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On the reactivity of subvalent compounds of the Group 13 elements: exploration of the mechanism for the reactions of MCl (M = Ga or In) with dihydrogen to give H_2MCl†

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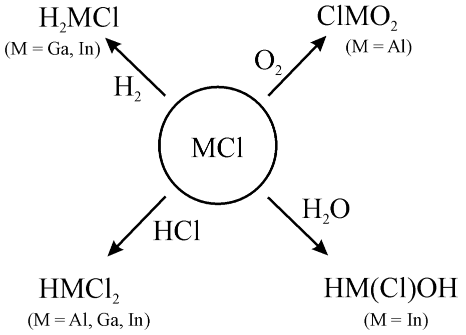
Motivated by recent experimental results on the reactivity of the diatomic Group 13 subhalogenides GaCl and InCl in solid Ar matrices, the mechanisms for spontaneous and photoactivated reactions of these species are studied herein by means of quantum chemical methods as applied to their reactions with H_2. The experimental results show that reaction with H_2 in a solid Ar matrix does not occur spontaneously, but requires photoactivation, the trivalent derivatives H_2MCl (M = Ga or In) being the detectable products. Furthermore, these results indicate that the photoactivated reactions proceed in a concerted fashion. Quantum chemical calculations are employed to explain the observed reactivities and provide quantitative estimates for the barriers to reaction. Calculations were performed for several electronic states and multiplicities of the $GaCl/H_2$ and $InCl/H_2$ systems likely to be of relevance and enable a detailed overall analysis of the reaction mechanisms to be made. The reactions of Group 13 subhalogenides with other molecules are anticipated to follow the same pattern and, thus, the results reported herein should be of relevance to the reactivity of Group 13 subhalogenides in general.

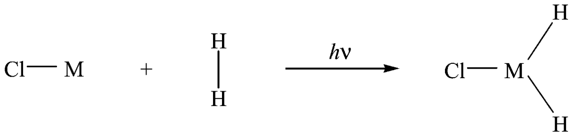
Introduction

Subvalent compounds of Group 13 elements excite attention not only because of their interesting electronic structure and bonding properties, the evaluation of which has been the topic of many studies in recent years,[1,2] but also because of the potential of these species as reagents in chemical reactions, once they can be produced on the preparative scale.[2] Compounds like BF or AlF, for example, invite comparison with the formally isoelectronic molecule CO,[3] and the hydrides $M(\mu\text{-}H)_2M$ and their isomers HMMH (M = Ga or In), which have both been characterized recently in matrix isolation experiments,[4] were investigated for possible M ··· M interactions or even M–M multiple bonding.[5] As to the applications of subvalent species in chemical synthesis, it has been shown that a variety of new cluster compounds can be formed by thermal decomposition of metastable solutions of subvalent Group 13 halides in an ether–THF mixture in the presence of suitable stabilizing ligands, for example.[2,6] Matrix isolation is now well established as an extremely useful technique for the exploration of the reactivities of such species, since the matrix offers the possibility of characterizing even highly reactive intermediates at leisure.[7] In addition, the matrix-isolated species are generally prevented from oligomerization or interaction with anything other than the reagent of interest (with the exception, of course, of the interaction with the matrix material, *e.g.* Ar). Therefore, the experiments give information not only about the properties of the observed products formed in the matrix, but also about the mechanism leading to their formation. For example, it has been shown on the basis of the experimental results that the concerted matrix reaction of Ga_2 with H_2 to give $Ga(\mu\text{-}H)_2Ga$ is subject to a barrier of about 30 kJ mol^{-1},[4] which enables the reaction to happen spontaneously for H_2, but not for D_2. With the aid of quantum chemical calculations, an almost complete analysis of the mechanism of this quite complicated reaction has been presented recently.[8] Among the matrix reactions of subvalent halides MX (M = Al, Ga or In; X = F, Cl or Br) that have been studied in the past are the reactions with HX (X = F, Cl or Br),[9,10] H_2,[10,11] O_2,[12] and H_2O[10] (see Scheme 1), which were all shown to lead directly to trivalent, monomeric Group 13 compounds. Strikingly, all attempts to generate H_2AlCl by reaction of AlCl with H_2 have failed so far, although this reaction is calculated to be exothermic by 75.6 kJ mol^{-1}. A detailed analysis of this reaction will be the topic of a separate report.[13]



Scheme 1 Scheme summarizing the reactivity of GaCl and InCl as observed in matrix isolation experiments.

