Supplementary Information

Stabilizing hydrogen-mediated sextuple bond by quintuple superatomic bonding and a σ_{dz^2} bond

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Table S1. Benchmark on the distances (Å) of metal to metal, metal to bridging H and metal to Cp ring in **5**-**8** under CCSD(T) and different DFT methods with def2tzvp basis set.

Distances / Methods	$[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**)			$[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**)			$[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**)			$[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**)		
	Sc-Sc	Sc-H	Sc-Cp	Mn-Mn	Mn-H	Mn-Cp	Ti-Ti	Ti-H	Ti-Cp	V-V	V-H	V-Cp
bp86	2.394	2.013	2.217	2.239	1.728	1.690	2.268	1.879	2.129	2.129	1.783	1.9301
tpss	2.379	2.014	2.207	2.230	1.728	1.681	2.252	1.883	2.120	2.118	1.783	1.918
pbe	2.398	2.016	2.210	2.239	1.728	1.68	2.274	1.878	2.120	2.132	1.783	1.9226
pbe-D3	2.388	2.014	2.199	2.233	1.727	1.675	2.269	1.877	2.110	2.126	1.782	1.9161
tpssh	2.372	2.012	2.203	2.230	1.719	1.686	2.234	1.879	2.118	2.096	1.775	1.912
b3lyp	**2.392**	**2.015**	**2.240**	**2.254**	**1.712**	**1.743**	**2.225**	**1.881**	**2.166**	**2.087**	**1.774**	**1.945**
b3lyp-D3	2.376	2.012	2.222	2.242	1.715	1.733	2.217	1.879	2.149	2.078	1.771	1.932
cam-b3lyp	2.362	2.005	2.216	2.246	1.704	1.730	2.192	1.873	2.145	2.052	1.760	1.921
cam-b3lyp-D3	2.352	2.002	2.208	2.241	1.703	1.726	2.188	1.872	2.136	2.048	1.759	1.916
CCSD(T)	**2.388**	**2.033**	**2.233**	**2.236**	**1.697**	**1.719**	**2.200**	**1.888**	**2.159**	**2.057**	**1.751**	**1.918**

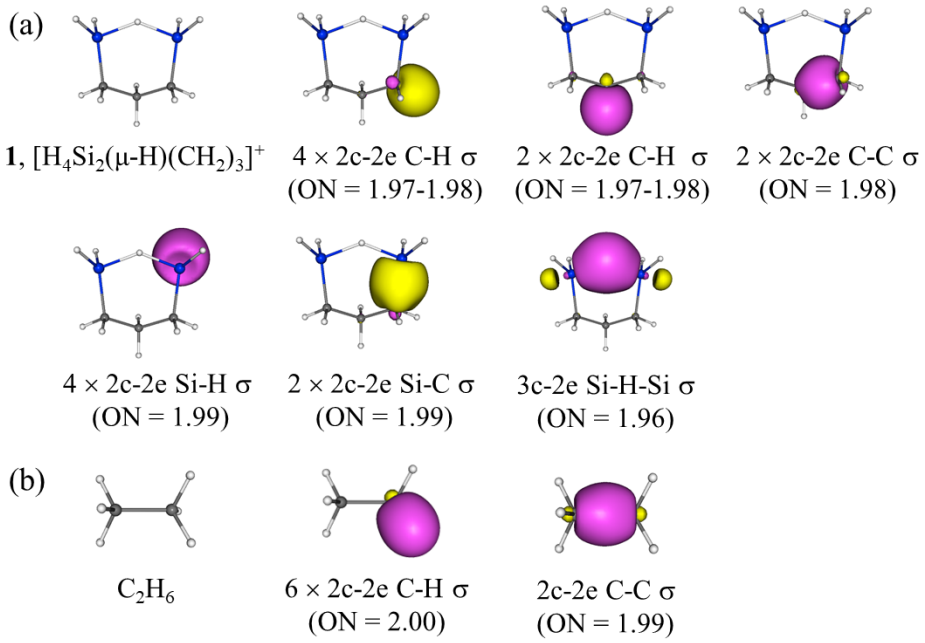

Fig. S1 AdNDP bonding frameworks of (a) $[H_4Si_2(\mu\text{-}H)(CH_2)_3]^+$ (**1**) and (b) C_2H_6.

