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# Investigating CN<sup>-</sup> cleavage by three-coordinate M[N(R)Ar]<sub>3</sub> complexes

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Three-coordinate Mo[N(<sup>t</sup>Bu)Ar]<sub>3</sub> binds cyanide to form the intermediate [Ar(<sup>t</sup>Bu)N]<sub>3</sub>Mo–CN–Mo[N(<sup>t</sup>Bu)Ar]<sub>3</sub> but, unlike its N<sub>2</sub> analogue which spontaneously cleaves dinitrogen, the C–N bond remains intact. DFT calculations on the model [NH<sub>2</sub>]<sub>3</sub>Mo/CN<sup>-</sup> system show that while the overall reaction is significantly exothermic, the final cleavage step is endothermic by at least 90 kJ mol<sup>-1</sup>, accounting for why C–N bond cleavage is not observed experimentally. The situation is improved for the [H<sub>2</sub>N]<sub>3</sub>W/CN<sup>-</sup> system where the intermediate and products are closer in energy but not enough for CN<sup>-</sup> cleavage to be facile at room temperature. Additional calculations were undertaken on the mixed-metal [H<sub>2</sub>N]<sub>3</sub>Re<sup>+</sup>/CN<sup>-</sup>/W[NH<sub>2</sub>]<sub>3</sub> and [H<sub>2</sub>N]<sub>3</sub>Re<sup>+</sup>/CN<sup>-</sup>/Ta[NH<sub>2</sub>]<sub>3</sub><sup>-</sup> systems in which the metals ions were chosen to maximise the stability of the products on the basis of an earlier bond energy study. Although the reaction energetics for the [H<sub>2</sub>N]<sub>3</sub>Re<sup>+</sup>/CN<sup>-</sup>/W[NH<sub>2</sub>]<sub>3</sub> system are more favourable than those for the [H<sub>2</sub>N]<sub>3</sub>W/CN<sup>-</sup> system, the final C–N cleavage step is still endothermic by 32 kJ mol<sup>-1</sup> when symmetry constraints are relaxed. The resistance of these systems to C–N cleavage was examined by a bond decomposition analysis of [H<sub>2</sub>N]M–L<sub>1</sub>≡L<sub>2</sub>–M[NH<sub>2</sub>]<sub>3</sub> intermediates for L<sub>1</sub>≡L<sub>2</sub> = N<sub>2</sub>, CO and CN<sup>-</sup> which showed that backbonding from the metal into the L<sub>1</sub>≡L<sub>2</sub> π\* orbitals is significantly less for CN<sup>-</sup> than for N<sub>2</sub> or CO due to the negative charge on CN<sup>-</sup> which results in a large energy gap between the metal d<sub>π</sub> and the π\* orbitals of CN<sup>-</sup>. This, combined with the very strong M–CN<sup>-</sup> σ interaction which stabilises the CN<sup>-</sup> intermediate, makes C–N bond cleavage in these systems unfavourable even though the C≡N triple bond is not as strong as the bond in N<sub>2</sub> or CO.

## Introduction

Cyanide binds to almost all transition metals<sup>1</sup> and the resulting complexes are among the most stable transition metal compounds known.<sup>2</sup> Despite the large number of cyanide complexes, and the fact that the C≡N triple bond is not as strong as the bond in carbon monoxide, there are relatively few examples of cyanide cleavage in the literature. The difference between the reactivity of CN<sup>-</sup> and that of isoelectronic CO, has often been attributed to differences in the π acceptor capacity of these two ligands. Although cyanide can act as both a σ donor and π acceptor ligand, its anionic nature results in it being a stronger σ donor but a weaker π acceptor than CO.<sup>3,3</sup>

Cleavage of the C≡N triple bond in coordinated CN<sup>-</sup> has been achieved by Fehlhammer *et al.*<sup>4</sup> The reaction of the [Fe<sub>2</sub>]–CN complex, [Fe<sub>2</sub>] = Fe<sub>2</sub>(η-Cp)<sub>2</sub>(CO)<sub>3</sub>, with phthaloyl dichloride gives [Fe<sub>2</sub>]–C≡N=C–[Fe<sub>2</sub>]<sup>+</sup> and phthalimide between –60 °C and room temperature.<sup>4</sup> The most likely mechanism involves cleavage of the C–N bond in [Fe<sub>2</sub>]–CN to give [Fe<sub>2</sub>]–C<sup>2+</sup> which is then trapped by [Fe<sub>2</sub>], while the N atom is incorporated in the phthalimide bi-product. However, in this reaction, the cleavage of cyanide does not yield isolatable carbide and nitride products.

In the search for systems capable of cleaving cyanide, it is worth noting that the three-coordinate complexes, Mo[N(R)Ar]<sub>3</sub>, are well known for their ability to cleave N<sub>2</sub>.<sup>5–8</sup> These complexes also bind and activate a range of other small molecules, including CO,<sup>9,10</sup> NO<sup>6</sup> and notably CN<sup>-</sup>,<sup>11</sup> but to date only the cleavage of the N–N bond in N<sub>2</sub>O and N<sub>2</sub> has been reported. Although CN<sup>-</sup> cleavage has not been observed for these complexes, the cleavage of organic nitriles to alkylidyne and nitride complexes by the related cyclometalated complex Mo(H)(η<sup>2</sup>-Me<sub>2</sub>C=NAr)(N[<sup>i</sup>Pr]Ar)<sub>2</sub> has been achieved.<sup>33</sup> Given that Mo[N(R)Ar]<sub>3</sub> cleaves N<sub>2</sub> under very mild conditions, with judicious choice of metals, it may be possible to design related systems which are capable of cleaving CN<sup>-</sup>.

Since the thermodynamic driving force for the cleavage of a small molecule, L<sub>1</sub>≡L<sub>2</sub>, using M[N(<sup>t</sup>Bu)Ar]<sub>3</sub> complexes is the formation of very strong M–L bonds in the product, a sensible approach would be to choose metals that result in the greatest stabilization of the products. Recently we carried out a systematic study of the strength of M–N, M–C and M–O bonds in model L–M[NH<sub>2</sub>]<sub>3</sub> complexes.<sup>12</sup> The results of this study show that d<sup>3</sup> metals form the strongest M–N bonds, while d<sup>4</sup> and d<sup>2</sup> metals form the strongest M–C and M–O bonds, respectively. The strength of the M–L bonds also increases down a group and to the left of a period. In principle, the results of this study can be used to predict which metals are best suited to cleaving a variety of small molecules, L<sub>1</sub>≡L<sub>2</sub>, when L<sub>1</sub>, L<sub>2</sub> = N, C or O.

