

FULL PAPER

The Amide Route in Imine Metathesis with Imidomolybdenum Catalysts: A Model DFT Study

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Abstract Gradient-corrected density-functional computations (BP86/ECP1 level) confirm the viability of the recently proposed reaction pathway for imine metathesis with imidomolybdenum(VI) species $[\text{Mo}(\text{NR})_2\text{L}_x]$ (e.g., $\text{L}_x = \text{Cl}_2, \text{DME}$; $\text{R} = t\text{Bu}$). In addition to a Chauvin-type [2+2] addition-elimination mechanism, model calculations for the $[\text{MoCl}_2(\text{NH})_2] + \text{NH}_3 + \text{CH}_2\text{NH}$ system corroborate the suspected involvement of amido intermediates such as $[\text{MoCl}_2(\text{NH})(\text{NH}_2)_2]$ and

$[\text{Mo}(\text{NHCH}_2\text{NH}_2)\text{Cl}_2(\text{NH})(\text{NH}_2)]$. Several catalytic cycles are characterised that differ in the stereochemistry of the ligands about Mo. The lowest computed rate-determining barriers are only a few kcal mol^{-1} higher than that obtained for the Chauvin-type mechanism in the $[\text{MoCl}_2(\text{NH})_2] + \text{CH}_2\text{NH}$ system via $[\text{Mo}(\text{NHCH}_2\text{NH})\text{Cl}_2(\text{NH})]$, provided the necessary H-atom transfers are catalysed efficiently by traces of base.

Keywords Metathesis, Homogeneous catalysis, Density functional calculations, Reaction mechanisms

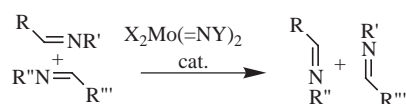
Introduction

Elucidation of reaction mechanisms in homogeneous catalysis is difficult, but may be rewarding when specific tailoring

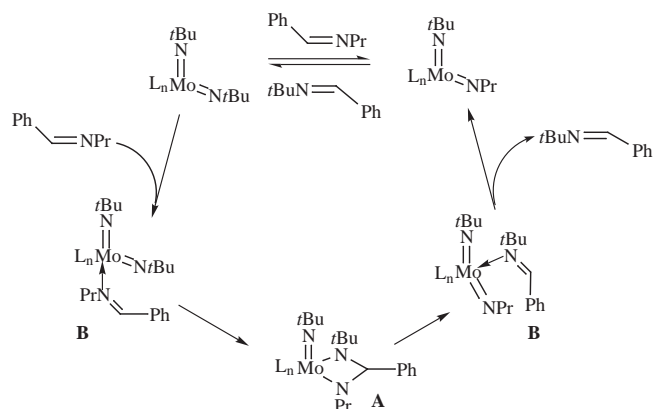
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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

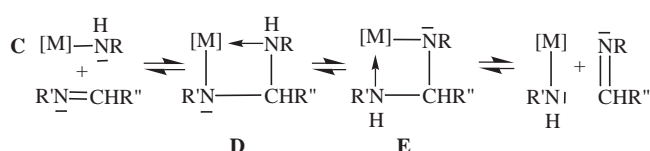
of activities or selectivities is sought. With the advent and establishment of the powerful tools of computational chemistry [1] (especially those based on quantum mechanics) important mechanistic information can now be obtained theoretically. In particular, mechanistic proposals, sometimes based on circumstantial evidence or on pure speculation, can be tested computationally and can either be corroborated or, if unsurmountable barriers are obtained, refuted. For instance, the recently reported imine metathesis promoted by imidomolybdenum(VI) catalysts [2] (Scheme 1) has initially been suggested to proceed, in analogy to the well-known olefin metathesis catalysed by related Mo complexes [3], via a Chauvin-type [2 + 2] addition-elimination



Scheme 1 Imine metathesis promoted by imidomolybdenum catalysts



Scheme 2 Proposed mechanism for imine metathesis based on a Chauvin-type [2 + 2] addition-elimination sequence



Scheme 3 Alternative mechanism for imine metathesis involving amido- rather than imidometal species

sequence involving diazametallacyclobutane [4] and imine Lewis-adduct intermediates (**A** and **B**, respectively, in Scheme 2).

