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Activation and Cleavage of Dinitrogen by Three-coordinate Metal Complexes Involving Mo(III) and Nb(II/III)

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Activation and cleavage of dinitrogen by three-coordinate metal complexes involving Mo(III) and Nb(II/III)

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Density functional calculations have been employed to rationalize why the heteronuclear N_2-bridged $Mo^{III}Nb^{III}$ dimer, $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Nb[N(^iPr)Ar]_3$ (Ar = 3,5-$C_6H_3Me_2$), does not undergo cleavage of the dinitrogen bridge in contrast to the analogous $Mo^{III}Mo^{III}$ complex which, although having a less activated N–N bond, undergoes spontaneous dinitrogen cleavage at room temperature. The calculations reveal that although the overall reaction is exothermic for both systems, the actual cleavage step is endothermic by 144 kJ mol^{-1} for the $Mo^{III}Nb^{III}$ complex whereas the $Mo^{III}Mo^{III}$ system is exothermic by 94 kJ mol^{-1}. The reluctance of the $Mo^{III}Nb^{III}$ system to undergo N_2 cleavage is attributed to its d^3d^2 metal configuration which is one electron short of the d^3d^3 configuration necessary to reductively cleave the dinitrogen bridge. This is confirmed by additional calculations on the related d^3d^3 $Mo^{III}Nb^{II}$ and $Nb^{II}Nb^{II}$ systems for which the cleavage step is calculated to be substantially exothermic, accounting for why in the presence of the reductant KC_8, the $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Nb[N(^iPr)Ar]_3$ complex was observed to undergo spontaneous cleavage of the dinitrogen bridge. On the basis of these results, it can be concluded that the level of activation of the N–N bond does not necessarily correlate with the ease of cleavage of the dinitrogen bridge.

Introduction

Despite the overall favourable thermodynamics, development of an energy-efficient process for nitrogen fixation continues to present a significant chemical challenge, namely due to the high kinetic barrier to breaking the extremely strong N≡N triple bond.[1] Given the crucial role played by transition metal ions in maintaining the mild conditions for the reduction of dinitrogen in the biological enzyme nitrogenase, numerous efforts have been made synthetically to develop transition metal based catalysts that activate dinitrogen under similar conditions.[2,3]

A recent discovery of interest in the activation of dinitrogen is the reaction involving the coordinatively unsaturated, three-coordinate Mo(III) complex developed by Laplaza and Cummins.[4,5] In this reaction, the sterically-hindered, three-coordinate molybdenum(III) complex $Mo[N(R)Ar]_3$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$) spontaneously reacts with dinitrogen resulting in its cleavage at room temperature to form the nitrido product $[Ar(R)N]_3MoN$. The cleavage reaction proceeds *via* the dimeric intermediate $[Ar(R)N]_3Mo(\mu\text{-}N_2)Mo[N(R)Ar]_3$ which, on the basis of magnetic measurements on the related $[Ph(^tBu)N]_3Mo(\mu\text{-}N_2)Mo[N(^tBu)Ph]_3$ complex, is assumed to possess a spin triplet ground state.[5] The intermediate dimer can be isolated at lower temperatures and its structural characterization[5] by extended X-ray absorption fine structure (EXAFS) has revealed a linear Mo–N–N–Mo core containing an end-on dinitrogen bridge unit with a N–N bond length of 1.19(2) Å (*cf.* 1.10 Å in free N_2), and an approximately trigonal arrangement of the bulky N(R)Ar amide groups.

More recently, the related heteronuclear $Mo^{III}Nb^{III}$ dinitrogen-bridged dimer $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Nb[N(^iPr)Ar]_3$ has been isolated and structurally characterized by single-crystal X-ray diffraction.[6] The ground state of the complex is a spin doublet and surprisingly, although the dintrogen bridge is significantly more activated (N–N distance of 1.235(10) Å) than in the above dimolybdenum(III) intermediate, the complex does not undergo N_2 cleavage. However, in the presence of the reductant KC_8, the dinitrogen bridge is cleaved resulting in the formation of the nitrido products $[Ar(^tBu)N]_3MoN$ and $[Ar(^iPr)N]_3NbN^-$.

