Table S 1. Comparison of density functional dependence of geometric parameters (N-N and M-N distances in pm) and relative stability (ΔE in kJ mol^{-1}) of calculated $[(Cy_2N)_3Nb(\mu\text{-}NN)Nb(NCy_2)_3]$ structures based on experimentally observed species.

Functional	N-N	M-N	ΔE [a]	Comments
BP	127.9	185.7	0	fully optimized
	134.0	184.6	+6	N-N fixed
BP with dispersion corrections	127.1	183.5	0	fully optimized
	134.0	182.3	+8	N-N fixed
OLYP with dispersion corrections	127.6	184.6	0	fully optimized
	134.0	183.9	+12	N-N fixed
PBE with dispersion corrections	127.7	184.8	0	fully optimized
	134.0	183.8	+10	N-N fixed
PBE0	127.9	185.7	0	fully optimized
	134.0	184.6	+8	N-N fixed

[a] energy difference relative to fully optimized structure

Notes for results included in Table S 1

- Dispersion corrections as given by Grimme, Antony, Ehrlich, and Krieg (Journal of Chemical Physics 2010, 132, 154104).

- BP corresponds to Becke exchange (Physical Review A 1988, 38, 3098) and Perdew correlation (Physical Review B 1986, 33, 8822) functionals.

- OLYP corresponds to Handy-Cohen exchange (Molecular Physics 2001, 99, 403) and Lee-Yang-Parr correlation (Physical Review B 1988, 37, 785) functionals.

- PBE corresponds to Perdew-Burke-Ernzerhof exchange and correlation (Physical Review Letters 1996, 77, 3865) functionals.

- PBE0 corresponds to the hybrid form given by Adamo and Barone (Journal of Chemical Physics 1999, 110, 6158).

  Due to the extremely intensive computational demands associated with hybrid functional calculations with the Amsterdam Density Functional package, PBE0 results correspond to single-point calculations employing a BP optimized geometry.