The bond strengths of a number of diatomic molecules are tabulated in Table 1. Of these, the C≡O, N≡N and C≡N bonds are the strongest, and hence the most challenging to break. The strategy outlined above has already been applied to both N<sub>2</sub> and

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**Table 1** Bond lengths and dissociation energies for diatomics<sup>14</sup>

Diatomic	Bond length/Å	Dissociation energy/kJ mol <sup>-1</sup>
CO	1.128	1072
N <sub>2</sub>	1.098	942
CN <sup>-</sup>	1.16	887
NO	1.21	607
O <sub>2</sub>	1.207	493

CO cleavage.<sup>12,13</sup> For N<sub>2</sub>, the overall reaction thermodynamics and activation barrier to N–N bond cleavage were shown to follow the trends in bond strengths,<sup>12</sup> validating the use of the latter to predict the ease of N<sub>2</sub> cleavage. For CO, Re[NH<sub>2</sub>]<sub>3</sub> (d<sup>4</sup>) and Ta[NH<sub>2</sub>]<sub>3</sub> (d<sup>2</sup>) were predicted to give the strongest M–C and M–O bonds, respectively, in the L–M[NH<sub>2</sub>]<sub>3</sub> products for a neutral system. When the CO reaction profile involving these two metal systems was explored computationally in detail, C–O cleavage was calculated to be exothermic by 467 kJ mol<sup>-1</sup> and barrierless,<sup>13</sup> making it both thermodynamically and kinetically more favourable than N<sub>2</sub> cleavage by Mo[N(‘Bu)Ar]<sub>3</sub>. The cleavage of CO by Mo[N(‘Bu)Ar]<sub>3</sub>, however, was calculated to be unfavourable,<sup>34</sup> consistent with the bond energy results, and demonstrates that the choice of metal is important in achieving C–O cleavage. Since the above strategy has been successful for CO and N<sub>2</sub>, the next challenge is to design a three-coordinate metal complex capable of cleaving the CN<sup>-</sup> triple bond.

The cleavage of the C–N bond by M[N(‘Bu)Ar]<sub>3</sub> complexes has been attempted experimentally for Mo.<sup>11</sup> [Ar(‘Bu)N]<sub>3</sub>Mo–CN was prepared by the reaction of I–Mo[N(‘Bu)Ar]<sub>3</sub> with [N<sup>n</sup>Bu<sub>4</sub>][CN]. This was followed by reaction with additional Mo[N(‘Bu)Ar]<sub>3</sub> to give the neutral dinuclear species [Ar(‘Bu)N]<sub>3</sub>Mo–CN–Mo[N(‘Bu)Ar]<sub>3</sub>. Since this complex has one electron less than the corresponding N<sub>2</sub> bridged dimer which spontaneously cleaves dinitrogen at room temperature, it was reduced in the hope of forming [Ar(‘Bu)N]<sub>3</sub>Mo–CN–Mo[N(‘Bu)Ar]<sub>3</sub><sup>-</sup> and cleaving the C–N bond. However, no C–N cleavage was observed and instead, it has been postulated that one of the Ar(‘Bu)N ligands undergoes ejection of a ‘Bu radical. The closely related [Ar(Ad)N]<sub>3</sub>Mo–CN–Mo[N(‘Bu)Ar]<sub>3</sub> and [Ar(Ad)N]<sub>3</sub>Mo–CN–V[N(‘Bu)Ar]<sub>2</sub> intermediates were also synthesised but once again, C–N cleavage was not observed for either complex.

While the first attempts at CN<sup>-</sup> cleavage have not been successful, it may be possible to design related systems in which the metal ions are electronically more suited to cleaving the C–N bond. On the basis of our earlier bond energy study, the d<sup>3</sup> Mo centre in the above Mo[N(R)Ar]<sub>3</sub> complexes is capable of forming strong Mo–N bonds but not strong Mo–C bonds. Consequently, although CN<sup>-</sup> is isoelectronic with N<sub>2</sub> and Mo[N(R)Ar]<sub>3</sub> is able to provide the electrons required to reductively cleave the C–N bond, the products are not necessarily stable enough for the cleavage reaction to be favourable. From the tabulated M–C bond energies, d<sup>4</sup> metals such as Re<sup>III</sup> are much better suited to forming strong metal–carbide bonds and therefore stabilizing the products sufficiently for C–N bond cleavage to be possible.<sup>12</sup>

In the first part of this study, the reaction of CN<sup>-</sup> with Mo[N(R)Ar]<sub>3</sub> is investigated in order to rationalize why C–N cleavage is not observed experimentally for this system given that the same complex is able to cleave the stronger N–N bond in N<sub>2</sub>. The latter part of this study then examines whether C–N cleavage

is possible with other metals, using the results of the M–L bond energy study to optimise the choice of metal ions. Since CN<sup>-</sup> is a heteronuclear diatomic, it is likely that a mixed-metal system will be best suited to C–N cleavage in which one metal is electronically tuned for binding to N, and the other metal tuned for binding to C.

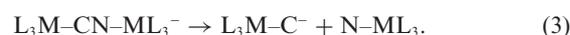
## Computational details

The calculations carried out in this work were performed using the Amsterdam density functional (ADF)<sup>15–17</sup> program (version 2002.03 and 2006.01) running on either Linux-based Pentium IV computers or the Australian National University Supercomputing Facility. All calculations used the local density approximation (LDA) to the exchange potential, the correlation potential of Vosko, Wilk and Nusair (VWN),<sup>18</sup> the Becke<sup>19</sup> and Perdew<sup>20</sup> corrections for non-local exchange and correlation, and the numerical integration scheme of te Velde and co-workers.<sup>21</sup> Geometry optimisations were performed using the gradient algorithm of Versluis and Ziegler.<sup>22</sup> All electron, triple- $\zeta$  Slater type orbital basis sets (TZP) were used for all atoms. Relativistic effects were incorporated using the zero order relativistic approximation (ZORA)<sup>23–25</sup> functionality. Solvent corrected calculations were carried out using the COSMO method<sup>35</sup> to accommodate the bulk effects of the ether solvent used in the experimental work. For these calculations the solvent dielectric constant was set at 4.34 and the radius (rigid sphere) at 3.46 Å. Frequencies were computed by numerical differentiation of energy gradients in slightly displaced geometries.<sup>26,27</sup> All calculations were carried out in a spin-unrestricted manner. Frequency calculations were used to confirm that the optimized structures of lowest energy were true minima. Optimised structures were corrected for zero point vibrational energy. The convergence criteria for geometry optimisations were 10<sup>-3</sup> Hartrees for energy and 10<sup>-2</sup> Hartrees Å<sup>-1</sup> for gradient. SCF convergence was set at 10<sup>-6</sup>. The integration parameter, accint, was set to 4.0 for geometry optimisations and to 6.0 for frequency calculations. Bond energies were analysed using the fragment-based bond decomposition scheme available in ADF.<sup>28–30</sup>

