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On the assistance of the heterolytic cleavage of H_2 by an external base: a theoretical assessment†

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The assistance, by a Lewis base, of the heterolytic cleavage of co-ordinated H_2 during a σ-bond metathesis process involving late transition-metal complexes has been analysed with the aid of *ab initio* Møller–Plesset second-order perturbation (MP2) calculations on the $[Rh(H_2)(PH_3)_2(HCO_2)]\cdots NH_3$ model system. It is found that both the kinetics and the thermodynamics of the metathesis process are favoured in the presence of the amine. The structures of the various intermediates and transition states, which show how the amine mediates the proton transfer, are discussed.

σ-Bond metathesis reactions of H_2 taking place through a four-centre transition state are now gaining wide acceptance for complexes of electron-poor transition metals or of early f-block elements.[1,2] In these reactions a dihydrogen complex is believed to be a precursor intermediate. Since the protons of such complexes are known to be more acidic than those of free H_2,[1a,3] the heterolytic cleavage of the H−H bond can be accelerated by bases such as amines.[4–6] In addition to these reactions involving early transition-metal complexes there have been some more recent experimental[7] and theoretical[8] findings which suggest that σ-bond metathesis reactions could also occur with middle or late transition-metal complexes. Here too the presence of a base seems to be beneficial.[4] However, the intimate mechanism of this assistance has not yet been ascertained. Quite recently we reported, on the basis of theoretical calculations, that a σ-bond metathesis reaction of H_2 with a rhodium(I) formate intermediate [reaction (1)] could bypass a

$$[Rh(PH_3)_2(HCO_2)] + H_2 \longrightarrow [RhH(PH_3)_2(HCO_2H)] \quad (1)$$

sequence of Rh^{I}–Rh^{III} oxidative-addition/reductive-elimination steps [reactions (2) and (3)] in the transformation of $H_2 + CO_2$

$$[Rh(PH_3)_2(HCO_2)] + H_2 \longrightarrow [Rh(H_2)(PH_3)_2(HCO_2)] \quad (2)$$

$$[Rh(H_2)(PH_3)_2(HCO_2)] \longrightarrow [RhH(PH_3)_2(HCO_2H)] \quad (3)$$

into formic acid homogeneously catalysed by a hydrido(diphosphine)rhodium(I) complex.[9] Particularly the energy barrier for the [2 + 2] addition of H_2 to the Rh−O bond of the three-co-ordinate d^8 $[Rh(PH_3)_2(HCO_2)]$ intermediate, reaction (1), was computed to be smaller than the barrier for the reductive elimination of HCO_2H from $[RhH_2(PH_3)_2(HCO_2)]$, reaction 3: 14.8 instead of 24.7 kcal mol^{-1}, QCISD(T)//MP2 values.[9b] It was also shown that the dissociation of the incipient H^+ was triggered by the p lone pair on the formate ligand. This lone pair could therefore be considered as playing the same role as an external base.[9b] Interestingly, experimental investigations of this catalytic reaction had indicated that the hydrogenation is enhanced by the presence of an amine in the reaction cell.[10] Among the various roles that the amine could play in such a multistep catalytic process, one might be to accelerate further the heterolytic splitting of H_2 by mediating proton transfer between the co-ordinated H_2 and the ancillary ligand. The results that we report here pertain to this mechanistic issue. They have also a broader scope since they can be applied to this whole class of metathesis reactions. They show how an additional Lewis base can indeed act as a relay, by first abstracting a proton from the co-ordinated H_2 to form an ion pair from which the proton is subsequently released to the ancillary ligand.

Results and Discussion

The calculations were carried out at the MP2 level ‡ starting from the model system *cis*-$[Rh(H_2)(PH_3)_2(HCO_2)] + NH_3$ **1** using the GAUSSIAN 92 program system.[11] The geometries were optimized by the gradient technique with the all-electron basis set that we previously used.[9b] This basis set was made of a (15, 10, 8) ⟨6, 4, 4⟩ basis §'[12] for Rh, of the standard (10, 6) and (9, 5) basis sets of Huzinaga[13a] contracted into ⟨4, 3⟩ and ⟨3, 2⟩ for the phosphorus, carbon and oxygen atoms respectively. The hydrogen atoms were described by a (4) ⟨2⟩ basis set.[13b] Polarization functions (of exponent 0.63, 0.95, 1.33 and 0.8 for C, N, O and H respectively) were added to NH_3 and to the ligands atoms (with the exception of the two spectator PH_3 ligands which were left unpolarized). All stationary points (intermediates and transition states) were characterized by a numerical frequency analysis. Our previous calculations have shown that the MP2//MP2 level of calculation seemed appropriate for this type of reaction.[9b] In particular, improving the level of the calculation of the energies to the QCISD(T) level did not modify substantially the energy differences computed at the MP2 level.