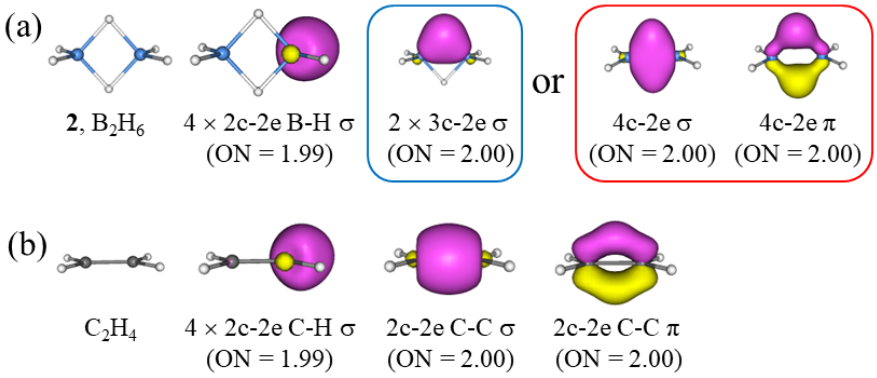

Fig. S2 AdNDP bonding frameworks of (a) B_2H_6 (**2**) and (b) C_2H_4.

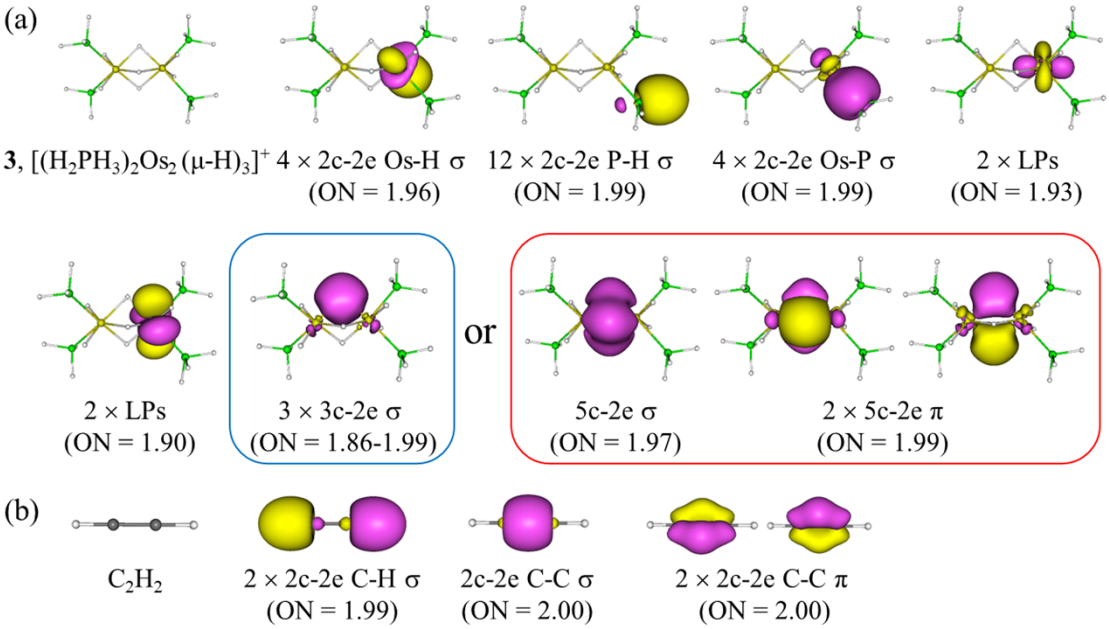

Fig. S3 AdNDP bonding frameworks of (a) $[(H_2PH_3)_2Os_2(\mu\text{-}H)_3]^+$ (**3**) and (b) C_2H_2.

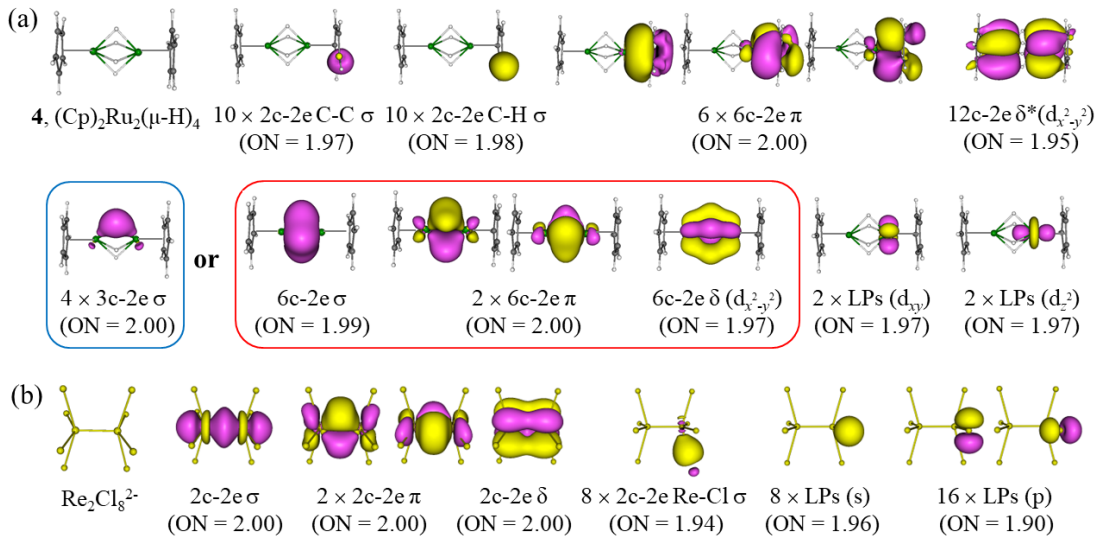

Fig. S4 AdNDP bonding frameworks of (a) $(Cp)_2Ru_2(\mu\text{-}H)_4$ (**4**) and (b) $Re_2Cl_8^{2-}$.

