From chelating to bridging diphosphine ligands in quadruply-bonded bimetallic complexes: a non-dissociative phosphine exchange mechanism

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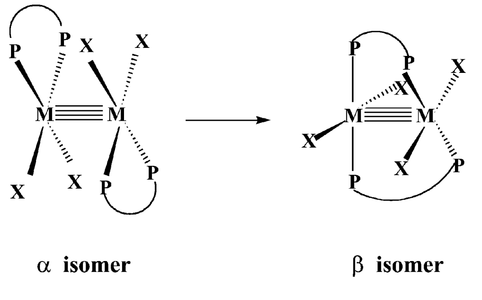
The exchange of phosphine ligands in the bimetallic $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$ complex was studied by means of DFT calculations with the B3LYP functional. A non-dissociative mechanism was fully characterized (minima, transition states) for the isomerization reaction, which transforms the α isomer, with two chelating diphosphines, into the β isomer, with two bridging diphosphines. It involves the non-concerted migration of one end of each diphosphine ligand from one metal center to the other. The computed activation energy (about 30 kcal mol^{-1}) is associated with the jumping of the first phosphine end, which bridges the two metal centers in the transition state structure (**TS1**).

Quadruply-bonded complexes of the $Mo_2X_4(dpe)_2$ 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). The α to β isomerization, which requires at least that one end of each dpe ligand migrates from one metal center to the other, has been observed both in solution[2–5] and in the solid state.[4,6] The activation energies measured in solution lie between 20 and 29 kcal mol^{-1},[2,3] while, in the solid state, a much higher value of 80 ± 7 kcal mol^{-1} has been reported for the $Mo_2Cl_4(dppe)_2$ complex [dppe = 1,2-bis(diphenylphosphino)ethane].[6] From the experimental data on this $Mo_2Cl_4(dppe)_2$ complex, a unimolecular non-dissociative process was believed to be the most likely in solution and in the solid phase, although a dissociative mechanism, with the initial breaking of a single M–P bond, could not be definitely ruled out for the reaction in solution.[4] Until recently, an internal flip of the Mo_2 unit inside the cavity formed by the eight ligand atoms has been proposed to be the rate-determining step of the non-dissociative process[3–6] and was also invoked for other ligand exchange processes in related bimetallic complexes.[7,8]

In a previous communication,[9] we reported a DFT study of the exchange of two phosphines in the quadruply-bonded dimer $Mo_2Cl_4(PH_3)_4$ used as a model for complexes of the $Mo_2Cl_4(P–P)_2$ type. This study led us to conclude that the internal flip was a too high energy process to be operative in solution. An alternative mechanism was proposed for the non-dissociative process, which involved the non-concerted jumping of two phosphine ligands from one metal center to the other, the computed activation energy (28.8 kcal mol^{-1}) being in the range of experimental barriers. These two results were supported by a recent Car–Parrinello study of the isomerization processes in a related triply-bonded ditungsten complex with two monodentate phosphine ligands.[10]



α isomer β isomer

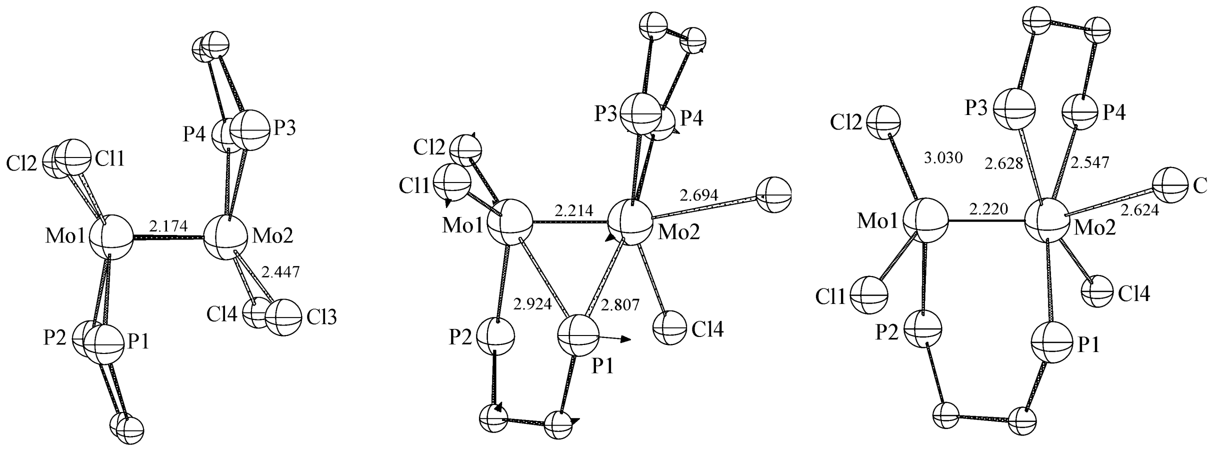
Fig. 1 Schematic structure of the α and β isomers in $Mo_2X_4(dpe)_2$ complexes.