A subsequent density-functional study for the model system $[\text{MoCl}_2(\text{NH})_2]$ (**1**) + CH_2NH [**5**] has confirmed the viability of such a mechanism by characterisation of the corresponding intermediates $[\text{Mo}(\text{NHCH}_2\text{NH})\text{Cl}_2(\text{NH})]$ (**2**) and $[\text{MoCl}_2(\text{NH})_2(\text{NHCH}_2)]$ (**3**), as well as the transition state between them (**TS23**). A notable rate-determining barrier has been computed, 23.1 kcal mol⁻¹, in apparent consistency with the modest catalytic activity, i.e. with the more drastic reaction conditions (higher temperature and longer reaction times) required for imine vs olefin metathesis.

Detailed kinetic studies of the imine-metathesis process with the Mo-based catalyst have proven to be difficult, presumably due to the occurrence of more than one pathway [6]. This conjecture has received support from results for a related Ta-based system, $[\text{TaCl}_2\text{Cp}^*(\text{NR})]$ [7]: the rate of imine metathesis has been found to depend decisively on the

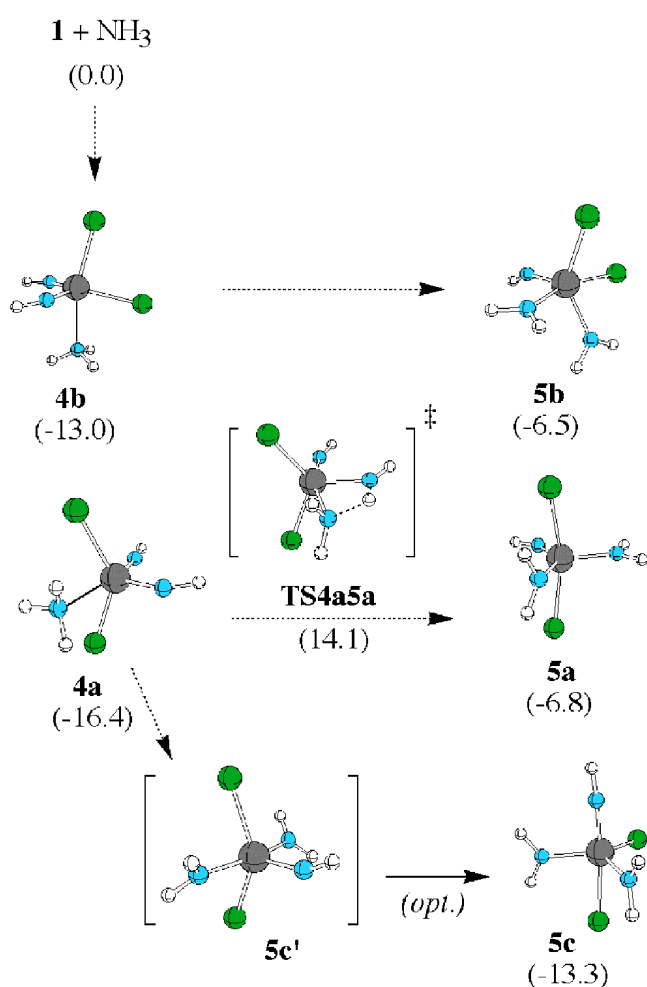


Figure 1 Initiation of the amide route: formation of the bis(amido) species **5** via the amine complexes **4** (in parentheses: energies in kcal mol⁻¹ relative to the reactants, BP86/ECPI + ZPE level)

amount of amine in the imine substrates (which is always present as contaminant). Therefore, the actual, active catalyst should arise from the reaction of the imidotantalum complex with amine, affording most probably an amidotantalum species (cf. **C** in Scheme 3). The key metathesis step of such a pathway has been suggested by Meyer and co-workers [7] to be the reversible formation of diazametallacyclobutane intermediates **D** and **E**, which differ from **A** by the presence of an additional H atom at one of the N donors. In order to achieve metathesis, this H atom must be transferred from the amine N atom to the amide N atom of the metallacycle.

Could such an amide-mediated mechanism also be competitive and operative in the imidomolybdenum system? A density-functional study is now presented for the model reaction of **1** with NH_3 (as parent amine) and for the involvement of the possible reaction products in subsequent metathesis reaction with imine, CH_2NH . Several possible path-

ways are considered, and indeed the lowest barriers are found to be comparable to those of the Chauvin mechanism *via* **2** and **3**.