As to the mechanisms, the experimental results provide the following information: (i) the reactions do not occur spontaneously, although they can be set in train by UV photolysis [see eqn. (1) for the case of reaction with H_2]; and (ii) the reactions occur in a concerted fashion.



$$Cl—M + H—H \xrightarrow{h\nu} Cl—MH_2 \quad (1)$$

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† Dedicated to Professor D. Fenske on the occasion of his 60th birthday.

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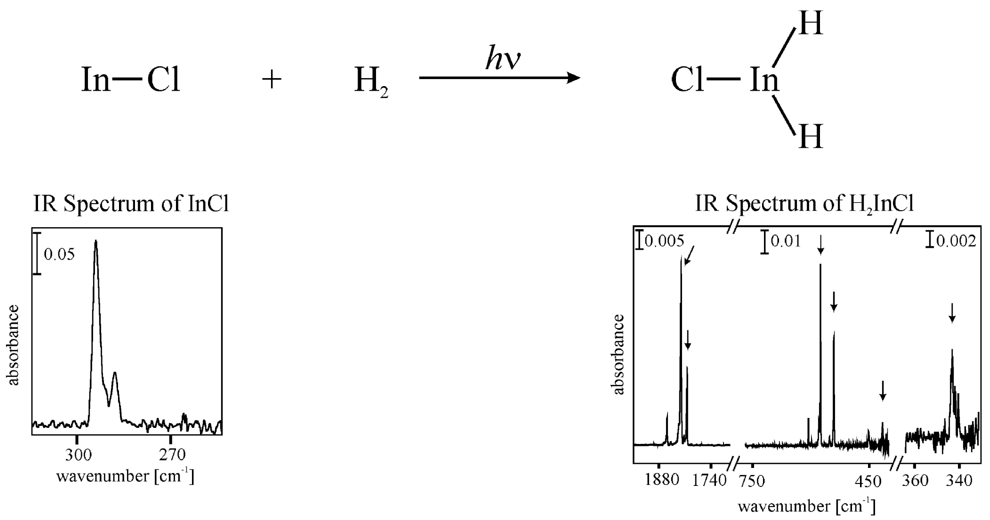

Fig. 1 IR spectra for the reaction of InCl with H_2 to give H_2InCl in a solid Ar matrix at 12 K.

As a first step in the evaluation of the mechanisms for the reactions of the subvalent halides MX (M = Ga or In), consideration is given here to the response of these species to H_2. Reactions with agents other than H_2 (*e.g.* H_2O or NH_3) are anticipated to follow a similar pattern and, thus, the results of this study should shed light on the reactivity of the MX species in general.

Experimental

Experimental details concerning the matrix studies can be found elsewhere.[10,14]

Ab initio MP2 and CCSD(T) calculations were carried out with the aid of the Gaussian 98 program package.[15] For the elements Al, Ga, Cl, and H, a 6-311+G(df,p)-type basis set was used, and an ECP46MWB basis set was used for In.[16] The reaction coordinate, defined as the separation of the M atom (M = Ga or In) in MCl from the centroid of the H_2 molecule (see below for more detailed information) was scanned and, for each step, the optimized energy and structure analysed. The calculations at each step were performed for different electronic states and multiplicities of relevance to simulate the effect of photoactivation. Although multireference methods were not used in this work, the results will be shown to give a satisfactory explanation for the experimentally achieved results of the reactions.

Results and discussion

Fig. 1 shows the characteristic IR absorptions of InCl and H_2InCl obtained for the reaction of InCl with H_2 in a solid Ar matrix. It has already been shown in detail previously how the spectra together with the results of quantum chemical calculations, resulted in the identification and characterization of the product, the In(III) species H_2InCl.[10] All six vibrational fundamentals of this planar molecule (C_{2v} symmetry) have been traced (see labeled absorptions in the IR spectrum contained in Fig. 1). They are located at 1804.0 [$\nu_1(a_1)$], 575.8 [$\nu_2(a_1)$], 343.4 [$\nu_3(a_1)$], 541.4 [$\nu_4(b_1)$], 1820.3 [$\nu_5(b_2)$], and 415.7 cm^{-1} [$\nu_6(b_2)$]. The identification and characterization of the reaction product being well established, the focus now lies on the exploration of the reaction mechanism leading to it. The strong absorption due to the stretching fundamental of the InCl monomer found in the IR spectrum taken upon deposition of a matrix containing InCl and H_2 in an excess of Ar was observed to decay upon exposure of the matrix to broad-band UV-visible photolysis ($200 < \lambda < 800$ nm). At the same time, the spectrum evidenced the appearance of the absorptions due to H_2InCl. It can thus be concluded that the reaction does not occur spontaneously, but requires photoactivation. Experiments were also conducted with D_2, HD, and equimolar mixtures of H_2 and D_2. In the experiments using equimolar mixtures of H_2 and D_2, only H_2InCl and D_2InCl, but *not* H(D)InCl, were found to be formed upon photolysis, indicating that the reaction occurs in a concerted fashion. Similar conclusions can be drawn from the experimental results obtained for the system $GaCl/H_2$.[11]