## Results and discussion

### 1 [H<sub>2</sub>N]<sub>3</sub>M–CN–M[NH<sub>2</sub>]<sub>3</sub> (M = Mo, W) systems

To explore the possibility of cyanide cleavage by Mo[N(R)Ar]<sub>3</sub> complexes, calculations were undertaken on a model system where the bulky N(R)Ar groups were replaced with NH<sub>2</sub>. The overall reaction of CN<sup>-</sup> with a metal complex, ML<sub>3</sub> (L = [N(R)Ar]), is then modelled as:

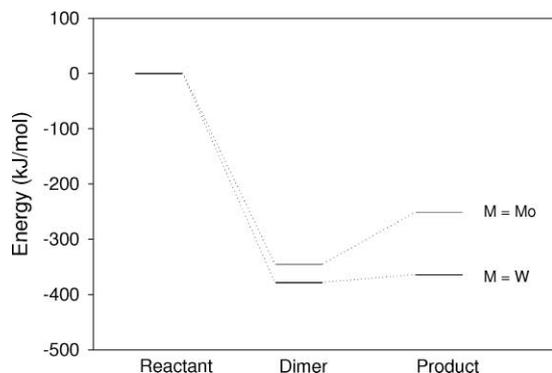


While the model reaction does not exactly mimic the experimental conditions, it allows us to determine whether cyanide cleavage would be possible in the ideal case, using the L<sub>3</sub>M–CN–ML<sub>3</sub><sup>-</sup> intermediate, and also reduces the complexity of the calculations

since it is not necessary to account for changes in charge along the reaction pathway. Furthermore, this reaction sequence makes it possible to directly compare the  $\text{CN}^-$  system with the previously studied  $\text{N}_2$  and  $\text{CO}$  cleavage reactions by  $\text{M}[\text{N}(\text{R})\text{Ar}]_3$  complexes.<sup>13,31,32</sup>

In the case of the analogous  $[\text{H}_2\text{N}]_3\text{M}-\text{N}_2-\text{M}[\text{NH}_2]_3$  dimers, the extent of  $\text{N}_2$  activation was shown to increase down any one transition metal group. This trend was rationalised in terms of the increasing metal orbital dilation on descending the group, and thus enhanced back donation from the metal d-orbitals into the  $\pi^*$  orbitals of  $\text{N}_2$ . A similar trend is also expected for C–N activation in  $[\text{H}_2\text{N}]_3\text{M}-\text{CN}-\text{M}[\text{NH}_2]_3^-$  intermediates, and therefore, in principle, a system with  $\text{M} = \text{W}$  should be better suited to cleaving the C–N bond than Mo. Consequently, the cleavage reaction was investigated for both  $\text{M} = \text{Mo}$  and  $\text{W}$ .

The structure and energy of the reactants,  $[\text{H}_2\text{N}]_3\text{Mo}$  and  $[\text{H}_2\text{N}]_3\text{W}$  and potential products,  $[\text{H}_2\text{N}]_3\text{Mo}-\text{C}^-$ ,  $[\text{H}_2\text{N}]_3\text{Mo}-\text{N}$ ,  $[\text{H}_2\text{N}]_3\text{W}-\text{C}^-$  and  $[\text{H}_2\text{N}]_3\text{W}-\text{N}$  have already been reported.<sup>12</sup> In the current study, calculations were initially undertaken on the  $[\text{H}_2\text{N}]_3\text{Mo}-\text{CN}-\text{Mo}[\text{NH}_2]_3^-$  and  $[\text{H}_2\text{N}]_3\text{W}-\text{CN}-\text{W}[\text{NH}_2]_3^-$  intermediates within the constraints of  $C_{3v}$  symmetry to determine whether C–N cleavage was a possibility for these two systems. The relative energies of reactants, intermediate and products obtained from these calculations are plotted in Fig. 1.



**Fig. 1** Relative energies of reactant, intermediate and products for the reaction  $[\text{H}_2\text{N}]_3\text{M} + \text{CN}^- + \text{M}[\text{NH}_2]_3 \rightarrow [\text{H}_2\text{N}]_3\text{M}-\text{CN}-\text{M}[\text{NH}_2]_3^- \rightarrow [\text{H}_2\text{N}]_3\text{M}-\text{C}^- + \text{N}-\text{M}[\text{NH}_2]_3$  ( $\text{M} = \text{Mo}, \text{W}$ ) within the constraints of  $C_{3v}$  symmetry.

Based on these preliminary calculations, the final C–N cleavage step is endothermic by at least  $90 \text{ kJ mol}^{-1}$  for  $\text{Mo}[\text{NH}_2]_3$ . Therefore, even though the  $[\text{H}_2\text{N}]_3\text{Mo}-\text{CN}-\text{Mo}[\text{NH}_2]_3^-$  intermediate is isoelectronic with  $\text{N}_2-\{\text{Mo}[\text{NH}_2]_3\}_2$  and has the  $d^3/d^3$  configuration best suited to breaking the C–N bond, cleavage of  $\text{CN}^-$  is still unfavourable. On the basis of earlier work<sup>31</sup> involving the analogous  $\text{N}_2$  cleavage reaction by  $\text{Mo}[\text{NH}_2]_3$ , relaxing of  $C_{3v}$  symmetry constraints to allow rotation of the  $\text{NH}_2$  ligands and bending of the  $\text{Mo}-\text{N}-\text{N}-\text{Mo}$  core will only stabilise the intermediate further relative to the products and thus increase the endothermicity of the C–N cleavage step. These calculations therefore account for why C–N bond cleavage is not observed experimentally for the  $\text{Mo}[\text{N}(\text{tBu})\text{Ar}]_3/\text{CN}^-$  system.

