Density Functional Study of Tetraphenolate and Calix[4]arene Complexes of Early Transition Metals

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Density functional calculations have been performed on some calix[4]arenes complexes of early transition metals. Particular emphasis has been placed on the comparison of the main properties of these metal complexes with the analogous metal complexes based on four monodentate phenolate ligands to study the effect of the geometrical constraints imposed by the calixarenes framework on the electronic structure. The results show that the most stable geometry of titanium and molybdenum tetraphenolates is pseudotetrahedral (slightly flattened for molybdenum) and that the distortion to a square planar coordination requires, respectively, 52.0 and 21.5 kcal mol^{-1}. However, a significant energy decrease is found when the four phenolate groups are bent in the same hemisphere, reproducing the calix[4]arene geometry. Such a coordination determines the energy decrease of the unoccupied metal d orbitals of σ and π symmetry, which leads to an increase of the electron-accepting properties of these metal fragments.

1. Introduction

Calix[*n*]arenes are a family of macrocyclic molecules consisting of *n* para-substituted phenol units connected through methylene bridges in their ortho positions[1] (see Scheme 1). The calix[*n*]arenes can bind transition metal ions through their deprotonated phenolate groups. These groups are hard donor ligands and are therefore expected to show a preference for hard metal ions such as early transition metals in high oxidation states, although mid-transition metal complexes are known. While calix[6]arenes or larger calix[*n*]arenes, because of their conformational flexibility, can fully encapsulate the metal ion to form stable complexes, calix[4]arenes are conformationally rigid and could in principle act as a macrocyclic tetradentate ligand. Free calix[4]arenes can adopt four main conformations, the cone, the partial cone, the 1,2-alternate, and the 1,3-alternate,[2] whose energy order depends on the substituents on the upper rim. For a canonical calix[4]arene, where protons are bound to oxygen atoms, the cone conformation is the most stable.[3] For metallacalix[4]arenes, where the four oxygen atoms are coordinated to the metal center, the cone conformation is still the more stable, as revealed by several X-ray studies.[4] Actually, the first transition metal calix[4]arene complexes, such as [(Ti{*p*-Bu^t-calix[4]arene})$_2$], [(Fe(NH$_3$){*p*-Bu^t-calix[4]arene-OSiMe$_3$})$_2$], and [Co$_3${*p*-Bu^t-calix[4]-OSiMe$_3$}$_2$(THF)],[5] show dimeric structures in which the metals are bridged by a phenolate group from each of the two calixarene ligands.

Mononuclear complexes in which the calix[4]arene acts as one tetradentate macrocyclic ligand are much less common because of the high reactivity of the electron-deficient metal center.[6] The latter complexes have recently been exploited as polioxo matrices for reactive organometallic functionalities.[4] Although the anchoring groups in calixarenes are methylene-bridged phenolate anions, the metal supported by calix[4]arene has anomalous coordination and reactivity compared to metals

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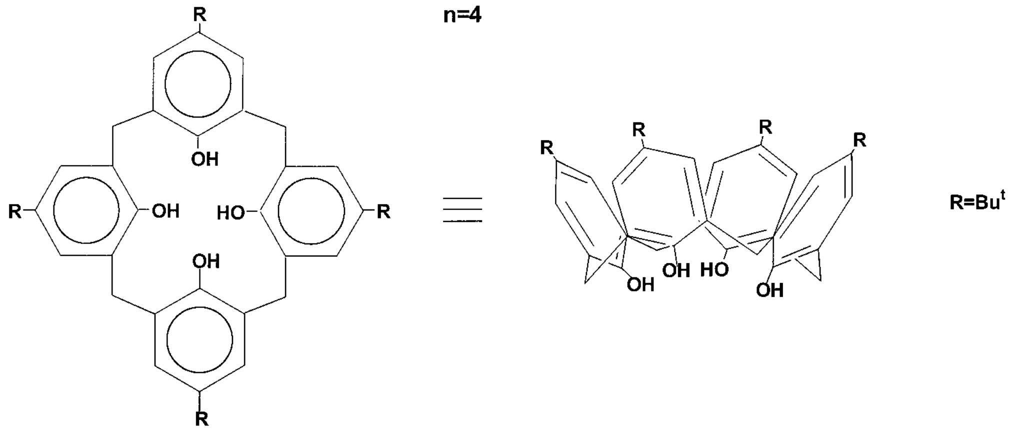
Scheme 1