The X-ray structure of the $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Nb[N(^iPr)Ar]_3$ dimer reveals significant deviation from the trigonal structure found for the related dimolybdenum intermediate. The $[Ar(^iPr)N]$ ligands do not have the expected trigonal arrangement around the Nb center and instead have undergone significant rotation about the Nb–N(amide) axes. Furthermore, the Mo–N–N–Nb core is not linear but bent by approximately 13° at the Nb end. The rotated ligand structure is of interest as our previous DFT study[7] of the model dimolybdenum(III) system $(NH_2)_3Mo(\mu\text{-}N_2)Mo(NH_2)_3$ showed that a 90° rotation of one of the amide ligands on each Mo center resulted in a 60 kJ mol^{-1} stabilization of the spin singlet structure making it the preferred ground state over the spin triplet structure which adopts a trigonal arrangement of the NH_2 ligands.

In this study, we have used DFT methods to calculate and compare the structures and energetics of the heteronuclear $Mo^{III}Nb^{III}$ and $Mo^{III}Nb^{II}$ systems with those of the analogous dimolybdenum(III) and diniobium(II) complexes in order to rationalise the differing reactivities of the above experimentally known $Mo^{III}Mo^{III}$ and $Mo^{III}Nb^{III}$ systems towards cleavage of the dinitrogen bridge.

Computational details

The calculations carried out in this work were performed using the Amsterdam Density Functional (ADF)[8–10] program (version 2002.03) running on either Linux-based Pentium IV computers or the Australian National University Supercomputing Facility. All calculations employed the local density approximation (LDA) to the exchange potential, the correlation potential of Vosko, Wilk and Nusair (VWN),[11] the Becke[12] and Perdew[13] corrections for non-local exchange and correlation, and the numerical integration scheme of te Velde and coworkers.[14] Geometry optimisations were performed using the gradient algorithm of Versluis and Ziegler.[15] All electron, triple-ζ Slater type orbital basis sets with polarization functions (TZP) were used for all atoms. Relativistic effects were incorporated using the zero order relativistic approximation (ZORA)[16–18] functionality in ADF. Frequencies were computed in ADF by numerical differentiation of energy gradients in slightly displaced geometries[19,20] to confirm that optimized structures were true minima. All calculations were carried out in a spin-unrestricted manner.

Results and discussion

Analogous to our previous study on the $Mo^{III}Mo^{III}$ system, the calculations employed model complexes where the bulky $[Ar(^tBu)N]$ and $[N(^iPr)N]$ groups were replaced with simple amide ligands NH_2. For all three systems, $Mo^{III}Nb^{III}$, $Mo^{III}Nb^{II}$ and $Nb^{II}Nb^{II}$, geometry optimizations were completed for four of the five species along the reaction path shown schematically in Fig. 1, including the reactants, $M'(NH_2)_3$ and $M''(NH_2)_3$, encounter complexes, $N_2\text{–}M'(NH_2)_3$ and

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Table 1

System	N–N/Å	Spin	Symmetry	E_R/eV	E_I/eV	E_P/eV	E_A/kJ mol^{-1}	E_s/kJ mol^{-1}
Mo^{III}/Mo^{III}	1.221	0	C_{2h}	−126.2967	−128.7946	−129.7692	66	335
Mo^{III}/Nb^{III}	1.237	1/2	$C_1(C_s)$	−126.5837	−129.7269	−128.2367	—	160
Mo^{III}/Nb^{II}	1.270	0	$C_1(C_s)$	−126.8259	−130.5610	−131.0328	70	406
Nb^{II}/Nb^{II}	1.279	1	C_{2h}[a]	−127.3669	−128.1416	−132.2981	54	476

[a] Ligands are approximately trigonal.

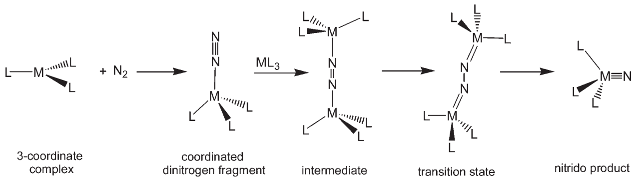


Fig. 1 Proposed reaction sequence associated with N_2 cleavage by the Laplaza and Cummins three-coordinate complex Mo(N[R]Ar)$_3$.

N_2–M″(NH$_2$)$_3$ intermediate dimer, (NH$_2$)$_3$M′–N=N–M″(NH$_2$)$_3$, and products (NH$_2$)$_3$M′≡N and (NH$_2$)$_3$M″≡N, and compared with our earlier calculations on the $Mo^{III}Mo^{III}$ system.

