Dinitrogen fixation and activation by Ti and Zr atoms, clusters and complexes†

Navaratnarajah Kuganathan,[a] Jennifer C. Green[a] and Hans-Jörg Himmel*[b]

Received (in Montpellier, France) 5th May 2006, Accepted 27th June 2006
First published as an Advance Article on the web 10th August 2006
DOI: 10.1039/b606328d

This perspective deals with dinitrogen fixation and activation (a) by complexes of the early transition metals Ti and Zr as synthesized by solution techniques, and (b) by ligand-free Ti and Zr atoms and small clusters as generated using the matrix isolation technique. The two approaches are very different, and not many attempts have yet been made to connect the two different research areas, although a detailed understanding of dinitrogen activation and fixation can only be achieved if all efforts are combined. One of the most striking results that emerged from the research of one of us is that the ligand-free dimer Ti_2, which can be stabilized and studied in matrix isolation experiments, is able to cleave the strong NN triple bond without a significant activation barrier in just one step, leading to the cyclic bis-nitrido species $Ti(\mu\text{-}N)_2Ti$. In this perspective we are discussing possibilities to use this unusually high reactivity for catalytic processes.

Introduction

The discovery of the first transition metal complex which catalytically reduces dinitrogen to ammonia[1,2] together with new high-resolution data of the nitrogenase MoFe protein[3] have renewed interest in dinitrogen activation. In the last few years several new Ti and Zr complexes of N_2 have been synthesized and shown to be relevant for dinitrogen reduction.[4] Detailed studies of the reactions of atoms, dimers, and, latterly, small clusters with N_2 using matrix isolation techniques are now also available. The matrix isolation technique[5] has on several occasions been at the very heart of new developments in chemistry (*e.g.* in the case of noble gas compounds[6] and molecular Al and Ga cluster compounds[7]). In this article we attempt to highlight similarities between the "worlds" of matrix isolation and of preparative solution chemistry. We propose that the results from matrix isolation experiments could also in the case of dinitrogen activation give some interesting new ideas for future experiments in preparative chemistry. Possibilities to bind N_2 and activate the NN triple bond by compounds which include the early transition metal elements Ti and Zr are discussed herein. The discussion includes:

(1) Activation by synthesised complexes in solution.
(2) Activation by bare atoms.
(3) Activation by dimers.
(4) Activation by trimers or larger clusters.
(5) Perspectives.

Navaratnarajah Kuganathan was awarded his BSc (Hons 1st class) from the University of Jaffna, Sri Lanka in 2001. He subsequently taught for three years in the Department of Chemistry, University of Jaffna while he was trained in teaching and research skills under the guidance of Prof. R. Mageswaran, Dr M. Senthilnanthanan, Dr R. Srikaran and Dr J. P. Jeyadevan. In 2004, he was awarded a Felix Scholarship to read for a D. Phil degree at the University of Oxford where he is currently studying in the Inorganic Chemistry Laboratory. His research concerns electronic structure calculations of filled nanotubes under the supervision of Prof. Jennifer Green. He is a member of Wolfson College, Oxford.

Jennifer Green (née Bilham) studied Chemistry at the University of Oxford where she was awarded a BA (Hons 1st class) in 1964. She remained at Oxford for her D.Phil. (awarded 1967) under the supervision of Jack Linnett and Peter Atkins. She was subsequently a Turner and Newall Research Fellow (1967–1970) and became a Fellow and Tutor of St. Hugh's College, Oxford in 1969, a post that she holds to the present day. She was appointed Professor of Chemistry at Oxford University in 1999. Her research centres on the electronic structure of inorganic molecules, which she investigates by spectroscopic and computational methods.

---

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. E-mail: hans-jorg.himmel@aci.uni-heidelberg.de*

† The HTML version of this article has been enhanced with additional colour images.

Hans-Jörg Himmel studied Chemistry in Heidelberg, Germany, where he received his diploma in 1994. In that year he started work for his Ph.D., first in Heidelberg then in Bochum under the supervision of Prof. Christof Wöll at the Institute of Physical Chemistry; this work, completed in 1998, was in the field of surface science. From 1998 to 2000 he joined the group of Prof. Tony Downs at the Inorganic Chemistry Laboratory in Oxford, U.K., with funding from the Deutsche Forschungsgemeinschaft (DFG), and received a D.Phil. degree from the University of Oxford in 2000. Then he moved to the University of Karlsruhe, Germany, to start work for his habilitation. For his work on the reactivity of small ligand-free metal clusters he was awarded the ADUC prize (given by the Association of German University Professors in Chemistry) of the year 2003. After completion of his habilitation in April 2004 he was Privatdozent at the Institute of Inorganic Chemistry of the University of Karlsruhe, receiving a Heisenberg Fellowship from the DFG since September 2004. In October 2005 he returned to Oxford as a Lecturer in Inorganic Chemistry and a Fellow of The Queen's College. Since June 2006 he has been a Professor of Chemistry (W3) at the Ruprecht-Karls-University of Heidelberg.

1. Activation by complexes

Many authoritative review articles already cover the field of N_2 fixation and activation by mononuclear as well as dinuclear complexes of Ti and Zr.[4] Therefore here we concentrate on more recent examples, some of which have not yet been reviewed. Fig. 1 gives an overview of bonding modes of N_2 realized so far; no differentiation has been made between single, double or triple bonds in this overview. To date, the only known example for bonding mode (8) is the gold cluster $[(LAu)_6(N_2)]^{2+}$ (where *e.g.* L = PPh_2iPr).[8] Bonding mode (6) is realized in the dinitrogen complex $[(NPN)Ta(\mu\text{-}H)]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N_2)$, where NPN is $PhP(CH_2SiMe_2NPh)_2$.[9] In this complex, N_2 adopts a side-on end-on dinuclear bonding mode. Examples for the other modes are provided below.