Since both the intermediate and products involve charged species, the effect of the bulk properties of the ether solvent on the reaction pathway was also studied using the COSMO model. However, the relative energies only changed by approximately

$50 \text{ kJ mol}^{-1}$ , in favour of the product, compared to the unsolvated calculations, and the final cleavage step is still calculated to be endothermic by over  $40 \text{ kJ mol}^{-1}$ .

The above calculations do not take into account the steric effects of the bulky amide ligands. However, the influence of the full ligands on the energetics of the analogous  $\text{N}_2$  and  $\text{CO}$  cleavage reactions by  $\text{Mo}[\text{N}(\text{tBu})\text{Ar}]_3$  have been studied using QM/MM methods.<sup>34</sup> In both cases, the overall reaction enthalpy was found to decrease between 20 and  $40 \text{ kJ mol}^{-1}$  when the full ligands were included and, as far as the energies of the intermediate and products are concerned, the effect is of the same magnitude but in the opposite direction to the solvent effects, with the products destabilised relative to the intermediate by approximately  $40 \text{ kJ mol}^{-1}$ . Accordingly, because of cancellation effects, we anticipate that the model calculations will produce relative energies similar to calculations which incorporate both the steric bulk of the ligands and solvent effects.

Within the constraints of  $C_{3v}$  symmetry, the overall reaction is calculated to be more exothermic when  $\text{M} = \text{W}$ , consistent with the predictions of the bond energy study,<sup>12</sup> and the final C–N cleavage step is more favourable with the intermediate and products reasonably close in energy. Given the more favourable reaction energetics, calculations on the  $[\text{H}_2\text{N}]_3\text{W}-\text{CN}-\text{W}[\text{NH}_2]_3^-$  intermediate were repeated without symmetry constraints. Further calculations on the  $[\text{H}_2\text{N}]_3\text{W}-\text{C}^-$  and  $[\text{H}_2\text{N}]_3\text{W}-\text{N}$  product species were not necessary as previous studies<sup>12</sup> have shown that the  $C_{3v}$  structures correspond to the lowest energy minima. The lowest energy optimised structure of the intermediate was over  $80 \text{ kJ mol}^{-1}$  more stable than the  $C_{3v}$  structure, implying that the C–N cleavage step will be endothermic by at least  $80 \text{ kJ mol}^{-1}$ . In the low symmetry structure, the  $\text{NH}_2$  ligands rotate, breaking the three-fold symmetry in a similar way to that observed for the corresponding  $\text{N}_2$  and  $\text{CO}$  bridged intermediates.<sup>13,31</sup>

Although these results predict that C–N cleavage is thermodynamically unfavourable for both  $\text{M} = \text{Mo}$  and  $\text{W}$ , they demonstrate that the reaction energetics can be improved with different metal systems, as was shown for  $\text{N}_2$  activation and cleavage by  $\text{M}[\text{NH}_2]_3$  complexes. Since C–N cleavage is not favourable for either the Mo or W systems, the reaction profiles for these metals were not investigated further.

## 2 C–N Cleavage by a mixed-metal $[\text{H}_2\text{N}]_3\text{Re}-\text{CN}-\text{W}[\text{NH}_2]_3$ system

In designing a system which is optimised for cleaving the CN– bond, we adopt the same strategy which was successfully applied to the cleavage of  $\text{N}_2$  and  $\text{CO}$ ,<sup>12,13</sup> namely a system where the metals are chosen to maximise the strength of the metal–carbide and metal–nitride bonds in the products. Based on the results of our earlier bond energy study, the  $d^4$  metals  $\text{W}^{\text{II}}$  and  $\text{Re}^{\text{III}}$  are predicted to give the strongest M–C bonds, and the  $d^3$  metals  $\text{Ta}^{\text{II}}$  and  $\text{W}^{\text{III}}$  the strongest M–N bonds in  $\text{C}-\text{M}[\text{NH}_2]_3$  and  $\text{N}-\text{M}[\text{NH}_2]_3$  complexes, respectively. Since charged complexes can lead to destabilized intermediates relative to the reactants,<sup>31</sup> the best choice is an overall neutral system which also avoids some of the complications encountered in the attempted synthesis of  $[\text{Ar}(\text{R})\text{N}]_3\text{Mo}-\text{CN}-\text{Mo}[\text{N}(\text{R})\text{Ar}]_3^-$ .<sup>11</sup> Therefore, a system involving  $\text{Re}[\text{NH}_2]_3^+$  and  $\text{W}[\text{NH}_2]_3$  with Re bound to C and W bound to N, has the greatest potential for cleaving the C–N bond.

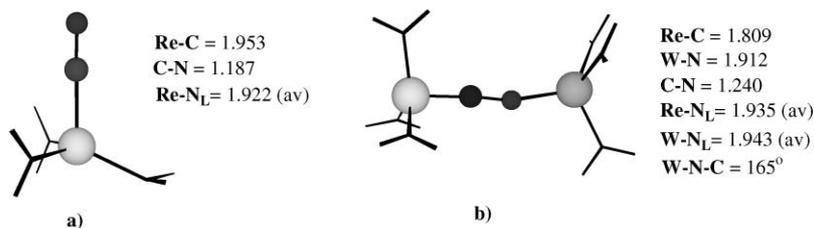
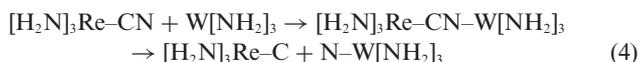


Fig. 2 Optimised structures of a)  $[\text{H}_2\text{N}]_3\text{Re-CN}$  and b)  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$ .

The choice of metals is further complicated by the tendency of cyanide to retain its negative charge throughout the reaction sequence. Thus, since  $\text{CN}^-$  is isoelectronic with  $\text{N}_2$ , it is more appropriate to consider the neutral  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  intermediate as possessing two  $d^3$  metal centres,  $\text{Re(IV)}$  and  $\text{W(III)}$ , providing the six electrons required to cleave the C–N triple bond. However, the final cleavage step necessitates a redistribution of the negative charge on cyanide, and the resulting neutral  $[\text{H}_2\text{N}]_3\text{Re-C}$  carbide product which contains a  $\text{Re(III)}$  centre, will involve a very strong M–C bond due to the  $d^4$  metal configuration.