Computational details

Density-functional theory (DFT) is now well established as a tool to compute geometries and energetics of transition-metal compounds reliably [8]. The same DFT-based methods and basis sets as in the previous study of the title reaction [5] have been employed, i.e. geometries have been fully optimised using the exchange and correlation functionals of Becke[9] and Perdew [10], respectively, together with a fine integration grid (75 radial shells with 302 angular points per shell), a relativistic MEFIT effective core potential with the corresponding [6s5p3d] valence basis for Mo [11], and standard 6-31G* basis set [12] for all other elements. This level is denoted BP86/ECP1. The nature of the stationary points has been verified by calculations of harmonic vibrational frequencies (none and one imaginary frequency for minima and transition structures, respectively), from which zero-point energies (ZPEs) have also been obtained. Geometries and energies (including ZPEs) are given as Supplementary Material. Unless otherwise noted, energies are reported relative to the isolated reactants at the BP86/ECP1 + ZPE level, i.e. including zero-point corrections. All computations have been performed with the Gaussian suite of programs [13].

Results and discussion

In the first step, **1** reacts with ammonia NH₃ under formation of Lewis-base complexes **4** (Figure 1). As with imine CH₂NH, complexation can occur either *trans* to a Cl ligand (**4b**) or, slightly lower in energy, *trans* to an imido moiety (**4a**). As expected, formation of the amine complex **4a** is computed to be more favourable than formation of the corresponding imine adduct ($\Delta E = -16.4$ vs -12.5 kcal mol⁻¹ [5], respectively). Hence, the Mo catalyst would indeed preferentially bind any amine present, rather than the imine substrates.

Conversion of the initial amine complex(es) to the proposed amido intermediates requires the transfer of a H atom from the amine to an imido ligand. The corresponding transition state for intramolecular H-transfer in **4a** has been located (TS4a5a, Figure 1). Due to the strain in the four-membered cyclic transition structure the barrier on the potential-energy surface (PES) is considerable, 30.5 kcal mol⁻¹ with respect to **4a**. However, this value certainly represents an upper limit since tunnelling (not accounted for in the present approach) would reduce the barrier significantly. Moreover, proton transfer can often be catalysed very efficiently by traces of Brønsted acids or, in the present case, Brønsted bases (amines and imines). It is therefore unclear at this point if this process would actually be rate-determining in the Mo system. In any event it is noteworthy that formation of the

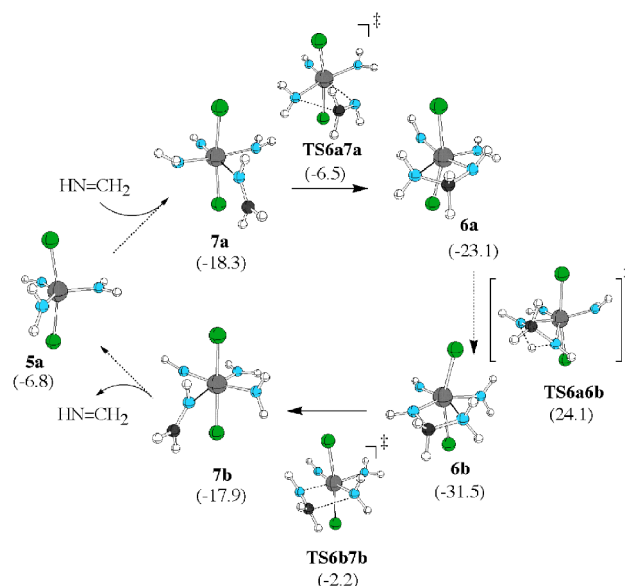


Figure 2 Catalytic cycle (path I) for imine metathesis involving bis(amide) **5a** (in parentheses: energies in kcal mol⁻¹ relative to the reactants, BP86/ECP1 + ZPE level)

bis(amide) **5a** from **4a** is computed to be endothermic by almost 10 kcal mol⁻¹ (Figure 1). A corresponding H transfer in **4b** (location of the transition structure not attempted) affords **5b**, slightly less stable than **5a**.