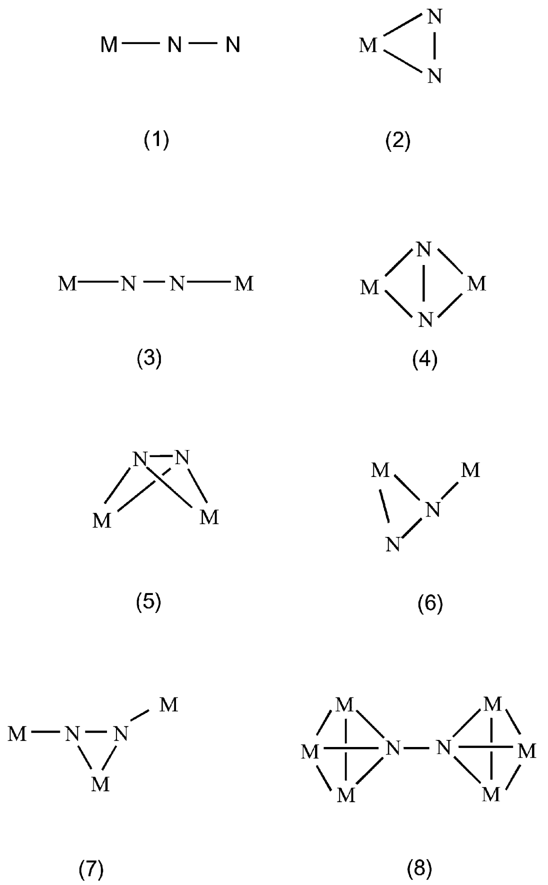
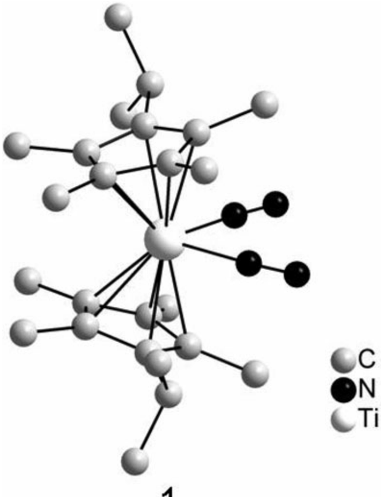


Fig. 1 Experimentally verified bonding modes of N_2. Note that no differentiation was made between single, double or triple bonds. Examples for the nomenclature used in the text are (1) $M(\eta^1\text{-}N_2)$, (2) $M(\eta^2\text{-}N_2)$, (3) $M_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, (4) and (5) $M_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, and (6) $M_2(\mu_2,\eta^1,\eta^2\text{-}N_2)$.

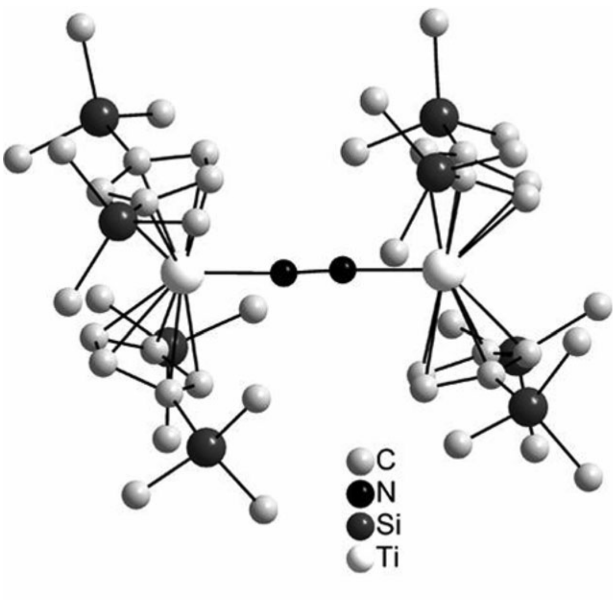
Metallocene derivatives have been proven to be particularly interesting. Small modifications in the cyclopentadienyl substitution have great influence on the reactivity toward dinitrogen. N_2 prefers a bridging η^1,η^1-coordination in dinuclear Ti complexes.[10] From early experiments it has already been known that bis(pentamethylcyclopentadienyl)-titanium(II) reacts with N_2 to give either the mononuclear N_2 complex $Cp^*{}_2TiN_2$ or the dinuclear dark blue N_2 complex $\{Cp^*{}_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ [$Cp^* = C_5(CH_3)_5$].[11] In the crystalline phase, $\{Cp^*{}_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ exhibits NN and TiN bond distances of 116.5(1.4) and 200.5(1.0)/201.6(1.0) pm.[12]

Recently it has been shown that two N_2 units reversibly bind in an end-on fashion to Ti(II) in complexes of the form $[C_5Me_4R]_2Ti$ (R = CMe_3, $SiMe_3$, $CHMe_2$, or CH_3).[13] For example, **1**, $\{C_5Me_4[CH(CH_3)_2]\}_2Ti(N_2)_2$ [featuring TiN and NN bond distances of 204.3(1) and 111.0(2) pm] is stable at temperatures of up to −30 °C, but releases N_2 at higher temperatures. Interestingly, the temperature up to which these complexes are stable increases in the order R = Cme_3 < $SiMe_3$ < $CHMe_2$ < CH_3. The short NN distance and the high wavenumber of the NN stretching fundamental (1986 cm^{-1}) indicate a weak degree of N_2 activation.



1

There are now several examples of dinuclear titanocene complexes, featuring a bridging N_2 unit. One early example is $\{Cp_2Ti(p\text{-tolyl})\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, for which NN and TiN bond distances of 116.2(1.2) and 196.2(0.6) pm were measured.[14] The well known precursor for low-valent titanocene complexes $Cp_2Ti(PMe_3)_2$[15] reacts with N_2 to form the dinuclear complex $\{Cp_2Ti(PMe_3)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, featuring NN and TiN bond distances of 119.1(8) and 192.0(6)/192.1(5) pm.[16] Recently the paramagnetic complex $[(C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, **2**, has been prepared according to eqn (1) [with an NN bond distance of 116.4(5) pm].[17]



2

This complex has an interesting chemistry. Treatment with Me_3SiN_3 results in liberation of N_2 and formation of the imido complex $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Ti{=}NSiMe_3$, which takes up H_2 to form $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Ti(H)NSiMe_3(H)$. Finally, $[(C_5Me_4H)_2Ti]_2(\mu\text{-}\eta^1,\eta^1\text{-}N_2)$, featuring TiN and NN bond distances of 198.7(3) and 117.0(4) pm and an almost perfectly linear Ti–N–N–Ti chain, is also known.[18] Synthesis was achieved from the hydride $(C_5HMe_4)_2TiH$.