supported by four monomeric phenolate moieties. This is mainly due to geometrical constraints imposed by the calixarene ligand, which provides an oxo surface nearly planar to the metal center, so the metallacalix[4]arenes can be considered as a molecular model of metal oxide surfaces. The aim of this work is to investigate how the geometrical constraint, imposed by this ancillary ligand, influences the electronic structure and the reactivity of early transition metals such as titanium and molybdenum. To achieve this goal, we have first considered some tetraphenolate complexes of early transition metals and studied their geometric and electronic structure. Mononuclear d^0-d^2 complexes supported by four homoleptic alkoxide and thiolate ligands have been intensively studied in the past[7] and structurally characterized.[8] It has been found that the d^0 complexes of group IV metals, such as $Ti(OAr)_4$,[9] are essentially tetrahedral while the d^2 complexes of group VI metals, such as $W(OAr)_4$,[10] show a flattened tetrahedral geometry. We have then considered the effect on the electronic structure and the reactivity of these complexes of gradually forcing the four phenolate groups to be in the same hemisphere, i.e. to reach the same geometry found for the corresponding metal calix[4]arenes.

2. Computational Details

The calculations reported in this paper are based on the ADF (Amsterdam density functional) program package described elsewhere.[11−13] Its main characteristics are the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each SCF cycle, the accurate and efficient numerical integration of the effective one-electron Hamiltonian matrix elements, and the possibility of freezing core orbitals. The frozen cores were 1s−2p for Ti, 1s−3d for Mo, and 1s for C and O. The molecular orbitals were expanded in an uncontracted DZ STO basis set for all atoms with the exception of the transition metal orbitals for which we used a DZ STO basis set for *n*s and *n*p and a TZ STO basis set for *n*d and $(n + 1)$s. As polarization functions, one $(n + 1)$p, one 3d, and one 2p STO were used for transition metals, O, and H, respectively.

The nonlocal (NL) exchange correlation potential and energy were used; the Becke's nonlocal correction[14] to the local exchange expression and the Perdew's nonlocal correction[15] to the local expression of correlation energy were included together with Vosko−Wilk−Nusair parametrization[16] for homogeneous electron gas correlation. It has been demonstrated that excellent metal−metal and ligand−metal bond energies are obtained from this density functional based approach.[17] Molecular structures were optimized by the NLDA method, thanks to the successful implementation of analytical energy gradients, within different symmetry constraints. It has already been demonstrated that the nonlocal corrections improve optimized geometries of transition metal complexes, especially metal−ligand bond lengths, otherwise almost uniformly too short (by about 0.05 Å) if calculated by local methods.[17] Electron affinities have been estimated as the energy difference between the total energies of anion and neutral species.

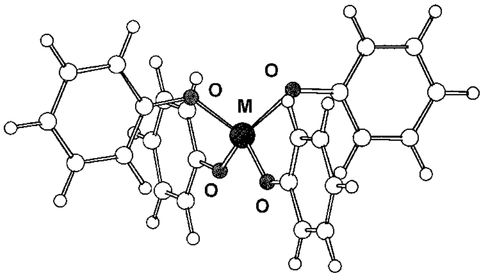


Figure 1. Structure of $M(OPh)_4$.