Finally, in **4a** an H atom can be transferred from the NH₃ ligand to the imino group in *trans* position. This process would have to take place inter-, rather than intramolecularly or under acid/base catalysis. Upon optimisation of the presumed product of such a transfer, **5c'** in Figure 1, **5c** was obtained. The coordination geometry in **5a** and **5b** could be described as trigonal bipyramidal (tbp) and square pyramidal (sp) with the imido group in equatorial and apical positions, respectively. In contrast, **5c** adopts a tbp conformation with the imido ligand in axial position and is by far the most stable of these isomers. This result comes to a surprise since in pentacoordinate complexes, ligands with the strongest *trans*-effect [14] tend to avoid sites in direct opposition to other ligands [15]. Formation of **5c** from **4a** is only slightly endothermic (by ca. 3 kcal mol⁻¹) and should be easily achievable under the experimental conditions.

Starting from **5a**, the most stable isomer accessible *via* intramolecular H-transfer, a catalytic cycle (path I) was computed according to Scheme 3. Both envisaged intermediates **D** and **E** are indeed true minima on the PES (**6a** and **6b**, Figure 2). In both metallacycles, the Mo-N(H₂R) distances are significantly longer than the Mo-N(HR) bond lengths (e.g. 2.500 vs 1.982 Å in **6b**); **6a** and **6b** should therefore be described as intramolecular Lewis-base adducts, rather than as true diazametallacyclobutanes [16].

Dissociation of the imine from **6a** and **6b** does not afford the diamide **5a** directly, but proceeds *via* the imine Lewis

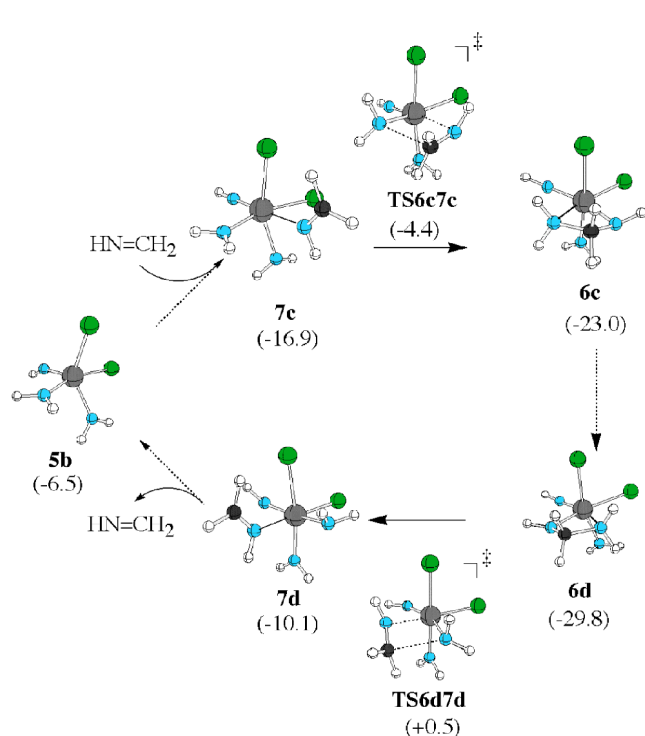


Figure 3 Alternative catalytic cycle (path II) for imine metathesis involving bis(amide) **5b** (in parentheses: energies in kcal·mol⁻¹ relative to the reactants, BP86/ECPI + ZPE level)

adducts **7a** and **7b**, via the transition structures **TS6a7a** and **TS6b7b**, respectively. Little activation (other than the endothermicity of the process) is expected for imine dissociation from **7a** and **7b** to the common products **5a** + CH₂NH. A preliminary search for the corresponding transition states indicated that their energies on the potential energy surface would be similar to or even slightly lower¹⁷ than those of **5a** and CH₂NH combined. Formation or dissociative decay of the Lewis adducts **7x** should therefore not be rate-determining and no attempts have been made to compute the corresponding barriers in the catalytic cycles.

