_6$, (O_h)
BP86/def-QZVPPD, Singlet
Energy = -748.814 a.u.
Gibbs free energy = -748.808 a.u.

C	0.000000	0.000000	2.059978
C	0.000000	0.000000	-2.059978
C	0.000000	2.059978	0.000000
C	-2.059978	0.000000	0.000000
O	0.000000	0.000000	3.211504
O	0.000000	0.000000	-3.211504
O	0.000000	3.211504	0.000000
O	-3.211504	0.000000	0.000000
C	2.059978	0.000000	0.000000
C	0.000000	-2.059978	0.000000
O	3.211504	0.000000	0.000000
O	0.000000	-3.211504	0.000000
Mo	0.000000	0.000000	0.000000

(12) $W(CO)_6$, (O_h)
BP86/def-QZVPPD, Singlet
Energy = -747.716 a.u.
Gibbs free energy = -747.710a.u.

C	0.000000	0.00000	2.071393
C	0.000000	0.000000	-2.071393
C	0.000000	2.071393	0.000000
C	-2.071393	0.000000	0.000000
O	0.000000	0.000000	3.224167
O	0.000000	0.000000	-3.224167
O	0.000000	3.224167	0.000000
O	-3.224167	0.000000	0.000000
C	2.071393	0.000000	0.000000
C	0.000000	-2.071393	0.000000
O	3.224167	0.000000	0.000000
O	0.000000	-3.224167	0.000000
W	0.000000	0.000000	0.000000

Methods and Materials

Crystals of $[K([2.2.2]crypt)]_2[Cr(CO)_5]\cdot en$ were obtained by the reaction of K_4Pb_9 and $Cr(CO)_6$ in ethylenediamine in the presence of 2.2.2-crypt in a very low yield (< 7%). Similarly, crystals of $[K([2.2.2]crypt)]_2[Mo(CO)_5]$ were obtained by the reaction of K_4Pb_9 and $Mo(CO)_6$ in DMF in the presence of 2.2.2-crypt in < 5% yield.

General:

All manipulations were performed under a nitrogen atmosphere by using standard Schlenk-line or glove box techniques. K_4Pb_9 was synthesized by heating the corresponding mixture of the stoichiometric elements at 800 ℃ for 36 h in sealed niobium tubes.1,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ([2.2.2]crypt, Sigma-Aldrich 98%) was dried under vacuum for several hours and transfer to glove box for use. Toluene (Aldrich, 99.8%), Ethylenediamine (en) (Aldrich, 99%) and Dimethylformamide (DMF) (Aldrich, 99.8%) were distilled by sodium in a nitrogen atmosphere and stored in a glove box prior to use. $Cr(CO)_6$ and $Mo(CO)_6$ were purchased from Aldrich.

X-ray Diffraction:

Suitable single crystals were selected for X-ray diffraction analyses. Crystallographic data were collected on Rigaku XtalAB Pro MM007 DW diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54184 Å). Structures were solved using direct methods and then refined using SHELXL-2014 and Olex2 to convergence, in which all the non-hydrogen atoms were refined anisotropically during the final cycles.[1-3] All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The CCDC numbers of compounds **1** and **2** are 2059985 and 2059986.

Synthesis of $[K([2.2.2]crypt)]_2[Cr(CO)_5]\cdot en$ (**1**)

In a 10 mL vial, 150 mg (0.074 mmol) of K_4Pb_9, 80 mg (0.212 mmol) of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and 22 mg (0.099 mmol) of $Cr(CO)_6$ were dissolved in ethylenediamine (2 mL) and the green solution was allowed to stir vigorously at room temperature for 4 h. The resulting brown solution was filtered through glass wool and transferred to a test tube. After 7 days, brown plate-like crystals of $[K([2.2.2]crypt)]_2[Cr(CO)_5]\cdot en$ were obtained by layering with toluene (3 mL) (< 7% crystalline yields based on Cr). The crystals are very air-sensive, and the very low yield hindered further characterizations.

Synthesis of $[K([2.2.2]crypt)]_2[Mo(CO)_5]$ (**2**)

In a 10 mL vial, 150 mg (0.074 mmol) of K_4Pb_9, 80 mg (0.212 mmol) of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and 26 mg (0.098 mmol) of $Mo(CO)_6$ were dissolved in DMF (2 mL) and the green solution was allowed to stir vigorously at room temperature for 5 h. The resulting brown-black solution was filtered through glass wool and transferred to a test tube. After 14 days, brown plate-like crystals of $[K([2.2.2]crypt)]_2[Mo(CO)_5]$ were obtained by layering with toluene (3 mL) (< 5% crystalline yields based on Mo). The crystals are very air-sensive, and the very low yield hindered further characterizations.