3. Results and Discussion

3.1. Titanium and Molybdenum Tetraphenolates. In this section we will consider the d^0 and d^2 tetraphenolates of groups IV and VI, taking Ti and Mo as examples. We first carried out a geometry optimization within the D_{2d} symmetry constraint. A $^1A_1$ singlet ground state has been found for both systems with two electrons occupying the d_{z^2} orbital in the Mo d^2 complex. The computed structures (see Figure 1) can be described in terms of two "W" moieties intersecting orthogonally, as a "gull's wings" structure; the main geometrical parameters are given in Table 1. These structures correspond to a distorted tetrahedral coordination around the metal, the distortion from the tetrahedral geometry being stronger for the molybdenum complex. In particular, the OMO angle increases slightly in passing from Ti to Mo, changing from 107.4° for

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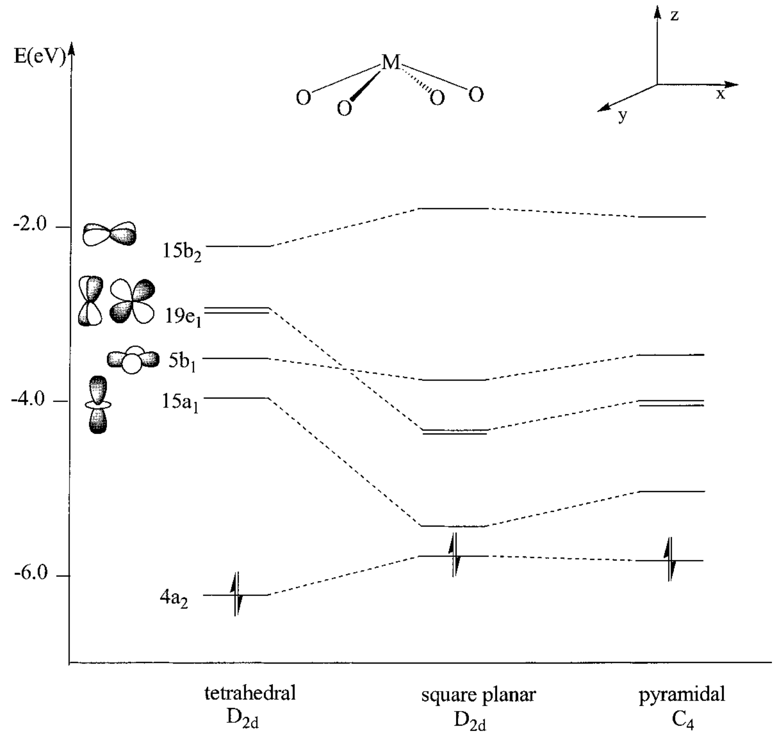

Figure 2. Frontier molecular orbitals diagram for Ti(OPh)$_4$ in (a) pseudotetrahedral, (b) square planar, and (c) square pyramidal coordination.

Table 1. Main Geometrical Parameters Calculated for Pseudotetrahedral M(OPh)$_4$ and for [Calix[4]O$_4$M] (M = Ti, Mo)

	symmetry	MO (Å)	OC (Å)	∠OMO (deg)	∠MOC (deg)
Ti(OPh)$_4$	D_{2d}	1.835	1.375	107.4	137.8
Mo(OPh)$_4$	D_{2d}	1.972	1.388	116.4	120.9
Ti(OAr-*i*-Pr$_2$)$_4$[9,a]		1.781		110.1	165.3
[calix[4]areneTi]	C_{4v}	1.866	1.357	159.7	135.6
[calix[4]areneMo]	C_{4v}	1.945	1.356	155.7	134.5

[a] The corresponding experimental parameters for Ti(OAr-*i* -Pr$_2$)$_4$ are reported for comparison.

