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A dissociative mechanism for phosphine exchange in quadruply bonded bimetallic complexes

Isabelle Demachy,*[a] Yves Jean[b] and Agusti Lledos[c]

[a] *Laboratoire de Chimie-Physique (CNRS UMR 8000), Université Paris-Sud 11, 91405 Orsay cedex, France. E-mail: isabelle.demachy@lcp.u-psud.fr; Fax: +33 169 15 61 88; Tel: +33 169 15 44 45*
[b] *Laboratoire Hétéroéléments et Coordination (CNRS UMR 7653), Ecole Polytechnique, 91128 Palaiseau cedex, France. E-mail: yves.jean@polytechnique.fr*
[c] *Departament de Quimica, Universitat Autonoma de Barcelona, 08193 Bellaterra, (Catalonia), Spain. E-mail: agusti@klingon.uab.es*

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The exchange of two phosphine ligands in the metal dimer [$Mo_2Cl_4\{H_2P–(CH_2)_2–PH_2\}_2$] was studied by means of DFT calculations with the B3LYP functional. A dissociative mechanism was fully characterized (minima, transition states) for the reaction that transforms the **α** isomer with two chelating diphosphines into the **β** isomer with two bridging diphosphines. It is essentially a two-step mechanism, each step involving the breaking of a Mo–P bond at a metal centre, followed by the formation of a new Mo–P bond with the other metal centre. This Mo–P bond exchange processes are found to be accompanied by the migration of a chloride ligand in the opposite direction. The activation energy computed at the unrestricted UB3LYP-bs level (24 kcal mol^{-1}) is found to be in the range of experimental values.

Introduction

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** → **β** isomerization 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} (ref. 2 and 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 the $Mo_2Cl_4(dppe)_2$ complex, a unimolecular non-dissociative process was believed to be likely in solution and in the solid phase but a dissociative mechanism, with the initial breaking of a single M–P bond, was also believed to take place for the reaction in solution.[4]

In previous studies,[7,8] we reported the DFT characterization of a non-dissociative mechanism for the exchange of two phosphines in such quadruply bonded dimers with either monodentate phosphines (PH_3)[7] or actual (diphosphino)ethane ligands (dpe) linked to the metal centres.[8] This mechanism, which involves the non-concerted jumping of two phosphine ligands from one metal centre to the other, has been supported by a recent Car–Parrinello study of the isomerization processes in a related triply bonded ditungsten complex.[9] Furthermore, the computed activation energy (28.5 kcal mol^{-1} with dpe ligands)[8] was found to be in the range of the experimental barriers.

In this paper, we now report the characterization by DFT-based B3LYP calculations of a multi-step dissociative mechanism leading to the **α** → **β** isomerization in the [$Mo_2Cl_4\{H_2P–(CH_2)_2–PH_2\}_2$] complex. All the stationary points (minima and transition states) were optimized and characterized by frequency calculations.

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Computational details

Calculations were performed with the GAUSSIAN 98 series of programs,[10] 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).[8,11] Density functional theory (DFT)[12,13] was applied with the B3LYP functional.[14–16] 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). 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. Since $^1\langle S^2\rangle$ values close to 1 were found in our singlet state UB3LYP-bs calculations, spin-projected energies were calculated with the approximate spin correction procedure proposed by Yamaguchi and coworkers[18,19]and already applied to UB3LYP-bs calculations.[7,8,11,20] Assuming that the contamination of the singlet wavefunction is only from the lowest $^3\delta\delta^*$ triplet state,[11b,11c]

