DFT Study of the Role of Bridging Diphosphine Ligands in the Structure and the Internal Rotation in Quadruply Bonded Metal Dimers of the $Mo_2Cl_4(P-P)_2$ Type

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The structure of the quadruply bonded β-$Mo_2Cl_4(H_2PCH_2CH_2PH_2)_2$ complex, with two bridging diphosphine ligands, is studied by means of DFT calculations with the B3LYP functional. Full geometry optimization is first performed for both the lowest singlet (δ^2) and triplet ($^3\delta\delta^*$) states. In agreement with the data on related experimental complexes, an essentially staggered conformation is found, the singlet state being the electronic ground state. The potential energy curves associated with the internal rotation around the Mo−Mo bond are then computed for both the singlet and the triplet states, the geometry being fully optimized for each value of the rotational angle. The singlet state is always found to be the electronic ground state, but the singlet−triplet energy separation (ΔE(S−T) depends on the rotational angle. Comparison with the available experimental data on β-$Mo_2Cl_4(P-P)_2$ complexes for seven complexes with an internal rotational angle ranging from 24.7° to 69.4° reveals a satisfactory agreement between theoretical and experimental values provided approximate spin-projected broken-symmetry calculations are used for the singlet state.

Introduction

Complexes of the $M_2X_4(dpe)_2$ type (M = Mo, W; X = halide; dpe = 1,2-bis(dialkyl or diarylphosphino)ethane) may exist in two isomeric forms:[1] the α isomer with two chelating diphosphines and the β isomer with two bridging diphosphines (Figure 1). In the former, the $MX_2(dpe)$ units are always found to be essentially eclipsed,[2] leading to a quadruply bonded metal dimer ($\sigma^2\pi^4\delta^2$ electronic configuration). In contrast, internal rotational angles (χ) between 26.8° [3d] and 59.5° [3b] are found in the major conformation of the β isomers, depending on the substituents on the phosphines and carbon atoms and on the nature of the halide ligands.[2a,3] An eclipsed conformation is however restored in complexes with the diphosphinomethane (dpm) ligand.[4] Therefore, it appears that the bridging dpe ligand in the β-M_2X_4-$(dpe)_2$ complexes imposes an internal rotation around the M−M quadruple bond at the expense of the δ bonding, which actually vanishes in the staggered conformation ($\chi = 45°$).
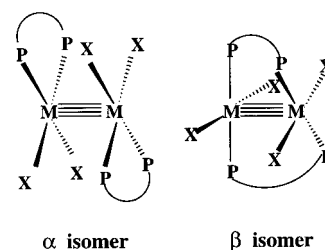
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Figure 1. Schematic structure of α and β isomers in $Mo_2X_4(P-P)_2$ complexes.

Since various structures which differ by the relative orientation of the $MX_2(dpe)$ units have been characterized, some electronic and geometrical changes associated with the internal rotational process are available from experiments.[5,6] Measurement of the singlet (δ^2)−triplet ($^3\delta\delta^*$) energy difference by ^{31}P NMR spectroscopy showed the singlet state to be the electronic ground state in all the range of observed χ angle values.[5] The energy separation was however found to depend on this angle, the smallest one being found for $\chi \cong 45°$, i.e., for the staggered conformation in which the δ bond is removed.

In previous theoretical studies,[7,8] the $Mo_2Cl_4(PH_3)_4$ complex was used as a model for the β isomer of $Mo_2X_4(dpe)_2$ complexes. Although both CASSCF[7] and our more recent DFT calculations[8a] properly reproduced the singlet−triplet energy separation as a function of the rotational angle χ, the singlet

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and the triplet potential energy curves dramatically suffer from the lack of the constraints exerted by the bridged diphosphine ligands in the real β isomers: an eclipsed (quadruply bonded) conformation ($\chi = 90°$) in which the M−P bonds on one metal unit eclipse the M−Cl bonds on the other was found for both electronic states, a result in strong variance with the staggered or nearly staggered (triply bonded) conformations characterized for the β-$Mo_2X_4(dpe)_2$ complexes. It is thus clear that the presence of diphosphinoethane ligands is required to obtain the proper shape for the singlet and the triplet energy curves associated with the internal rotational process in these complexes.