Table S2. HOMO-LUMO energy gaps (E_{HL}) of **5**-**8** under different DFT methods with def2tzvp basis set.

	$[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**)	$[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**)	$[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**)	$[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**)
bp86	1.74	1.48	0.78	1.17
tpss	1.89	1.89	0.88	1.26
pbe	1.73	1.46	0.77	1.16
pbe-D3	1.75	1.47	0.76	1.16
tpssh	2.72	3.13	1.73	2.21
b3lyp	3.42	3.81	2.61	3.11
b3lyp-D3	3.47	3.81	2.59	3.11
cam-b3lyp	6.25	6.17	5.05	6.15
cam-b3lyp-D3	6.28	6.17	5.03	6.15

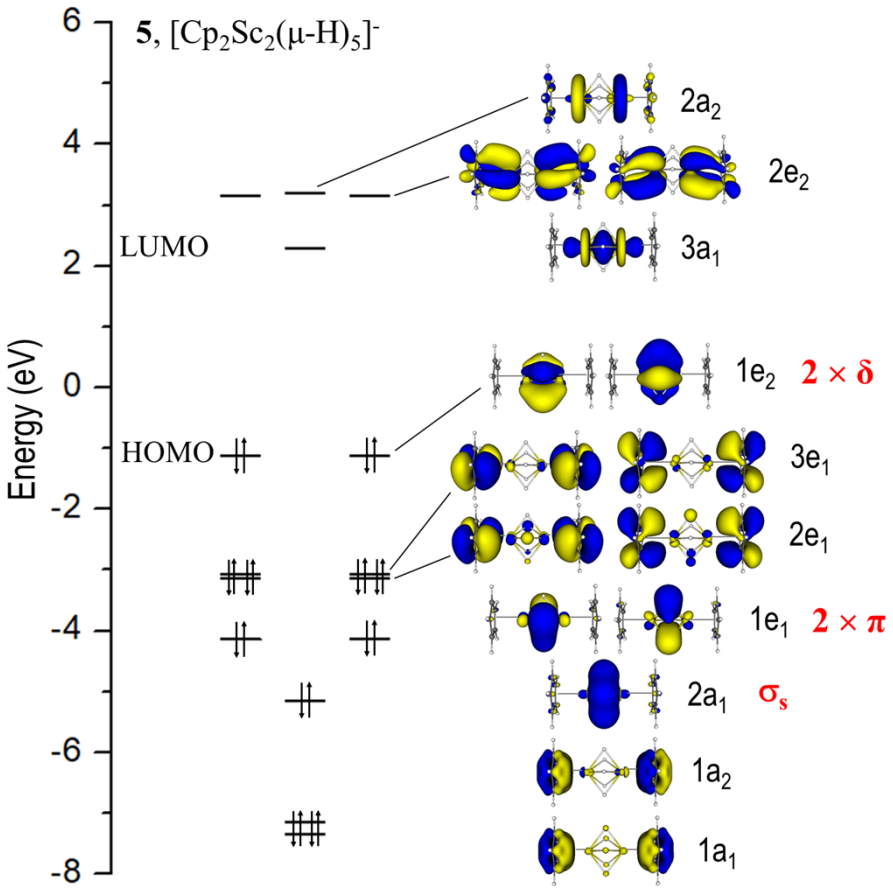

Fig. S5 Canonical molecular orbital diagram of $[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**).