For a mixed-metal system there are four possible reaction pathways depending on whether  $\text{CN}^-$  binds to the Re or W centre first. This leads to four possible  $\text{L}_3\text{M-CN-ML}_3$  intermediates, and four sets of products. In our study of CO cleavage by  $\text{Re}[\text{NH}_2]_3$  and  $\text{Ta}[\text{NH}_2]_3$ , cleavage of the C–O bond was found to be favourable only when  $\text{Re}^{\text{III}}$  was bound to C and  $\text{Ta}^{\text{III}}$  bound to O in the intermediate. In the case of the other three possible intermediates, either the products were destabilized, making the C–O cleavage step endothermic, or the activation barrier associated with C–O cleavage was comparatively large. A similar situation is very likely for  $\text{CN}^-$  cleavage if all reaction pathways are considered. However, since it should be possible to control the reaction conditions to form the desired intermediate and products by first synthesizing  $[\text{H}_2\text{N}]_3\text{Re-CN}$  and then adding  $\text{W}[\text{NH}_2]_3$  to form  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$ , the other possible reactions were not pursued and only the following reaction profile was investigated in detail:



The optimised structures of  $[\text{H}_2\text{N}]_3\text{Re-CN}$  and the  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  intermediate are shown in Fig. 2 and relative energies of the reaction species are plotted in Fig. 3. The structures of the products  $[\text{H}_2\text{N}]_3\text{Re-C}$  and  $[\text{H}_2\text{N}]_3\text{W-N}$  have already been reported.<sup>12</sup> The initial reactants,  $[\text{H}_2\text{N}]_3\text{Re}^+ + \text{CN}^- + \text{W}[\text{NH}_2]_3$ , are not included in Fig. 3 as they are over 700  $\text{kJ mol}^{-1}$  higher in energy than  $[\text{H}_2\text{N}]_3\text{Re-CN} + \text{W}[\text{NH}_2]_3$  due to the charge on  $\text{CN}^-$ .

The  $[\text{H}_2\text{N}]_3\text{Re-CN}$  complex is calculated to have  $C_s$  symmetry with a spin doublet ground state. Like the related  $[\text{H}_2\text{N}]_3\text{Mo-N}_2$  complex, one  $\text{NH}_2$  ligand is rotated around the M–N<sub>amide</sub> axis by  $90^\circ$  resulting in slight bending of the Re–C–N core. The intermediate,  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$ , also has  $C_s$  symmetry with a spin singlet ground state (the analogous triplet structure lies 9  $\text{kJ mol}^{-1}$  to higher energy). The intermediate has approximately trigonal symmetry at the Re centre but  $C_s$  symmetry at the W centre due to the rotation of two  $\text{NH}_2$  ligands. The singlet structure also exhibits a distinct bend in the geometry of the Re–C–N–W core with a W–N–C bond angle of  $165^\circ$ . The C–N bond length of 1.187 Å for  $[\text{H}_2\text{N}]_3\text{Re-CN}$  indicates only slight activation

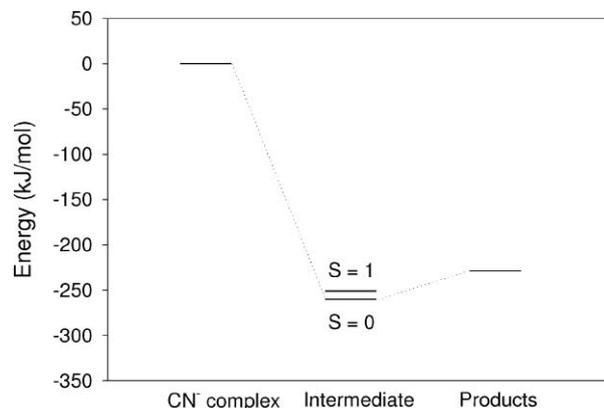


Fig. 3 Relative energies of  $\text{CN}^-$  complex, intermediate and potential products for the reaction  $[\text{H}_2\text{N}]_3\text{Re-CN} + \text{W}[\text{NH}_2]_3 \rightarrow [\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3 \rightarrow [\text{H}_2\text{N}]_3\text{Re-C} + \text{N-W}[\text{NH}_2]_3$ .

compared to free  $\text{CN}^-$  (1.185 Å) but the C–N bond length of 1.240 Å in the intermediate structure shows more significant activation, as may be expected when two metals are available to reduce the C–N bond.

Reaction 4 is calculated to be exothermic by 229  $\text{kJ mol}^{-1}$  but the  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  intermediate is more stable than the products making the C–N cleavage step endothermic by 32  $\text{kJ mol}^{-1}$ . However, when  $C_{3v}$  symmetry is enforced, the intermediate is approximately equi-energetic with the products, analogous to the  $[\text{H}_2\text{N}]_3\text{W-CN-W}[\text{NH}_2]_3^-$  system. Although the final cleavage step involving the  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  intermediate is still endothermic, it is more favourable than the  $[\text{H}_2\text{N}]_3\text{W-CN-W}[\text{NH}_2]_3^-$  system where the same step is over 80  $\text{kJ mol}^{-1}$  endothermic when symmetry constraints are relaxed.

While the C–N cleavage step for  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  is unfavourable thermodynamically, the endothermicity of this step is offset by the entropy term, based on calculated values of  $\Delta S = 146 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $T\Delta S = 44 \text{ kJ mol}^{-1}$  at room temperature. Therefore C–N cleavage may still be possible if the activation barrier is not large. To investigate this possibility, the barrier to C–N bond cleavage was estimated from a linear transit, the results of which are plotted in Fig. 4. In the singlet spin state, the calculated barrier to C–N bond cleavage is approximately 90  $\text{kJ mol}^{-1}$ , about one and half times that calculated for the corresponding  $\text{N}_2$  reaction which is observed to undergo spontaneous N–N cleavage at room temperature.<sup>5,7</sup> Consequently, although the barrier is higher, C–N cleavage may still be achievable as long as the barriers to other side reactions, for example  $^t\text{Bu}$  ejection from the  $\text{N}(\text{tBu})\text{Ar}$  ligands, are not lower in energy. The linear transit for the corresponding triplet spin state proved problematic and as

