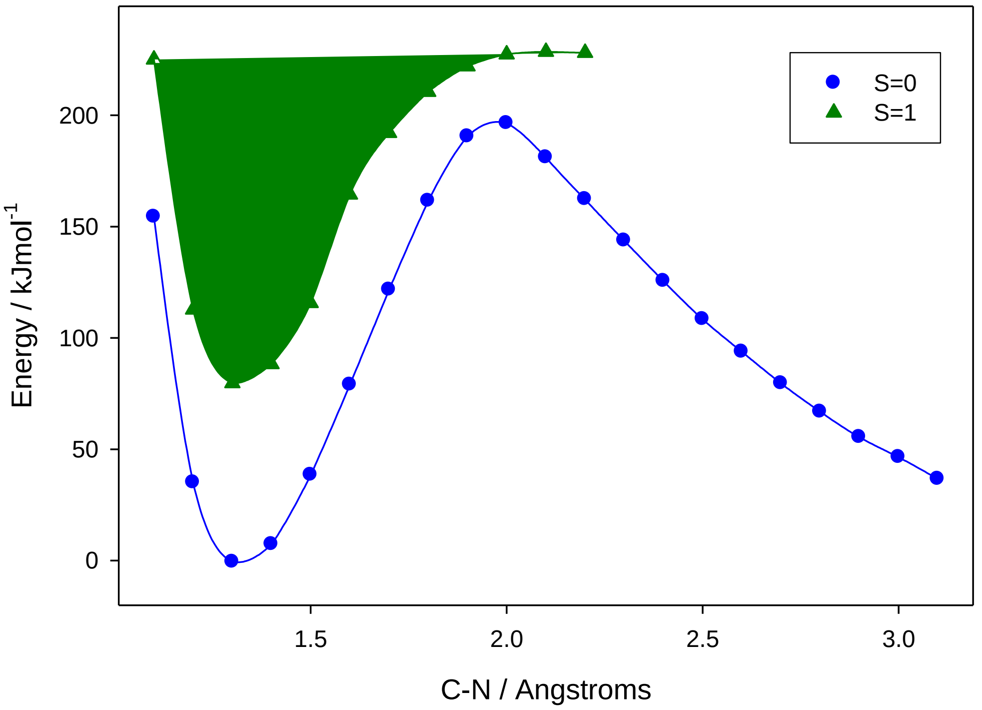
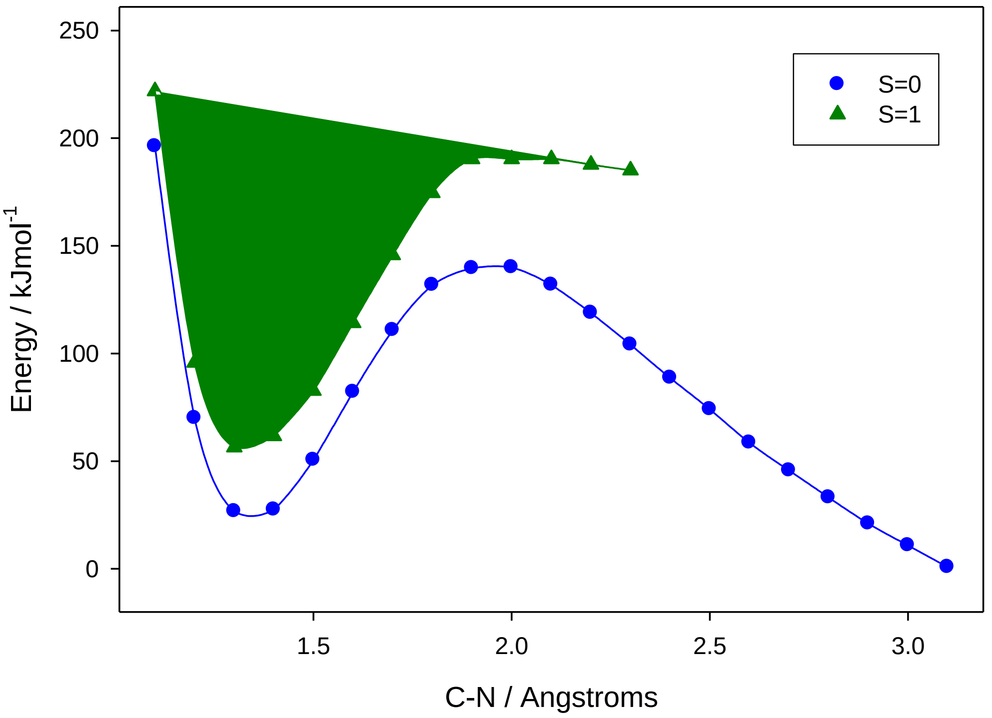
Supplementary Data

Page S2:	Potential energy scans for the dissociation of the dinuclear species into carbide and nitride products, in the [L_3Nb-CN-NbL_3] and [L_3Ta-CN-TaL_3] (L=[NH_2]) systems.
Pages S3 and S4:	Comparison of the influence of the solvent model (toluene or water) and ligand (L=NH_2 or L=NMe_2) on the energy gaps between the relevant π-like [$\Delta E(\pi)$] fragment orbitals in [L_3M-CN-M'L_3] (L = NH_2) species.
Pages S5 and S6:	Comparison of reaction energy profiles for [L_3M-CN-ML_3] (L=[NH_2]) systems of Mo and Ta, calculated using the Becke-Perdew and B3-LYP functionals.