However, regarding the actual α to β isomerization reaction in $Mo_2X_4(dpe)_2$ complexes (Fig. 1), our preliminary study suffered from the replacement of each diphosphine by two monodentate ligands (PH_3). The constraints exerted by the bidentate ligands were thus lacking, in particular in the β isomer for which the conformation of the two metal units was found to be *eclipsed* in the model system and essentially *staggered* in the complex with two ligands of the dpe type (Fig. 1). It was therefore recognized that the exchange mechanism found for the $Mo_2Cl_4(PH_3)_4$ complex might well be changed in some way (energetics, stereoselectivity) when bidentate ligands are involved.[9]

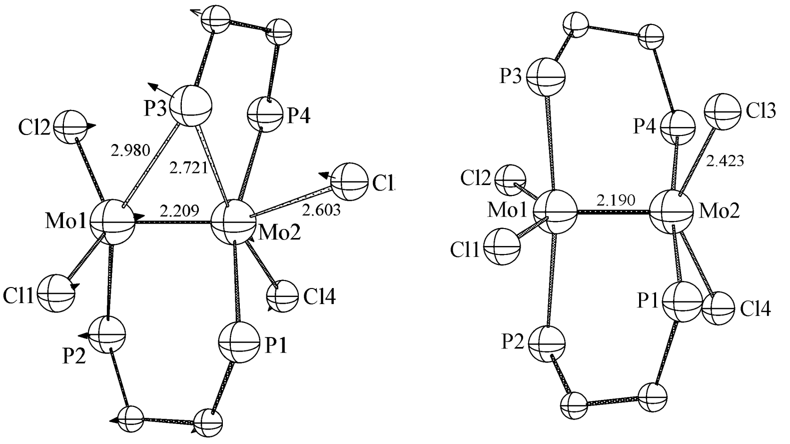
In this paper, we now report the theoretical study of the direct phosphine exchange mechanism leading to the α to β isomerization in the $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$ complex, that is a quadruply-bonded bimetallic complex with two real diphosphine ligands.

Computational details

Calculations were performed with the GAUSSIAN 98 series of programs,[11] using the same methodology as in our previous works on the structural properties of $Mo_2Cl_4(PH_3)_4$ and $Mo_2Cl_4[H_2P–(CH_2)_n–PH_2]_2$ complexes (n = 1, 2).[9,12] Density functional theory (DFT)[13,14] was applied with the B3LYP functional.[15–17] Both the spin-restricted (R) and spin-unrestricted



(a) Isomer α **(b) TS1** **(c) Min**



(d) TS2 **(e) Isomer β**

Fig. 2 Optimized structures of the α isomer (a), **TS1** (b), **Min** (c), **TS2** (d) and the β isomer (e) of the $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$ complex. Geometries for the α and the β isomers are taken from ref. 12*d* and 12*c*, respectively. The transition vector is pictured for the transition states **TS1** and **TS2.** Hydrogen atoms on P and C atoms are omitted for clarity.

(U) forms of the B3LYP functional were used. In the unrestricted formalism, we made use of the broken-symmetry approach proposed by Noodleman[18] (indicated as UB3LYP-bs hereafter). Geometry optimizations of the stationary points and frequency calculations were performed at the RB3LYP level, the energies being recomputed at the UB3LYP-bs level by means of single-point energy-only calculations. A quasi-relativistic effective core potential operator was used to represent the 28 innermost electrons of the molybdenum atom[19] as well as the electron core of Cl and P atoms.[20] The basis set for the metal was that associated with the pseudopotential,[19] with a standard double-ζ LANL2DZ contraction.[11] The basis set for the P and Cl atoms was that associated with the pseudopotential,[20] with a standard double-ζ LANL1DZ contraction[11] supplemented with a set of d-polarization functions.[21] A 6-31G basis set was used for the C and H atoms.[22] Solvent effects were taken into account by means of PCM calculations[23] using the standard options of PCM and cavity keywords.[11] Keeping the geometry optimized for the isolated species (single-point calculations), free energies of solvation were calculated with CH_2Cl_2 ($\varepsilon = 8.93$), that is the solvent used in the experiments reported in ref. 2–4.