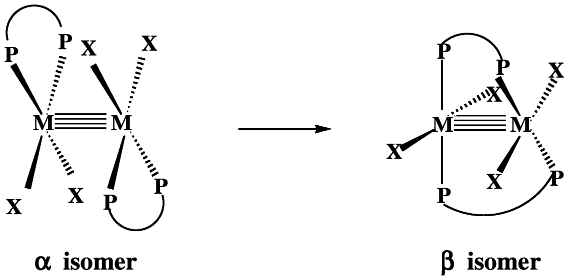


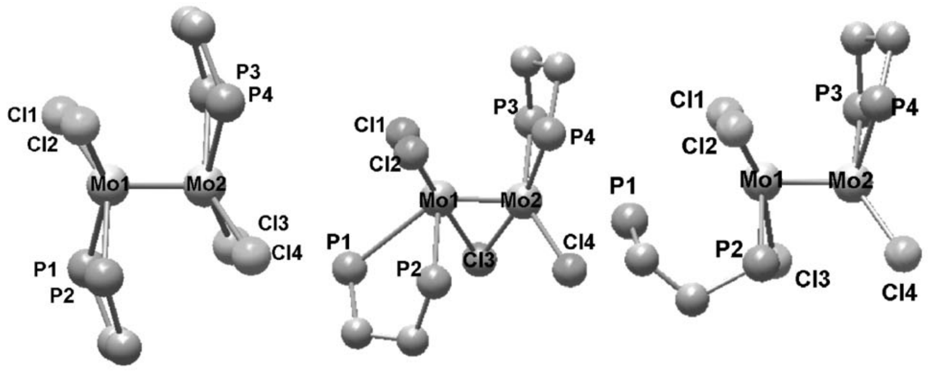
Fig. 1 Schematic structures of the **α** and **β** isomers in $Mo_2X_4(dpe)_2$ complexes.

the spin-corrected energy ($^1E_{SC}$) is given by: $^1E_{SC} = {}^1E_{UB3LYP} + f_{SC}({}^1E_{UB3LYP} - {}^3E_{UB3LYP})$, in which the fraction of spin contamination f_{SC} is given by $^1\langle S^2\rangle/({}^3\langle S^2\rangle - {}^1\langle S^2\rangle)$. A quasirelativistic effective core potential operator was used to represent the 28 innermost electrons of the molybdenum atom[21] as well as the electron core of the Cl and P atoms.[22] The basis set for the metal was that associated with the pseudopotential,[21] with a standard double-ζ LANL2DZ contraction.[10] The basis set for the P and Cl atoms was that associated with the pseudopotential,[22] with a standard double-ζ LANL1DZ contraction[10] supplemented with a set of d-polarization functions.[23] A 6-31G basis set was used for the C and H atoms.[24]

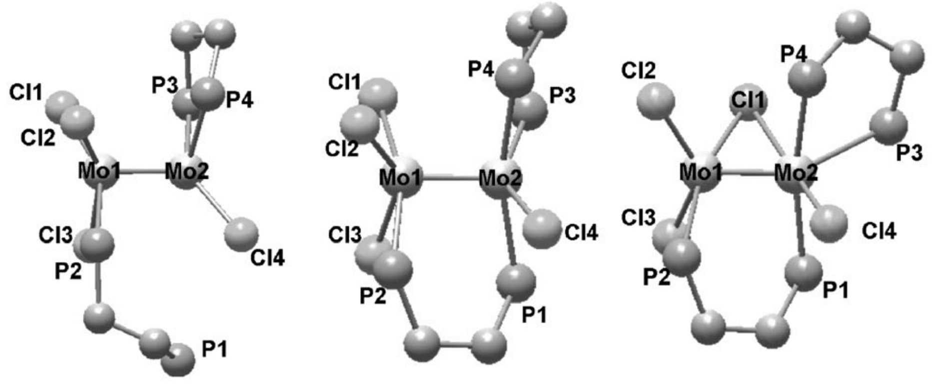
Results and discussion

The structure of the stationary points (minima and transition states) are depicted in Fig. 2; more detailed geometries and energetic results (ΔE, ΔH and ΔG) are reported in Table 1. In the following description of the reaction mechanism, only the energies computed at the RB3LYP level are given.