Scrambling of the two N atoms in the cyclic adducts **6a** and **6b** (and, thus, imine metathesis) is accomplished by H-atom transfer from the NH₂ to the NH group within the ring. The transition state for the corresponding intramolecular process, **TS6a6b**, has been located and is included in Figure 2. Compared to the preceding H-transfer from **4a** to **5a**, an even larger activation barrier is found, 47 kcal mol⁻¹ (relative to **6a**), due to the increased strain in the bicyclic **TS6a6b**. Similarly large barriers have been computed for intramolecular H-transfer processes in cationic zirconocene complexes with comparable topology [18]. Even when allowing for appreciable decrease due to tunnelling, a 47 kcal mol⁻¹ barrier would seem excessively high. The catalytic cycle in Figure 2 would therefore be only viable if the critical H-transfer from **6a** to **6b** would be catalysed efficiently by the Brønsted bases present, as discussed above.

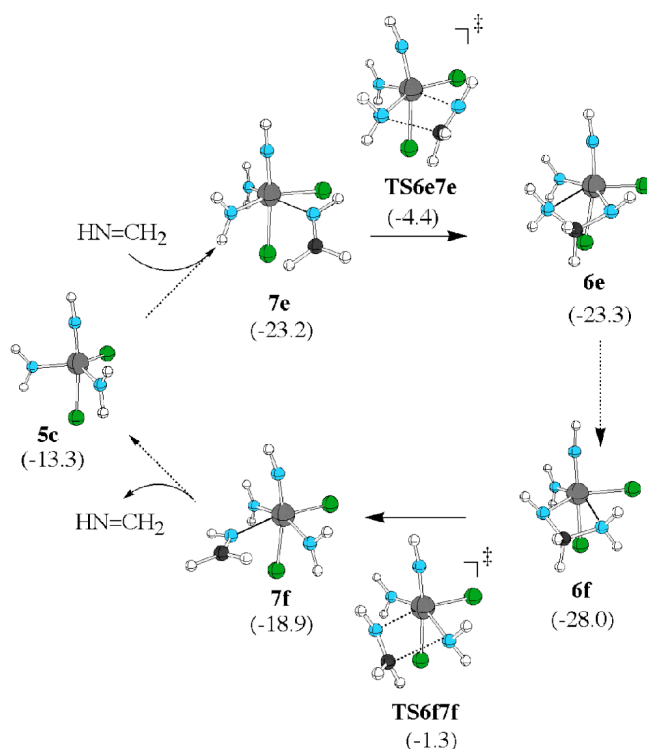


Figure 4 Alternative catalytic cycle (path III) for imine metathesis involving bis(amide) **5c** (in parentheses: energies in kcal·mol⁻¹ relative to the reactants, BP86/ECPI + ZPE level)

The driving force for the **6a** → **6b** rearrangement is considerable, more than 8 kcal mol⁻¹, and **6b** has the lowest energy in the whole cycle and would thus be the resting state. The highest point (excluding H-transfer) is **TS6b7b**, i.e. imine dissociation from **6b**. The energy between the two, 29.3 kcal mol⁻¹, would thus be the rate-determining barrier for this cycle. This value is noticeably higher than that computed for the parent Chauvin-type mechanism, 23.1 kcal mol⁻¹ [5], apparently disfavouring the amide route for the Mo system.

However, path I displayed in Figure 2 is not the only conceivable one for the model system. Using the {Mo(NCH₂N)} ring as reference, several permutations of the remaining four ligands about Mo are possible. These will be discussed in the remainder of this section.

For instance, exchanging the terminal NH₂ and one of the Cl ligands affords a new set of stationary points, path II (Figure 3, no further transition structures for H-transfer have been optimised). Minima and transition states along paths I and II share the same salient features. Thus, the lowest point on path II is **6d**, from which imine dissociation via **TS6d7d** would be rate-determining. The resulting barrier, 30.3 kcal mol⁻¹, is similar to, and even slightly higher than that for path I.