Ti(OPh)$_4$ to 116.4° for Mo(OPh)$_4$, i.e., from an essentially tetrahedral to a flattened tetrahedral geometry. This trend is in agreement with the X-ray structures found for mononuclear d^0 and d^2 complexes supported by aryloxo and thiolate ligands.[8] For instance, while Ti(OAr-*i*-Pr$_2$)$_4$ is essentially tetrahedral,[9] W(SBu)$_4$, Mo(SAr)$_4$, and W(OAr)$_4$[10,18] display a variable degree of flattening from the tetrahedral geometry. This effect has been already studied at the semiempirical level[7] and has been attributed to the strong energy decrease of the lowest d$_{z^2}$ metal orbital upon tetrahedral to square planar deformation. It is worth noting that the optimized geometry calculated for the titanium phenolate is in reasonable agreement with the experimental X-ray structure available for the analogous Ti(OAr)$_4$ compounds[9] (see Table 1). The only discrepancies between experimental and computed data, shorter MO bond lengths and quite different ∠MOC, are due to ortho position substituents of experimental compounds. To the best of our knowledge, no mononuclear molybdenum aryloxo compound has been structurally characterized, the closest species being the Mo[S-2,4,6-C$_6$H$_2$(CHMe$_2$)$_3$]$_4$ tetrathiolate[18] displaying a ∠SMoS of 114.1 very close to that calculated for Mo(OPh)$_4$.

The frontier orbital energies of the titanium tetraphenolate are illustrated on the left of Figure 2. The lowest metal orbitals show a distorted three-over-two pattern, typical of pseudotetrahedral coordination, well above a group of low-lying symmetry combinations of the oxygen lone pairs. The lowest metal orbital is the 15a$_1$(d$_{z^2}$) with the 5b$_1$(d$_{x^2-y^2}$) slightly higher in energy, while the 19e$_1$(d$_{xz}$, d$_{yz}$) and the 15b$_2$(d$_{xy}$) are significantly higher. A similar metal orbital pattern is also observed for the molybdenum tetraphenolate.

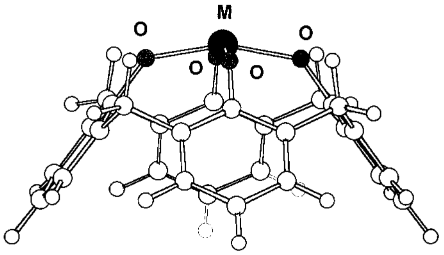

Figure 3. Structure of metal calix[4]arene.

3.2. Titanium and Molybdenum Calix[4]arenes. We have then considered titanium and molybdenum calix[4]arene complexes using a realistic model ligand where only the four *p*-Bu^t substituents are neglected (see Figure 3). A geometry optimization has been performed on both molecules, imposing C_{4v} symmetry, and the main optimized parameters for the lowest singlet states are reported in Table 1. A direct comparison with experimental geometries is difficult because most of the structurally characterized early transition metal calixarenes refer to dinuclear structures in which the metal shows a pseudotetrahedral coordination.[5] However, a few mononuclear titanium(IV) complexes with a monomethylated calix[4]arene ligand and an apical halogen or alkyl groups have been structurally characterized[19] and show geometrical parameters in satisfying agreement with the calculated values. For instance, the [Ti(calix)O$_3$(OMe)*p*-MeC$_6$H$_4$] complex shows the following average geometrical parameters concerning the phenolate oxy-

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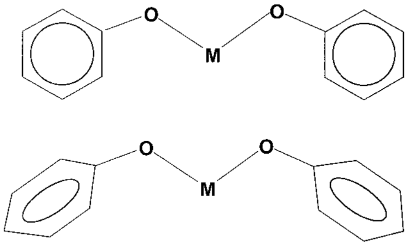
Scheme 2



gen: Ti−O = 1.81 Å, ∠OTiO = 156.0°, O−C = 1.36°, ∠TiOC = 131.0°, which agree reasonably well with the calculated values in Table 1. The energies of the frontier orbitals of titanium differ significantly from those of the corresponding metal tetraphenolate in its optimized pseudotetrahedral structure, showing the typical one-over-four pattern of square planar complexes[20] with a high-lying $12b_2(d_{xy})$.

Since negligible electronic effects may be foreseen for the four bridging methylenes, the differences between calixarenes and tetraphenolates can be essentially attributed to the effects of the peculiar coordination geometry imposed by the rigid macrocyclic structure on the four phenolate moieties; therefore, in the next chapters we will consider the tetraphenolate complexes by studying the effect of gradually forcing the four phenolate groups until they reach the same coordination found in the metal calixarenes.