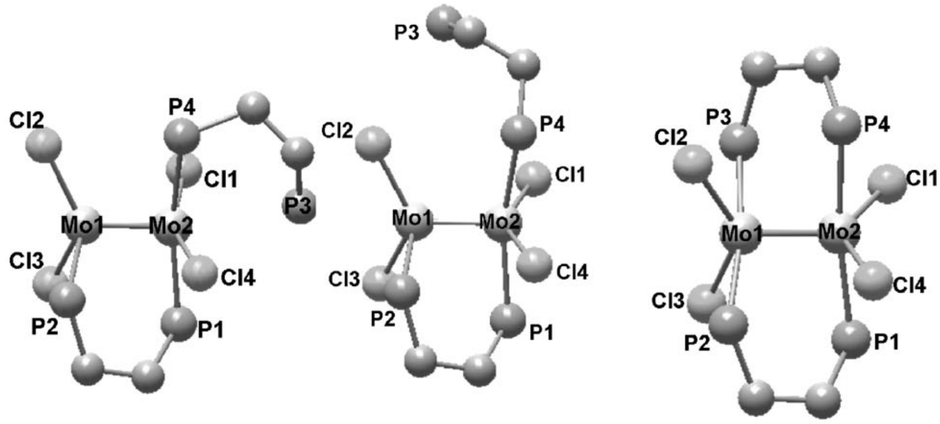
Starting from the **α** isomer [Fig. 2(a)], the elongation of the Mo1–P1 bond leads to a transition state [**TS1**, Fig. 2(b)] located 14.6 kcal mol^{-1} above the **α** isomer. Surprisingly, the lengthening of the Mo1–P1 bond (Mo1–P1 = 3.072 Å) is accompanied by the migration of a chloride ligand (Cl3) from Mo2 to Mo1 so that it is bridging the two metal centres in **TS1**



(a) α isomer **(b) TS1** **(c) Min 1**



(d) TS2 **(e) Min 2** **(f) TS3**



(g) Min 3 **(h) TS4** **(i) β isomer**

Fig. 2 Optimized structures of the **α** isomer (a), **TS1** (b), **Min 1** (c), **TS2** (d), **Min 2** (e), **TS3** (f), **Min 3** (g), **TS4** (h) and the **β** isomer (i) of the $[Mo_2Cl_4\{H_2P–(CH_2)_2–PH_2)_2]$ complex. Hydrogen atoms are omitted for clarity.

Table 1 Main geometrical parameters and energetic results (kcal mol^{-1}) for the **α** (ref. 11*d*), **TS1**, **Min 1**, **TS2**, **Min 2**, **TS3**, **Min 3**, **TS4** and **β** (ref. 11*c*) structures of the [$Mo_2Cl_4\{H_2P–(CH_2)_2–PH_2\}_2$] complex. Distances are in Å and angles in degrees

	α	**TS1**	**Min 1**	**TS2**	**Min 2**	**TS3**	**Min 3**	**TS4**	**β**
Mo1–Mo2	2.174	2.171	2.181	2.189	2.212	2.198	2.183	2.181	2.200
Mo1–P1	2.515	3.072	3.321	5.179	3.503	3.402	3.422	3.415	3.474
Mo1–P3	3.489	3.497	3.518	3.497	3.519	4.571	5.336	5.106	2.561
Mo2–P1	3.489	4.835	5.441	4.810	2.521	2.525	2.559	2.557	2.561
Mo2–P3	2.515	2.500	2.477	2.470	2.477	2.725	3.176	5.340	3.474
Mo1–Cl1	2.448	2.417	2.407	2.394	2.399	2.593	3.288	3.575	3.835
Mo1–Cl3	3.800	2.760	2.473	2.393	2.410	2.405	2.397	2.392	2.423
Mo2–Cl1	3.800	3.751	3.720	3.738	3.745	2.836	2.438	2.383	2.423
Mo2–Cl3	2.448	2.620	2.982	3.319	3.774	3.835	3.838	3.838	3.835
Mo2–Mo1–P1	95.9	133.8	162.5	68.1	45.8	47.9	48.4	48.4	47.4
Mo1–Mo2–P3	95.9	96.7	98.0	97.1	97.1	136.2	169.2	72.0	47.4
Mo2–Mo1–Cl1	110.4	109.6	108.2	109.2	108.5	72.1	47.8	40.5	35.7
Mo1–Mo2–Cl3	110.4	69.6	54.6	46.1	37.0	35.3	34.9	34.7	35.7
ΔE (RB3LYP)	0.0	14.6	13.2	17.8	−2.7	10.3	9.3	13.8	−6.6
ΔH (298.3 K)[a]	0.0	13.9	13.0	17.1	−2.3	9.9	9.5	13.5	−5.9
ΔG (298.3 K)[a]	0.0	12.7	9.5	15.1	−2.2	10.0	7.3	11.4	−5.0
ΔE (UB3LYP-bs)[b]	0.0	13.3	19.4	24.0	3.6	8.6	6.2	11.2	−11.0
ΔE_{sp} (UB3LYP-bs)[c]	0.0	13.0	23.9	28.4	8.0	9.0	6.2	11.2	−9.4

[a] ZPE and thermal corrections are computed using the characterization of the stationary points at the RB3LYP level. [b] Single-point calculation using the geometry optimized at the RB3LYP level. [c] Spin-corrected (UB3LYP-bs) calculation (see computational details).

