Relative reactivity of the metal-amido versus metal-imido bond in linked cp-amido and half-sandwich complexes of vanadium

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			M(ins)	M(ins)#	M(HCCH)	M + HCCH	M(HCCH)	M(met)#	M(met)	M(2+3)#	M(2+3) s	M(2+3) t
CpTiHNNH ₂	Etot	Hartrees	-440.47	-440.43	-440.44	-440.43	-440.44	-440.44	-440.48	-440.41	-440.46	-440.48
		kcal/mol	-24.69	-0.46	-9.12	0.00	-9.12	-8.73	-31.72	10.59	-17.65	-32.95
	thermal corr	Hartrees	0.12	0.12	0.11	0.10	0.11	0.12	0.12	0.12	0.12	0.12
	deltaG	kcal/mol	-10.47	11.41	1.35	0.00	1.35	3.01	-18.53	24.73	-1.14	-17.63
CpVNHNH ₂	Etot	Hartrees	-453.44	-453.41	-453.42	-453.38	-453.42	-453.42	-453.44	-453.40	-453.46	-453.52
		kcal/mol	-37.30	-17.70	-21.87	0.00	-23.22	-21.74	-33.45	-13.20	-51.00	-85.79
	thermal corr	Hartrees	0.12	0.12	0.12	0.10	0.12	0.12	0.12	0.12	0.13	0.13
	deltaG	kcal/mol	-22.40	-5.04	-11.38	0.00	-11.85	-9.03	-19.03	0.83	-34.67	-68.33
CpC ₂ H ₄ NHVNH	Etot	Hartrees	-530.88	-530.85	-530.86	-530.82	-530.86	-530.86	-530.88	-530.83	-530.91	-530.95
		kcal/mol	-34.14	-15.77	-22.86	0.00	-22.86	-22.04	-35.73	-6.30	-52.26	-78.19
	thermal corr	Hartrees	0.16	0.16	0.15	0.14	0.15	0.16	0.16	0.16	0.16	0.16
	deltaG	kcal/mol	-19.29	-3.14	-11.84	0.00	-11.84	-9.68	-21.50	7.32	-35.11	-61.75
CpC ₂ H ₄ NHVNMe	Etot	Hartrees	-570.21	-570.18	-570.19	-570.16	-570.19	-570.19	-570.21	-570.16	-570.23	-570.27
		kcal/mol	-33.43	-14.61	-21.92	0.00	-21.92	-20.87	-30.25	-0.09	-43.74	-69.81
	thermal corr	Hartrees	0.18	0.18	0.18	0.16	0.18	0.18	0.18	0.18	0.19	0.19
	deltaG	kcal/mol	-19.97	-2.90	-12.43	0.00	-12.43	-8.44	-16.53	13.16	-27.05	-53.85

Abbreviations used:

ins	insertion reaction
met	[2+2] cycloaddition reaction
2+3	[2+3] cycloaddition reaction
s	singlet state
t	triplet state
Etot	Energy obtained from single point calculation
thermal corr	Thermal correction to Gibbs Free Energy at 298.15 K obtained from frequency calculation
deltaG	Calculated Gibbs Free Energy at 298.15 K

Transition states are denoted with #