In this paper we report the first theoretical study (DFT calculations) of the β isomer of the unsubstituted $Mo_2Cl_4(dpe)_2$ complex (dpe = $H_2PCH_2CH_2PH_2$). Full geometry optimization was first performed for both the lowest singlet (δ^2) and triplet ($^3\delta\delta^*$) electronic states, the results being compared to the structures characterized for the real β-$Mo_2X_4(dpe)_2$ complexes. The singlet and triplet potential energy curves associated with the rotation around the Mo−Mo bond were then studied, the shape of these curves and the way the singlet−triplet energy difference depend on the internal rotation being discussed with respect to the available experimental data.

Method of Calculation

Calculations were performed with the GAUSSIAN 94 series of programs,[9] using the same methodology as in our previous works on $Mo_2Cl_4(PH_3)_4$ model complexes. The density functional theory (DFT)[10,11] was applied with the B3LYP functional.[12−14] It has very recently been proved that accurate values of structural properties of quadruply bonded dinuclear second-row complexes can be obtained with this functional.[8a,15,16] Both the spin-restricted (R) and spin-unrestricted (U) forms of the B3LYP functional were used. In the unrestricted formalism, we made use of the broken-symmetry approach proposed by Noodleman[17] (indicated as UB3LYP-bs hereafter). This approach in combination with the DFT theory has been recently successfully applied to the study of the electronic structure of bridged Cu(II), Ni(II), and Mn(II) binuclear compounds,[18] oxo-bridged manganese dimers,[19] and $M_2Cl_9{}^{3-}$ and $M_2Cl_{10}{}^{4-}$ bimetallic systems.[20] Values of $^1\langle S^2\rangle$ ranging from 0.900 to 1.095 being found in our broken-symmetry calculations, spin-projected energies were calculated for the δ^2 singlet state. Two methods were used, both assuming that the contamination of the singlet state came mainly from the triplet $^3\delta\delta^*$ state. This assumption was based on the spin densities computed for the metal d orbitals: depending on the rotational angle, values ranging from 0.74 to 0.82 were found for the

d orbital involved in the δ molecular orbital, while much smaller values (between 0.14 and 0.17) were found for the d orbitals involved in the π molecular orbitals. The approximate spin correction was therefore calculated by using (i) the procedure proposed by Yamaguchi and co-workers[21,22] and already applied to UB3LYP-bs calculations,[8,23] in which the spin-corrected energy ($^1E_{SC}$) is given by $^1E_{SC} = {}^1E_{UB3LYP} + f_{SC}[{}^1E_{UB3LYP} - {}^3E_{UB3LYP}]$, the fraction of spin contamination f_{SC} being given by $^1\langle S^2\rangle/[^3\langle S^2\rangle - {}^1\langle S^2\rangle]$, and (ii) the equation given by Illas and co-workers[24] which relates the spin correction to the overlap (S_{ab}) between the magnetic α and β orbitals of the broken-symmetry solution: $^1E_{SC} - {}^3E_{UB3LYP} = 2[{}^1E_{UB3LYP} - {}^3E_{UB3LYP}]/[1 + S_{ab}{}^2]$. A quasirelativistic effective core potential operator was used to represent the 28 innermost electrons of the molybdenum atom[25] as well as the electron core of Cl and P atoms.[26] The basis set for the metal was that associated with the pseudopotential,[25] with a standard double-ζ LANL2DZ contraction.[9] The basis set for the P and Cl atoms was that associated with the pseudopotential,[26] with a standard double-ζ LANL1DZ contraction[9] supplemented with a set of d-polarization functions.[27] A 6-31G basis set was used for the C and H atoms.[28]