The relative energies of the species along the reaction pathway for the $Mo^{III}Nb^{III}$ system are shown in Fig. 2. The first step in the lowest energy pathway is the binding of N_2 to $Nb^{III}(NH_2)_3$, with a triplet ground state, to form the encounter complex N_2–$Nb^{III}(NH_2)_3$ also in the triplet spin state. Unlike the $Mo^{III}Mo^{III}$ system, spin crossover is not required to form the encounter complex. $Mo^{III}(NH_2)_3$ then binds to the encounter complex to form the intermediate dimer (NH$_2$)$_3$Nb–N=N–Mo(NH$_2$)$_3$ with a doublet ground state. Unlike the $Mo^{III}Mo^{III}$ system where the singlet and triplet spin states of the intermediate dimer are relatively close in energy, the quartet spin state for the $Mo^{III}Nb^{III}$ dimer is calculated to lie 132 kJ mol^{-1} higher in energy.

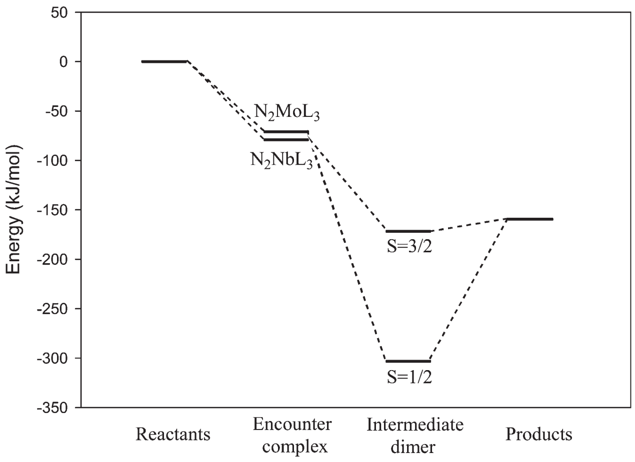


Fig. 2 Calculated energies of the species involved in the N_2 cleavage reaction relative to the reactants for the $Mo^{III}Nb^{III}$ system.

Experimentally the intermediate dimer is formed by the reaction of NbCl(N(^{i}Pr)Ar)$_3$ with a [(N$_2$)Mo(N[R]Ar)$_3$]$^-$ salt, however, calculations on the encounter complex (NH$_2$)$_3$M–N≡N reveal that in the case of the heteronuclear $Mo^{III}Nb^{III}$ and $Mo^{III}Nb^{II}$ systems, it is energetically more favorable by approximately 8 kJ mol^{-1} and 56 kJ mol^{-1}, respectively, for the dinitrogen to bind first to the (NH$_2$)$_3$Nb^{III} ($S = 1$) or (NH$_2$)$_3$Nb^{II} ($S = 3/2$) reactant rather than (NH$_2$)$_3$Mo^{III}. This result can be attributed to the greater radial extension of the valence d orbitals of Nb^{III} and Nb^{II} relative to Mo^{III} and therefore a larger propensity for metal–dinitrogen backbonding.

The calculated energies for the reactants, intermediate dimer and products for the $Mo^{III}Mo^{III}$, $Mo^{III}Nb^{III}$, $Mo^{III}Nb^{II}$ and $Nb^{II}Nb^{II}$ systems are given in Table 1 along with the ground spin state and N–N bond length for the intermediate dimer, and the overall stabilization energy of the products relative to the reactants. The computed activation energies associated with the cleavage of the dinitrogen bridge to form the nitrido products, are also tabulated, and are based on linear transit calculations on the intermediate dimer where the N–N bond length was progressively incremented in steps of 0.05 Å with all other geometrical parameters being allowed to optimize. The energies of the intermediate dimer and products for each system are plotted relative to the reactants in Fig. 3.