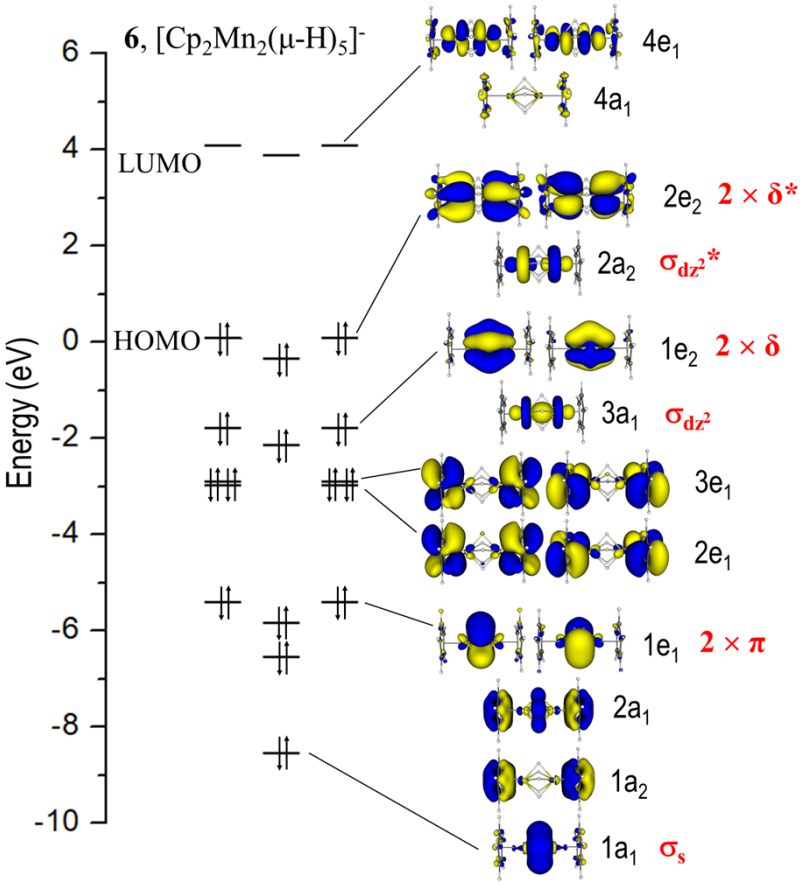

Fig. S6 Canonical molecular orbital diagram of $[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**).

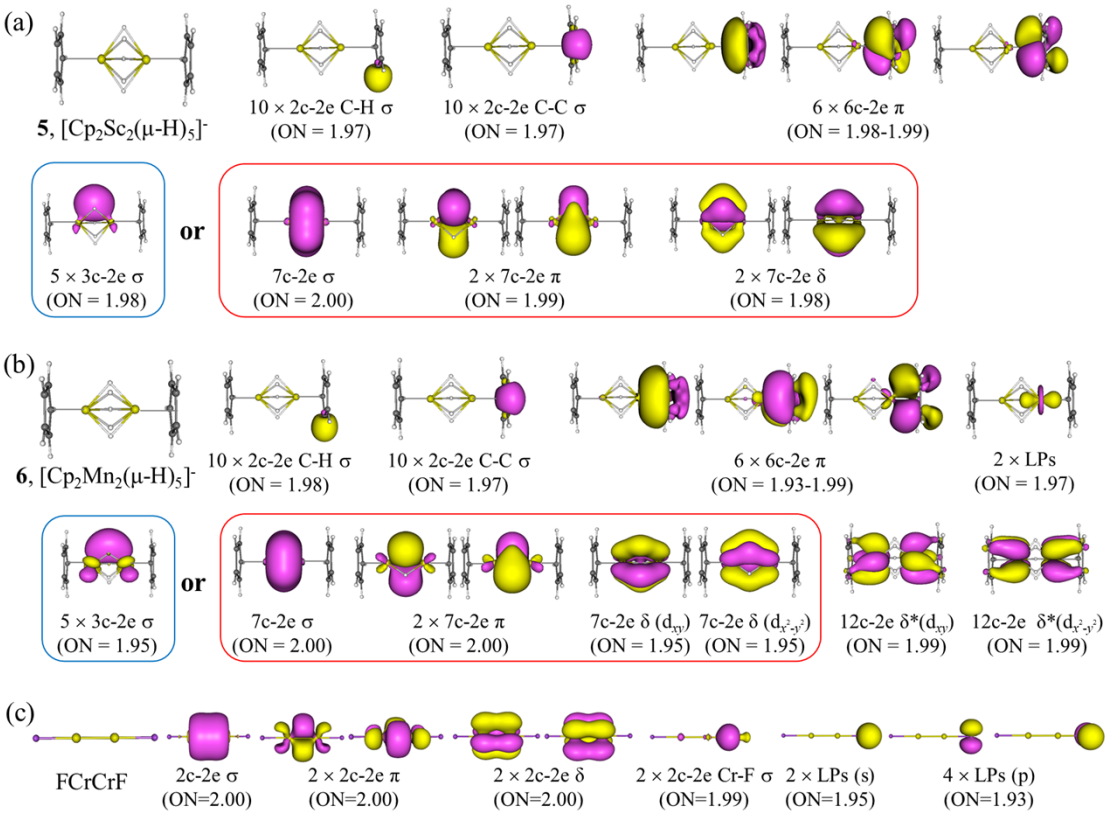

Fig. S7 AdNDP bonding frameworks of (a) $[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**), (b) $[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**) and (c) Cr_2F_2.