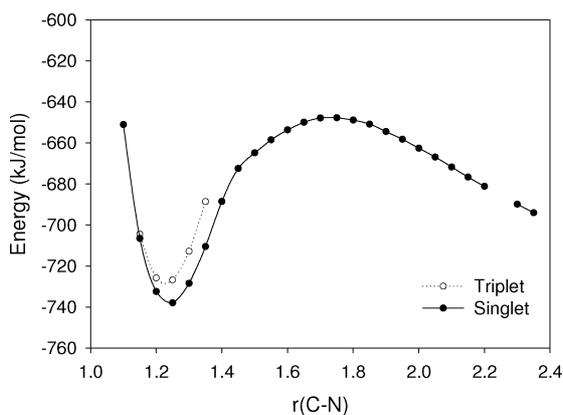


Fig. 4 Linear transit results for C–N cleavage in  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$ .

a result, it was not possible to calculate the curve over the same range of C–N distances. Nonetheless, the results in Fig. 4 show that the triplet state lies higher in energy than the singlet, at least for short C–N distances. In fact, C–N cleavage in the triplet state is extremely unfavourable, as the products lie over  $200 \text{ kJ mol}^{-1}$  higher in energy than the intermediate.

Calculations were also undertaken on the isoelectronic  $[\text{H}_2\text{N}]_3\text{Re-CN-Ta}[\text{NH}_2]_3^-$  system to ascertain whether C–N cleavage was more favourable for a different third-row metal combination. However, the C–N cleavage step was calculated to be endothermic by approximately  $25 \text{ kJ mol}^{-1}$  when  $[\text{H}_2\text{N}]_3\text{Re-CN-Ta}[\text{NH}_2]_3^-$  was constrained to  $C_{3v}$  symmetry. In comparison, the intermediate and products are calculated to be approximately equivalent in energy for  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  in  $C_{3v}$  symmetry and therefore this system still appears to be the one best suited to cyanide cleavage.

### 3 Comparisons between $\text{N}_2$ , CO and $\text{CN}^-$ complexes

Although the above results indicate that it may be possible to cleave  $\text{CN}^-$  using  $\text{M}[\text{N}(\text{R})\text{Ar}]_3$  complexes, it is apparent that C–N cleavage is less favourable, both thermodynamically and kinetically, than either  $\text{N}_2$  or CO cleavage by related systems. In some respects, this is an unexpected result as the  $\text{C}\equiv\text{N}$  bond is actually weaker than either the  $\text{N}\equiv\text{N}$  or  $\text{C}\equiv\text{O}$  bonds. An indication of the reluctance of  $\text{CN}^-$  to cleave is apparent from the lower level of activation of the C–N bond in the  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  intermediate where the C–N bond is only  $0.055 \text{ \AA}$  longer than in free  $\text{CN}^-$ . This can be compared to the analogous  $\text{N}_2$  bridged  $[\text{H}_2\text{N}]_3\text{W-N}_2\text{-W}[\text{NH}_2]_3$  intermediate where the N–N bond is activated by over  $0.17 \text{ \AA}$ .

It is likely that the lower activation of  $\text{CN}^-$  and consequently, the difficulty in cleaving the C–N bond using  $\text{M}[\text{N}(\text{R})\text{Ar}]_3$  complexes, can be attributed to the poorer  $\pi$  acceptor ability of  $\text{CN}^-$  compared to  $\text{N}_2$  and CO.<sup>13</sup> This aspect was explored in more detail by comparing the energy of the  $\pi^*$  orbitals in  $\text{N}_2$ , CO and  $\text{CN}^-$  with the energies of the metal  $d_\pi$  ( $d_{xz}$  and  $d_{yz}$ ) orbitals for the relevant encounter complexes  $[\text{H}_2\text{N}]_3\text{W-N}_2\text{-W}[\text{NH}_2]_3$ ,  $[\text{H}_2\text{N}]_3\text{Re-CO}$  and  $[\text{H}_2\text{N}]_3\text{Re-CN}$ . In each case, the metal–C and metal–N distances were set at  $3.0 \text{ \AA}$  in order to obtain the approximate energies of the orbitals when CO,  $\text{CN}^-$  or  $\text{N}_2$  are essentially unbound. The difference in energy,  $\Delta E$ , of the metal  $d_\pi$  orbitals and the  $\pi^*$  orbitals of  $\text{N}_2$ , CO and  $\text{CN}^-$  are summarised in Table 2.

Table 2 Energy gap,  $\Delta E$ , between the  $L_1\equiv L_2 \pi^*$  orbitals and the metal  $d_\pi$  orbitals in  $[\text{H}_2\text{N}]_3\text{M-L}_1\equiv\text{L}_2$  (M = W, Re) complexes. Calculations were carried out in  $C_{3v}$  symmetry with M– $L_1$  fixed at  $3.0 \text{ \AA}$

$L_1\equiv L_2$	Complex	$\Delta E/\text{eV}$
$\text{N}_2$	$[\text{H}_2\text{N}]_3\text{W-N}_2$	1.90
CO	$[\text{H}_2\text{N}]_3\text{Re-CO}$	2.43
$\text{CN}^-$	$[\text{H}_2\text{N}]_3\text{Re-CN}$	8.54

The energy gap between the metal  $d_\pi$  orbitals and the  $L_1\equiv L_2 \pi^*$  orbitals is clearly much larger for  $\text{CN}^-$  than for CO and  $\text{N}_2$ , and this is primarily due to the negative charge on  $\text{CN}^-$ . The increased energy gap reduces the interaction between the metal  $d_\pi$  and the  $\pi^*$  orbitals of  $\text{CN}^-$  and as a result, backdonation from the metal into the  $L_1\equiv L_2 \pi^*$  orbitals should be less significant for  $\text{CN}^-$  than either  $\text{N}_2$  or CO.