While the reaction of GaCl with H_2 (eqn. 3) is calculated to be weakly exothermic by −11.3 kJ mol^{-1}, the reaction of InCl (eqn. 4) is calculated to be endothermic by +59.0 kJ mol^{-1}. Thus, at least in the case of the $InCl/H_2$ system, the barrier to reaction has to be considerable to prevent the product from decomposing back to InCl and H_2 immediately after it has been formed. As already mentioned, up to now, the Al homologue H_2AlCl has escaped detection, although eqn. 2 is exothermic by some −75.6 kJ mol^{-1}.[13]

$$\mathrm{AlCl}\,(^1\Sigma_g) + \mathrm{H_2} \xrightarrow[-75.6\ \mathrm{kJ\,mol^{-1}}]{h\nu} \mathrm{H_2AlCl}\,(^1A_1) \qquad (2)$$

$$\mathrm{GaCl}\,(^1\Sigma_g) + \mathrm{H_2} \xrightarrow[-11.3\ \mathrm{kJ\,mol^{-1}}]{h\nu} \mathrm{H_2GaCl}\,(^1A_1) \qquad (3)$$

$$\mathrm{InCl}\,(^1\Sigma_g) + \mathrm{H_2} \xrightarrow[+59.0\ \mathrm{kJ\,mol^{-1}}]{h\nu} \mathrm{H_2InCl}\,(^1A_1) \qquad (4)$$

In the following, the energies and structures for the systems $GaCl/H_2$ and $InCl/H_2$ are discussed as a function of a reaction coordinate, *r*, which was chosen to be the separation of the M atom of MCl from the centroid of the H_2 molecule (see Fig. 2).

Fig. 2 Definition of the reaction coordinate *r* used in the calculations as the distance between the M atom (M = Ga or In) in MCl and the centroid of the H_2 molecule.

The calculations were firstly employed to satisfactorily explain the observation that an MCl (M = Ga or In) molecule does not react spontaneously with H_2, and to establish quantitative estimates for the barriers to reaction of the ground state molecules. Fig. 3 shows the potential energy as a function of *r* for the approach of GaCl [Fig. 3(a)] and InCl [Fig. 3(b)] in its singlet electronic ground state ($^1\Sigma_1$) towards H_2. The H–H and Ga–Cl distances are plotted in Fig. 4(a) and (b) for the reaction of GaCl with H_2; the corresponding distances for $InCl/H_2$ follow the same pattern. A significant repulsive interaction between MCl and H_2 commences for values of the reaction coordinate smaller than about 3.5 Å. For values of *r* smaller than 2.5 Å, the energy rapidly increases for the system in its $^1A_1$ electronic state