Table S4. X-ray measurements and structure solutions of compound **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{43}H_{80}O_{17}N_6K_2Cr$	$C_{41}H_{72}O_{17}N_4K_2Mo$
Formula weight	1083.33	1067.16
Temperature /K	100	100
Wavelength /Å	1.54184	1.54184
Crystal system	Triclinic	Triclinic
Space group	*P*1	*P*1
a /Å	10.9523(3)	10.8840(3)
b /Å	11.6300(4)	11.6242(3)
c /Å	12.6749(4)	12.7269(3)
α /°	63.886(3)	64.679(2)
β /°	66.660(3)	68.734(2)
γ /°	86.853(2)	88.896(2)
V /Å^3	1316.98(8)	1339.97(7)
Z	1	1
ρ_{calc} /g·cm^{-3}	1.366	1.322
μ /mm^{-1}	3.814	3.955
F(000)	578.0	562.0
2θ range /°	8.54 to 133.996	8.346 to 133.982
Reflections collected / unique	11491/6070	13672/7011
Data / restraints / parameters	6070/3/623	7011/1707/587
R_1/wR_2 ($I>2\sigma(I)$)[a]	0.0465/0.1313	0.0315/0.0827
R_1/wR_2 (all data)	0.0526/0.1362	0.0317/0.0829
GooF (all data)[b]	1.048	1.034
Data completeness	0.995	0.994
Max. peak/hole /e$^-$·Å^{-3}	0.62/-0.66	0.76/-0.40

[a] $R_1 = = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$. [b] GooF = $\{\sum w[(Fo)^2-(Fc)^2]^2/(n-p)\}^{1/2}$

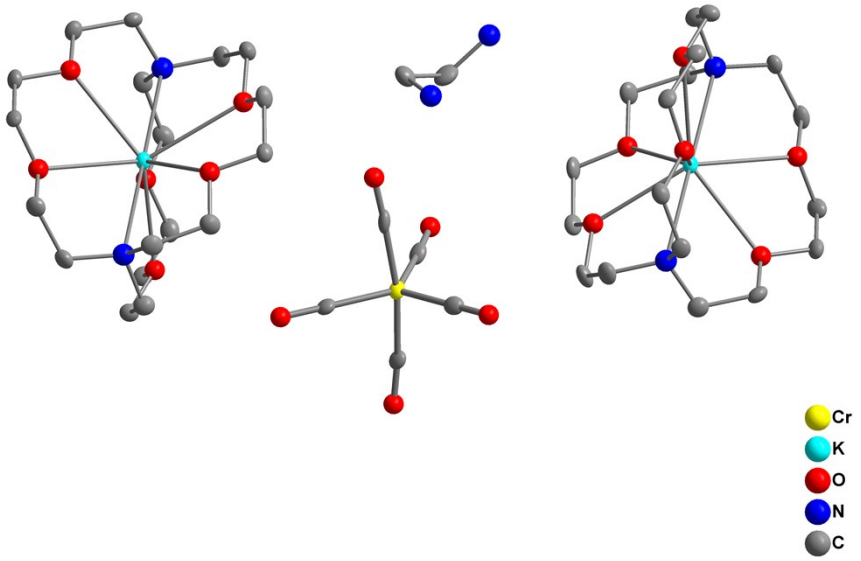

Fig. S8. Asymmetric unit of compound **1** with the cluster fragment. Thermal ellipsoids are drawn at 50% probability.

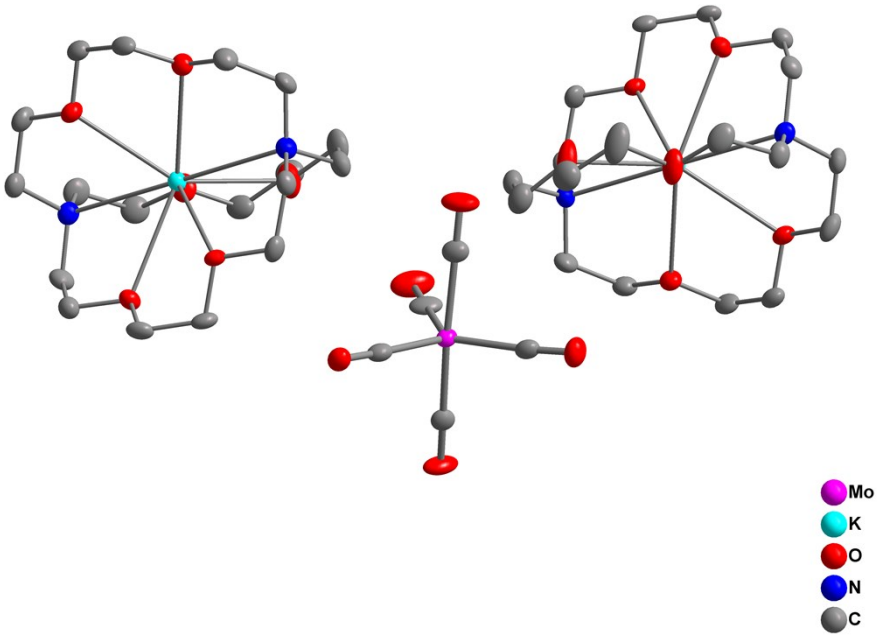

Fig. S9. Asymmetric unit of compound **2** with the cluster fragment. Thermal ellipsoids are drawn at 50% probability.

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