To test the above hypothesis, a fragment bonding analysis was carried out to measure the extent of backbonding from the metal into the  $\pi^*$  orbitals of  $\text{N}_2$ , CO and  $\text{CN}^-$  in the intermediates  $[\text{H}_2\text{N}]_3\text{W-N}_2\text{-W}[\text{NH}_2]_3$ ,  $[\text{H}_2\text{N}]_3\text{Re-CO-Ta}[\text{NH}_2]_3$  and  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$ . In this analysis, the intermediate was divided into three fragments,  $[\text{H}_2\text{N}]_3\text{M}_1$ ,  $[\text{H}_2\text{N}]_3\text{M}_2$  and  $L_1\equiv L_2$ , and the interaction energy between the fragments determined from a single point calculation corresponding to the optimised  $C_{3v}$  geometry of the relevant intermediate,  $[\text{H}_2\text{N}]_3\text{M}_1\text{-L}_1\equiv\text{L}_2\text{-M}_2[\text{NH}_2]_3$ .

Using the above approach, the interaction energy,  $E_{\text{int}}$ , between the fragments can be broken down according to the following expression

$$E_{\text{int}} = E_{\text{elect}} + E_{\text{Pauli}} + E_{\text{orb}}$$

where  $E_{\text{elect}}$  measures the electrostatic interactions between the fragments,  $E_{\text{Pauli}}$  is the four-electron two-orbital repulsive term, and  $E_{\text{orb}}$  is the orbital interaction term which can be further partitioned into contributions from each of the irreducible representations of the point group. As the calculations were carried out in  $C_{3v}$  symmetry, the  $E_{\text{orb}}$  term has contributions spanning  $A_1$ ,  $A_2$  and E irreducible representations. The  $A_1$  contribution arises from the  $\sigma$  interaction between the fragments whereas the E contribution is associated with the  $\pi$  interaction. The  $A_2$  contribution is negligible as there are no bonding orbitals of this symmetry. Since the  $\sigma$  and  $\pi$  interactions span different irreducible representations, it is possible to examine  $\sigma$  and  $\pi$  bonding effects independently. In  $C_{3v}$  symmetry, the E contribution is the sum of both the  $\pi$  forward- and back-bonding interactions. Thus, in order to distinguish between these two contributions, it is necessary to perform an additional calculation where the  $\pi^*$  orbitals of the  $L_1\equiv L_2$  fragment are removed and the bond decomposition analysis repeated. The difference in the relative contributions to  $E_{\text{int}}$  between the two calculations can then be attributed to backbonding interactions involving the  $\pi^*$  orbitals of  $L_1\equiv L_2$ . Although the  $C_{3v}$  structure for these complexes is not the true minimum, the calculations still provide a good indication of the trends in bonding. Furthermore, a clean separation of  $\sigma$  and  $\pi$  contributions would not be possible in a lower symmetry point group.

The Pauli, electrostatic and orbital contributions to the interaction energy for  $[\text{H}_2\text{N}]_3\text{W-N}_2\text{-W}[\text{NH}_2]_3$ ,  $[\text{H}_2\text{N}]_3\text{Re-CO-Ta}[\text{NH}_2]_3$  and  $[\text{H}_2\text{N}]_3\text{Re-CN-W}[\text{NH}_2]_3$  are given in Table 3 while the contributions of  $A_1$  and E symmetry to the orbital interaction

**Table 3** Bond decomposition analysis for  $L_3W-N_2-WL_3$ ,  $L_3Re-CO-TaL_3$  and  $L_3Re-CN-WL_3$ ,  $L = NH_2$ 

Intermediate	$E_{\text{Pauli}}/\text{eV}$	$E_{\text{elect}}/\text{eV}$	$E_{\text{orb}}/\text{eV}$	$E_{\text{int}}/\text{eV}$
$L_3W/N_2/WL_3$	15.098	-8.201	-15.651	-8.754
$L_3Re/CO/TaL_3$	13.528	-9.188	-11.361	-7.021
$L_3Re/CN^-/WL_3^+$	22.284	-24.433	-11.978	-14.127

energy,  $E_{\text{orb}}$ , and the changes in these contributions,  $\Delta A_1$  and  $\Delta E$ , when the  $\pi^*$  orbitals are removed, are listed in Table 4.

For the  $L_3Re-CN-WL_3$  intermediate, the charges on the fragments were assigned on the basis of the Mulliken charges for the optimised structure which show that the negative charge is largely localised on the CN fragment and that the  $WL_3$  fragment carries a higher positive charge overall than the  $ReL_3$  fragment. However, the bond analysis for  $L_3Re^+/CN^-/WL_3$  gave similar results and therefore the overall trends discussed below for  $L_3Re/CN^-/WL_3^+$  are not affected.

While the interaction energy,  $E_{\text{int}}$ , is similar for the  $N_2$  and CO intermediates, it is significantly larger for the  $CN^-$  system. This difference can be attributed to the charges on the  $L_3W^+$  and  $CN^-$  fragments, and is reflected in the much greater electrostatic contribution to the bonding.

From Table 4, the  $A_1(\sigma)$  contribution to the interaction energy is very similar for the  $N_2$  and CO bridged intermediates, and is also comparable to that calculated for the  $[H_2N]_3Mo-N_2-Mo[NH_2]_3$  dimer from an earlier study.<sup>31</sup> The  $A_1(\sigma)$  contribution is considerably larger for the  $CN^-$  intermediate implying a much stronger  $\sigma$  interaction between the metals and the CN fragment. The stronger  $\sigma$  bonding can again be attributed to the charge on  $CN^-$  which raises the energy of the C and N based  $\sigma$  orbitals such that they lie closer in energy to the  $d_{z^2}$  orbitals on the metals. The  $E(\pi)$  contribution, on the other hand, shows a steady decrease from approximately -12 eV for  $N_2$  to almost half this value for  $CN^-$ . Comparing the above results for  $[H_2N]_3W-N_2-W[NH_2]_3$  with those calculated earlier for  $[H_2N]_3Mo-N_2-Mo[NH_2]_3$ ,<sup>31</sup> reveals that the  $E(\pi)$  contribution increases on descending a group, and this trend can be attributed to the higher energy and greater dilation of the valence d orbitals on the heavier congeners.