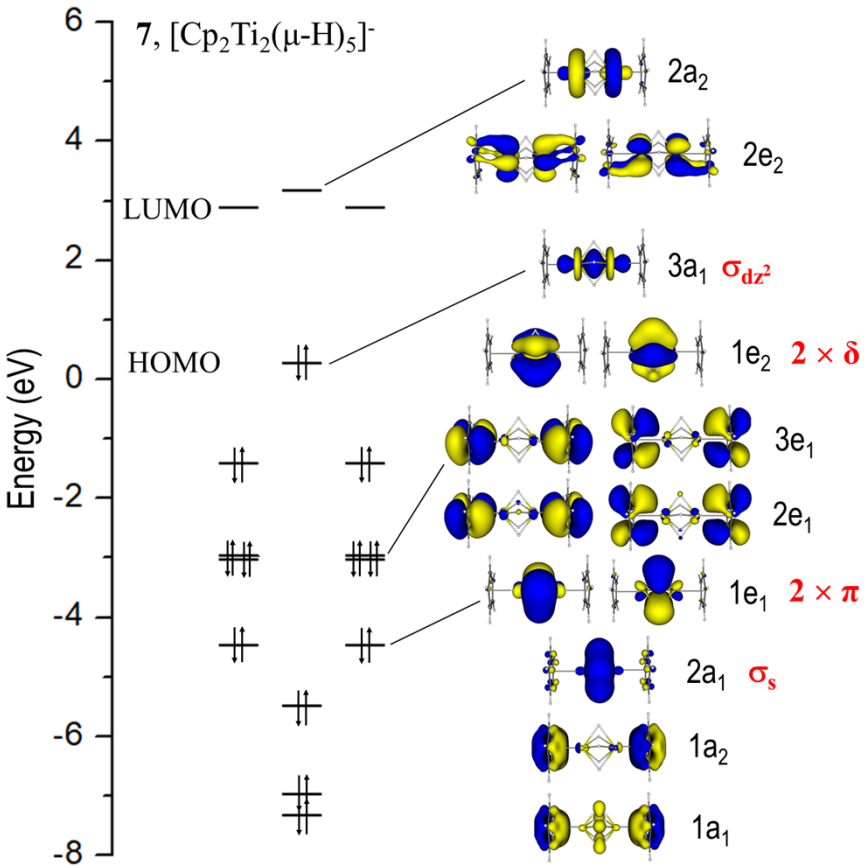

Fig. S8 Canonical molecular orbital diagram of $[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**).

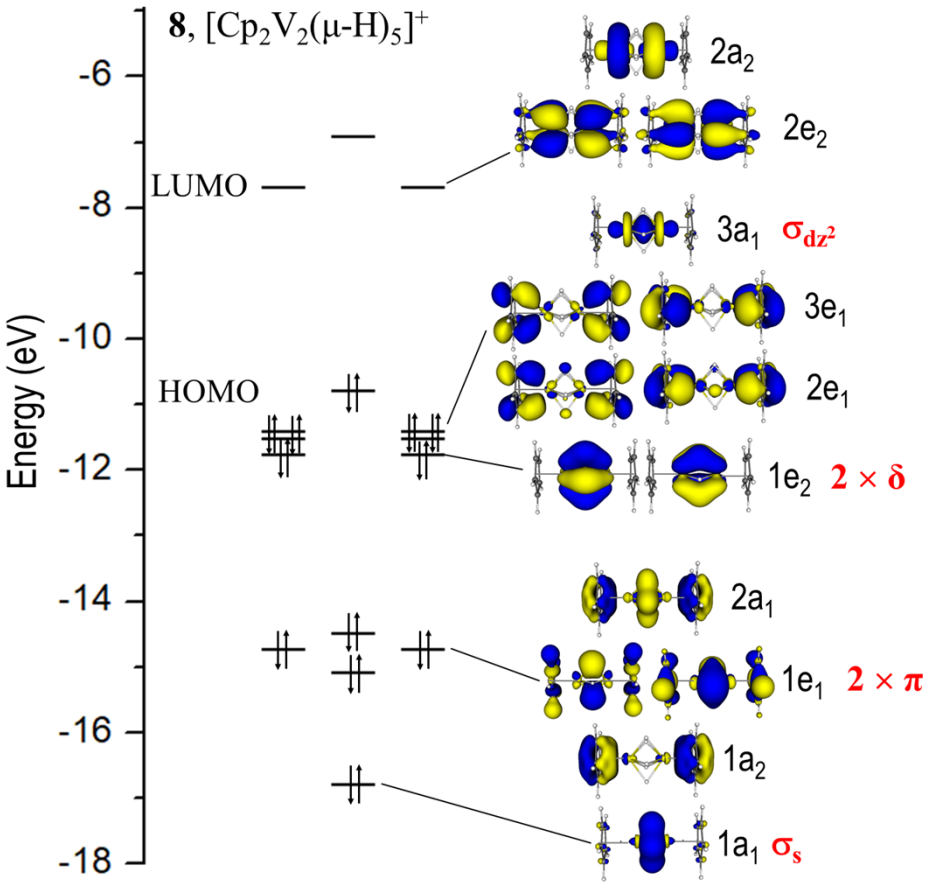

Fig. S9 Canonical molecular orbital diagram of $[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**).