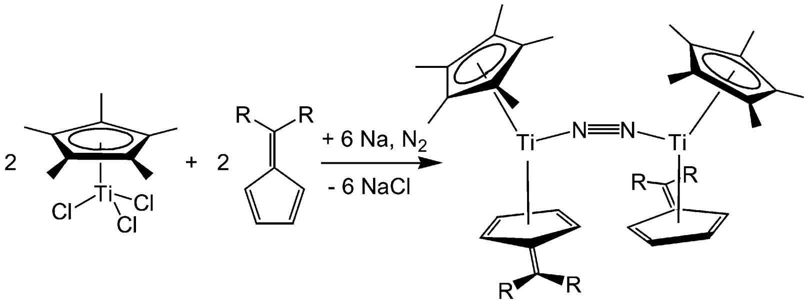
There are also examples with ligands other than Cp derivatives, leading to lower formal oxidation states of the Ti atoms. In $\{(\eta^5\text{-}C_5Me_5)Ti(\eta^6\text{-}C_5H_4{=}CR_2)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, obtained from eqn (2), one of the Cp ligands attached to each of the Ti atoms is replaced by pentafulvenes $C_5H_4{=}CR_2$ (R = p-tolyl or CR_2 = adamantyl).[19]

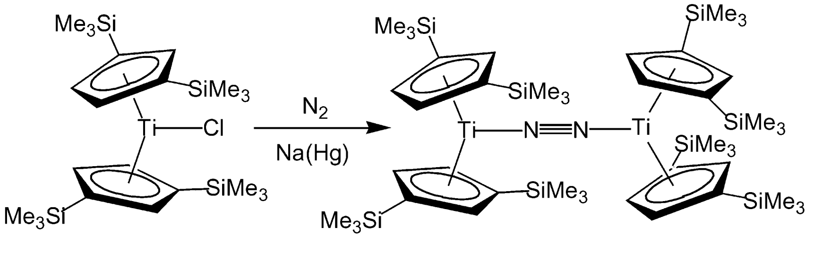
However, although the formal oxidation state is lower, the NN bond distance (measuring about 116.0 pm) is not larger than in compounds with two Cp-ligands on each of the Ti atoms. This has been explained by MO theory, indicating that the reduced degree of π-bonding between the Ti atoms and the bridging N_2 is caused by interactions between the d-orbitals on the Ti atoms and the pentafulvene ligands.[10] Reduction of $[(Me_2N)C(N\textit{i}Pr)_2]_2TiCl_2$, which can be prepared from $Ti(NMe_2)_2Cl_2$ and *i*PrNCN*i*Pr in diethylether, with Mg powder in THF under an atmosphere of dinitrogen affords the dinuclear complex $\{[Me_2NC(N\textit{i}Pr)_2]_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ with an NN bond distance of 128.0(8) pm.[20] Another example is $\{[(Me_3Si)_2N]TiCl(TMEDA)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (TMEDA = *N*,*N*,*N′*,*N′*-tetramethyl-ethylene-diamine), which can be isolated in the form of brown crystals.[21] The TiN and NN bond distances were measured to be 202.3(5) and 128.9 pm.

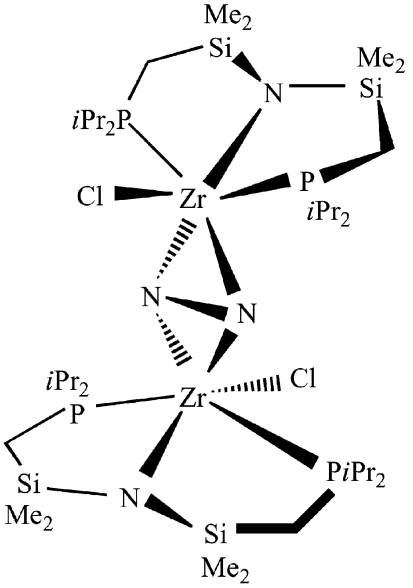
There are also known dinuclear complexes with two bridging N_2 units. Such a complex is the anion of the salt $[Li(TMEDA)_2]^+\{[(Me_3Si)_2N]_2Ti\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)_2Ti[N(SiMe_3)_2]_2\}^-$, which can be obtained in the form of paramagnetic, deep-purple/black crystals as one of the products of the reaction between $trans(TMEDA)_2TiCl_2$ with $(Me_3Si)_2NLi$ and N_2.[21] The TiN and NN bond distances were found to be 223.6/229.0 and 137.9(2.1) pm, respectively.

Finally, in the Ti complex $[\{(C_{10}H_8)Cp_2\text{–}Ti_2\}\{(C_5H_4)Cp_3Ti_2\}(\mu_3\text{-}N_2)]$, the N_2 unit, with an NN distance of 130(1) pm, exists as a $\mu_3\text{-}\eta^1,\eta^1,\eta^2$-ligand.[22] This is an example of bonding mode (7) (see Fig. 1).

Similar to the situation for the pair Fe/Ru,[23] complexes of Zr are potentially even more interesting for N_2 activation. N_2 complexes of Zr have also been known for a long time now. In the case of binuclear complexes the bridging η^2,η^2 bonding







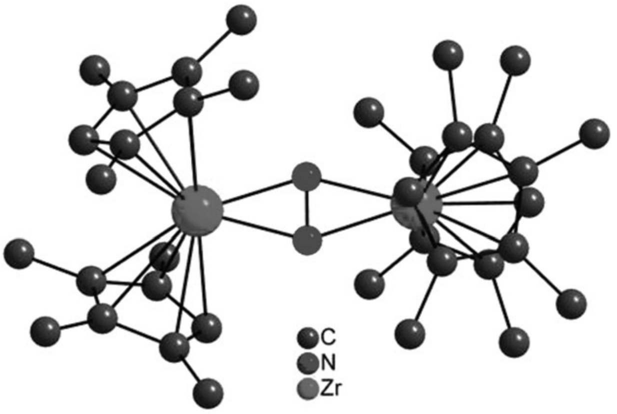
$\{[(i\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}\}_2(\mu,\eta^2,\eta^2\text{-N}_2)$

Fig. 2 Structural models of $\{[(i\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}\}_2(\mu,\eta^2,\eta^2\text{-N}_2)$ [with experimentally determined NN and ZrN separations of 154.8(7) and 202.4(4)/217.5(3) pm].

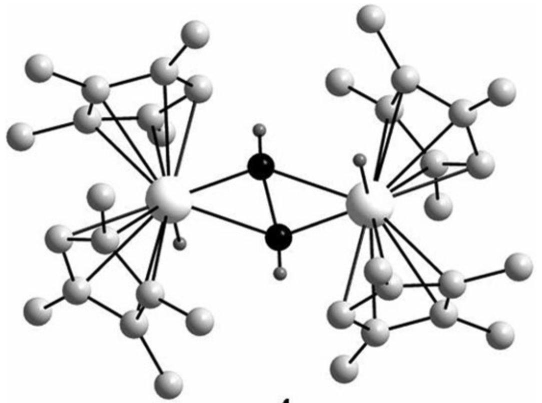
mode is more common than for Ti. One early example for the bridging η^1,η^1 mode is $\{\text{Cp*}_2\text{Zr(N}_2)\}_2(\mu\text{-}\eta^1,\eta^1\text{-N}_2)$ featuring two terminal and one bridging N_2.[24] The NN bond distance of the terminal and bridging N_2 units are 111.6(8) and 118.2(5) pm. The ZrN bond distances were found to be 218.8(4) pm for the terminal N_2 and 208.7(3)/207.5(3) pm for the bridging N_2. The two end-on bonded N_2 ligands adopt a *gauche* conformation, which can be explained by π-interactions between the two π-orbitals of the N_2 unit and suitable orbitals at the Zr. In the IR spectrum (KBr disk) the symmetric and antisymmetric combinations of the two NN stretches of the terminal N_2 ligands occur at 2040 and 2003 cm^{-1}, respectively.[25] The significant energetic separation of the two modes, together with the high intensity of the band assigned to the NN stretch of the bridging N_2 unit (at 1578 cm^{-1}) means substantial electronic coupling, in agreement to the suggested π-interactions.[25] The terminal N_2 ligands can be replaced by CO or PF_3. It proved difficult to add H_2 to such complexes. The normal result, if any, is the formation of a metal–hydrogen bond with expulsion of free N_2.[4]