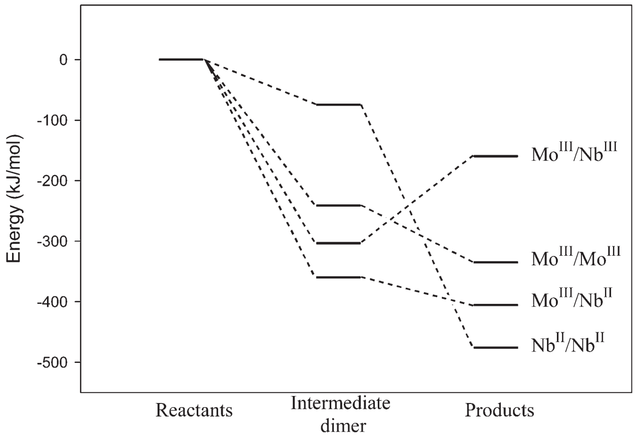
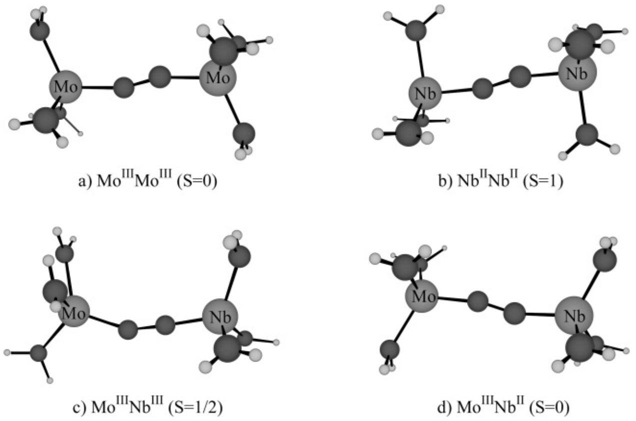


Fig. 3 Calculated energies of the intermediate dimers and products relative to the reactants for the $Mo^{III}Mo^{III}$, $Mo^{III}Nb^{III}$, $Mo^{III}Nb^{II}$, and $Nb^{II}Nb^{II}$ systems.

The reactants adopt D_{3h} symmetry and the products C_{3v} symmetry for Mo^{III} and Nb^{II} whereas for Nb^{III}, both the reactants and products have C_s symmetry. The encounter complexes for all four systems have approximately C_s symmetry with one ligand rotated by 90°. The lowest energy structure for the intermediate dimer (see Fig. 4) possessed C_{2h} symmetry for the $Mo^{III}Mo^{III}$ and $Nb^{II}Nb^{II}$ systems but C_s symmetry for $Mo^{III}Nb^{III}$ and $Mo^{III}Nb^{II}$. In all dimer structures except $Nb^{II}Nb^{II}$, rotation of the NH$_2$ ligands away from a trigonal arrangement was observed on both metal centers. The $Mo^{III}Nb^{III}$ dimer was calculated to have a spin doublet ground state, in agreement with experiment, while the $Mo^{III}Nb^{II}$ and $Mo^{III}Mo^{III}$ systems are predicted to have spin singlet ground states. The $Nb^{II}Nb^{II}$ dimer is calculated to have a spin triplet ground state but with the singlet lying only 7 kJ mol^{-1} higher in energy. The quartet and doublet spin states of the $Nb^{II}(NH_2)_3$ reactant also lie very close in energy unlike $Mo^{III}(NH_2)_3$, where they are separated by 59 kJ mol^{-1}.



a) $Mo^{III}Mo^{III}$ (S=0)
b) $Nb^{II}Nb^{II}$ (S=1)
c) $Mo^{III}Nb^{III}$ (S=1/2)
d) $Mo^{III}Nb^{II}$ (S=0)

Fig. 4 Optimized structures for the $Mo^{III}Mo^{III}$, $Mo^{III}Nb^{III}$, $Mo^{III}Nb^{II}$, and $Nb^{II}Nb^{II}$ intermediate dimers in their ground state.

The level of dinitrogen activation, as measured by the N–N bond length which varies between 1.22 and 1.28 Å, is smallest for the $Mo^{III}Mo^{III}$ system and greatest for the $Nb^{II}Nb^{II}$. The calculated N–N bond length of 1.237 Å for the $Mo^{III}Nb^{III}$ complex is very close to the experimental value of 1.235 Å. The larger N_2 activation for the $Nb^{II}Nb^{II}$ complex is consistent with our earlier work on other dinitrogen-bridged d^3d^3 dimers which revealed that for isoelectronic metals in any one transition series, the degree of N_2 activation increases towards the LHS of the period due to the increased size of the valence d orbitals and thus the capacity of the metal to back donate into the dinitrogen π^* orbitals.