Scheme 1 summarizes the computed geometries and energies of the stationary points (intermediates and transition states) along the reaction path of the σ-bond metathesis reaction assisted by NH_3. The corresponding energy profile is displayed in Fig. 1 and compared to that obtained without the assistance of the amine.¶

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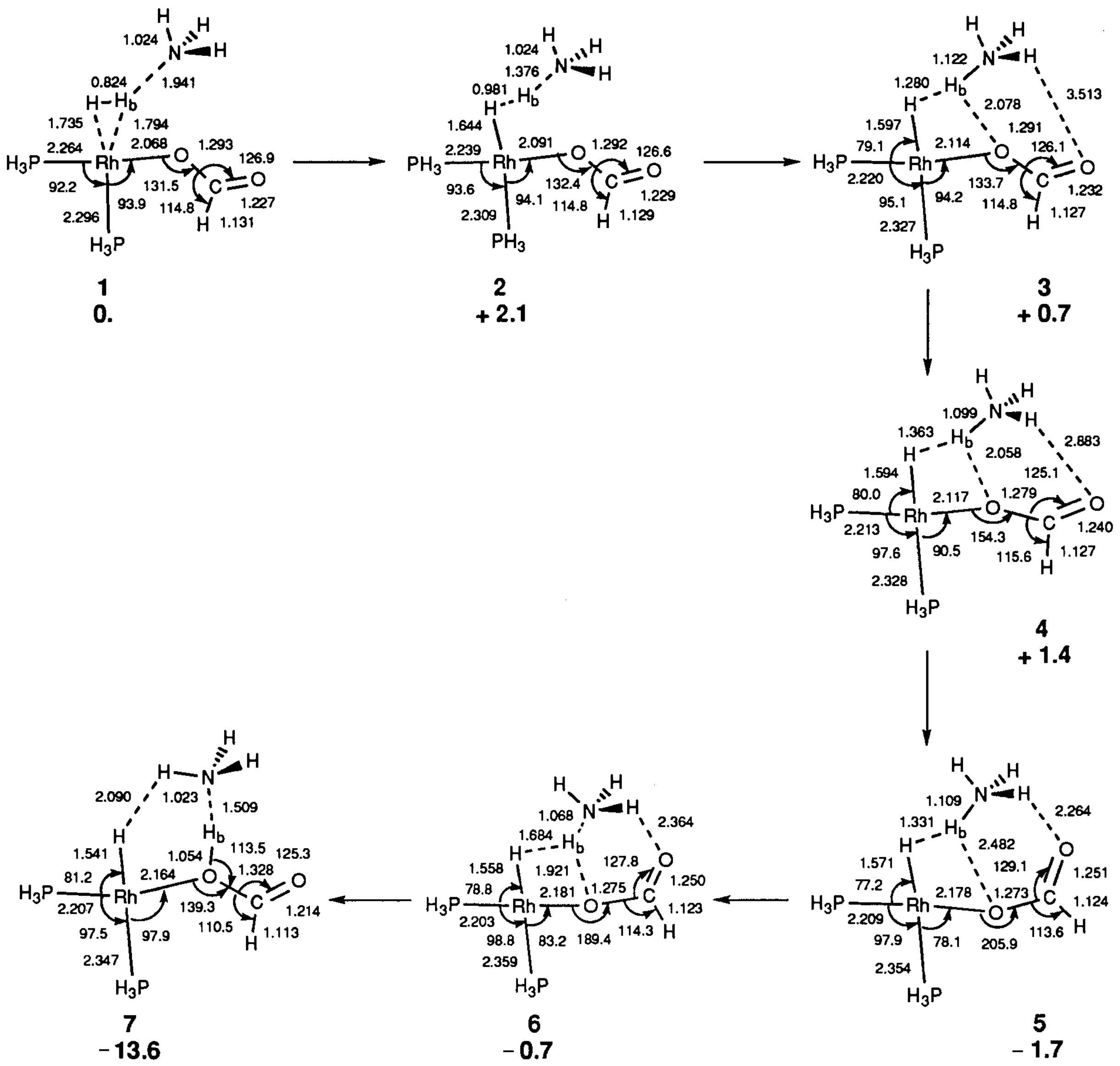
† *Non-SI units employed:* cal = 4.184 J, au ≈ 4.36×10^{-18} J.

‡ Using the six cartesian d functions and the frozen-core approximation.