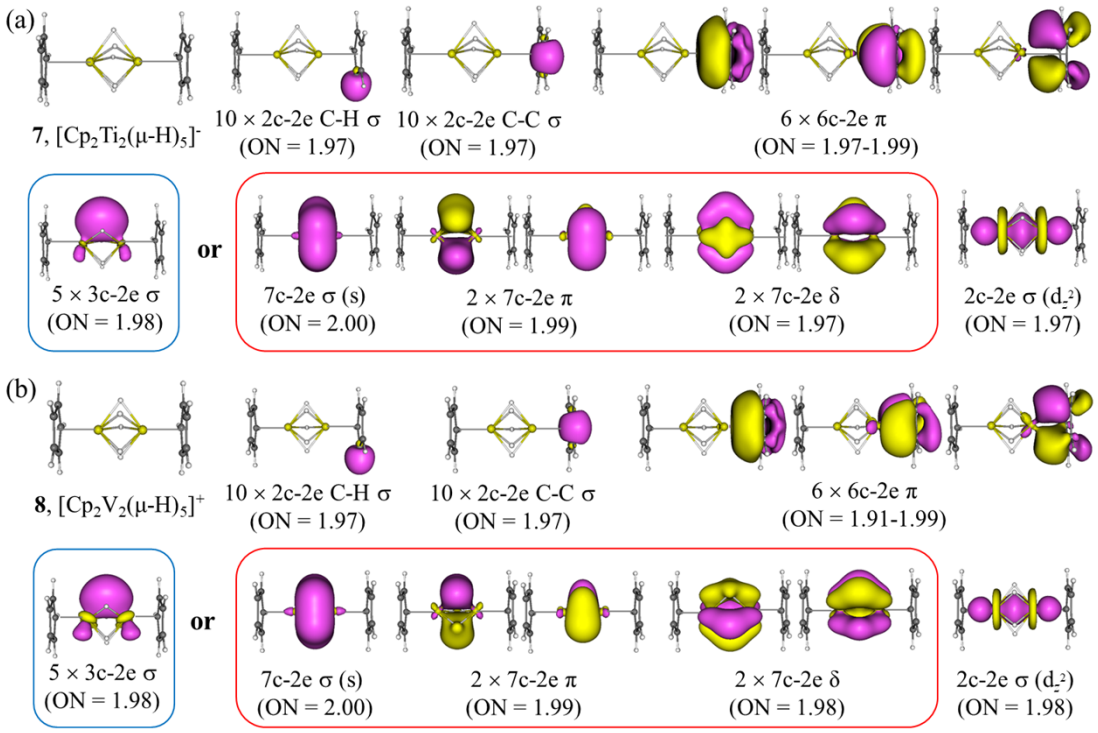

Fig. S10 AdNDP bonding frameworks of (a) $[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**) and (b) $[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**).

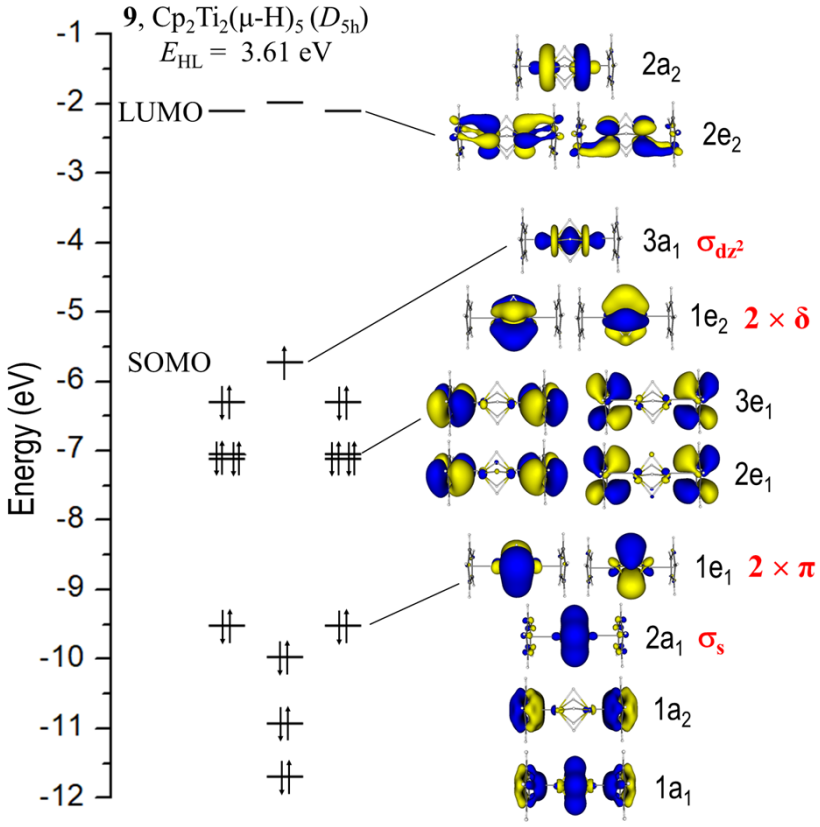

Fig. S11 Canonical molecular orbital diagram of $(Cp)_2Ti_2(\mu\text{-}H)_5$ (**9**).