Another cycle, path III (Figure 4), can be constructed from path II by exchanging the terminal NH and NH₂ ligands (or from path I by a 120° rotation of the {MoCl(NH)(NH₂)} “tripod”). Again, the energetic profile of path III is very similar to those of the other two pathways. Imine dissociation from

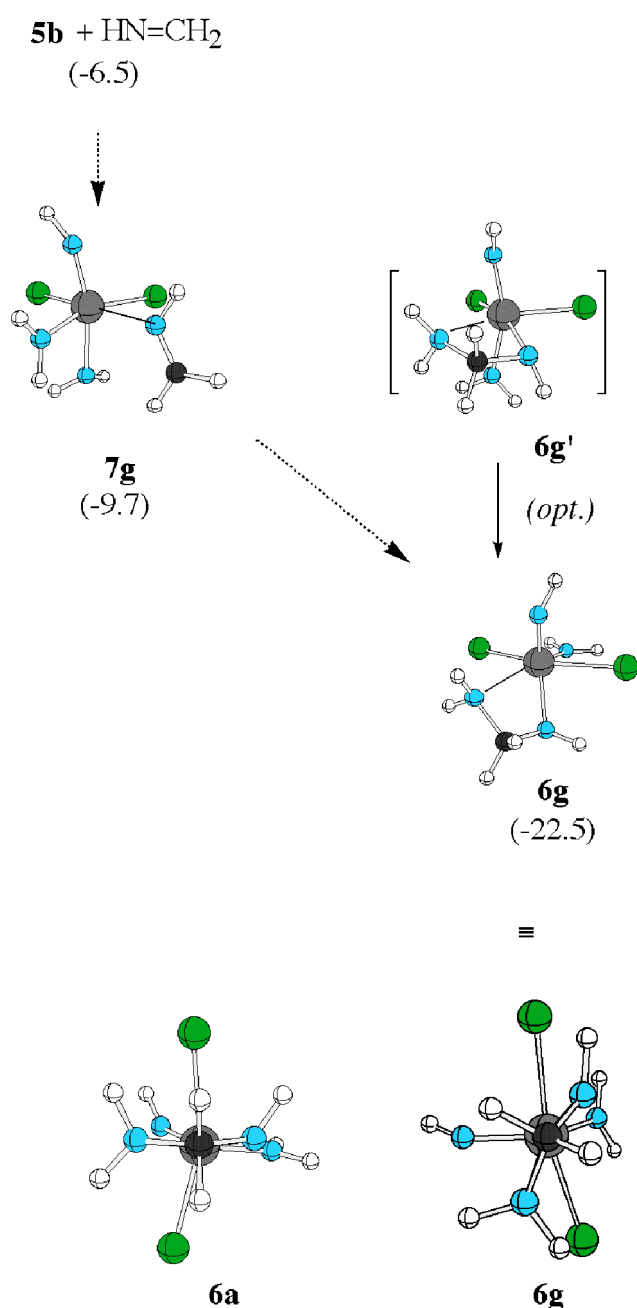


Figure 5 Entry into alternative catalytic cycle (path IV) for imine metathesis involving bis(amide) **5b** and relation of the key intermediate **6g** to **6a** on path I (in parentheses: energies in kcal·mol⁻¹ relative to the reactants, BP86/ECPI + ZPE level)

the resting state **6f** is indicated to be rate-determining with a barrier of 26.7 kcal mol⁻¹, the lowest value so far in the amide route. Entry into path III would occur via **5c**, the most stable of the bis(amido) isomers, providing additional kinetic preference for this route.

In an attempt to construct the fourth and last cycle from path III by exchanging the terminal NH₂ and the Cl ligand

trans to NH, an unexpected result was obtained: starting from **6g'** with an octahedral arrangement about Mo and terminal NH and NH₂ moieties *trans* to each other, the optimisation afforded **6g** (Figure 5). In the course of this optimisation, the terminal NH₂ group *trans* to the imido function is pushed up in between the two Cl ligands, resulting in an unusual coordination geometry, somewhere in between that of a pentagonal pyramid and an octahedron. When viewed along an axis passing through the Mo and C atoms, **6g** appears to be related to **6a** by a 60° rotation of the four-membered ring with respect to the remainder of the molecule (compare the two structures on bottom of Figure 5). In fact, in an attempt to dissociate CH₂NH from **6g** (i.e. to locate the transition state by elongating the appropriate N-C and Mo-N bonds), the structure collapsed to **TS6a7a** during optimisation. Only when the search was started from a hypothetical structure like **6g'**, a transition state connecting to the Lewis adduct **7g** could be located (**TS6g7g**, not shown in Figure 5). Among the respective isomeric forms **TS6x7x** and **6x**, both **TS6g7g** and **6g** are the least stable species (relative energies +8.3 and -22.5 kcal mol⁻¹, respectively). Moreover, the energetic separation between the two, 30.8 kcal mol⁻¹, is higher than the barriers of paths I - III discussed above. Hence, it is unlikely that a path involving intermediates such as **6g** would be favourable for imine metathesis.