Geometrical Model

Experimental structures of β-$M_2X_4(dpe)_2$ molecules possess in their major conformation an idealized or a rigorous overall D_2 symmetry.[2a,3] The experimental values of the internal rotation angle, χ, have been calculated by averaging the two P−M−M−P and the two Cl−M−M−Cl angles[5] obtained from the structural determinations[2a,3] (notice however that sometimes the rotational angle values reported are equal to the mean value of Cl−Mo−Mo−P angles, i.e., $90° - \chi$).[2a,3]

In our calculations on the β-$Mo_2Cl_4(H_2PCH_2CH_2PH_2)_2$ complex, the P−Mo−Mo−P dihedral angle (θ) was chosen to describe the internal rotation around the Mo−Mo bond. For a given value of θ, the corresponding theoretical value of χ (i.e., the mean value between θ and the optimized value of the Cl−Mo−Mo−Cl angle) will also be given for the sake of comparison with the experimental data. We will see however that, for a given structure, the values of θ and χ differ at most by a few degrees. According to the D_2 symmetry requirement, the structure of the complex was fully optimized in its lowest singlet (δ^2) and triplet ($^3\delta\delta^*$) states. The rotational energy curves associated with these two electronic states were then calculated by varying the θ angle from 0° to 90° in steps of 15°, the geometry being fully optimized for each value of θ.

Results and Discussion

Geometry Optimizations. The values of the main geometrical parameters optimized for the singlet state (RB3LYP and UB3LYP-bs calculations) and for the triplet state are reported in Table 1, as well as the values for the related experimental complex β-$Mo_2Cl_4(dmpe)_2$ (dmpe = 1,2-bis-(dimethylphosphino)ethane).[3a] This complex is actually that which most resembles our unsubstituted model complex since it is the less hindered in the series of β-$Mo_2Cl_4(dpe)_2$ complexes

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Table 1. Main Geometrical Parameters Optimized for the β-Mo$_2$Cl$_4$(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$ Complex in Its Lowest Singlet (S(RB3LYP) and S(UB3LYP-bs) Calculations) and Triplet (T) States[a]

	S(RB3LYP)	S(UB3LYP-bs)	T	exptl[b]
Mo−Mo	2.190	2.253	2.248	2.183(3)
Mo−Cl	2.423	2.425	2.423	2.403(5)
Mo−P	2.561	2.564	2.558	2.526(5)
Mo−Mo−Cl	112.4	109.7	109.4	111.2(1)
Mo−Mo−P	93.6	95.2	95.5	98.4(2)
C−C	1.547	1.545	1.545	1.41(2)
P−Mo−P	172.7	169.8	169.1	163.3(2)
Cl−Mo−Cl	135.3	140.6	141.2	137.6(2)
P−Mo−Mo−P (θ)	60.6	53.9	53.0	
Cl−Mo−Mo−Cl	72.0	60.0	58.2	
χ	66.3	56.9	55.5	50.0(1)

[a] Both θ and χ angle values are given to describe the internal rotation around the Mo−Mo bond (see the Geometrical Model). [b] Experimental parameters (ref 3a) are given for the β-Mo$_2$Cl$_4$(dmpe)$_2$ complex (singlet state).

for which experimental parameters are also available: β-Mo$_2$Cl$_4$(dppe)$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane)[3b] and β-Mo$_2$Cl$_4$(depe)$_2$ (depe = 1,2-bis(diethylphosphino)ethane).[3c]