Table S3. WBI bond orders of metal-metal and metal-bridging H in **5**-**8**.

	$[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**)	$[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**)	$[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**)	$[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**)
M-M	1.7	1.0	2.6	2.9
M-H	0.5	0.4	0.5	0.4

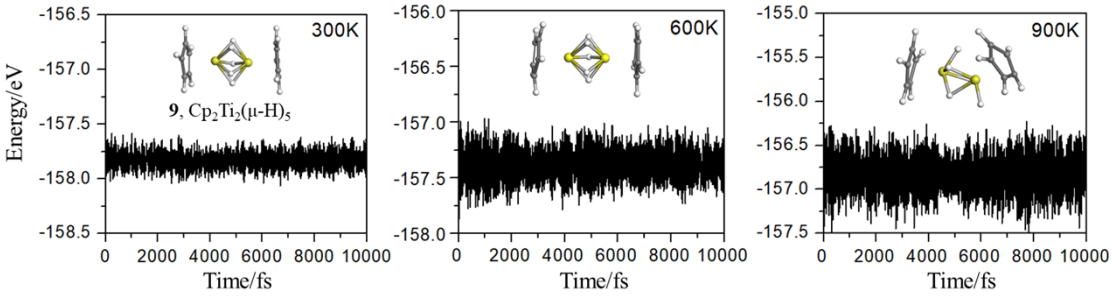

Fig. S12 Energy fluctuation depending on simulated time in molecular dynamics simulation at 300 (left), 600 (middle) and 900 (right) K of $(Cp)_2Ti_2(\mu\text{-}H)_5$ (**9**) after 10 ps simulation.

Table S4. Natural population analysis (NPA), Mulliken population analysis (MPA) and Atomic Dipole Moment Corrected Hirshfeld (ADCH) atomic charges of metals and bridging H atoms in **5-8**.

Charge	$[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**)		$[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**)		$[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**)		$[(Cp)_2V_2(\mu\text{-}H)_5]^+$(**8**)	
	Sc	H	Mn	H	Ti	H	V	H
NPA	-0.13	-0.01	-0.34	0.34	-0.45	0.10	-0.63	0.30
MPA	0.30	-0.08	-0.02	0.06	0.13	-0.01	-0.20	0.19
ADCH	0.16	-0.19	-0.17	-0.03	0.07	-0.15	0.03	-0.01

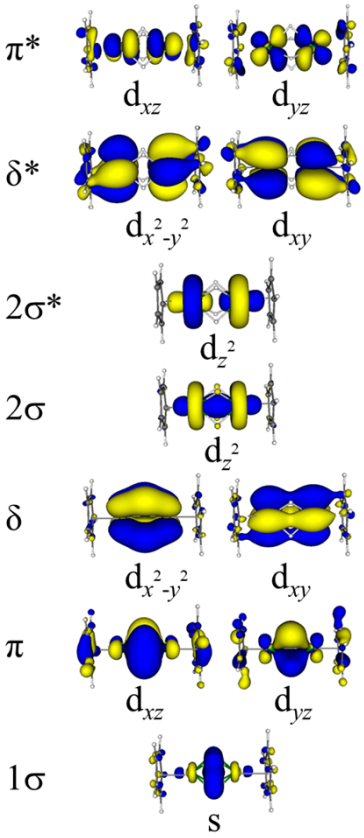

Fig. S13 The active-space molecular orbitals for the cas(18,11) calculation on $(Cp)_2Ru_2(\mu\text{-}H)_4$ (**4**).

Cartesian coordinates (in Å) of $[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**), $[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**), $[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**) and $[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**) at the B3LYP/def2tzvp level.