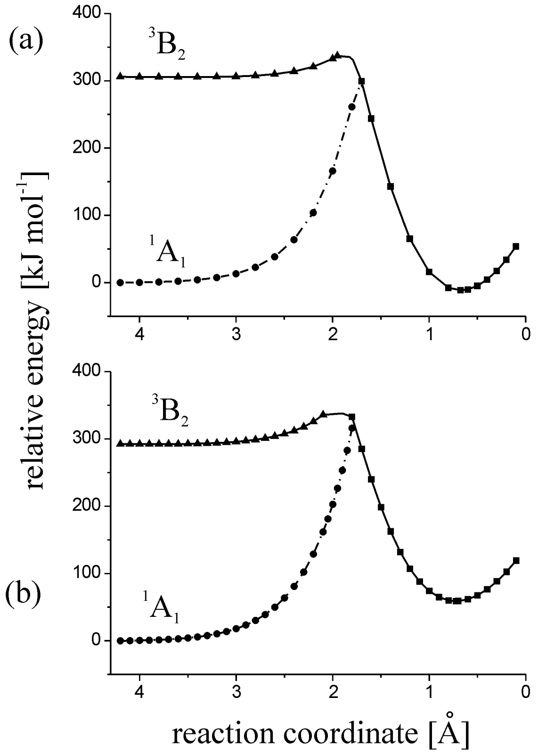

Fig. 3 Plots showing the optimized potential energy relative to the educts as a function of the reaction coordinate for the reaction between H_2 and (a) GaCl and (b) InCl in their $^1\Sigma$ electronic ground states and $^3\Pi$ electronic states to give H_2GaCl and H_2InCl, respectively.

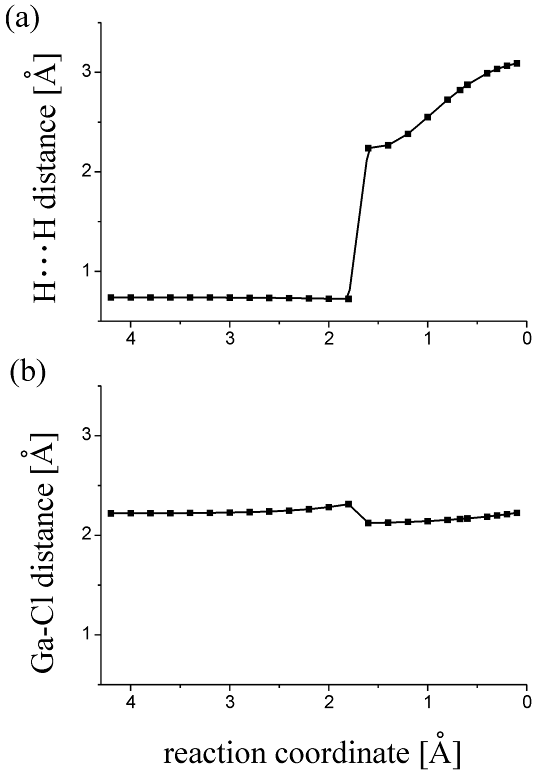

Fig. 4 Plots showing the H ··· H and Ga–Cl distances as a function of the reaction coordinate for the reaction between GaCl ($^1\Sigma$) and H_2.

and electron configuration . . .$a_1^2b_2^2b_1^2a_1^2$. For values of *r* smaller than 1.7 and 1.8 Å for GaCl/H_2 and InCl/H_2, respectively, another configuration (. . .$a_1^2b_2^2b_1^2b_2^2$) is energetically preferred. The transition state is thus reached for *r* values of 1.7 and 1.8 Å for GaCl and InCl, respectively, and at this point the electronic state changes from . . .$a_1^2b_2^2b_1^2a_1^2$ to . . .$a_1^2b_2^2b_1^2b_2^2$. As in the reaction of Ga atoms with H_2, which has previously been examined, the barrier is caused by rehybridization.[8,17] Concomitantly, the H–H distance increases dramatically at this point [see Fig. 4(a)]. At 295 and 320 kJ mol^{-1} for GaCl/H_2 and InCl/H_2, respectively, the barriers for both reactions under consideration are too high to allow them to occur spontaneously, whether in an inert gas matrix or in the gas phase at reasonable temperatures. The energy curve calculated for the configuration . . .$a_1^2b_2^2b_1^2b_2^2$ leads directly to the product H_2MCl in its global minimum structure, which is characterized by *r* values of 0.674 and 0.724 Å, M–H distances of 1.565 and 1.696 Å, H ··· H distances of 2.823 and 3.067 Å, and M–Cl distances of 2.163 and 2.328 Å for GaCl and InCl, respectively.

We now shift our attention to the effect of photoactivation. Obviously, the UV radiation used in the experiments does not have sufficient energy to cause excitation of the H_2 molecule. Therefore, there has to be an electronic state of the MCl monomer which is accessible through photolysis in the range $\lambda = 200$–800 nm. Fig. 5(a) shows the frontier orbitals of GaCl.