§ The original (15, 9, 8) basis set was modified by the addition of a p function of exponent 0.15.

¶ The zero-point energies are not taken into account. The corresponding MP2 total energies (in au) are: $[Rh(H_2)(PH_3)_2(HCO_2)]$, −5555.9701; NH_3, −56.3603; **1**, −5612.3479; **2**, −5612.3445; **3**, −5612.3468; **4**, −5612.3456; **5**, −5612.3506; **6**, −5612.3490; **7**, −5612.3696; $[RhH(PH_3)_2(HCO_2H)]$, −5555.9722.



Scheme 1 The MP2 optimized geometries and relative energies (with respect to system **1**, in kcal mol^{-1}) of the intermediates and transition states along the reaction path of the σ-bond metathesis in the presence of the amine. Bond distances and angles are in Å and ° respectively

One first notes in the reactant **1** a stabilizing interaction between NH_3 and the co-ordinated H_2, through the hydrogen atom adjacent to the formate ligand. This hydrogen is the most acidic in the $[Rh(H_2)(PH_3)_2(HCO_2)]$ system. It has a charge of +0.16e (according to a Mulliken population scheme), whereas the other hydrogen atom is slightly negative (−0.03e). The interaction between $[Rh(H_2)(PH_3)_2(HCO_2)]$ and NH_3 is quite weak and mostly electrostatic. The H–H bond is only slightly lengthened, from 0.798 Å in the absence of NH_3 to 0.824 Å in **1** and the binding energy between NH_3 and $[Rh(H_2)(PH_3)_2(HCO_2)]$ is computed to be 1 kcal mol^{-1} when the basis set superposition error (BSSE) is taken into account through the counterpoise method.[14] Since the computed BSSE is most likely overestimated by 2 to 3 kcal mol^{-1},[||] the stabilization of the dihydrogen complex by the amine is probably of the order of 3 to 5 kcal mol^{-1}. The N···H distance amounts to 1.941 Å. This value is in the range expected for a hydrogen bond involving NH_3 and a hydrogen atom with a partial positive charge, as for instance in $H_3N\cdots HOH$.[16]

In the product **7**, NH_3 interacts primarily with the formic acid which is itself co-ordinated to the Rh atom. The N···H distance is 1.509 Å. One might argue that this computed value is too short due to some calculational artefact. Pilot calculations carried out on the metal-free adduct $HCO_2H\cdots NH_3$ yield a value of 1.702 Å when using the same basis set, and a value of 1.754 Å (*i.e.* a lengthening of only 0.052 Å) with the much larger 6-311+G** basis set. In fact one finds in **7** an additional attractive interaction between the hydride and one hydrogen atom of NH_3: the H···H distance is 2.09 Å and there is clearly some tilting of one N–H bond towards the hydride (the angle made by this bond with the O–H···N axis is 105.8°, whereas the two other N–H bonds make an angle of 112.9°). This intermolecular N–H···H–Rh interaction is very similar to the one found in the crystal structure of $[ReH_5(PPh_3)_3]\cdot$indole C_8H_6NH where the H···H distance is 2.212 Å.[17] It probably accounts for the short N···H distance. One should nevertheless note that this additional interaction is linked to our choice of NH_3 as a model of the amine. A tertiary amine such as NEt_3 would interact only through its lone pair and would probably give a longer N···H distance.

Two local minima, **3** and **5**, have been found for the RhH-

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[||] The BSSE in system **1** is computed to be 10.0 kcal mol^{-1}. Related calculations involving weak interactions of an external molecule with the co-ordination sphere of a transition-metal complex show an increase of the interaction energy (corrected from the BSSE) of about 2 kcal mol^{-1} when going to a full double-zeta + polarization functions basis set.[15] Note also that the effect of the BSSE on the proton transfer *within* the composite system is most likely at least an order of magnitude smaller. This is confirmed by the value of the BSSE *difference* between **7** and **1** which is computed to be only 0.5 kcal mol^{-1}.