(Mo2–Cl3 = 2.62 Å and Mo1Cl3 = 2.76 Å). The complete breaking of the Mo1–P1 bond leads to a shallow secondary minimum [**Min 1**, Fig. 2(c)] in which Cl3 is now linked to Mo1 instead of to Mo2 as in the **α** isomer. The reorientation of the P1 free end of the diphosphine ligand through the **TS2** transition state [Fig. 2(d)] allows formation of the new Mo2–P1 bond [**Min 2**, Fig. 2(e)]. This minimum, found to be 2.7 kcal mol^{-1} more stable than the starting **α** isomer, is a mixed-valence complex [Mo(I)–Mo(III)] with one chelating and one bridging diphosphine ligand. The second part of the mechanism, leading to the **β** isomer with two bridging diphosphines, is very similar to the first one. The breaking of the Mo2–P3 bond is accompanied by the migration of Cl1 from Mo1 to Mo2 [**TS3**, Fig. 2(f) and **Min 3**, Fig. 2(g)]. **TS3** is located 13.0 kcal mol^{-1} above **Min**

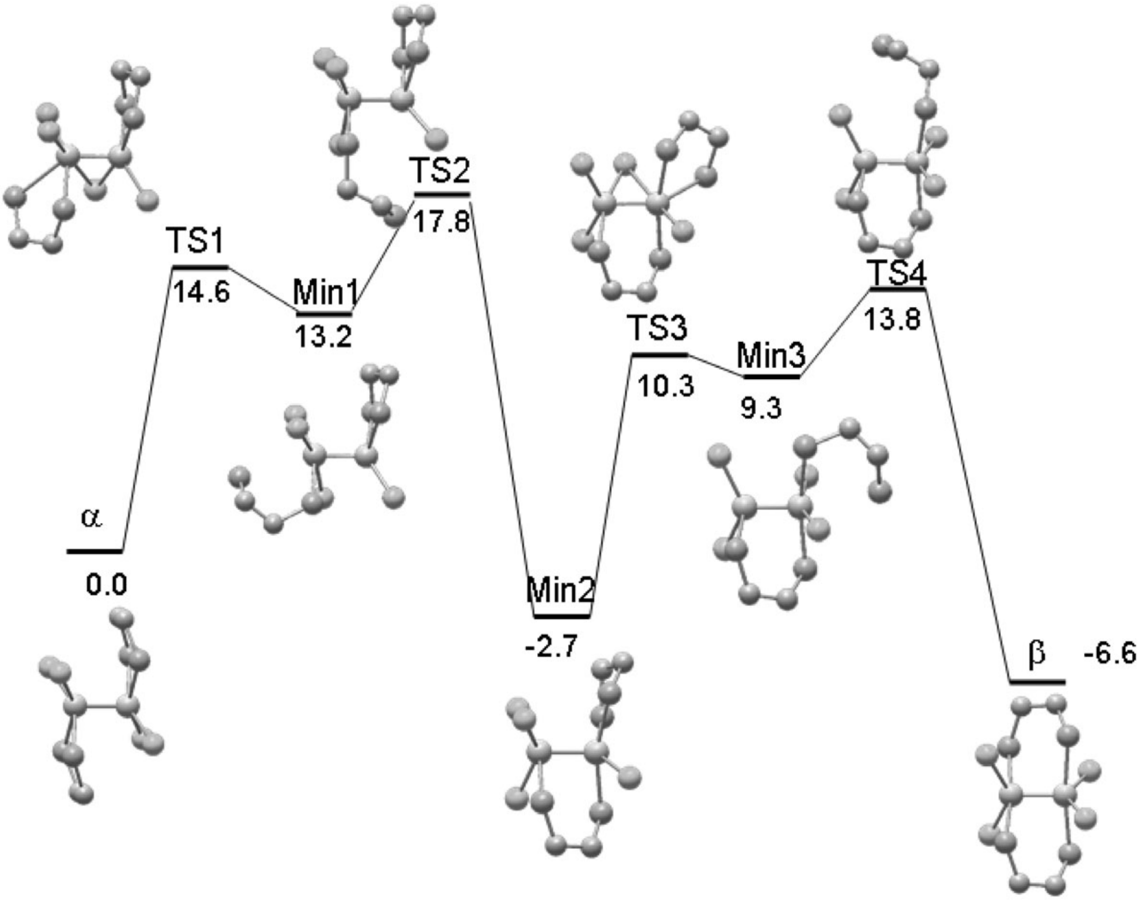


Fig. 3 Energy profile associated with the **α**-to-**β** isomerization (dissociative mechanism) in the [$Mo_2Cl_4\{H_2P–(CH_2)_2–PH_2\}_2$] complex. The energies (in kcal mol^{-1}) are given at the RB3LYP level.

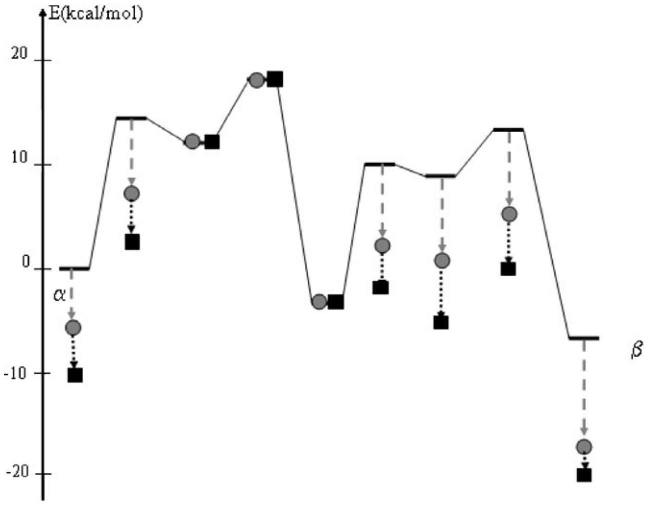


Fig. 4 Changes in the RB3LYP energy profile given by single-point calculations at the UB3LYP-bs (grey circles) and spin-corrected UB3LYP-bs (black squares) levels.

2, a value very similar to that found for the breaking of the first Mo–P bond (14.6 kcal mol^{-1}). After a reorientation of the P3 end [**TS4**, Fig. 2(h)], the Mo1–P3 bond is formed leading to the **β** isomer [Fig. 2(i)], which is more stable than the **α** isomer by 6.6 kcal mol^{-1}.

The whole energy profile for this dissociative mechanism is shown in Fig. 3. It can be described essentially as a two-step mechanism. Each step involves the breaking and the reformation of a Mo–P bond with the other metal centre, each Mo–P bond exchange being accompanied by the migration of a chloride ligand in the opposite direction. From an energetic point of view, the activation energy along the reaction pathway is equal to 17.8 kcal mol^{-1} (ΔH = 17.1, ΔG = 15.1 kcal mol^{-1}). These are significantly lower than the values found previously at the same RB3LYP level for the non-dissociative mechanism (28.3, 27.6 and 28.8 kcal mol^{-1} for ΔE, ΔH and ΔG, respectively)[8] and also lower than the experimental activation energies for the reaction in solution,[2,3] between 20 and 29 kcal mol^{-1} (see next section).