The overall cleavage reaction is found to be exothermic for all four systems (see Fig. 3) but the stabilization energy for the $Mo^{III}Nb^{III}$ system is significantly lower by at least 175 kJ mol^{-1}, even though the N–N bond is more activated than in the $Mo^{III}Mo^{III}$ system. More importantly, whereas the N_2 cleavage step for the $Mo^{III}Mo^{III}$, $Nb^{II}Nb^{II}$ and $Mo^{III}Nb^{II}$ systems is exothermic, with the barriers to bond cleavage (calculated activation energies, E_A, between 50 and 70 kJ mol^{-1}) all accessible at room temperature, the corresponding step in the $Mo^{III}Nb^{III}$ system is endothermic by 144 kJ mol^{-1}. The dependence of the total energy on the N–N bond length is plotted in Fig. 5 for the $Mo^{III}Nb^{III}$ and $Mo^{III}Nb^{II}$ dimers. For $Mo^{III}Nb^{II}$, the N_2 cleavage step is favourable in the singlet spin state with a barrier of 70 kJ mol^{-1}. Analogous to the $Mo^{III}Mo^{III}$ system, the triplet and singlet spin states are relatively close for the dimer but N_2 cleavage is endothermic in the triplet spin state. However, for the $Mo^{III}Nb^{III}$ system, the reverse cleavage reaction, from products to intermediate dimer, is barrierless in the doublet spin state. N_2 cleavage is even less favourable in the quartet state as the products are destabilized relative to the reactants.

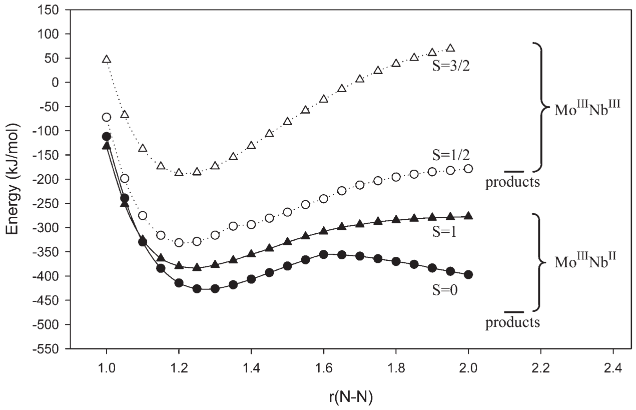


Fig. 5 Dependence of total energy on the N–N bond length for the $Mo^{III}Nb^{III}$ and $Mo^{III}Nb^{II}$ intermediate dimers. Energy is plotted relative to the energy of the $Mo^{III}Nb^{III}$ reactants.

The endothermicity of the N_2 cleavage step for $Mo^{III}Nb^{III}$ accounts for the observed resistance of the $Mo^{III}Nb^{III}$ dimer to cleavage of the bridging dinitrogen in the absence of a reductant. This is in agreement with our earlier calculations on the analogous $Ta^{III}Ta^{III}$ dimer which showed that although the complex has a very activated N–N bond of 1.277 Å, the N_2 bond cleavage step is endothermic by nearly 460 kJ mol^{-1}. On the basis of these results, it can be concluded that the level of activation of the N–N bond does not necessarily correlate with the ease of cleavage of the dinitrogen bridge.

Our previous study compared the level of N_2 activation and energetics associated with the N_2 cleavage reaction for the third row metals Ta^{III}, W^{III} and Re^{III} which possess d^2, d^3 and d^4 configurations, respectively. The results of that study showed that the cleavage reaction was most favored for d^3 metals as this configuration provides the six electrons necessary to reduce the dinitrogen to form the nitrido products. Calculations in the current study on the d^3d^3 $Mo^{III}Nb^{II}$ and $Nb^{II}Nb^{II}$ intermediate dimers were found to be consistent with this finding in that, unlike the d^3d^2 configuration of the $Mo^{III}Nb^{III}$ dimer, the reaction step involving cleavage of the dintrogen bridge to form the nitrido products was exothermic in both cases by 45 and 401 kJ mol^{-1}, respectively (see Table 1 and Fig. 2). Furthermore, the calculated N–N bond lengths of 1.270 and 1.279 Å are more activated than the value of 1.221 Å predicted for the $Mo^{III}Mo^{III}$. The exothermic cleavage step for the $Mo^{III}Nb^{II}$ dimer accounts for why the $Mo^{III}Nb^{III}$ complex, in the presence of the reductant KC_8, results in the cleavage of the dinitrogen bridge as the reduction step is most likely metal-centred with Nb^{III} being reduced to Nb^{II}.