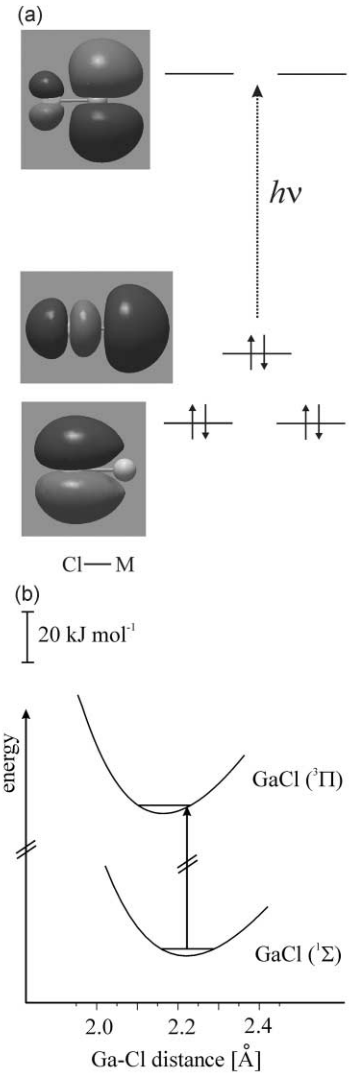

Fig. 5 (a) Frontier orbitals of GaCl ($^1\Sigma$). (b) Potential energy curves calculated for GaCl in its $^1\Sigma$ electronic ground state and its $^3\Pi$ excited state.

The HOMO exhibits σ symmetry, and the LUMO π symmetry. Photolysis is most likely to cause excitation of one electron of the HOMO into the LUMO, resulting in a species exhibiting a $^3\Pi$ electronic state. According to the calculations, the energy differences between the singlet electronic ground states and the excited triplet states amount to 305.9 and 292.4 kJ mol^{-1} (391 and 410 nm) for GaCl and InCl, respectively. Thus, the $^3\Pi$ electronic state should be accessible through photolysis. The M–Cl

Table 1 M–Cl, M–H, and H · · · H distances (M = Ga or In) for the reactants and products (in Å) of the reactions studied in this work and computed reaction energies (in kJ mol^{-1})

				Reaction energy	
	M–Cl	M–H	H · · · H	MP2	CCSD(T)
H_2			0.738		
GaCl ($^1\Sigma$)	2.221				
GaCl ($^3\Pi$)	2.164				
H_2GaCl ($^1A_1$)	2.163	1.565	2.823		
GaCl ($^1\Sigma$) $\longrightarrow$ GaCl ($^3\Pi$)				+305.9	+319.9
GaCl ($^1\Sigma$) + $H_2 \longrightarrow H_2$GaCl ($^1A_1$)				−11.3	−6.1
GaCl ($^1\Pi$) + $H_2 \longrightarrow H_2$GaCl ($^1A_1$)				−317.2	−326.0
InCl ($^1\Sigma$)	2.414				
InCl ($^3\Pi$)	2.330				
H_2InCl ($^1A_1$)	2.328	1.696	3.067		
InCl ($^1\Sigma$) $\longrightarrow$ InCl ($^3\Pi$)				+292.4	+309.2
InCl ($^1\Sigma$) + $H_2 \longrightarrow H_2$InCl ($^1A_1$)				+59.0	+66.1
InCl ($^1\Pi$) + $H_2 \longrightarrow H_2$InCl ($^1A_1$)				−233.4	−243.1

distances decreases from 2.221 and 2.414 Å for the $^1\Sigma$ states to 2.164 and 2.330 Å for the $^3\Pi$ states of GaCl and InCl, respectively. The HOMO orbital can be described as a combination between the s valence orbital at the M atom (lone pair) and a p orbital with a lower contribution centered at the Cl atom. The LUMO mainly consists of an empty p orbital at the M atom. The HOMO is certainly more antibonding with respect to the M–Cl bond than the LUMO. Therefore, the M–Cl bond distance is reduced in the triplet excited state in comparison to the singlet electronic ground state. Calculations were also performed using the CCSD(T) method. Using this method, we obtained energy differences between the $^1\Sigma$ and $^3\Pi$ states of 319.9 kJ mol^{-1} for GaCl and 309.2 kJ mol^{-1} for InCl, in fair agreement with the energy differences computed with MP2.

