Phosphines exchange in quadruply bonded metal dimers: theoretical proposal for an alternative to the internal flip mechanism

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The non-concerted jumping of two phosphine ligands from one metal center to the other in [Mo$_2$Cl$_4$(PH$_3$)$_4$] is found to be < 30 kcal mol^{-1} (1 cal = 4.184 J) energy costing process (DFT calculations).

Quadruply bonded complexes of [Mo$_2$X$_4$(dpe)$_2$] type (X = halide, dpe = diphosphinoethane) may exist in two isomeric forms:[1] the α isomer with two chelating diphosphines and the β isomer with two bridging diphosphines (Fig. 1). In the former, the Mo$_2$X$_2$P$_2$ units are essentially eclipsed while internal rotational angles between 25 and 65° have been found in the latter.[2]
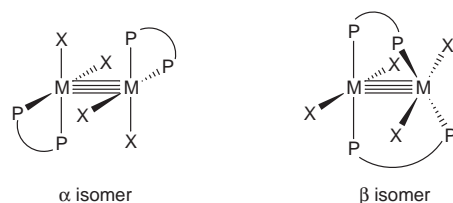

Fig. 1 Schematic structure of α and β isomers in [Mo$_2$X$_4$(P–P)$_2$] complexes

The α → β isomerization has been observed both in solution[3–6] and in the solid state.[5,7] From the experimental data on [Mo$_2$Cl$_4$(dppe)$_2$],[5] two mechanisms are believed to be competitive in solution: (*i*) a dissociative process in which one or both dppe ligands would break one of their M–P bonds; (*ii*) a unimolecular non-dissociative process. In the solid state, only the latter would be at work.[5] A fascinating mechanism has been proposed[4–6] for the non-dissociative process, the so-called internal flip mechanism. It involves as the rate-determining step the internal rotation of the Mo$_2$ unit inside the cavity formed by the eight ligand atoms (Scheme 1), followed by some internal rotation around the Mo–Mo bond. At the mid-point structure, four ligands (2P, 2X) would bridge the two metal centers. An activation energy of *ca.* 24 kcal mol^{-1} has been estimated for the non-dissociative mechanism in [Mo$_2$Br$_4$(dppe)$_2$] (solution).[4] In the related [Mo$_2$Cl$_4$(dppe)$_2$] complex, a similar activation energy has been measured in solution (28.9 ± 1 kcal mol^{-1}).[3] However, a much higher value (80 ± 7 kcal mol^{-1}) has been found for the solid-state reaction,[7] although the flip mechanism was believed to be at work in both phases. Since 1985 until very recently, this mechanism has been invoked for ligands exchange processes in various bimetallic complexes,[8]
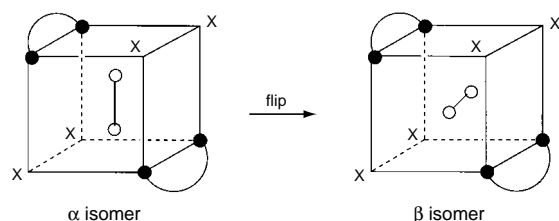

Scheme 1 Schematic picturing of the internal flip mechanism in [M$_2$X$_4$-(P–P)$_2$] complexes

the activation energies in solution lying between 20 and 29 kcal mol^{-1}.[8c,e,f]

Cayton and Chisholm have addressed the feasibility of such an intriguing process *via* an orbital symmetry analysis.[9] Fenske–Hall calculations on the [Mo$_2$Cl$_8$]$^{4-}$ complex have shown the rigid rotation of the Mo$_2$ unit to be a symmetry allowed process, but the Walsh diagram revealed that one π bonding MO was destabilized by about 2.5 eV and that the Mo–Mo bond should be elongated in the intermediate structure. These calculations did not however allow the authors to estimate the energy barrier associated to this mechanism.

Here we report the results of DFT calculations on the [Mo$_2$Cl$_4$(PH$_3$)$_4$] complex used as a model for the real Mo$_2$X$_4$(P–P)$_2$ systems. Calculations were performed with the B3LYP functional[10] within both the restricted (RB3LYP) and the unrestricted broken-symmetry (UB3LYP-bs) formalisms.§[11,12] Structures **1** and **2**, with *cis* and *trans* phosphines on

1(α)   **2**(β)
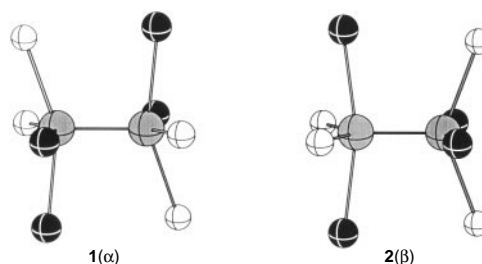
each metal center, respectively, were used as models for the α and β isomers. Full geometry optimizations led to structures of C_{2h} and D_{2d} symmetry, respectively.[13] The β isomer (**2**) was found to be the most stable, the energy difference being almost independent of the method of calculation (12.3 and 13.2 kcal mol^{-1} for RB3LYP and UB3LYP-bs methods, respectively).