In the singlet state, good agreement was found between experimental and theoretical parameters with both RB3LYP and UB3LYP-bs methods, in particular for Mo−Cl and Mo−P bond lengths and for Mo−Mo−Cl and Cl−Mo−Cl bond angles (mean deviations between 0.020 and 0.035 Å for bond distances, and between 1° and 3° for bond angles). Slightly larger but still acceptable deviations were found for the bond angles involving phosphine ligands (Mo−Mo−P and P−Mo−P, Table 1). The only large difference involved the C−C bond length in the bridging dmpe ligand: a value of 1.547 Å, usual for a C−C single bond, was given by our calculations while a surprisingly short distance (1.41(2)) has been derived from X-ray data.[3a] For this geometrical parameter, the theoretical value is likely to be more reliable than the experimental one (large uncertainty). The Mo−Mo distance (experimental, 2.183 Å) was almost perfectly reproduced by RB3LYP calculations (2.190 Å) but overestimated by 0.07 Å by UB3LYP-bs calculations. Such a lengthening of the Mo−Mo distance in the broken-symmetry calculations has already been found in our previous studies of quadruply bonded dimers with monodentate phosphine ligands.[8a,c] Last but not least, both RB3LYP and UB3LYP-bs methods led to an essentially staggered conformation for the complex, in agreement with the experimental data: θ values of 60.6° and 53.9° were given by RB3LYP and UB3LYP-bs calculations, respectively, leading to χ values (see the Geometrical Model) of 66.3° and 56.9°, respectively (Table 1). The latter compares rather well to the experimental value for the β-Mo$_2$Cl$_4$(dmpe)$_2$ (χ$_{exptl}$ = 50.0°)[3a] and also to those reported for the related β-Mo$_2$Cl$_4$(depe)$_2$ and β-Mo$_2$Cl$_4$(dppe)$_2$ complexes (χ$_{exptl}$ = 41.4° and 59.5°, respectively).[3c,b] We will see in the next section how one can understand such large variations for the experimental rotational angle χ (from about 40° to 60°) for complexes differing only in the nature of the substituents on the phosphine groups.

Two drawings of the minimal energy structure are given in Figure 2. In agreement with the major orientation found in the experimental structures,[3a−c] each ring has a nearly ideal chair conformation. It is particularly clear in Figure 2b (view directly down the Mo−Mo axis) where it is apparent that the C−C bonds are almost parallel to the Mo−Mo bond.

Finally, the geometry optimized for the $^3\delta\delta^*$ triplet state is very similar to that given by the UB3LYP-bs calculations for
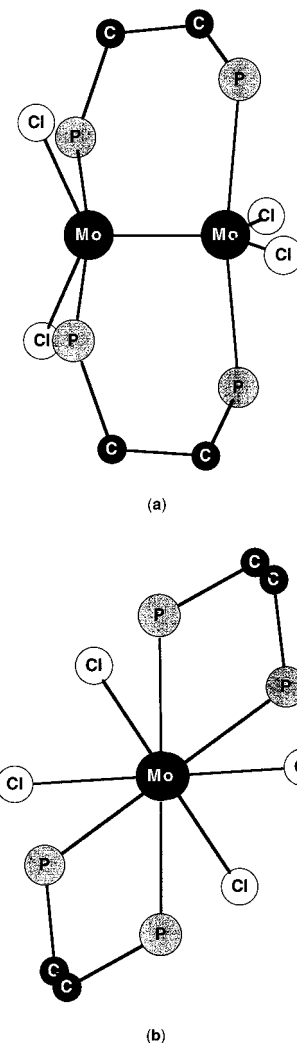

Figure 2. Two drawings of the minimal energy structure of the β-Mo$_2$Cl$_4$(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$ complex (singlet state). Hydrogen atoms have been omitted for the sake of clarity.

the δ^2 singlet state (Table 1). In both cases, the internal rotational angle χ (55.5° and 56.9°, respectively) was found to be close to the value associated with the idealized staggered conformation (45°), and both can thus be described approximately as triply bonded dimers. However, it has already been noticed that spin contamination in the UB3LYP-bs singlet state might contribute to making the geometries of the singlet and the triplet states too close to each other.[8a,c] As a matter of fact, the geometries are less similar if the RB3LYP results are used for the singlet state. In going from the singlet (RB3LYP) to the triplet state, the internal rotational angle χ decreases from 66.3° to 55.5° (motion toward the staggered conformation) and the Mo−Mo distance increases by 0.058 Å (Table 1).