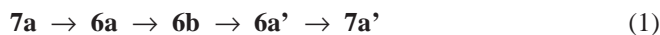
Proton transfer in **6g** would afford the mirror image thereof (this can be seen more easily in the hypothetical structure **6g'** with the same topology, Figure 5); formation of the mirror image of **7g** and imine dissociation would complete this cycle, path IV. Schematic energy profiles for all paths are compared in Figure 6, illustrating the overall similarity of paths I - III, but also the variations in relative stabilities of the corresponding isomers.

The lowest barrier is obtained for path III, 26.7 kcal·mol⁻¹. This value is not much higher than that computed for the Chauvin mechanism, 23.1 kcal mol⁻¹ [5], thereby confirming the amide route at least as viable alternative. Computed differences in activation energies of less than 4 kcal mol⁻¹ for the two mechanistic alternatives may well be within the uncertainty of the chosen theoretical method. In addition, kinetic preferences in the chain initiation (e.g. preferred formation of amine over imine Lewis adducts) could well be important for the overall observed rates.

Thus, in the real system, both Chauvin and amide pathways could indeed be operative in parallel. For the model Chauvin mechanism, substitution of the Cl ligands with other groups (F, Br, OMe, OCF₃) has resulted in only minor changes of the computed rate-determining barrier. It would be interesting to probe computationally if the same would be true in the amide route or if other substituents could actually lower the barrier and could, thus, increase the catalytic activity. Unfortunately, the complexity of the amide mechanism with its manifold of possible pathways makes such a study of substituent effects very cumbersome.

It has been assumed so far that the crucial H-transfer occurs within the four-membered ring, for instance leading from **6a** to **6b** (Figure 2). For the model system it is also conceivable, however, that such a transfer could involve the terminal NH and NH₂ groups. If an H atom could be transferred from

the latter to the former in **6b**, intermediate **6a** would be formed back, but now with scrambled N atoms in the ring (denoted **6a'**). Thus, the following reaction sequence,



would also bring about imine metathesis. Since intermediate **7b** and the transition state for its formation are bypassed on this path, the point with highest energy is **TS6a7a**. The resulting rate-determining barrier (with respect to **6b**) is only 25.0 kcal mol⁻¹, the lowest barrier of all the pathways studied here.

In the real system, such a process would require the presence of two Mo-NHR groups in the initial bis(amide) (cf. **C** in Scheme 3), which could arise from the initiation reaction with primary amines (traces of which could always be present). Mixed Mo imido/amido complexes are known, for instance [Mo(NAr)₂(NHAr₂)] (Ar = 2,6-C₆H₃iPr₂) [19], but no H-transfer between these two types of ligands can be detected on the NMR time scale. Thus, the central step in Eq. (1), the **6b** → **6a'** conversion, is unlikely to occur. The expected low basicity of the imido nitrogen atom [20] would probably preclude the necessary efficient acid/base catalysis of this proton transfer. H-transfer within the four-membered ring is not affected by this argument since the lone pair at the "target" N atom is not involved in the bonding to the metal (note the degree of pyramidalisation of the N atom in question in **6a**, **6c**, and **6e** in Figures 2-5) and could participate in such acid/base reactions.

Conclusion

The viability of a new proposed mechanism for catalytic imine metathesis, the amide route, has been investigated computationally for the model system [MoCl₂(NH)₂] (**1**) + NH₃ + CH₂NH. Chain initiation can occur by rearrangement of the primary [MoCl₂(NH)₂(NH₃)] adduct to a bis(amido) species, [MoCl₂(NH)(NH₂)₂], which subsequently adds the imine under formation of a



intramolecular Lewis adduct). H transfer within the four-membered ring, from the NH₂ to the NH group, and elimination of imine results in a scrambling of the N atoms between the Mo complex and the imine and, thus, in overall imine metathesis.