Results and discussion

The structures of the stationary points (minima and transition states) are pictured in Fig. 2 together with a few selected geometrical parameters. More detailed geometries and the energetic results (ΔE, ΔH, ΔG) are reported in Table 1.

Starting from the α isomer (Fig. 2*a*), a stationary point was localized and further characterized as a transition state (**TS1**, Fig. 2*b*) with a single imaginary frequency of 144*i* cm^{-1}. In this structure, one end (P1) of one of the chelating ligands in the α isomer (P1–P2) is now bridging the two metal centers, with Mo1–P1 and Mo2–P1 distances of 2.924 and 2.807 Å, respectively. The transition vector drawn in Fig. 2*b* confirms that this transition state is associated with the motion of the P1 end from the Mo1 to the Mo2 metal center. The ligand that is the most affected by the phosphine motion is the chloride Cl3, linked to Mo2 and lying almost exactly in the P1–Mo1–Mo2 plane. It is displaced by the phosphine approach so that the Mo2–Cl3 bond becomes almost collinear to the metal-metal axis and significantly elongated, from 2.447 Å in the α isomer to 2.694 Å in **TS1**. From an energetic point of view (Table 1), this transition state was found to be located 28.3

Table 1 Main geometrical parameters and energetic results (kcal mol^{-1}) for the α (ref. 12*d*), **TS1**, **Min**, **TS2** and β (ref. 12*c*) structures of the $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$ complex. Distances are in Å and angles in °

	α	**TS1**	**Min**	**TS2**	β
Mo1–Mo2	2.174	2.214	2.220	2.209	2.190
Mo2–Cl3	2.447	2.694	2.624	2.603	2.423
Mo2–Cl4	2.447	2.447	2.440	2.429	2.423
Mo1–Cl1	2.447	2.389	2.417	2.425	2.423
Mo1–Cl2	2.447	2.346	2.363	2.367	2.423
Mo1–P1	2.515	2.924	3.423	3.419	3.474
Mo2–P1	3.487	2.807	2.534	2.536	2.561
Mo1–P3	3.487	3.479	3.030	2.980	2.561
Mo2–P3	2.515	2.539	2.625	2.721	3.474
Mo2–Mo1–P1	95.8	64.5	47.7	47.9	47.4
Mo1–Mo2–P3	95.8	93.9	76.9	73.5	47.4
ΔE(RB3LYP)	0.0	28.3	13.0	13.0	−6.6
ΔE(UB3LYP-bs)[a]	0.0	32.4	12.9	13.1	−11.0
ΔH(298.3 K)[b]	0.0	27.6	13.1	12.5	−6.5
ΔG(298.3 K)[b]	0.0	28.8	14.2	15.0	−3.7

[a] Single-point calculation using the geometry optimized at the RB3LYP level. [b] ZPE and thermal corrections are computed using the characterization of stationary points at the RB3LYP level.

kcal mol^{-1} above the α isomer at the RB3LYP level (32.4 kcal mol^{-1} at the UB3LYP-bs level), similar values being calculated for ΔH and ΔG (27.6 and 28.8 kcal mol^{-1}, respectively).

Following the transition vector on both sides of **TS1** showed that this transition state connects the α isomer (as expected) and a secondary minimum (**Min**, Fig. 2*c*), which was located 13.0 kcal mol^{-1} above the α isomer at the RB3LYP level (12.9 kcal mol^{-1} at the UB3LYP-bs one). In this structure, the P1 phosphine end is definitely bound to the Mo2 center, with a normal Mo2–P1 distance of 2.535 Å, intermediate between those optimized in the α and the β isomers (2.515 and 2.561 Å, respectively). Therefore, half of the α to β isomerization has been achieved since one of the chelating diphosphine ligands in the α isomer (P1–P2) is now bridging the two metal centers. A distorted octahedral arrangement is found around the Mo2 center and there is a vacant site at Mo1. It is noteworthy that, among the two phosphine ends of the remaining chelating diphosphine ligand (P3–P4) on Mo2, P3 seems more suitable than P4 for a further migration toward the vacant site at Mo1 (Fig. 2*c*). As a matter of fact, the Mo2–P3 bond is weakened (2.628 Å instead of 2.547 Å for Mo2–P4) and oriented toward the Mo1 center, the small value of the Mo1–Mo2–P3 angle (76.9°) leading to a Mo1···P3 distance of 3.030 Å (instead of 3.776 Å for Mo1···P4). In **Min**, the P3 center is actually not far from being in a bridging position.