However, there are some exceptions. One of them is the dinuclear Zr complex $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-N}_2)$, with P_2N_2 = $\text{PhP(CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$.[26] The NN and ZrN bond distances were measured to be 143(1) and 220.3(4)/201.0(2) pm. This complex adds dihydrogen at pressures of 1–4 bar to give $[\text{P}_2\text{N}_2]\text{Zr}(\mu\text{-}\eta^2\text{-N}_2\text{H})(\mu\text{-H})\text{Zr}[\text{P}_2\text{N}_2]$. The bonding properties within the planar Zr_2N_2 core of this dinitrogen complex have been analysed recently in detail by resonance Raman, IR and UV-vis spectroscopy.[27] With 154.8 nm, the NN bond distance in the complex $\{[(i\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}\}_2(\mu,\eta^2,\eta^2\text{-N}_2)$ (see Fig. 2) is one of the largest known NN bond length in a metal–dinitrogen complex.[28]

Very recently, the complex $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu\text{-}\eta^2,\eta^2\text{-N}_2)$, **3**, was synthesized by reduction of $(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrCl}_2$[29] with sodium amalgam under one atmosphere of N_2.[30] This complex was shown to react immediately at 22 °C with H_2 leading to the complex $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrH}]_2\{\mu_2,\eta^2,\eta^2\text{-N}_2\text{H}_2\}$, **4**.[30,31] **4** reacts at 85° with H_2 to give the hydride $(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrH}_2$ and NH_3. The work was also extended to Hf complexes.[32] However, we restrict ourselves to Ti and Zr in this review.



3



4

2. Activation by the bare atoms

Ti atoms can be stabilized with the help of matrix isolation techniques. The metal atoms can either be generated thermally or with the aid of the laser-ablation technique. The laser-ablation technique generates, besides neutral species in their electronic ground state, a high percentage of charged and/or electronically excited species. Furthermore, N_2 is cleaved in the course of the laser-ablation process, so that the matrix also contains N atoms. Therefore thermal evaporation is more suitable to study coordination compounds, the generation of which requires mild conditions. Nevertheless, we will also discuss the results of laser-ablation studies. In our experiments, Ti vapour, thermally evaporated by resistive heating of a Ti or Ti/Mo filament, is codeposited in a vacuum apparatus together with a large excess of a noble gas (such as Ar or Ne) onto a freshly polished Cu surface kept at temperatures in the region 6–12 K (see Fig. 3a). Fig. 3b shows an UV-vis spectra of an Ar matrix containing small quantities (0.1%) of Ti. The absorptions can be assigned to electronic excitations of single Ti atoms, which are slightly shifted from their gas phase values

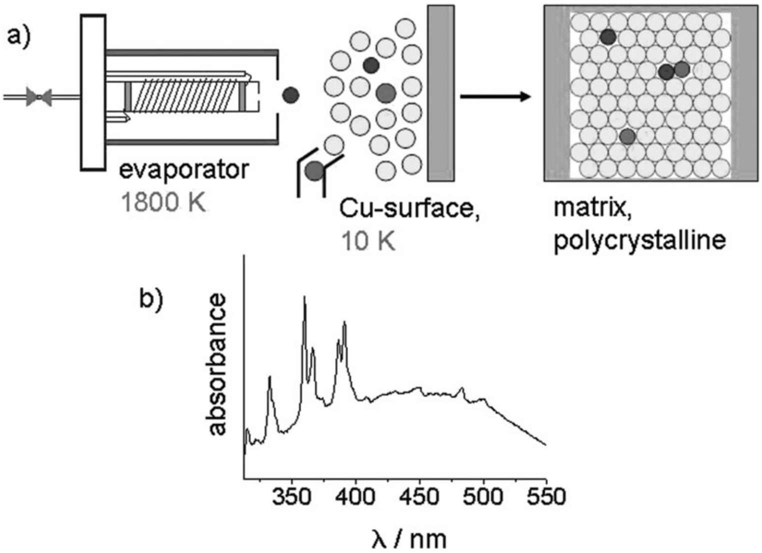


Fig. 3 (a) Preparation of a matrix containing Ti atoms and N_2. The Ti atoms are emitted from a hot filament. The N_2 is admixed to the matrix gas. In the resulting matrix the reactants are distributed statistically in defect sites. (b) UV-Vis spectrum of Ti atoms in an Ar matrix.

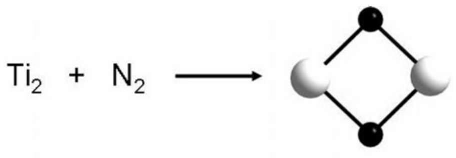
(matrix-shift).[33,34] Matrix experiments have shown that a Ti atom in its ^3F electronic ground state (electronic configuration $3d^24s^2$) does not form any complex with N_2 presumably due to significant σ-repulsion (see the discussion in the case of the monocarbonyl complex).[35] Only after photolytic activation of the Ti atom (excitation of one electron out of the 4s orbital) can the formation of a weakly end-on bonded N_2 complex be observed,[36] which according to DFT calculations exhibits a $^5\Delta$ electronic ground state. The DFT calculations also found side-on bonded complexes with $^3A_2$ and $^5B_1$ electronic states. However, they are 14 and 65 kJ mol^{-1} higher in energy, respectively.

Matrix-isolation studies of the interaction of laser-ablated Zr and Hf atoms with dinitrogen[36] indicate the formation of both η^1- and η^2-coordinated complexes. According to BP86 calculations, the side-on bonded $Zr(N_2)$ complex exhibits a $^1A_1$ ground electronic state. The degree of dinitrogen activation in the side-on bonded complexes increases in the order Ti < Zr < Hf, a trend which has been rationalized by the increasing size of the valence nd orbitals. A bis-η^2:η^2-dinitrogen complex of Zr, presumably with a $^5B_{3g}$ ground electronic state, has also been sighted in these experiments. There is, furthermore, some indication that bent NZrN and NHfN species are generated as a consequence of the laser-ablation process.

