Electronic Supplementary Information (ESI)

Probing the CO bonding to heteronuclear group 4 metal-nickel clusters by photoelectron spectroscopy

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Table S1. Comparison of experimental VDE and ADE values (eV) to BP86 calculated ones of the five lowest-energy isomers for $ZrNi(CO)_n^-$ (n = 3-7).

Cluster	Isomer	VDE		ADE	
		Exp.[a]	Calc.	Exp.[a]	Calc.
n=3	3-I	2.04(7)	2.32	1.86(8)	2.11
	3-II		1.89		1.79
	3-III		2.16		2.05
	3-IV		1.85		1.71
	3-V		1.93		1.88
n=4	4-I	2.62(4)	2.51	2.31(6)	2.15
	4-II		2.37		2.23
	4-III		2.69		2.47
	4-IV		2.27		2.05
	4-V		2.38		2.01
n=5	5-I	3.01(2)	3.21	2.62(4)	2.67
	5-II		3.13		2.60
	5-III		2.91		2.65
	5-IV		2.63		2.49
	5-V		2.58		2.43
n=6	6-I	—	3.28	—	2.90
	6-II		3.01		2.62
	6-III		2.79		2.64
	6-IV		2.90		2.62
	6-V		2.83		2.56
n=7	7-I	—	3.23	—	2.81
	7-II		3.09		2.80
	7-III		3.39		3.06
	7-IV		2.99		2.65
	7-V		2.89		2.57

[a] Numbers in parentheses represent the uncertainty in the last digit.

Table S2. Comparison of experimental VDE and ADE values (eV) to BP86 calculated ones of the five lowest-energy isomers for $HfNi(CO)_n^-$ (n = 3-7).

Cluster	Isomer	VDE		ADE	
		Exp.[a]	Calc.	Exp.[a]	Calc.
n = 3	3-i	2.09(8)	2.24	1.91(8)	2.02
	3-ii		2.00		1.93
	3-iii		2.34		2.10
	3-iv		1.95		1.74
	3-v		2.25		2.18
n = 4	4-i	2.68(4)	2.69	2.40(5)	2.44
	4-ii		2.40		2.27
	4-iii		2.32		2.20
	4-iv		2.24		2.10
	4-v		2.39		2.16
n = 5	5-i	3.11(2)	3.37	2.67(4)	2.69
	5-ii		2.76		2.58
	5-iii		2.87		2.63
	5-iv		2.64		2.17
	5-v		2.56		2.43
n = 6	6-i	—	3.36	—	3.01
	6-ii		2.97		2.66
	6-iii		2.81		2.54
	6-iv		2.92		2.60
	6-v		2.83		2.51
n = 7	7-i	—	3.22	—	2.87
	7-ii		3.10		2.82
	7-iii		3.37		3.07
	7-iv		3.03		2.69
	7-v		2.88		2.53

[a] Numbers in parentheses represent the uncertainty in the last digit.