From an energetic point of view, the RB3LYP singlet state was found to be higher in energy than the triplet state, by 11.7 kcal/mol (4090 cm^{-1}). Such a result, already found at this level of calculation for complexes with monodentate phosphine ligands,[8a,c] is in disagreement with the experimental data.[5] A singlet ground state was however restored by using the UB3LYP-bs method for the singlet state.[29] It is located 820 cm^{-1}

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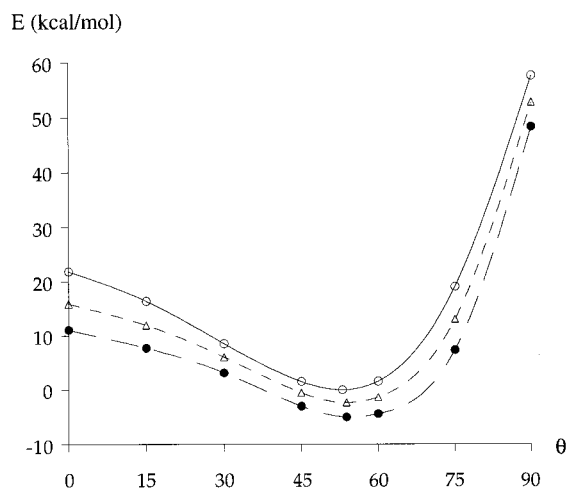
E (kcal/mol)

Figure 3. Potential energy curves associated with the internal rotation (θ) in the β- $Mo_2Cl_4(H_2PCH_2CH_2PH_2)_2$ complex: triplet state (hollow circles) and singlet state at the UB3LYP-bs (hollow triangles) and spin-projected UB3LYP-bs (Yamaguchi procedure, solid circles) levels. The origin of energies is that of the triplet state in its optimized geometry ($-383.237\ 17$ au).

below the triplet state (each electronic state being in its optimized geometry). Although the ordering of the two electronic states is now correct, the computed energy difference is about 2 times smaller than the experimental energy differences reported for the experimental complexes with similar internal rotational angles: 1290(50) and 1650(40) cm^{-1} for β-Mo_2Cl_4-(dmpe)$_2$ ($\chi_{exptl} = 50.0°$) and β-Mo_2Cl_4(dppe)$_2$ ($\chi_{exptl} = 59.5°$) complexes, respectively.[5] A much better agreement was found by calculating the approximate spin-projected energy of the singlet state (see the Method of Calculation). As a matter of fact, the computed singlet−triplet energy difference increases to 1750 and 1575 cm^{-1} using the procedures proposed by Yamaguchi[21,22] and Illas,[24] respectively.

Internal Rotation around the Mo−Mo Bond. The potential energy curves associated with the lowest singlet (δ^2) and triplet ($^3\delta\delta^*$) states are given in Figure 3. For the singlet state, both the UB3LYP-bs and the spin-corrected UB3LYP-bs curves are reported. For the latter, only that obtained using the correction procedure proposed by Yamaguchi and co-workers[21,22] is reported: taking into account the energy scale required for this figure, this curve is essentially undistinguishable from that obtained by using the equation given by Illas and co-workers.[24] We will return to this point in more detail when discussing the singlet−triplet energy separation as a function of the internal rotational angle.