3. Activation by dimer

The generation of a "naked" Ti dimer in the absence of a ligand sphere or another sort of protecting environment can only be achieved in the gas phase or by using matrix isolation techniques. Resonant-two-photon-ionization experiments of the dimer in the gas phase allowed the bond energy to be estimated to be 149 ± 19 kJ mol^{-1}.[37] The dimer has also been studied using mass spectrometry.[38] We employed matrix isolation which is now very well established as a powerful technique for stabilizing reactive molecules and intermediates, to study the dimer and its reactivity.[34,39] A series of overtones of the vibrational fundamental of the dimer in an Ar matrix were traced in resonance Raman experiments.[34,40] An analysis of these overtones by the method introduced by LeRoy, Bernstein and Lam[41] yielded a D_e value of *ca.* 120 kJ mol^{-1}. Quantum chemical multireference CI calculations argue for a somewhat higher value (*ca.* 150 kJ mol^{-1}).[40] The calculations predict the electronic ground state to be $^3\Delta_g$, in agreement with the results of the gas phase experiments.

We then recorded electronic absorption spectra of the dimer isolated in both Ne and Ar matrices.[40] In the obtained spectra allowed transitions to several electronically excited states (namely 1 $^3\Pi_u$, 1 $^3\Phi_u$, 2 $^3\Pi_u$ and 2 $^3\Phi_u$) were observed, each showing vibrational structure allowing useful information to be inferred about the excited states. The excitation energies are not more than 0.41, 0.43, 0.73, and 0.94 eV. A Franck–Condon analysis of the intensity patterns observed for transitions into different vibrational states reveals elongations of the Ti–Ti bond by 9 ± 2, 10 ± 2, 13 ± 2, 13 ± 4 pm in the 1 $^3\Pi_u$, 1 $^3\Phi_u$, 2 $^3\Pi_u$ and 2 $^3\Phi_u$ excited states, respectively.[40] These excited states are presumably very important for the reactivity of metal dimers. In the case of Ga_2 we have shown that low-lying electronic states are responsible for the very small barrier to reaction with H_2 of only 30 kJ mol^{-1}.[42]



5

Very surprisingly, the Ti dimer reacts without any significant activation barrier with N_2 to give the cyclic bis-nitrido-species $Ti(\mu\text{-}N)_2Ti$, **5**.[43] Thus the N≡N triple bond is completely cleaved in just one step. The experiments have been repeated with different dinitrogen isotopomers. The measured spectra do not only indicate the presence of two equivalent N atoms, but also allow an estimate of *ca.* 90° for the N–Ti–N bond angles and of 175 pm for the Ti–N distance. Quantum chemical (multireference CISD + Q) calculations clearly show that Ti_2N_2 exhibits a ^1A_g ground electronic state (in disagreement with earlier DFT results using the BP86 functional suggesting a $^3B_{1u}$ state).[36] The Ti–N bond order is 1.5. The reaction of Ti_2N_2 with H_2 under matrix isolation conditions is a topic of ongoing research.

The bond strength in the Zr dimer was experimentally determined to be 294 kJ mol^{-1} which is almost twice the value estimated for Ti_2.[44] From resonance Raman spectra of the matrix isolated molecule the force constant was estimated to be 251 N m^{-1}. It is a general scheme for the early transition metals that the dimers are stronger bound for the second row transition metals than for the first row ones.[45] The difference is most striking for Cr_2 and Mo_2, and has been explained by the electron configuration of the metal atoms.

The experimental data accumulated for the reaction between laser-ablated Zr and N_2 suggest the formation of the four-membered cyclic $Zr_2(\mu\text{-}N_2)$ species. DFT calculations suggest this species to have, like Ti_2N_2, a ^1A_g ground electronic state characterized by ZrN bond distances of 193.2 pm and NZrN bond angles of 87.2°.

4. Activation by small clusters

Unfortunately, the reactions of the trimers and larger clusters of Ti or Zr with N_2 have not yet been studied. However, information about the trimers themselves is available and provides some idea about the possible reactivity of these species. The Ti trimer has been studied by quantum chemical calculations. A triangular D_{3h} symmetric form with a $^7E'$ electronic ground state and Ti–Ti bond distances of about 230 pm defines the energy minimum according to DFT calculations.[46] Four excited electronic states are predicted to have energies very close by. These are the $^5E'$, $^3A_2'$, $^3E''$ and $^9A_2'$ states with 2.2, 8.1, 8.4 and 9.8 kcal mol^{-1}, respectively, higher energies than the $^7E'$ ground state. This density of electronic states in energetic proximity to the ground state indicates a high reactivity. The Zr trimer has been generated and studied experimentally by Raman spectroscopy using the matrix isolation technique.[47] The ZrZr valence force constant in this trimer was estimated to be 119 N m^{-1}. In summary the preliminary calculations on Ti_3 and Zr_3 suggest that the trimers should have a very interesting and rich chemistry.

Generally, the metal–metal force constant $k^{(n)}$ of a symmetric metal clusters with n atoms can be estimated by the formula $k^{(n)} = \beta_n k^{(2)}$, where $k^{(2)}$ denotes the force constant of the metal dimer, $\beta_n = 2/a_n$ and a_n is the sum of the number of atoms to which each atom in a bond is connected.[48] This rule is only applicable if the type of bonding or configuration does not change between the dimer and cluster. For Zr and $n = 3$, β_3 is $\frac{1}{2}$, and thus a force constant of 147 N m^{-1} is expected for Zr_3.[49] This value is reasonably close to the value of 119 N m^{-1} determined from the Raman spectra. The decrease of the force constant might suggest higher reactivity for the trimer and larger clusters. However, there is a limit, and this is when the onset of bulk behaviour occurs in the clusters. In the case of Ti, and with respect to properties such as electron affinities, ionization potentials, and chemical reactivity, the onset of bulk behaviour occurs already for a cluster comprised of ten atoms.[50] This means that Ti_2–Ti_9 are the species which are expected to show the most interesting chemistry with respect to dinitrogen activation.