To more accurately simulate the effect of photolysis, the potential energy curves for GaCl in both its $^1\Sigma$ electronic ground state and in its $^3\Pi$ excited electronic state were calculated, the results being shown graphically in Fig. 5(b). The potential energy curve for Ga–Cl bond elongation is rather flat for distances close to the energy minimum distances. Vertical excitation of an electron from the electronic ground state leads directly into the zero-point energy level of the GaCl ($^3\Pi$) potential energy curve.

With the effects of photolysis on the isolated MCl molecules being established, the potential energy curve for the approach of the excited MCl molecule towards H_2 was calculated. The reaction coordinate was again chosen to be the separation of the M atom in MCl from the centroid of the H_2 molecule. The results of these calculations are included in Fig. 3. It is clearly evident from this plot that the repulsive interaction between MCl in its $^3\Pi$ electronic state and H_2 is now much weaker than it is for the approach of the MCl molecule in its $^1\Sigma$ ground state, most likely because of a small but attractive interaction between MO 25 with π symmetry [see Fig. 5(a)], now containing one electron, and the σ* orbital of H_2. On the other hand, the repulsive interaction of MO 24 (σ symmetry) with the frontier orbitals of H_2 is reduced. The energy curves calculated for the approach of GaCl and InCl molecules in their $^3\Pi$ electronic states towards H_2 (symmetry of the GaCl/H_2 or InCl/H_2 systems: $^3B_2$) intersect at 1.8 and 1.9 Å, respectively, those derived for the systems in their singlet states and . . .$a_1{}^2b_2{}^2b_1{}^2b_2{}^2$ ($^1A_1$) configurations, leading directly to the products in their $^1A_1$ electronic ground states. At this point, the chances for triplet–singlet intersystem crossing should be increased. It has been shown previously that Ar is an efficient quenching material.[8,18] Therefore, it appears reasonable to believe that somewhere around this intersection point, the molecule changes from a triplet to a singlet electronic state, although this means a forbidden intersystem crossing.[19] In total, this process results in barriers to reaction of not more than 20 and 35 kJ mol^{-1} for M = Ga and In, respectively. Bearing in mind the additional energy provided by the differences between the zero-point energies of the reactants on the one hand and the product or the transition state on the other,[20] and with due allowance for the usual amount of calculational inaccuracy (especially as regards the singlet–triplet energy gap), the calculations argue for spontaneous reaction of excited MCl molecules with H_2, in agreement with what is observed experimentally.

Conclusions

A combination of hard experimental facts and quantum chemical calculations were used as a basis for a detailed evaluation of the mechanism of the reaction between a Group 13 subhalide (GaCl or InCl) and H_2 in a solid Ar matrix. Table 1 summarizes the bond distances and reaction energies for the species and reactions addressed in this work. Experimental and quantum chemical results agree that the reactions of the subhalides in their electronic ground states ($^1\Sigma$) are subject to substantial barriers (295 and 320 kJ mol^{-1} for GaCl/H_2 and InCl/H_2, respectively), preventing the reaction from proceeding spontaneously. These barriers are caused by rehybridization effects; at the transition state, the electronic configuration changes from . . .$a_1{}^2b_2{}^2b_1{}^2a_1{}^2$ to . . .$a_1{}^2b_2{}^2b_1{}^2b_2{}^2$ and the H · · · H distances increase dramatically. Reactions can, however, be set in train by photolytic activation of the subhalides, resulting in population of the $^3\Pi$ electronic state. The calculations suggest that reaction of MCl in its $^3\Pi$ electronic state with H_2 to give singlet H_2MCl ($^1A_1$) is subject to only a small barrier, allowing this process to occur spontaneously, although it is spin-forbidden, in an Ar matrix where quenching of the electronic state is likely to occur rapidly and efficiently. An alternative explanation is that spin–orbit interaction occurs. Reactions with molecules other than H_2 are anticipated to follow a similar pattern and, therefore, these results should be of relevance to the reactivity of these species in general.

Acknowledgements

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19 Another possible explanation for the triplet–singlet transition is the presence of substantial spin–orbit coupling. The $^3B_2$ state splits into three components with A_1, A_2 and B_1 symmetry and, thus, interaction with the singlet state can occur through the A_1 component.

20 Because of the differences in the zero-point energies of the reactants and the product, the intersection point between the potential energy curves for the $^3B_2$ electronic state and that for the $^1A_1$ electronic state leading directly to the product is shifted towards higher values of the reaction coordinate. At the same time, the energy barrier shrinks somewhat (accounting for an additional 5–10 kJ mol^{-1} of energy).