The mid-point structure associated with the flip mechanism was optimized within C_i constraint and keeping the four bridging ligands in a plane perpendicular to the Mo–Mo bond. The RB3LYP structure was found to be located 86.4 kcal mol^{-1} above the α isomer (**1**) with an Mo–Mo distance elongated to 2.525 Å. Single-point energy-only calculation of this structure using the UB3LYP-bs method led to a very similar result (89.2 kcal mol^{-1}). It is noteworthy that these values are close to the experimental activation energy reported for the α → β conversion of [Mo$_2$Cl$_4$(dppe)$_2$] in the solid state (80 ± 7 kcal mol^{-1}).[7] Although we failed in locating a stationary point in this region of the potential energy surface, the possibility for the flip mechanism to be operative in the solid state is, at least, left open by our calculations. However, it is unlikely on energetic grounds for the reaction in solution (E_a < 30 kcal mol^{-1}). Therefore, we searched for another mechanism for the α → β isomerization reaction.

Exploration of the potential energy surface for phosphine(s) migration processes led to the localization of a stationary point which was further characterized as a transition state (a single imaginary frequency of 124i cm^{-1}). Moving along the reaction coordinate on both sides of the transition state confirmed it
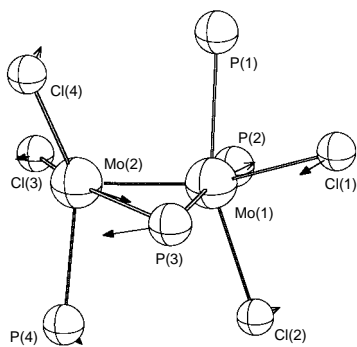
Fig. 2 Optimized geometry of the transition state for the α (**1**) → β (**2**) conversion. Hydrogen atoms of the phosphine ligands are omitted for clarity. The transition vector is also pictured.

connects the α (**1**) and β (**2**) isomers through a one-step mechanism. The main feature of the transition state structure (Fig. 2) is the presence of a single bridging phosphine (P3, initially bound to Mo2 in the α isomer), with Mo1–P3 2.820 Å and Mo2–P3 3.150 Å (UB3LYP-bs). Although P3 is closer to Mo1 than to Mo2, no Mo–P bond is fully broken at the transition state. Another interesting feature is that the Mo–Mo distance (2.181 and 2.240 Å at the RB3LYP and UB3LYP-bs levels, respectively) is *ca.* 0.3 Å shorter than in the mid-point associated with the flip mechanism and close to that found at the same level of calculations in the quadruply bonded structures **1** and **2**.[13] Last but not least, the computed activation energy (28.4 and 28.8 kcal mol^{-1} at the RB3LYP and UB3LYP-bs levels, respectively) is in good agreement with the experimental estimates for the α → β conversion of quadruply bonded metal dimers in solution.

The whole reaction mechanism is pictured in Scheme 2 (for the atom numbering, see Fig. 2). It involves first the migration of one phosphine (P3) from Mo2 toward Mo1, leading to the bridged transition state. Next P3 binds definitely Mo1, thus creating a vacancy at the Mo2 center and a distorted octahedral arrangement around Mo1. Finally P1, which is more suitably oriented than P2 with respect to the vacant site, migrates from Mo1 to Mo2 to form the β isomer. This mechanism can thus be described as the successive jumping of two phosphine ligands from one metal center to the other.

Although satisfactory in several aspects with respect to the experimental data in solution, there is however one result this
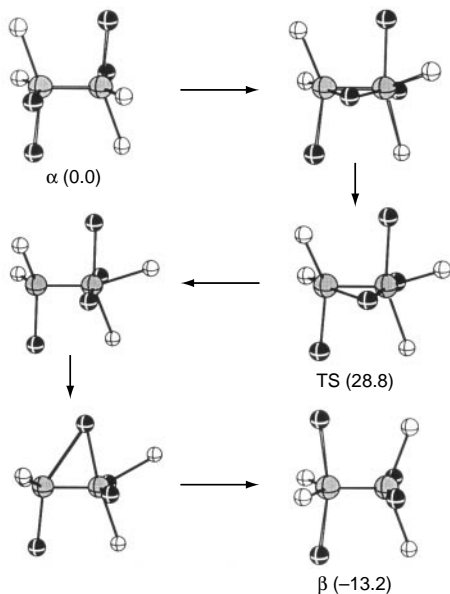
Scheme 2 Mechanism for the α (**1**) → β (**2**) conversion going through the transition state given in Fig. 2. Hydrogen atoms of the phosphine ligands are omitted for clarity.

mechanism does not account for: in the [Mo$_2$Cl$_4$(dpdbp)$_2$] complex, it has been shown that the α-*syn* and α-*anti* isomers convert to the β-*syn* and β-*anti* isomers, respectively.[6] Such a stereoselectivity would require the migration of P2 instead of that of P1 in the last stage of the reaction path (Scheme 2). Such change might be due to the constraints exerted by the bridging diphosphines in real β-[Mo$_2$X$_4$(P–P)$_2$] systems,[2] the P–Mo–Mo–P dihedral angles being smaller than in our model complex **2** (90°). These constraints should be at work not only at the very end of the reaction (β isomer) but just after the transition state has been reached, when P3 binds Mo1 (one 'bridging diphosphine' involving P4 and P3 atoms). Therefore, the reaction path for [Mo$_2$Cl$_4$(dpe)$_2$] systems should be modified in its last stage by an internal rotation around the Mo–Mo bond which might in turn make P2 more suitably oriented than P1 for migration from Mo1 to Mo2.

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