$[L_3Nb\text{-}CN\text{-}NbL_3]^{(3-)} \longrightarrow [L_3Nb\text{-}C]^{(2-)} + [N\text{-}NbL_3]^{(-)}$ (L=NH_2) (~C_{3v})



$[L_3Ta\text{-}CN\text{-}TaL_3]^{(3-)} \longrightarrow [L_3Ta\text{-}C]^{(2-)} + [N\text{-}TaL_3]^{(-)}$ (L=NH_2) (~C_{3v})

Figure S1. Potential energy scans for the dissociation of the dinuclear species into carbide and nitride products, in the Nb and Ta $[L_3M\text{-}CN\text{-}ML_3]$ (L=$[NH_2]$) systems.

(S3)

Table S1. Comparison of the influence of the solvent model (toluene or water) on the energy gaps (in eV) between the relevant π-like [ΔE(π)] fragment orbitals in [L_3M-CN-M'L_3] (L = NH_2) species. Calculations were performed on structures in which the values of the M-C and N-M' distances were fixed at 400 pm. Results correspond to C_{3v} symmetry.

Metal Elements	**Molecular Charge**	**toluene** [a]	**water** [b]
Nb, Nb	-3	3.15, 3.00	1.98, 2.02
Mo, Mo	-1	5.77, 5.68	4.40, 4.43
Tc, Mo	0	8.24, 4.80	6.95, 4.36
Re, W	0	7.69, 4.23	6.51, 3.90

[a] dielectric constant = 2.38, radius = 3.48

[b] dielectric constant = 78.4, radius = 1.90

(S4)

Table S2. Comparison of the influence of the ligand (L=NH_2 or L=NMe_2) on the energy gaps (in eV) between the relevant π-like [$\Delta E(\pi)$] fragment orbitals in [L_3M-CN-$M'L_3$] species. Calculations were performed on structures in which the values of the M-C and N-M' distances were fixed at 400 pm. Results correspond to C_{3v} symmetry.

Elements	**Molecular Charge**	**NH_2 [a]**	**NMe_2 [a]**
Nb, Nb	-3	1.98, 2.02	2.30, 2.13
Mo, Mo	-1	4.40, 4.43	4.34, 4.33
Tc, Mo	0	6.95, 4.36	7.28, 4.19
Re, W	0	6.51, 3.90	6.15, 3.75

[a] solvent dielectric constant = 78.4, radius = 1.90

(S5)

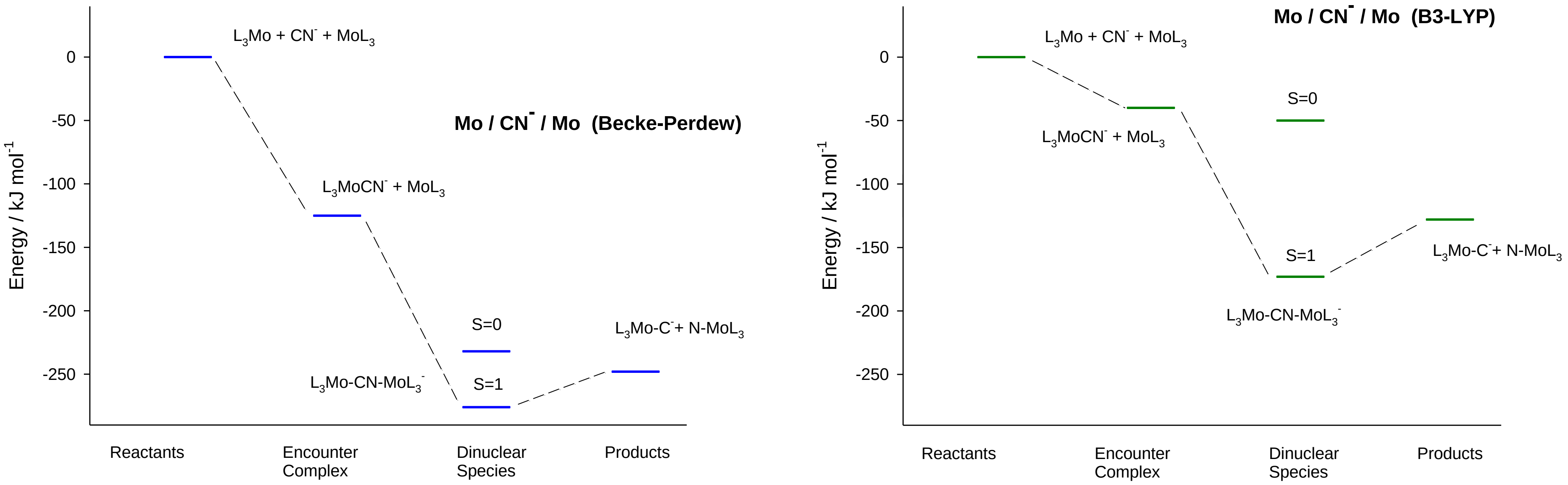


Figure S2. Reaction energy profiles for Mo [L_3M-CN-ML_3] (L=[NH_2]) systems.