5. Perspectives

How could one possibly make use of the striking reactivity of Ti_2 to bind N_2? One possible route to follow is the stabilization of the Ti dimer in robust thermally stable host systems such as zeolites or carbon nanotubes. Ti coated carbon nanotubes and fullerenes were recently discussed as possible hydrogen storage materials.[51] It might be possible to get access to the dimers or small clusters by CVD methods, *e.g.* starting with the Ti(0) compound bisbenzene titanium $[(C_6H_6)_2Ti]$.[52] As a first step in this direction we have calculated the structure and catalytic reactivity of $C_{60}Ti_2$.[53] Although it is of course speculative if such a compound could ever be prepared on a large scale, we think that the analysis gives some useful hints for future synthetic attempts. Compounds of the form $Ti_n(C_{60})(CO)_k^+$ (n = 1 or 2, k = 0–3) were generated in the gas phase and analysed by TOF mass spectrometry.[54] The ionization energy of $C_{60}Ti$ was determined to be 5.92–6.42 eV and is thus smaller than that of free Ti atoms (6.82 eV). The catalytic cycle as proposed in Fig. 4 illustrates the reduction of N_2 with H_2 to NH_3. Fig. 5 contains the relative energies for each of the steps. The formation of the catalytically active species $C_{60}Ti_2$ from C_{60} and Ti_2, is associated with an energy change of −262 kJ mol^{-1} according to our DFT calculations. $C_{60}Ti_2$ features a Ti–Ti distance of 242 pm. This value compares with 197.8 pm obtained in a previous calculation.[51b] The first step in the catalytic cycle then is the formation of $C_{60}[Ti(\mu\text{-}N)_2Ti]$ from $C_{60}Ti_2$ and N_2. DFT calculations predict this reaction to be highly exothermic (energy change of −517 kJ mol^{-1}). For comparison, the energy change for the reaction between free Ti_2 and N_2 to give Ti_2N_2 is calculated to be −539 kJ mol^{-1}. The fact that the reaction energy is only slightly reduced by the presence of C_{60} does of course not mean automatically that the reactivities of Ti_2 and $C_{60}Ti_2$ are similar and that $C_{60}Ti_2$ would also react without activation barrier, but it might make this likely. This indicates that C_{60} or a carbon nanotube would be the right choice. Another interesting comparison can be made between this reaction energy and that of the reaction between the V compound $[HN(CH_2CH_2NH)_2V]$ and N_2 to give the bridged nitride dimer $[HN(CH_2CH_2NH)_2V(\mu\text{-}N)]_2$.[55] According to DFT calculations, this reaction is exothermic by 684 kJ mol^{-1}. $C_{60}Ti_2N_2$ exhibits TiN bond distances of 180 pm. This is close to the value estimated on the basis of empirical correlations from the experimental vibrational spectra for free Ti_2N_2 (175 ± 3 pm).[44] The TiTi and NN separations amount to 245 and 250 pm, respectively (in agreement to the experimental estimate for the NN separation of 247 pm). When coordinated to C_{60}, the Ti_2N_2 unit is slightly bent.

Additional calculations were carried out to look at the products of the reaction with H_2.[54] The reaction energy of the next step of the imaginary catalytic cycle to give C_{60}[Ti

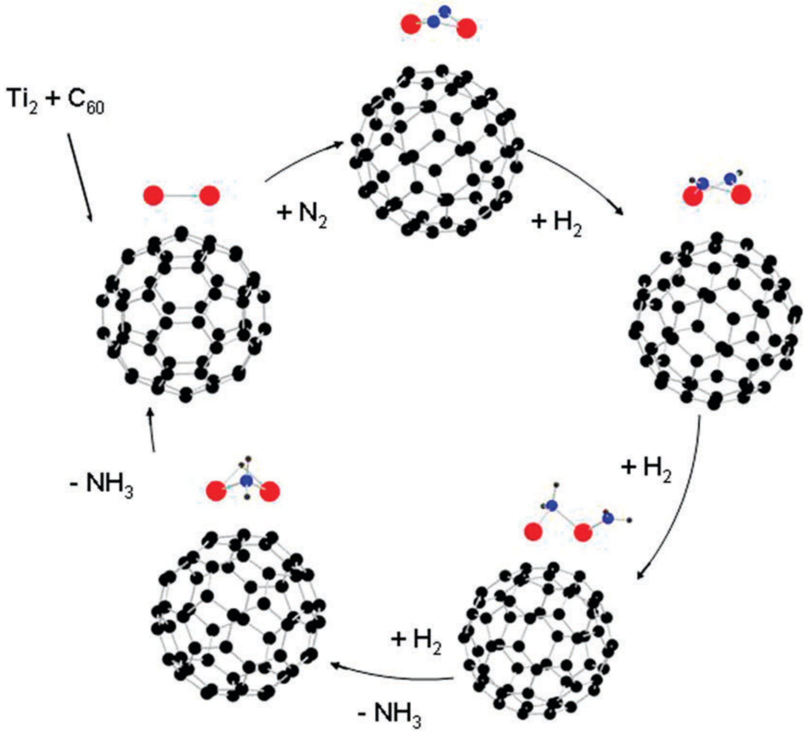


Fig. 4 Catalytic cycle for reduction of N_2 to NH_3 with $C_{60}Ti_2$ as catalyst.

(μ-NH)$_2$Ti] is also calculated to be exothermic (energy change of -93 kJ mol^{-1}). The TiN and NH bond distances are all 190 and 103 pm, respectively. The Ti–N–Ti bond angles are 75°. The TiTi and NN separations amount to 231 and 277 pm, respectively.

Addition of a second H_2 leads to $C_{60}Ti_2N_2H_4$. One of the NH_2 groups bridges the Ti_2 unit, while the other is more end-on coordinated. The TiTi bond distance increases to 252 pm. The TiN distances to the bridging NH_2 are 209 and 205 pm. For the end-on bonded NH_2 unit, TiN distances of 187 and 364 pm are adopted. This step is endoenergetic by $+99$ kJ mol^{-1}.

Reaction with a third H_2 molecule could proceed *via* two possible routes: (i) directly to two moieties of NH_3 and regeneration of the catalyst $C_{60}Ti_2$, or (ii) in a two step reaction first to $C_{60}Ti_2(NH)(H)$ and one moiety of NH_3, and then to another moiety of NH_3 and $C_{60}Ti_2$. The first route is endothermic by as much as 477 kJ mol^{-1} and therefore not likely to be followed. The second route, which gives in the second step the possibility of energetic assistance from further reaction with N_2, is much better. The first step of the second route is endothermic by 123 kJ mol^{-1}. The product of this reaction, the species $C_{60}Ti_2NH_3$, features TiH, TiN, NH and TiTi bond distances of 188, 208/209, 104 and 230 pm, respectively. The reaction energy for the second step is calculated to be 354 kJ mol^{-1}. Though this second step is unfavourable, if it were to be coupled with reaction with a further mole of N_2, the overall process would be exoenergetic.