Both singlet and triplet energy curves exhibit the same general features. The minima are found for the nearly staggered structures described in the preceding section ($\theta = 53.9°$ and $53.0°$ for the singlet and the triplet states, respectively), and the curves are very unsymmetrical with respect to these minima: although the angular variation is smaller, going to the eclipsed structure with $\theta = 90°$ costs much more energy than going to the eclipsed structure with $\theta = 0°$ (57.7 vs 21.7 kcal/mol for the triplet state and 53.4 vs 16.1 kcal/mol for the spin-corrected singlet state). These results are in marked contrast with those found for the complex with *monodentate* phosphine ligands[7,8a] for which the eclipsed conformation with $\theta = 90°$ (Mo−P bonds on one metal unit eclipsing Mo−Cl bonds on the other) was found to be the most stable structure for both the singlet and the triplet states. The nearly staggered conformation for the $Mo_2Cl_4(dpe)_2$ complex is thus imposed by the bidentate dpe ligand in a chair conformation, which makes the

Table 2. Main Geometrical Parameters Optimized for the Triplet State of the β-$Mo_2Cl_4(H_2PCH_2CH_2PH_2)_2$ Complex as a Function of the Internal Rotational Angle θ^a

θ	χ	Mo−Mo	Mo−Cl	Mo−P	Mo−Mo−Cl	Mo−Mo−P
90	85.8	2.332	2.409	2.506	119.8	85.5
75	75.2	2.286	2.413	2.537	114.4	89.5
60	61.4	2.259	2.419	2.555	110.8	93.4
53	55.5	2.248	2.423	2.558	109.4	95.5
45	48.4	2.239	2.427	2.559	108.3	97.9
30	34.4	2.235	2.431	2.559	108.1	101.8
15	18.6	2.238	2.429	2.560	107.6	104.2
0	1.3	2.242	2.425	2.568	107.4	105.1

^{a}The corresponding values computed for the χ angle (see the Geometrical Model) are also given.

Table 3. Main Geometrical Parameters Optimized for the Singlet Ground State (UB3LYP-bs Calculations) of the β-$Mo_2Cl_4(H_2PCH_2CH_2PH_2)_2$ Complex as a Function of the Internal Rotational Angle θ^a

θ	χ	Mo−Mo	Mo−Cl	Mo−P	Mo−Mo−Cl	Mo−Mo−P
90	86.6	2.301	2.412	2.510	119.9	85.7
75	72.8	2.264	2.417	2.551	115.1	89.0
60	62.8	2.255	2.422	2.561	111.0	93.3
53.9	56.9	2.253	2.425	2.564	109.7	95.2
45	49.0	2.247	2.429	2.563	108.2	97.8
30	33.4	2.239	2.431	2.561	107.8	101.7
15	16.7	2.225	2.430	2.563	108.0	104.2
0	1.1	2.217	2.429	2.551	107.7	105.3

^{a} The corresponding values computed for the χ angle (see the Geometrical Model) are also given.

eclipsed conformations very high in energy, especially that which was the most stable with monodentate phosphine ligands ($\theta = 90°$).

The constraints exerted by the bidentate dpe ligands also appear in the values optimized for some geometrical parameters in both the triplet and the singlet states (Tables 2 and 3, respectively). In the former, the metal−metal triple bonding (one σ and two π bonds) is not affected by the internal rotational process, so that the Mo−Mo distance would be expected to remain almost unchanged. It is actually what is found for θ varying from 0° to 60°, the bond length change being only 0.017 Å. A further increase of θ from 60° to 90° (the most unstable structure) entails however a significantly larger lengthening (0.073 Å) of the metal−metal distance (Table 2). Large variations in optimized angular parameters also reflect the constraints at work for $\theta \geq 75°$. The Mo−Mo−Cl angle, which was found to vary smoothly from 107.4° to 110.8° for θ varying from 0° to 60°, increases to 119.8° at $\theta = 90°$. In the same way, values smaller than 90° are found for the Mo−Mo−P angle for $\theta \geq 75°$. The same trends hold for the singlet δ^2 state (Table 3). In going from $\theta = 0°$ (eclipsed conformation) to $\theta = 45°$ (staggered conformation), the δ bond is destroyed so that a lengthening of the Mo−Mo distance is expected. The optimized metal−metal distance actually increases by 0.030 Å. However, while a further increase of θ from 45° to 90° restores the δ bonding, the Mo−Mo bond is lengthened by 0.054 Å. This result may still be traced to the constraints exerted by the bidentate dpe ligands when $\theta \geq 75°$ which are reflected by both a high-energy destabilization (Figure 3) and large variations of the optimized geometrical parameters, sometimes unexpected on electronic grounds.