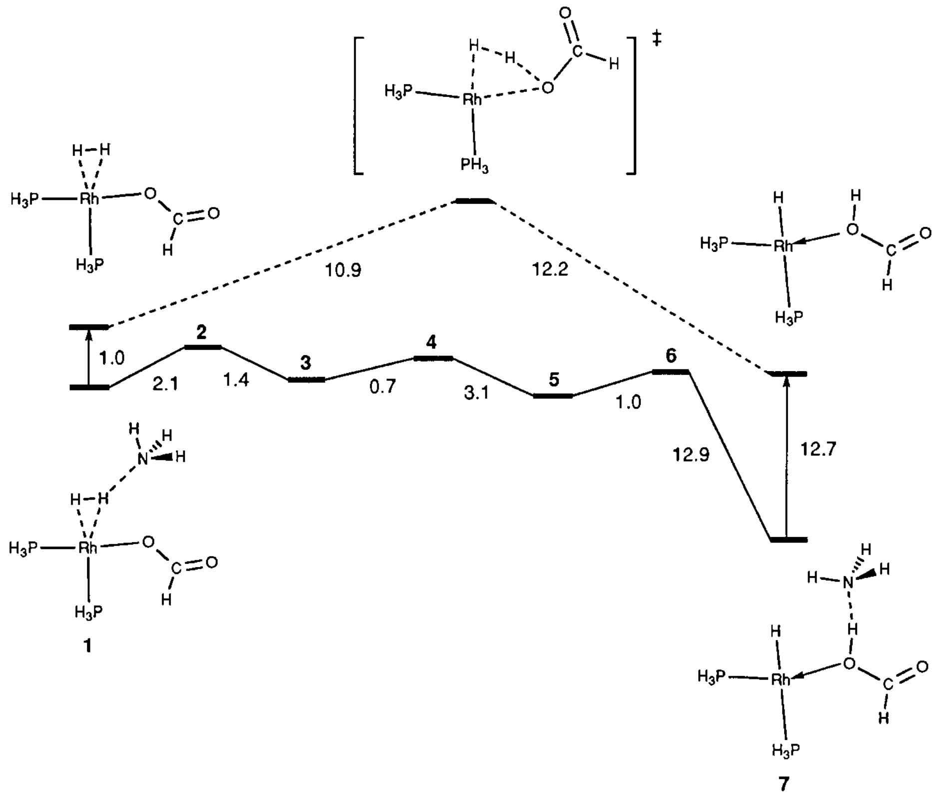

Fig. 1 The MP2 potential-energy profiles (in kcal mol^{-1}) of the assisted (——) and non-assisted (-----) σ-bond metathesis reaction

$(PH_3)_2(HCO_2)^- \cdots NH_4^+$ ion pair. In this ion pair the ammonium cation can interact with both the hydride and the formate ligand. The interaction with the hydride is the strongest one: the $O \cdots H$ distance between the oxygen atom which is bound to Rh and the ammonium proton is quite large, much larger than the one computed *e.g.* for either $NH_4^+ \cdots H_2O$[18] or $CH_3^+ \cdots CH_3OH$.[19] In fact **3** rearranges to **5** (*via* the transition state **4**) in order to achieve additional electrostatic attractions between the carbonyl oxygen atom and the other hydrogen atoms of NH_3. Similar electrostatic arguments, based on the greater proton affinity of the carbonyl oxygen atom of formic acid, have been used to account for the conformation of the $HCO_2H \cdots H_3O^+$ adduct.[20] Species **5** is slightly more stable than **3**, by 2.4 kcal mol^{-1}. The energy barrier between these two intermediates is also very small, see Scheme 1.

It is interesting to compare the geometry of the transition states **2** and **6** with that computed for transition states for proton transfer in various organic or inorganic compounds. Both **2** and **6** are characterized by relatively short $N \cdots H_b$ distances, H_b being the transferred proton. The value computed for **2**, 1.376 Å, is however somewhat longer than that of 1.31 Å found at the MP2 level for the proton transfer between two NH_3 in $[N_2H_7]^+$.[18a] One may be more worried about the $N \cdots H_b$ distance in **6**, 1.068 Å, since it is even shorter than in **5**. However, the $H_b \cdots H$ and $H_b \cdots O$ distances vary as expected between **5** and **6**. $H_b \cdots H$ is lengthened and $H_b \cdots O$ is shortened. The eigenvector associated with the imaginary frequency is consistent with these variations and an optimization for a true energy minimum starting from a very slightly modified geometry of **6** led directly to **7**. The step **5** ⟶ **6** ⟶ **7** is exothermic by about 12 kcal mol^{-1} and one therefore expects the transition state to be reactant-like. Moreover the proton displacement in transition states for proton transfer between two bases is known to be coupled with the internuclear distance between the two bases which in turn is related to other structural restraints of the entire system.[20,21] Thus the short $H_b \cdots N$ distance in **6** results most probably from the need of NH_4^+ to keep as long as possible on the reaction path its attractive electrostatic interactions with *both* oxygen atoms of the formate ligand. In agreement with this proposal one may note that the distance between the carbonyl oxygen atom and a non-reacting hydrogen atom is elongated by only 0.1 Å between **5** and **6**.