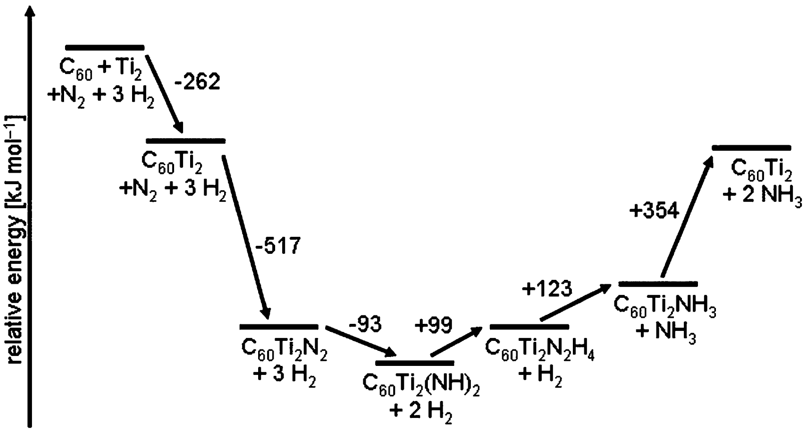


Fig. 5 Relative energies of the intermediates formed during the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ catalysed by $C_{60}Ti_2$.

Acknowledgements

H.-J. H. gratefully acknowledges the financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the DAAD Procope project. We thank the Oxford Supercomputer Centre for its facilities and the Felix Foundation for a scholarship (N. K.).

References

1 See, for example: (*a*) D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76; (*b*) R. R. Schrock, *Philos. Trans. R. Soc. London, Ser. A*, 2005, **363**, 959.

2 C. M. Kozak and P. Mountford, *Angew. Chem.*, 2004, **116**, 1206 (*Angew. Chem., Int. Ed.*, 2004, **43**, 1186).

3 (*a*) O. Einsle, F. A. Texcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard and D. C. Rees, *Science*, 2002, **297**, 1696; (*b*) D. C. Rees, F. A. Tezcan, C. A. Haynes, M. Y. Walton, S. Andrade, O. Einsle and J. B. Howard, *Philos. Trans. R. Soc. London, Ser. A*, 2005, **363**, 971; (*c*) J. Kästner and P. E. Blöchl, *ChemPhysChem*, 2005, **6**, 1724.

4 See, for example: (*a*) M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115; (*b*) M. D. Fryzuk and S. A. Johnson, *Coord. Chem. Rev.*, 2000, **200**, 379.

5 See, for example: I. R. Dunkin, *Matrix Isolation Techniques: A Practical Approach*, Oxford University Press, Oxford, UK, 1998.

6 See, for example: (*a*) R. N. Perutz, *Chem. Rev.*, 1985, **85**, 77; (*b*) M. Pettersson, J. Lundell and M. Räsänen, *Eur. J. Inorg. Chem.*, 1999, 729.

7 See, for example: (*a*) C. Dohmeier, D. Loos and H. Schnöckel, *Angew. Chem.*, 1996, **108**, 141 (*Angew. Chem., Int. Ed*, 1996, **35**, 129); (*b*) A. Schnepf and H. Schnöckel, *Angew. Chem.*, 2002, **114**, 3683 (*Angew. Chem., Int. Ed.*, 2002, **41**, 3533); (*c*) H. Köhnlein and H. Schnöckel, *Polyhedron*, 2002, **21**, 489; (*d*) H. Schnöckel, *Dalton Trans.*, 2005, **9**, 2653.

8 H. Shan, Y. Yang, A. J. James and P. R. Sharp, *Science*, 1997, **275**, 1460.

9 (*a*) M. D. Fryzuk, S. A. Johnson, O. B. Patrick, A. Albinati, S. A. Mason and T. F. Koetzle, *J. Am. Chem. Soc.*, 2001, **123**, 3960; (*b*) F. Studt, B. A. Mackay, M. D. Fryzuk and F. Tuczek, *J. Am. Chem. Soc.*, 2004, **126**, 280; (*c*) F. Studt, B. A. Mackay, M. D. Fryzuk and F. Tuczek, *Chem.–Eur. J.*, 2005, **11**, 604.

10 See, for example: F. Studt, N. Lehnert, B. E. Wiesler, A. Scherer, R. Beckhaus and F. Tuczek, *Eur. J. Inorg. Chem.*, 2006, **291** and references therein.

11 J. E. Bercaw, *J. Am. Chem. Soc.*, 1974, **96**, 5087.

12 R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8358.

13 (*a*) T. E. Hanna, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 14688; (*b*) T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter and P. J. Chirik, *Organometallics*, 2004, **23**, 3448.

14 J. D. Zeistra, J. H. Teuben and F. Jellinek, *J. Organomet. Chem.*, 1979, **170**, 39.

15 L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, U. Thewalt and B. Wolf, *Angew. Chem.*, 1985, **97**, 425 (*Angew. Chem., Int. Ed.*, 1985, **24**, 394).

16 D. H. Berry, L. J. Procopio and P. J. Caroll, *Organometallics*, 1988, **7**, 570.

17 T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter and P. J. Chirik, *Organometallics*, 2004, **23**, 3448.

18 J. M. deWolf, R. Blaauw, A. Meetsma, J. H. Teuben, R. Gyepes, V. Varga, K. Mach, N. Veldman and A. L. Spek, *Organometallics*, 1996, **15**, 4977.

19 A. Scherer, K. Kollak, A. Lützen, M. Friedemann, D. Haase, W. Saak and R. Beckhaus, *Eur. J. Inorg. Chem.*, 2005, 1003.

20 S. M. Mullins, A. P. Duncan, R. G. Bergman and J. Arnold, *Inorg. Chem.*, 2001, **40**, 6952.

21 R. Duchateau, S. Gambarotta, N. Beydoun and C. Bensimon, *J. Am. Chem. Soc.*, 1991, **113**, 8986.

22 G. P. Pez, P. Apgar and R. K. Crissey, *J. Am. Chem. Soc.*, 1982, **104**, 482.

23 (*a*) D. Sellmann, B. Hautsch, A. Rösler and F. W. Heinemann, *Angew. Chem.*, 2001, **113**, 1553 (*Angew. Chem., Int. Ed*, 2001, **40**, 1505); (*b*) D. Sellman, A. Hille, F. W. Heinemann, M. Moll, G. Brehm, M. Reiher, B. A. Hess and S. Schneider, *Inorg. Chim. Acta*, 2003, **348**, 194; (*c*) D. Sellmann, A. Hille, A. Rösler, F. W. Heinemann, M. Moll, G. Brehm, S. Schneider, M. Reiher, B. A. Hess and W. Bauer, *Chem.–Eur. J.*, 2004, **10**, 819; (*d*) M. Reiher and B. A. Hess, *Adv. Inorg. Chem.*, 2004, **56**, 55; (*e*) M. Reiher, B. Kirchner, J. Hutter, D. Sellmann and B. A. Hess, *Chem.–Eur. J.*, 2004, **10**, 4443; (*f*) B. Kirchner, M. Reiher, A. Hille, J. Hutter and B. A. Hess, *Chem.–Eur. J.*, 2005, **11**, 574.