Finally, the curves given in Figure 3 allow us to understand the rather large range of equilibrium values (from about 40° to 60°)[3a−c] measured for the internal rotational angle for Mo_2Cl_4-(dpe)$_2$ complexes differing only by the nature of the substituents on the phosphine groups. As a matter of fact, the energy cost for moving along the singlet energy curve from the minimum
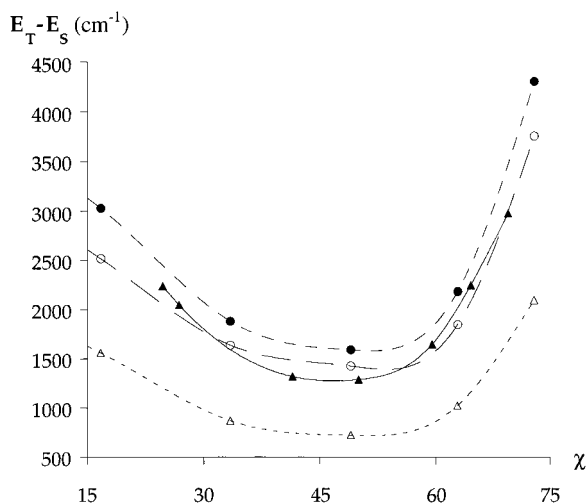
$E_T - E_S$ (cm^{-1})

Figure 4. Singlet–triplet separation (cm^{-1}) as a function of the internal rotation angle (χ) in the β-Mo₂Cl₄(H₂PCH₂CH₂PH₂)₂ complex. Computed values are given at the UB3LYP-bs (hollow triangles) and spin-projected UB3LYP-bs (solid circles and hollow circles for the procedures proposed by Yamaguchi and Illas, respectively) levels (see the Method of Calculation). Experimental values (taken from ref 5) for the related Mo₂X₄(P–P)₂ complexes are also reported (solid triangles).

Table 4. Computed Singlet–Triplet Energy Differences (cm^{-1}) as a Function of the Internal Rotational Angle θ^a

θ	χ	ΔE(S–T)^a	ΔE(S–T)^b	ΔE(S–T)^c	exptl
15.0	16.7	1563	3032	2521	
	24.7	*1214*	*2464*	*2054*	2240(90)
	26.8	*1143*	*2321*	*1938*	2050(10)
30.0	33.4	871	1883	1640	
	41.4	*741*	*1643*	*1482*	1320(20)
45.0	49.0	723	1592	1428	
	50.0	*714*	*1571*	*1411*	1290(50)
	59.5	*889*	*1821*	*1536*	1650(40)
60.0	62.8	1025	2186	1850	
	64.5	*1125*	*2393*	*2036*	2250(20)
	69.4	*1554*	*3214*	*2786*	2980(20)
75.0	72.8	2100	4309	3759	

$^{a-c}$ The corresponding value of the χ angle is also given (see the Geometrical Model). Experimental values for Mo₂X₄(P–P)₂ complexes, taken from ref 5, are reported together with the interpolated theoretical values (italic). In these calculations, the energy of the singlet state is computed by means of UB3LYP-bs (a) and the spin-projected procedure proposed by Yamaguchi (b) and Illas (c) (see the Method of Calculation).

energy structure ($\theta = 53.9°$, Table 1) to structures with $\theta = 40°$ or $\theta = 60°$ is only 1.8 and 1.0 kcal/mol, respectively. Small changes in the substitution pattern can thus cause rather large variations in the optimum value for the internal rotation angle.