Intramolecular H-transfer, both in the initiation and propagation steps, is computed to be highly unfavourable due to strain in the four-membered cyclic or bicyclic transition structures. It is suggested that under experimental conditions, the H-transfers occur intermolecularly or are catalysed efficiently by traces of Brønsted bases always present in the reaction mixture.

Four different metathesis pathways have been constructed by permutation of the terminal {Cl₂(NH)(NH₂)} ligands in

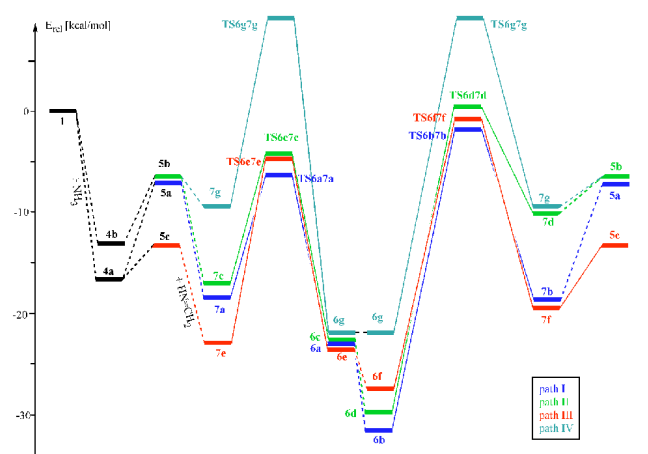


Figure 6 Schematic energy profile comparing paths I - IV

the octahedrally coordinated model complexes. Excluding H-transfer, rate-determining barriers between 26.7 and 30.8 kcal mol⁻¹ have been obtained for these pathways, the lowest value of which is not much higher than that computed previously for the Chauvin-type [2 + 2] mechanism, 23.1 kcal mol⁻¹. Initiation of the amide route is indicated to be favoured over the entry into the Chauvin pathway (since **1** forms a more stable Lewis adduct with NH₃ than with imine). Taken together, these results indicate that the recently proposed amide route is indeed a viable pathway for the Mo-based catalysts and that this route may well be competitive to the previously suggested Chauvin-type mechanism. The DFT results thus corroborate the conjecture that imidomolybdenum complexes are not well-defined single-site catalysts for imine metathesis.

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Supplementary Material available BP86/ECP1 optimised energies and Cartesian coordinates, as well as zero-point energies of all isomers of **4** - **7** and all transition structures discussed in the text are available in XYZ-format.

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 - The overwhelming majority of group VIa complexes with one π (oxo or imido) and four σ ligands have one additional donor attached, completing an octahedral environment; the same first coordination sphere as in **5** is realized in $[\text{WCl}_2(\text{NPh})(\{\text{NSiMe}_3\}_2\text{C}_6\text{H}_4)]$ which adopts an sp arrangement as in **5b** (Van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378-3380). The same arrangement is found in the gas phase for oxo halide complexes such as $[\text{MoOCl}_4]$ (Iijima, K.; Shibata, S. *Chem. Lett.* **1972**, 1033-1036).
 - There is at least one precedent for such a structure, namely in $[\text{V}(\text{N}t\text{BuSiMe}_2\text{NH}t\text{Bu})\text{Cl}_2(\text{N}t\text{Bu})]$, which shows a comparable inequivalence of the VN bond distances in the four-membered ring, ca. 1.85 vs 2.38 Å (Preuss, F.; Fuchslocher, E.; Sheldrick, W. S. *Z. Naturforsch.* **1985**, *40b*, 1040-1044).
 - The transition state can be lower in energy than the separated products because in the gas phase and without temperature effects, the latter would form a weak dipole-dipole complex. Little or no activation is to be expected on the free energy surface.
 - Lohrenz, J. C. W.; Bühl, M.; Weber, M.; Thiel, W. J. *Organomet. Chem.*, **1999**, *592*, 11-21.
 - Bryson, N.; Youinou, M.-T.; Osborn, J. A. *Organometallics* **1991**, *10*, 3389-3392.
 - For instance, in a related imidovanadium(V) complex, $[\text{VCl}_3(\text{N}t\text{Bu})]$, the basicity of the imido nitrogen is so low that no reaction occurs with HCl at room temperature: Preuss, F.; Towae, W. *Z. Naturforsch.* **1981**, *36b*, 1130-1135.