24 R. D. Sanner, J. M. Manriquez, R. E. Marsh and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351.

25 J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chang and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 3078.

26 (*a*) M. D. Fryzuk, J. B. Love, S. J. Rettig and V. G. Young, *Science*, 1997, **275**, 1445; (*b*) H. Basch, D. G. Musaev, K. Morokuma, M. D. Fryzuk, J. B. Love, W. W. Seidel, A. Albinati, T. F. Koetzle, W. T. Klooster, S. A. Mason and J. Eckert, *J. Am. Chem. Soc.*, 1999, **121**, 523.

27 F. Studt, L. Morello, N. Lehnert, M. D. Fryzuk and F. Tuczek, *Chem.–Eur. J.*, 2003, **9**, 520.

28 (*a*) M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *J. Am. Chem. Soc.*, 1990, **112**, 8185; (*b*) J. D. Cohen, M. Mylvaganam, M. D. Fryzuk and T. M. Loehr, *J. Am. Chem. Soc.*, 1994, **116**, 9529.

29 C. Janiak, U. Versteeg, K. C. H. Lange, R. Weiman and E. Hahn, *J. Organomet. Chem.*, 1995, **501**, 219.

30 J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527.

31 W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2005, **127**, 14051.

32 W. H. Bernskoetter, A. V. Olmos, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2006, **25**, 1021.

33 (*a*) D. M. Gruen and D. H. W. Carstens, *J. Chem. Phys.*, 1971, **54**, 5206; (*b*) R. Busby, W. Klotzbücher and G. A. Ozin, *J. Am. Chem. Soc.*, 1976, **98**, 4013.

34 H. J. Himmel and A. Bihlmeier, *Chem.–Eur. J.*, 2004, **10**, 627.

35 L. A. Barnes and C. W. Bauschlicher, Jr, *J. Chem. Phys.*, 1989, **91**, 314.

36 G. P. Kushto, P. F. Souter, G. V. Chertihin and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 9020.

37 L. M. Russon, S. A. Heidecke, M. K. Birke, J. Conceicao, M. D. Morse and P. B. Armentrout, *J. Chem. Phys.*, 1994, **100**, 4747.

38 (*a*) A. Kant and S.-S. Lin, *J. Chem. Phys.*, 1969, **51**, 164; (*b*) T. L. Haslett M. Moskovits and A. L. Weitzman, *J. Mol. Spectrosc.*, 1989, **135**, 259.

39 O. Hübner, H.-J. Himmel, L. Manceron and W. Klopper, *J. Chem. Phys.*, 2004, **121**, 7195.

40 C. Cossé, M. Fouassier, T. Mejean, M. Tranquille, D. P. DiLella and M. Moskovits, *J. Chem. Phys.*, 1980, **73**, 6076.

41 See, for example: R. J. LeRoy and W.-H. Lam, *Chem. Phys. Lett.*, 1980, **71**, 544.

42 (*a*) H.-J. Himmel, L. Manceron, A. J. Downs and P. Pullumbi, *Angew. Chem.*, 2002, **114**, 829 (*Angew. Chem., Int. Ed.*, 2002, **41**, 796); (*b*) H.-J. Himmel, L. Manceron, A. J. Downs and P. Pullumbi, *J. Am. Chem. Soc.*, 2002, **124**, 4448; (*c*) A. Köhn, B. Gaertner and H.-J. Himmel, *Chem.–Eur. J.*, 2003, **9**, 3909.

43 H.-J. Himmel, O. Hübner, W. Klopper and L. Manceron, *Angew. Chem.*, 2006, **118**, 2865 (*Angew. Chem., Int. Ed.*, 2006, **45**, 2799).

44 C. A. Arrington, T. Blume, M. D. Morse, M. Doverstål and U. Sassenberg, *J. Phys. Chem.*, 1994, **98**, 1398.

45 J. R. Lombardi and B. Davis, *Chem. Rev.*, 2002, **102**, 2431.

46 (*a*) S. H. Wei, Z. Zeng, J. Q. You, X. H. Yan and X. G. Gong, *J. Chem. Phys.*, 2000, **113**, 11127; (*b*) J. Zhao, Q. Qiu, B. Wang, J. Wang and G. Wang, *Solid State Commun.*, 2001, **118**, 157.

47 H. Haouari, H. Wang, R. Craig, J. R. Lombardi and D. M. Lindsay, *J. Chem. Phys.*, 1995, **103**, 9527.

48 G. A. Ozin and D. F. McIntosh, *J. Phys. Chem.*, 1986, **90**, 5756.

49 For a three-membered ring, a_3 is 4, and for a linear molecule, a_3 is 3.

50 S. R. Wu, L. S. Desai and L.-S. Wang, *Phys. Rev. Lett.*, 1996, **76**, 212.

51 See, for example: (*a*) T. Yildirim, J. Íñiguez and S. Ciraci, *Phys. Rev. B: Condes. Matter Mater. Phys.*, 2005, **72**, 153403; (*b*) Q. Sun, Q. Wang, P. Jena and Y. Kawazoe, *J. Am. Chem. Soc.*, 2005, **127**,

14582; (*c*) Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben and S. B. Zhang, *Phys. Rev. Lett.*, 2005, **94**, 155504.

52 (*a*) F. W. S. Benfield, M. L. H. Green, J. S. Ogden and D. Young, *J. Chem. Soc., Chem. Commun.*, 1973, 866; (*b*) M. T. Anthony, M. L. H. Green and D. Young, *J. Chem. Soc., Dalton Trans.*, 1975, 1419; (*c*) J. A. Bandy, A. Berry, M. L. H. Green, R. N. Perutz, K. Prout and J.-N. Verpeaux, *J. Chem. Soc., Chem. Commun.*, 1984, 729.

53 Calculations were carried out using the SIESTA code (D. Sanchez-Portal, E. Artacho and J. M. Soler, *Int. J. Quantum Chem.*, 1997, **65**, 453) using local density approximation (LDA) with the parameterization of Ceperley-Alder (D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566) and a double ζ basis set of numerical orbitals with pseudo potentials replacing the atomic cores. Energies were corrected for basis set superposition errors (A. Bende, A. Vobok, G. J. Halasz and S. Suhai, *Int. J. Quantum Chem.*, 2001, **84**, 617). The bond dissociation energy for H_2 has been corrected to the experimental value.

54 S. Nagao, T. Kurikawa, K. Miyajima, A. Nakajima and K. Kaya, *J. Phys. Chem. A*, 1998, **102**, 4495.

55 V. M. E. Bates, G. K. B. Clentsmith, F. G. N. Cloke, J. C. Green and H. D. Ll. Jenkin, *Chem. Commun.*, 2000, **927**.