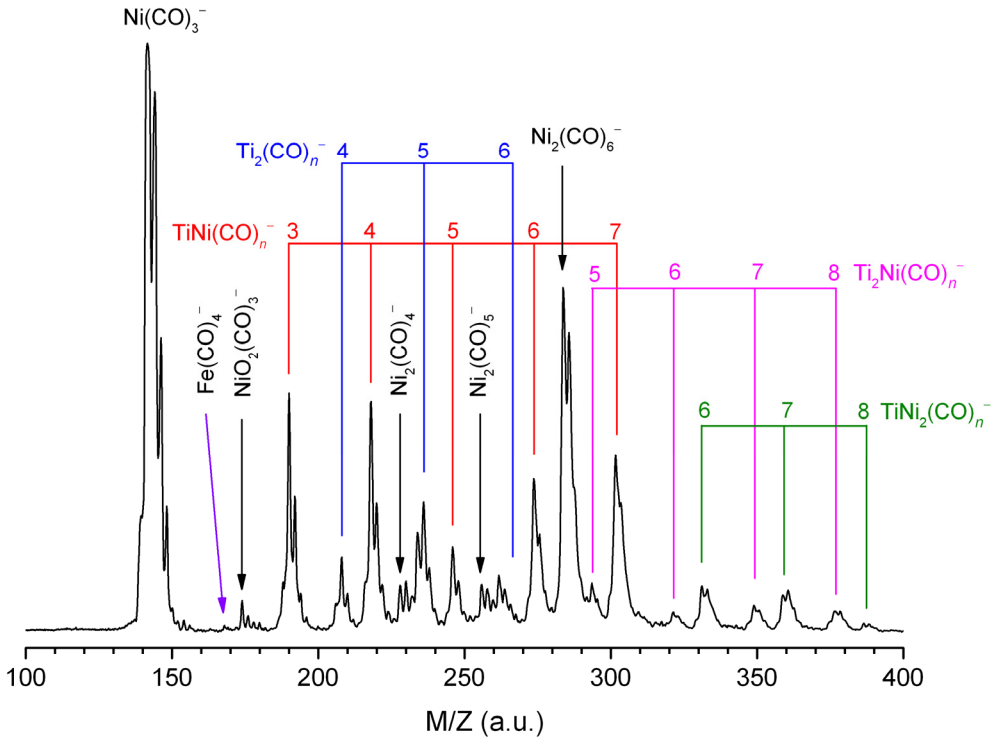

Fig. S1 Time-of-flight mass spectrum of the anions produced by pulsed laser vaporization of titanium metal target in an expansion of 5% CO seeded in He. Qualitatively similar time-of-flight spectra are obtained following ablation of zirconium and hafnium targets.

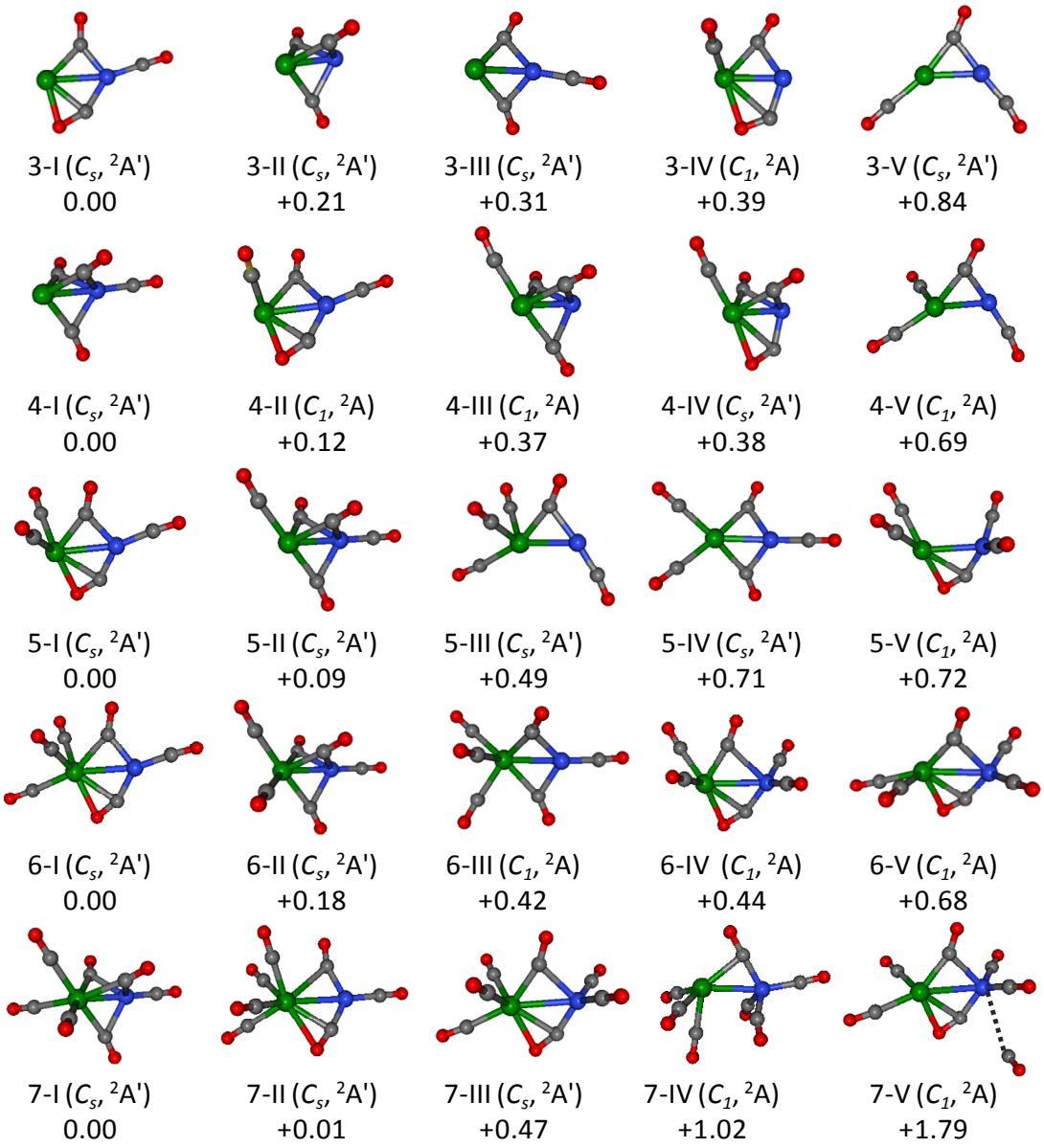

Fig. S2 Optimized structures of the $ZrNi(CO)_n^-$ (n = 3-7) anions (Zr, green; Ni, blue; C, gray; O, red). Relative energies are given in eV.