This analysis was supported by the characterization of a new transition state (**TS2**) with a single imaginary frequency of 68*i* cm^{-1} (Fig. 2*d*). In this structure, the P3 end of the (P3–P4) diphosphine ligand is now bridging the two metal centers, with Mo2–P3 and Mo1–P3 distances of 2.721 and 2.980 Å, respectively. The transition vector pictured in Fig. 2*d* confirms that **TS2** is associated with the motion of P3 from Mo2 to Mo1 and moving along this vector actually led to the secondary minimum **Min** on one side and to the β isomer on the other side. It is worth noting that the energy difference between **TS2** and **Min** was found to be less than 0.1 kcal mol^{-1} at the RB3LYP level and 0.2 kcal mol^{-1} at the UB3LYP-bs one. On the other hand, the free energy difference (ΔG) is only 0.8 kcal mol^{-1} and the transition state **TS2** disappears when considering the enthalpy change ($\Delta H = -0.6$ kcal mol^{-1}, Table 1). This means that the potential energy surface between **Min** and **TS2** is actually very flat and that the migration of the P3 end from Mo2 to Mo1 requires essentially no activation energy.

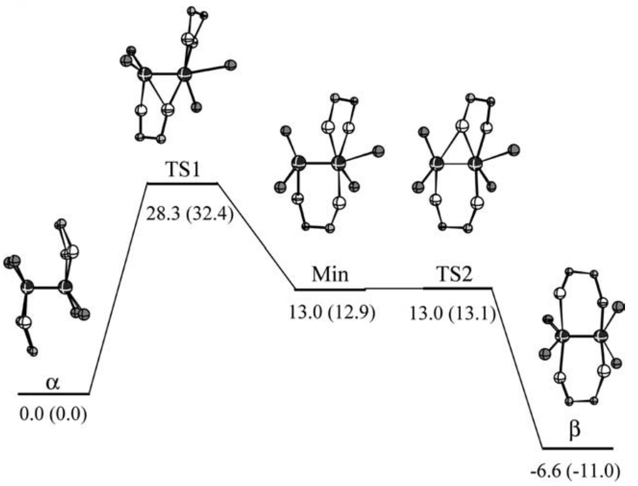


Fig. 3 Energy profile associated with the α to β isomerization by means of a non-dissociative phosphine exchange mechanism in the $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$ complex. The energies (in kcal mol^{-1}) are given at both the RB3LYP and UB3LYP-bs (in parenthesis) levels. Hydrogen atoms on P and C atoms are omitted for clarity.

The whole energy profile for this non-dissociative mechanism is reported in Fig. 3. Starting from the α isomer, it involves the successive migration of one phosphine end of each chelating diphosphine ligand, the rate-determining step being that associated with the first migration. Despite the finding of the secondary minimum **Min**, it is better described as a one-step process, with a metastable species in the second half of the reaction. The optimized values for the Mo–Mo distances, ranging from 2.174 to 2.220 Å, show that most of the metal–metal bonding is preserved in the course of this mechanism. The computed activation energy (28.3 and 32.4 kcal mol^{-1} at the RB3LYP and UB3LYP-bs levels, respectively), as well as the ΔH and ΔG values (27.6 and 28.8 kcal mol^{-1}, respectively) are in the range of the experimental barriers. A rough estimate of the solvent effect (CH_2Cl_2) by means of single-point calculations using the PCM model found this value almost unchanged (28.1 kcal mol^{-1} at the RB3LYP level). This mechanism resembles that we have found for the model complex with monophosphine ligands.[9] In particular, it involves the exchange of two Mo–P bonds with a dihedral angle of about 90° in the initial α isomer (P1–Mo1–Mo2–P3 in Fig. 2). The migration of two phosphine ends making a dihedral angle of 180° has been proposed for the α-Mo_2Cl_4(dpdbp)$_2$ complex [dpdbp = 1-diphenylphosphino-2-di(*p*-*tert*-butylphenyl)phosphinoethane]. Despite the fact that we have now taken into account the constraints exerted by the bidentate ligands, the stereoselectivity of this non-dissociative mechanism still does not agree with this experimental proposal.[5]

Conclusion

In the quadruply-bonded bimetallic complex $Mo_2Cl_4[H_2P–(CH_2)_2–PH_2]_2$, the successive migration of two phosphine ends is found to be a non-dissociative mechanism to connect the α isomer, with two chelating diphosphines, to the β isomer, with two bridging diphosphines. Starting from the α isomer, the activation energy (about 30 kcal mol^{-1}, DFT results) is associated with the jumping of the first phosphine group.

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