The most salient result of this study is that the two main steps of the process, *viz.* the capture of the proton by the amine from the co-ordinated H_2 (**1** ⟶ **2** ⟶ **3**) and its subsequent delivery to the co-ordinated formate ligand (**5** ⟶ **6** ⟶ **7**) are very easy: the corresponding energy barriers amount to 2.1 and 1.0 kcal mol^{-1}, see Fig. 1. The comparison with the reaction taking place in the absence of NH_3, which has an energy barrier of 10.9 kcal mol^{-1} (see Fig. 1), is the best indication that the assistance of the amine for the kinetics of the σ-bond metathesis process is quite efficient. The amine also assists the thermodynamics by stabilizing species **1** only weakly (see above) and **7** to a much larger extent. After correction from the basis set superposition error one gets a value of 12.7 kcal mol^{-1} for the interaction energy between NH_3 and $[RhH(PH_3)_2(HCO_2H)]$ in **7**. This value is somewhat greater than the value obtained for the metal-free adduct $HCO_2H \cdots NH_3$ 10.5 kcal mol^{-1} (after correction for the BSSE). Whether or not this is due to the co-ordination of HCO_2H to Rh and/or to the additional interaction of the hydride ligand with one hydrogen atom of NH_3 (see above) cannot be assessed precisely. Yet this quite large stabilization is certainly an important factor for the overall exothermicity of the process and for driving it to completion.

One may of course worry about the use of NH_3 as a model for the amine, since the amines that are known to accelerate the heterolytic cleavage of H_2 are usually tertiary amines, such as NEt_3. We have already stressed how some additional interactions of the hydrogen atoms of NH_3 may influence the geometry of species **7** or induce the rearrangement of **3** to **5**. These interactions should also contribute to the stabilisation of the transition state **6**. Thus the replacement of NH_3 by NEt_3 in our theoretical model would most likely suppress the rearrangement **3** ⟶ **4** ⟶ **5** from the reaction path. One would probably go directly from **3** to **7**, through a transition state perhaps higher in energy since it would be devoid of the stabilizing interactions betweeen the non-reacting hydrogen atoms and the carbonyl oxygen atom of **6**. On the other hand it is difficult, without carrying out calculations on the actual systems, to assess precisely the effect of this replacement on the *entire* energy profile. Factors other than electrostatic interactions (*e.g.* basicity of the amine, steric effects, solvent effects) may influence the proton-abstraction step and the proton-releasing step. They are not easy to estimate and their influence may be different in the two steps. On the basis of the relative gas-phase basicities of NH_3 and NEt_3, with the proton as the reference acid, one would expect the proton-abstraction step to be easier and the proton-releasing step to be more difficult in the case of NEt_3. However the magnitude and/or the order of base strength can change with the reference acid and more importantly with the solvent.**,[22] Thus the actual interactions of the amine with either the co-ordinated dihydrogen in **1** or with the co-ordinated formic acid in **7** may be quite different from the ones predicted on the basis of the usual gas-phase basicity scale.

Despite these limitations†† the present calculations show clearly the beneficial role of an external amine on both the kinetics and the thermodynamics of the heterolytic cleavage of dihydrogen complexes involved in σ-bond metathesis reactions.‡‡ They also provide a visualization of the corresponding mechanism. There is an obvious relationship to similar processes involving a base held in the vicinity of a M–H_2 unit by some arm,[7d,17,24,25] or an alcohol weakly interacting through its hydrogen atom with a hydride ligand.[26] Work along these lines for reactions of palladium-(II) and -(IV) complexes is currently underway.[27,28]

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** This is best seen through the comparison of the interaction of the amine with a proton and with formic acid. The protonation energy increases by 29.2 kcal mol^{-1} on going from NH_3 to NEt_3, whereas the stabilization by formic acid decreases by 0.9 kcal mol^{-1} [HF (Hartree–Fock)//HF values]. A theoretical treatment of the solvent effects on the proton affinities of methylamines, which accounts for their irregular ordering of basicity, has been performed recently.[23]

†† The non-inclusion of solvent effects in the calculations also prevents consideration for comparison of a channel that would deter the process from the σ-bond metathesis pathway. This channel would involve the dissociation of NH_4^+ from the intermediate **3**, thus leaving $[RhH(PH_3)_2(HCO_2)]^-$ as a product. The electrostatic interaction between these two ions, which are not solvated and of opposite charge, will be very strong, thus precluding any dissociation in the gas phase.[29]

‡‡ One may of course argue that the σ-bond metathesis process is no longer a genuine one. Its outcome corresponds however to a σ-bond metathesis. However since this reaction does not involve a four-centre transition state one cannot refer to it as a [2 + 2] process.

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