(S6)

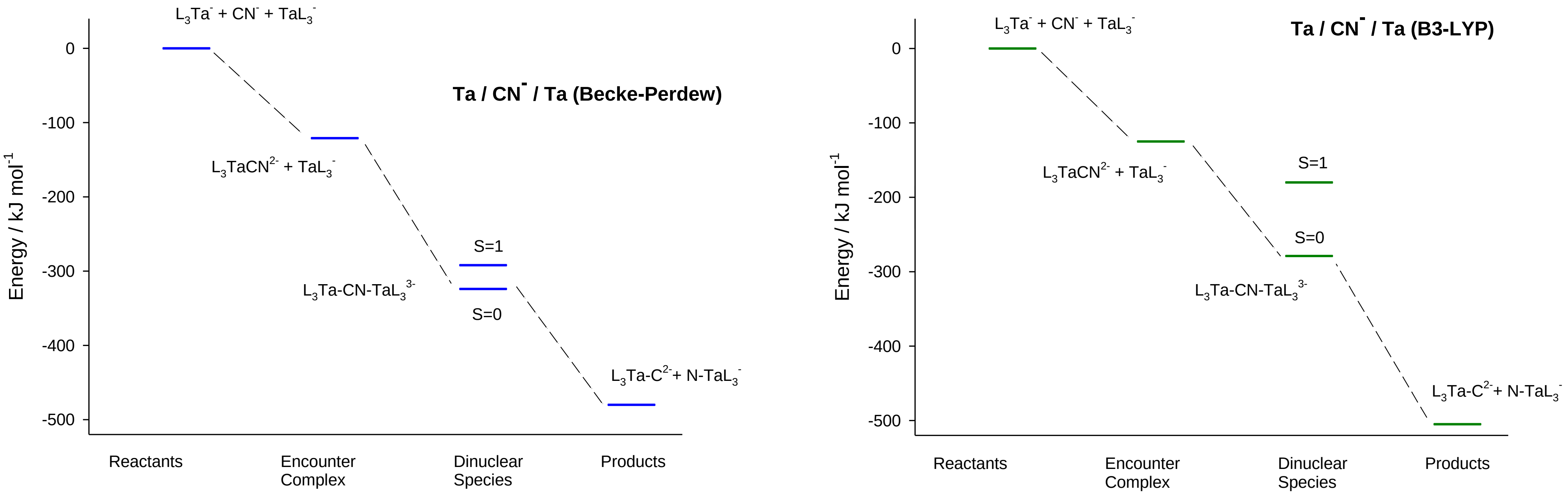


Figure S3. Reaction energy profiles for Ta [$L_3M\text{-}CN\text{-}ML_3$] (L=[$NH_2$]) systems.

(S7)

Comments on Comparison of Becke-Perdew and B3-LYP Results

The comparative plots included in Figures S2 and S3 show that, for both the Mo and Ta systems, the Becke-Perdew and B3-LYP approaches give qualitatively analogous energetic trends along the reaction profile. In general, only relatively small quantitative differences are found between the two calculation types in the Ta case, however, these differences are more significant for the Mo species.

For the molybdenum-cyanide system, the overall reaction is predicted to be approximately 120 kJ·mol^{-1} more exothermic if calculations employ the Becke-Perdew functional, relative to those involving hybrid (B3-LYP) methodology. This result is largely similar to that found for an analogous molybdenum-dinitrogen system, with the overall reaction energy being in this case -347 kJ·mol^{-1} (Becke-Perdew) and -229 kJ·mol^{-1} (B3-LYP) [s1].

An explanation for the observed differences between the Becke-Perdew and B3-LYP results for the Mo and Ta systems may lie in the fact that the reactant complexes have a relatively high spin (S=3/2) ground state compared with other species in the reaction profile, and in particular relative to the products, which have spin singlet (S=0) ground states. It is possible that exchange effects are enhanced in the B3-LYP case, leading to some degree of stabilization of reactants relative to products, which does not occur in the Becke-Perdew case.

The fact that this additional stabilization may be observed in the Mo system, but apparently not in the Ta system, could be related to the larger size of the metal atoms and the higher negative charge of the metal-containing species in the Ta case, as both factors should contribute to making the metal-based orbitals more dilated, thereby reducing the importance and influence of exchange effects.

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s1. N. J. Brookes, D. C. Graham, G. Christian, R. Stranger, B. F. Yates, J. Comp. Chem., 2009, 30, 2146.