Although the $Mo^{III}Nb^{III}$ and the $Ta^{III}Ta^{III}$ systems have unfavourable thermodynamics in relation to the cleavage of dinitrogen, the fact that, in principle, these systems can be isolated with significantly activated N_2 bonds is useful when controlled reactivities of the dinitrogen bridge are desired such as protonation reactions to form ammonia and hydrazine.

In the current study, model systems have been employed where the bulky N(R)Ar amide ligands have been replaced with NH_2. However, both the structures and reaction energetics will be influenced by the steric bulk of the N(R)Ar groups and we intend to investigate these effects in the $Mo^{III}Mo^{III}$ and $Mo^{III}Nb^{III}$ systems in a forthcoming paper using DFT based QM/MM methods.

Conclusion

DFT calculations have shown the importance of the metal d^3d^3 configuration in effecting cleavage of the dinitrogen bridge in $[Ar(R)N]_3M(\mu\text{-}N_2)M[N(R)Ar]_3$ complexes. Experimentally, the heteronuclear d^3d^2 $Mo^{III}Nb^{III}$ dimer $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)\text{-}Nb[N(^iPr)Ar]_3$ ($Ar = 3,5\text{-}C_6H_3Me_2$) does not undergo cleavage of the dinitrogen bridge, consistent with the theoretical calculations on the model complex $(NH_2)_3Mo(\mu\text{-}N_2)Nb(NH_2)_3$ which reveal that the cleavage step is significantly endothermic by 144 kJ mol^{-1}. In contrast, although the analogous $Mo^{III}Mo^{III}$ dimer $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Mo[N(^tBu)Ar]_3$ possesses a less activated N_2 bridge, this system is observed to undergo spontaneous cleavage at room temperature. The markedly differing reactivities of these two systems can be accounted for on the basis that the $Mo^{III}Nb^{III}$ dimer is one electron short of the six d-electrons necessary to reductively cleave the dinitrogen bridge. The necessity of the d^3d^3 configuration for N_2 cleavage is confirmed from calculations on the corresponding Nb^{II} containing d^3d^3 systems $Mo^{III}Nb^{II}$ and $Nb^{II}Nb^{II}$ which are calculated to have exothermic cleavage steps of 45 and 401 kJ mol^{-1}, respectively. The latter calculations provide a rationale for why $[Ar(^tBu)N]_3Mo(\mu\text{-}N_2)Nb[N(^iPr)Ar]_3$, in the presence of the reductant KC_8, undergoes spontaneous cleavage of the dinitrogen bridge since the reduction step is presumably centred on the Nb^{III}.

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References

1 J. B. Howard and D. C. Rees, *Chem. Rev.*, 1996, **96**, 2965–2982.
2 M. D. Fryzuk and S. A. Johnson, *Coord. Chem. Rev.*, 2000, **200**, 379–409.
3 M. P. Shaver and M. D. Fryzuk, *Adv. Synth. Catal.*, 2003, **345**, 1061–1076.
4 C. E. Laplaza and C. C. Cummins, *Science*, 1995, **268**, 861–863.
5 C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623.
6 D. J. Mindiola, K. Meyer, J.-P. F. Cherry, T. A. Baker and C. C. Cummins, *Organometallics*, 2000, **19**, 1622–1624.
7 G. Christian, J. Driver and R. Stranger, *Faraday Discuss.*, 2003, **124**, 331–341.
8 G. T. Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem*, 2001, **22**, 931–967.
9 C. F. Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391–403.

10 ADF2002.03, SCM, *Theoretical Chemistry*, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com/.

11 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.

12 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

13 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.

14 G. T. Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84–98.

15 L. Versluis and T. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322–328.

16 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597–4610.

17 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783–9792.

18 E. van Lenthe, A. Ehlers and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943–8953.

19 L. Y. Fan and T. Ziegler, *J. Phys. Chem.*, 1992, **96**, 6937–6941.

20 L. Y. Fan and T. Ziegler, *J. Chem. Phys.*, 1992, **96**, 9005–9012.