The change in  $E(\pi)$  when the  $\pi^*$  orbitals are removed,  $\Delta E$ , systematically decreases from  $N_2$  to  $CN^-$ , following the trend in  $E(\pi)$  contributions.  $\Delta E$  for  $N_2$  is approximately 5.5 eV larger than for  $CN^-$  indicating significantly less backbonding from the metal into the  $CN^- \pi^*$  orbitals. As noted above, the  $E(\pi)$  contribution is the sum of both the  $\pi$  forward and  $\pi$  backbonding from the metal to the  $L_1 \equiv L_2$  fragment. Since  $\Delta E$  is between 80–90% of the value of  $E(\pi)$  for  $N_2$  and CO, nearly all the  $\pi$  contribution can be attributed to backdonation from the metal into the  $\pi^*$  orbitals of the diatomic bridge. In addition, the relative magnitudes of the  $A_1(\sigma)$  and  $E(\pi)$  contributions for the  $N_2$  and CO bridged

intermediates indicate that  $\pi$  bonding from the metal to the  $L_1 \equiv L_2$  fragment is significantly more important than  $\sigma$  bonding in these two systems, particularly for the  $N_2$  bridged dimer. The situation is different for the  $CN^-$  bridged intermediate where the  $A_1(\sigma)$  and  $E(\pi)$  contributions are similar, approximately 6 eV, and therefore  $\sigma$  and  $\pi$  bonding are both important. Furthermore,  $\Delta E$  is now only slightly greater than half the  $E(\pi)$  contribution implying that the  $\pi$  forward and  $\pi$  backbonding contributions are more or less comparable for the  $CN^-$  system. Not unexpectedly, the  $\sigma$  bonding interaction is not greatly affected by the removal of the  $\pi^*$  orbitals, as reflected in the small values for  $\Delta A_1$  seen in Table 4.

Overall, these results are in accord with the backbonding from the metal into the  $\pi^*$  orbitals on  $L_1 \equiv L_2$  decreasing as the gap between the  $\pi^*$  and d orbitals increases. For  $CN^-$ , the backbonding is much less significant than for  $N_2$  and this is consistent with the weaker  $\pi$  acceptor behaviour of  $CN^-$ . On the other hand, while the increase in the energy of the  $CN^-$  orbitals reduces the degree of backbonding from the metal, it enhances the  $\sigma$  interaction with the metal, and it is this aspect of the bonding which ensures that the intermediate is very stable. Thus, both the stabilization of the intermediate due to strong metal- $CN^- \sigma$  bonding, and less efficient backbonding from the metal into the  $\pi^*$  orbitals on  $CN^-$ , combine to make C-N cleavage unfavourable.

## Conclusion

Our calculations on the model  $[H_2N]_3Mo/CN^-/Mo[NH_2]_3$  system have shown that although the overall reaction is significantly exothermic, the final cleavage step is endothermic by at least 90 kJ mol<sup>-1</sup>. This result is consistent with the fact that C-N cleavage is not observed experimentally when  $[Ar^tBu]N_3Mo-CN-Mo[N^tBuAr]_3$  is reduced in an attempt to form the mono-anion complex. For the analogous  $W[NH_2]_3$  system, the overall reaction is more energetically favourable but the C-N cleavage step is still endothermic and unlikely to be facile at room temperature.

To examine the possibility that C-N cleavage maybe feasible with a different choice of metals, the mixed-metal intermediate  $[H_2N]_3Re-CN-W[NH_2]_3$  was investigated. This system was chosen on the basis that C-Re $[NH_2]_3$  and N-W $[NH_2]_3$  have been shown to give the strongest M-C and M-N bonds, respectively, for  $M[NH_2]_3$  complexes and therefore should maximise the thermodynamics of the C-N cleavage reaction. For this system, C-N cleavage was calculated to be endothermic by 32 kJ mol<sup>-1</sup> with a barrier of approximately 90 kJ mol<sup>-1</sup>. Although the energetics are certainly improved on those for the analogous  $[H_2N]_3Mo/CN^-/Mo[NH_2]_3$  and  $[H_2N]_3W/CN^-/W[NH_2]_3$  systems, the question remains as to whether they are favourable enough to make C-N cleavage feasible for this system.

The calculations indicate that  $CN^-$  cleavage using three-coordinate  $ML_3$  complexes is less favourable than cleavage of either

**Table 4** Partitioning of the orbital interaction energy for  $L_3Mo-N_2-MoL_3$ ,  $L_3W-N_2-WL_3$ ,  $L_3Re-CO-TaL_3$  and  $L_3Re-CN-WL_3$  ( $L = NH_2$ ) into  $A_1(\sigma)$ ,  $A_2$  and  $E(\pi)$  contributions and the changes in these contributions,  $\Delta A_1$ ,  $\Delta A_2$  and  $\Delta E$  respectively, when the  $\pi^*$  orbitals are removed

Intermediate	$A_1(\sigma)/\text{eV}$	$A_2/\text{eV}$	$E(\pi)/\text{eV}$	$\Delta A_1/\text{eV}$	$\Delta A_2/\text{eV}$	$\Delta E/\text{eV}$
$L_3W/N_2/WL_3$	-3.957	0.001	-11.695	0.785	0.002	9.165
$L_3Re/CO/TaL_3$	-3.959	0.000	-7.402	0.659	0.001	6.535
$L_3Re/CN^-/WL_3^+$	-5.773	-0.014	-6.191	0.681	0.001	3.636

N<sub>2</sub> or CO even though the C≡N bond is actually weaker. Based on a comparison of orbital energies and a bond decomposition analysis for the N<sub>2</sub>, CO and CN<sup>-</sup> bridged intermediates, the reluctance to cleave cyanide can be largely attributed to the negative charge on the CN<sup>-</sup> ion which increases the energy of the π\* orbitals relative to the metal d orbitals and, as a result, significantly reduces the backdonation from the metal into the CN<sup>-</sup> π\* orbitals. At the same time, the higher energy of the CN<sup>-</sup> orbitals also enhances the σ interaction with the metal, making the intermediate very stable. Thus, the greater stability of the cyanide-bridged intermediate and less efficient backbonding from the metal into the π\* orbitals on CN<sup>-</sup> combine to make C–N cleavage less favourable.

Metals with higher lying d orbitals should provide a better match energetically with the π\* orbitals of CN<sup>-</sup> and hence facilitate C–N cleavage. In principle, this could be achieved by using metals in the third row but earlier in the period. However, moving towards the left of a period requires a lower charge on the metal to maintain the same d<sup>n</sup> configuration, and this necessarily leads to negatively charged intermediates which will be destabilized due to Coulombic repulsion. Consideration of these points indicates that the three-coordinate Re and W amide complexes investigated in this study are electronically the most suitable transition metal systems for activation and cleavage of CN<sup>-</sup>.

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