In our previous calculations on quadruply bonded transition metal dimers,[7,8,11] a lowering of the lowest singlet state energy was found by using the unrestricted broken symmetry formalism (UB3LYP-bs). As a matter of fact, such calculations allow the balance between covalent and antiferromagnetic coupling to be optimized by localizing the magnetic orbitals more or less on the metal centres. Single-point energy-only UB3LYP-bs calculations were thus performed on all the stationary points characterized at the RB3LYP level. An energy lowering was found for the **α** and **β** isomers and for structures **TS1**, **TS3**, **Min 3** and **TS4**. Therefore, the energies of these five structures on the reaction path are overestimated at the RB3LYP level. On the contrary, no broken symmetry solution of lower energy were found for **Min 1**, **TS2** and **Min 2** (Fig. 4). It is noteworthy that these three latter structures are the Mo(I)–Mo(III) mixed-valence complexes involved in the reaction mechanism. Therefore, the localization of the MOs on one of the two metal centres was already found at the RB3LYP level. The major consequences of these additional calculations are (i) the increase of the activation energy, from 17.8 (RB3LYP) to 24.0 (UB3LYP-bs) kcal mol^{-1} and to 28.4 kcal mol^{-1} when spin-corrected energies are used. These latter values are in better agreement with the experimental activation energies (20–29 kcal mol^{-1}) and in the range of that found previously for the non-dissociative mechanism (32.4 kcal mol^{-1} at the UB3LYP-bs level); (ii) the relative destabilization of the secondary minimum **Min 2**, which becomes less stable than the **α** and **β** isomers, by 3.6 and 14.6 kcal mol^{-1}, respectively (UB3LYP-bs), and by 8.0 and 17.4 kcal mol^{-1} using spin-corrected energies. Furthermore, the energy barrier to convert **Min 2** into the more stable **β** isomer is reduced to 7.6 kcal mol^{-1} (UB3LYP-bs) and to 3.2 kcal mol^{-1} with spin-corrected energies. This result is also in agreement with the experimental data since, to our knowledge, the **Min 2** isomer with one chelating and one bridging diphosphine has not been observed.