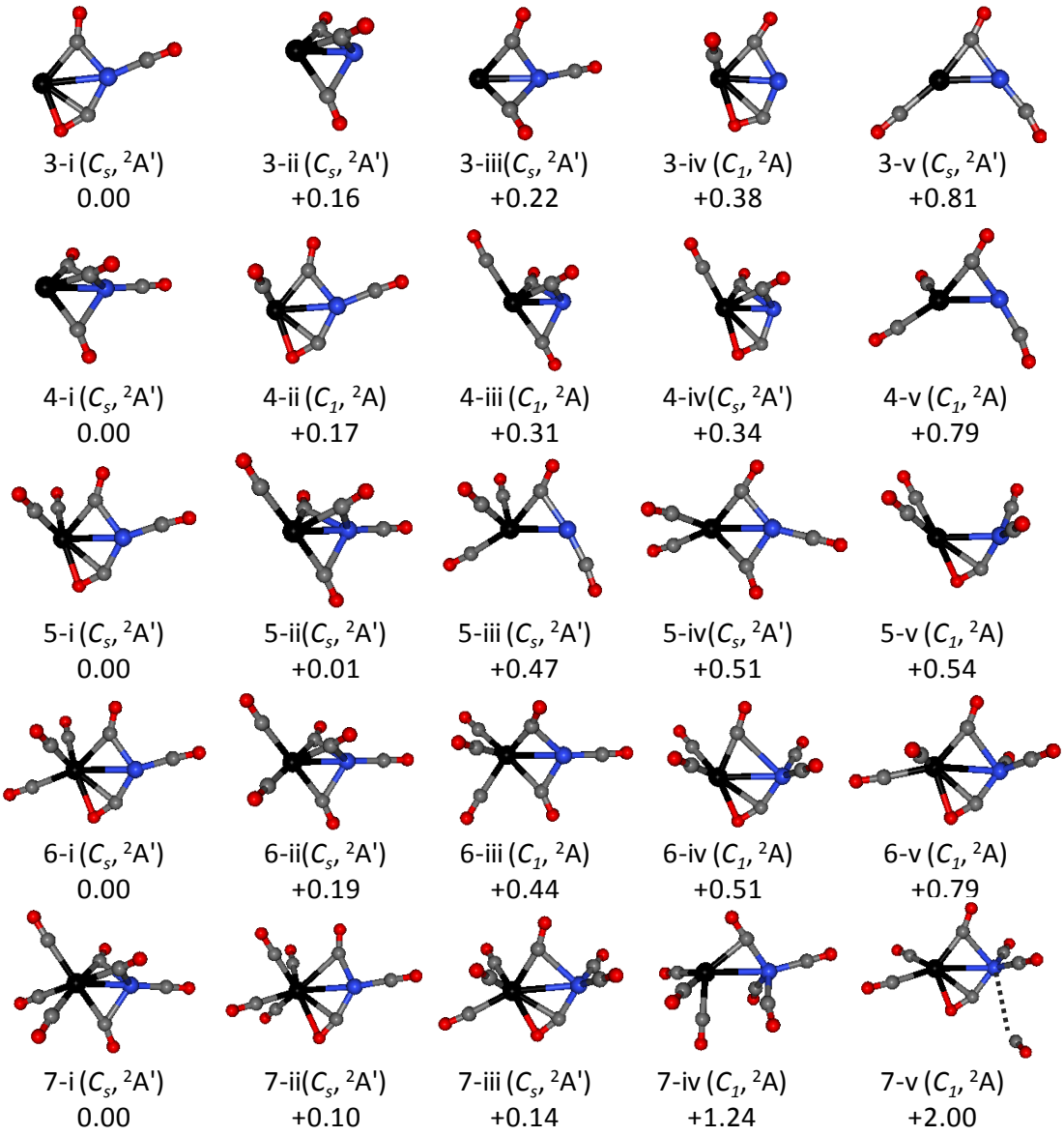

Fig. S3 Optimized structures of the $HfNi(CO)_n^-$ (n = 3-7) anions (Hf, black; Ni, blue; C, gray; O, red). Relative energies are given in eV.