1. $[(Cp)_2Sc_2(\mu\text{-}H)_5]^-$ (**5**)

H	-0.000000	1.622176	0.000000
H	-1.542781	0.501280	0.000000
H	0.953491	-1.312368	0.000000
H	1.542781	0.501280	0.000000
H	-0.953491	-1.312368	0.000000
C	0.707408	-0.973664	3.435584
C	-1.144611	0.371907	3.435584
C	1.144611	0.371907	3.435584
C	-0.707408	-0.973664	3.435584
C	0.000000	1.203515	3.435584
C	-1.144611	0.371907	-3.435584
C	0.707408	-0.973664	-3.435584
C	0.000000	1.203515	-3.435584
C	-0.707408	-0.973664	-3.435584
C	1.144611	0.371907	-3.435584
H	2.171064	0.705421	-3.413101
H	0.000000	2.282791	-3.413101
H	1.341791	-1.846817	-3.413101
H	-1.341791	-1.846817	-3.413101
H	-2.171064	0.705421	-3.413101
H	-1.341791	-1.846817	3.413101
H	-2.171064	0.705421	3.413101
H	0.000000	2.282791	3.413101
H	2.171064	0.705421	3.413101
H	1.341791	-1.846817	3.413101
Sc	0.000000	0.000000	1.196044
Sc	0.000000	-0.000000	-1.196044

2. $[(Cp)_2Mn_2(\mu\text{-}H)_5]^-$ (**6**)

H	-0.000000	1.296434	0.000000
H	-1.232982	0.400620	0.000000
H	0.762025	-1.048837	0.000000
H	1.232982	0.400620	0.000000
H	-0.762025	-1.048837	0.000000
C	0.712435	-0.980583	2.869890
C	-1.152744	0.374549	2.869890
C	1.152744	0.374549	2.869890
C	-0.712435	-0.980583	2.869890
C	0.000000	1.212067	2.869890
C	-1.152744	0.374549	-2.869890
C	0.712435	-0.980583	-2.869890
C	0.000000	1.212067	-2.869890
C	-0.712435	-0.980583	-2.869890
C	1.152744	0.374549	-2.869890
H	2.179348	0.708113	-2.858194
H	0.000000	2.291503	-2.858194
H	1.346911	-1.853865	-2.858194
H	-1.346911	-1.853865	-2.858194
H	-2.179348	0.708113	-2.858194
H	-1.346911	-1.853865	2.858194
H	-2.179348	0.708113	2.858194
H	0.000000	2.291503	2.858194
H	2.179348	0.708113	2.858194
H	1.346911	-1.853865	2.858194
Mn	0.000000	0.000000	1.127053
Mn	0.000000	-0.000000	-1.127053

3. $[(Cp)_2Ti_2(\mu\text{-}H)_5]^-$ (**7**)

H	0.000000	1.517235	0.000000
H	-1.442977	0.468852	0.000000
H	0.891809	-1.227469	0.000000
H	1.442977	0.468852	0.000000
H	-0.891809	-1.227469	0.000000
C	0.707730	-0.974107	3.278929
C	-1.145131	0.372076	3.278929
C	1.145131	0.372076	3.278929
C	-0.707730	-0.974107	3.278929
C	0.000000	1.204062	3.278929
C	-1.145131	0.372076	-3.278929
C	0.707730	-0.974107	-3.278929
C	0.000000	1.204062	-3.278929
C	-0.707730	-0.974107	-3.278929
C	1.145131	0.372076	-3.278929
H	2.171692	0.705626	-3.266854
H	0.000000	2.283452	-3.266854
H	1.342180	-1.847352	-3.266854
H	-1.342180	-1.847352	-3.266854
H	-2.171692	0.705626	-3.266854
H	-1.342180	-1.847352	3.266854
H	-2.171692	0.705626	3.266854
H	0.000000	2.283452	3.266854
H	2.171692	0.705626	3.266854
H	1.342180	-1.847352	3.266854
Ti	0.000000	0.000000	1.112484
Ti	0.000000	-0.000000	-1.112484

4. $[(Cp)_2V_2(\mu\text{-}H)_5]^+$ (**8**)

H	0.000000	1.435209	0.000000
H	-1.364965	0.443504	0.000000
H	0.843595	-1.161109	0.000000
H	1.364965	0.443504	0.000000
H	-0.843595	-1.161109	0.000000
C	0.709750	-0.976887	2.988063
C	-1.148399	0.373137	2.988063
C	1.148399	0.373137	2.988063
C	-0.709750	-0.976887	2.988063
C	0.000000	1.207498	2.988063
C	-1.148399	0.373137	-2.988063
C	0.709750	-0.976887	-2.988063
C	0.000000	1.207498	-2.988063
C	-0.709750	-0.976887	-2.988063
C	1.148399	0.373137	-2.988063
H	2.174829	0.706645	-2.995444
H	0.000000	2.286750	-2.995444
H	1.344118	-1.850020	-2.995444
H	-1.344118	-1.850020	-2.995444
H	-2.174829	0.706645	-2.995444
H	-1.344118	-1.850020	2.995444
H	-2.174829	0.706645	2.995444
H	0.000000	2.286750	2.995444
H	2.174829	0.706645	2.995444
H	1.344118	-1.850020	2.995444
V	0.000000	0.000000	1.043373
V	0.000000	-0.000000	-1.043373