3.3. Effects of Calixarene-like Geometrical Constraints on the Phenolate Ligands. For metal calix[4]arenes the presence of the methylene bridges imposes a strong geometry constraint to the four phenolate groups, which are forced to be in the same coordination hemisphere. The four oxygen atoms are nearly coplanar with the metal, the overall geometry being in most cases square pyramidal. This is quite different from both the pseudotetrahedral coordination shown by d^0 tetraphenolate complexes and the slightly flattened tetrahedral structure of d^2 complexes. Moreover, in the calixarene complexes the phenyl rings are oriented in a different way from that observed in the "gull's wings" structure of the free tetraphenolate (see Scheme 2). Indeed, the phenyl rings are arranged perpendicularly to the plane containing the two oxygens and the metal, while in the tetraphenolate complexes they lie in the same plane.

To understand how these geometrical constraints affect the electronic structure and the reactivity of the metal center, we analyzed the frontier orbitals of the investigated Ti and Mo tetraphenolates under the effects of two successive distortions: (i) from pseudotetrahedral to square planar and (ii) from square planar to pyramidal.

We first considered the pseudotetrahedral to square planar distortion, which has been realized by opening the two OMO angles, from an initial value of ca. 109.0° to 180.0° (see Scheme 3). The process has been carried out under D_{2d} symmetry constraints, keeping the phenyl rings oriented as in the optimized gull's wings structures. A steady energy rise has been observed on increasing ∠OMO from 109.0° to 180.0°.

Scheme 3

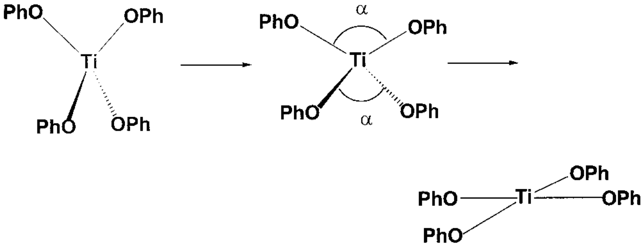


Table 2. Main Geometrical Parameters Calculated for $M(OPh)_4$ (M = Ti, Mo) in Constrained Square Planar and Pyramidal Coordination

	symmetry	MO (Å)	OC (Å)	∠OMO (deg)	∠MOC (deg)
square planar					
$Ti(OPh)_4$	D_{2d}	1.871	1.350	180.0	178.6
$Mo(OPh)_4$	D_{2d}	1.954	1.355	180.0	146.6
pyramidal					
$Ti(OPh)_4$	C_4	1.859	1.355	163.8	145.2
$Mo(OPh)_4$	C_4	1.938	1.357	160.6	145.8

The results of the constrained geometry optimization on the final square planar structure (with the ∠OMO frozen to 180.0°) are summarized in Table 2. In the planar $Ti(OPh)_4$ structure the axes of the phenyl rings are almost coplanar with the Ti−O bonds. On the other hand, the phenolate groups of the planar $Mo(OPh)_4$ remain bent as in the gulls wings structure, with ∠MOC of 145.0°. The square planar geometry for Ti has been calculated to be 52.0 kcal mol^{-1} higher in energy than the fully optimized pseudotetrahedral structure. A lower distortion energy has been found for $Mo(OPh)_4$ whose planar structure is only 21.5 kcal mol^{-1} less stable than the fully optimized geometry.