Conclusion

A dissociative mechanism has been fully characterized in the $[Mo_2Cl_4\{H_2P\text{–}(CH_2)_2\text{–}PH_2\}_2]$ complex for the reaction that connects the **α** isomer, with two chelating diphosphine ligands, to the **β** isomer with two bridging diphosphine ligands. It is essentially a two-step mechanism,with each step starting by the breaking of one Mo–P bond. The Mo–P bond exchange between the two metal centres is found to be accompanied by the simultaneous migration of a chloride ligand in the opposite direction. Therefore, the first step transforms the **α** isomer into an intermediate with one chelating and one bridging diphosphine ligand (**Min 2**) and the second step transforms **Min 2** into the **β** isomer. The activation energy computed at the unrestricted DFT-UB3LYP-bs level (24 kcal mol^{-1}) makes this dissociative mechanism competitive with the non-dissocative mechanism characterized previously.

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References

1 F. A. Cotton and R. A. Walton, in *Multiple Bonds between Metals Atoms*, Wiley, New York, 1982.
2 I. F. Fraser, A. McVitie and R. D. Peacock, *J. Chem. Res. (S)*, 1984, 420.
3 P. A. Agaskar, F. A. Cotton, D. R. Derringer, G. L. Powell, D. R. Root and T. J. Smith, *Inorg. Chem.*, 1985, **24**, 2786.
4 P. A. Agaskar and F. A. Cotton, *Inorg. Chem.*, 1986, **25**, 15.
5 F. A. Cotton and S. Kitagawa, *Polyhedron*, 1988, **7**, 463.
6 A. McVitie and R. D. Peacock, *Polyhedron*, 1992, **11**, 2531.
7 Y. Jean and A. Lledos, *Chem. Commun.*, 1998, 1443.
8 S. Blasco, I. Demachy, Y. Jean and A. Lledos, *New J. Chem.*, 2002, **26**, 1314.

9 J. VandeVondele, A. Magistrato and U. Rothlisberger, *Inorg. Chem.*, 2001, **40**, 5780.

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.6)*, Gaussian, Inc., Pittsburgh, PA, 1998.

11 (*a*) A. Lledos and Y. Jean, *Chem. Phys. Lett.*, 1998, **287**, 243; (*b*) I. Demachy, Y. Jean and A. Lledos, *Chem. Phys. Lett.*, 1999, **303**, 621; (*c*) I. Demachy, Y. Jean and A. Lledos, *Inorg. Chem.*, 1999, **38**, 5443; (*d*) S. Blasco, I. Demachy, Y. Jean and A. Lledos, *Inorg. Chim. Acta*, 2000, **300–302**, 837.

12 R. G. Parr and W. Yang, in *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, UK, 1989.

13 T. Ziegler, *Chem. Rev.*, 1991, **91**, 651.

14 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

16 P. J. Stephens, F. J. Delvin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

17 L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737.

18 K. Yamaguchi, F. Jensen, A. Dorigo and K. N. Houk, *Chem. Phys. Lett.*, 1988, **149**, 537.

19 S. Yamanaka, T. Kawakami, H. Nagao and K. Yamaguchi, *Chem. Phys. Lett.*, 1994, **231**, 25.

20 E. Goldstein, B. Beno and K. N. Houk, *J. Am. Chem. Soc.*, 1996, **118**, 6036.

21 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

22 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 28.

23 A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegman, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237.

24 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 225.