Whatever the value of θ, the singlet state (δ^2) is found to be lower in energy than the triplet state ($^3\delta\delta^*$) with both UB3LYP-bs and spin-projected calculations (Figure 3). This result is in agreement with the experimental data on d^4–d^4 M₂X₄(P–P)₂ complexes for which a singlet ground state has been found for internal rotational angles ranging from 24.7° to 69.4°.[5] It is also clear from Figure 3 that the singlet–triplet energy separation depends on θ and is about twice as large when spin-projected instead of UB3LYP-bs energies are used for the singlet state. Let us now compare, in more detail, these results with the available experimental data. The singlet–triplet energy differences are reported in Figure 4 and in Table 4 as a function of the internal rotational angle χ (which differs from θ by only a few degrees) for sake of comparison with the experimental data

(see the Geometrical Model). Three different values are given depending on the method of calculation for the singlet state: UB3LYP-bs and approximate spin-projected energy using either the procedure proposed by Yamaguchi[21,22] or that proposed by Illas.[24] Whatever the method of calculation, the computed energy curves nearly parallel the curve built from the experimental data (Figure 4): the smallest energy difference is found for $\chi \cong 45°$, i.e., the staggered conformation in which the δ bond is removed in the singlet state. Moving away from this structure increases the singlet–triplet energy separation since the δ bond is progressively restored in the singlet state while it is still lacking in the triplet state. From a more quantitative point of view, it is clear that the energy difference between the two electronic states is underestimated by nearly a factor of 2 by UB3LYP-bs calculations, whatever the internal rotational angle value. A satisfactory agreement is however found when approximate spin-projected energies are used for the singlet state (Figure 4 and Table 4). The average deviation for the seven structures for which the singlet–triplet energy difference has been measured (χ varying from 24.7° to 69.4°) is only 159 cm^{-1} with the Illas procedure (with a maximum of 214 cm^{-1}) and 235 cm^{-1} with the Yamaguchi one (with a maximum of 323 cm^{-1}) (Table 4).

Finally, it is noteworthy that the two procedures used to obtain the spin-projected energies lead to rather similar results, the lowering of the singlet-state energy being however slightly larger with the Yamaguchi one. The two methods would have given the same result provided $^1\langle S^2 \rangle = 1$ and $1 + S_{ab}^2 = 1$ (see the Method of Calculation). It is not far from being what is actually found in our calculations: in the range of χ values including all the experimental structures (Table 4), $^1\langle S^2 \rangle$ actually remains close to 1 (between 0.9 and 1.08) and $1 + S_{ab}^2$ varies from 1.01 to 1.25, the lowest value (strong orthogonal or localized limit) being found for the staggered conformation in which the two frontier orbitals are degenerate.

Concluding Remarks

The geometry optimized for the quadruply bonded β-Mo₂-Cl₄(H₂PCH₂CH₂PH₂)₂ complex, with two bridging diphosphine ligands, is in good agreement with the X-ray structure of related experimental complexes (β-Mo₂Cl₄(dmpe)₂, β-Mo₂Cl₄(dppe)₂, β-Mo₂Cl₄(depe)₂). In particular, the complex is found to adopt an essentially staggered conformation, in which the δ bonding is removed, in marked contrast with the eclipsed structure of complexes with monodentate phosphine ligands. The study of the internal rotation around the Mo–Mo bond shows that the singlet state is the electronic ground state, whatever the value of the rotational angle. This result is also in agreement with the experimental data on β-Mo₂Cl₄(P–P)₂ complexes since a singlet ground state has been found for a wide range of rotational angle values. Finally, the way the singlet–triplet energy separation varies upon internal rotation is well reproduced, with a minimum energy separation for the staggered conformation in which the δ and δ^* orbitals are degenerate. The agreement between theoretical and experimental values is satisfactory if spin-projected broken-symmetry calculations are used for the singlet ground state. These results prompt us to undertake new studies on the structure and the reactivity of transition metal dimer complexes at this level of calculation, which is shown to give reliable structural and energetic information.

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