The orbital energies of the titanium complex in pseudotetrahedral and planar coordination, computed in D_{2d} symmetry, are illustrated in Figure 2. We see that upon distortion from tetrahedral to square planar coordination the three-over-two orbital pattern changes completely, showing a strong stabilization of the $15a_1(d_{z^2})$ and $19e_1(d_{xz},d_{yz})$ due to the displacement of the ligands toward the *xy* plane. On the other hand, the $15b_2(d_{xy})$ is strongly destabilized and lies very high in energy in the square planar coordination where it points directly toward the oxygen atoms. A quite similar orbital reordering is also observed for the molybdenum complex and is responsible of the different geometrical features of this d^2 complex. Indeed, the occupation by two electrons of the nonbonding low-lying $a_1(d_{z^2})$ (strongly stabilized upon distortion from tetrahedral to square planar coordination) leads to the stabilization of the square planar geometry for d^2 configuration, thus explaining the observed flattening of these complexes.[10,18] The above orbital reordering is essentially due to the change of nature of the σ and π interactions upon distortion from tetrahedral to square planar geometries. Figure 4 shows the main σ and π antibonding interactions between the metal d orbitals and the symmetry-adapted linear combinations of oxygen s and p orbitals for the tetrahedral and square planar coordination, classified according to the irreducible representations of the D_{2d} group. In the tetrahedral geometry the $b_2(d_{xy})$ and $e(d_{xz},d_{yz})$ orbitals give both σ and π interactions while the $a_1(d_{z^2})$ and $b_1(d_{x^2-y^2})$ give only π interactions. On the other hand, in square planar geometry the $b_2(d_{xy})$ gives only σ interaction, the $e(d_{xz},d_{yz})$ and $b_1(d_{x^2-y^2})$ give only π interactions, and the $a_1(d_{z^2})$ is nonbonding. Upon the tetrahedral to square planar distortion, the $b_2(d_{xy})$ and $b_1(d_{x^2-y^2})$ are destabilized because of the stronger σ and π interactions, respectively, while the $e(d_{xz}, ,d_{yz})$ and $a_1(d_{z^2})$ are stabilized, the former because it gives only π interactions and the latter because it becomes nonbonding.

We then considered the square planar to pyramidal distortion. This has been achieved by reducing stepwise both the OTiO angles between opposite oxygen atoms from 180.0° to 140.0° (see Scheme 4). Moreover, to reproduce completely the

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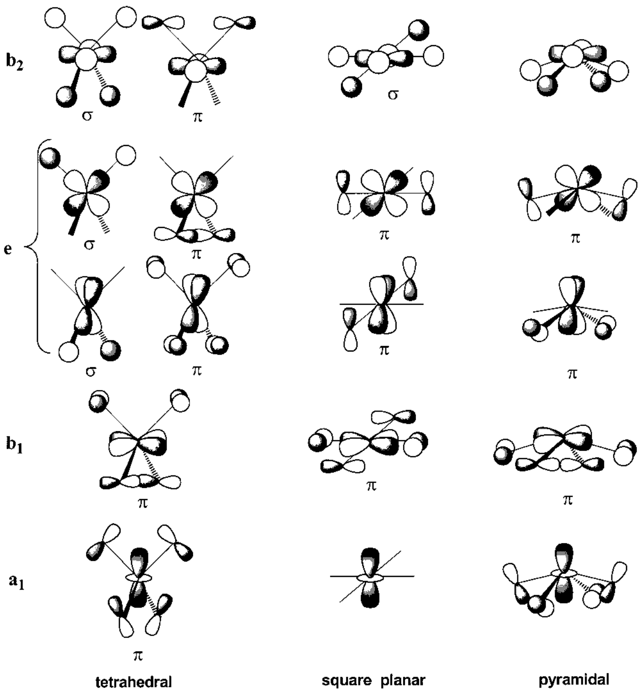
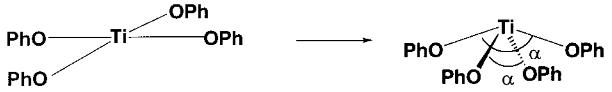


Figure 4. Main σ and π interactions between the metal d orbitals and the symmetry-adapted linear combinations of oxygen orbitals for the tetrahedral, square planar, and pyramidal coordination.

Scheme 4



geometry of the calixarene ligand, the phenyl rings should be rotated by 90° around the O$-$C(Ph) bond to be arranged perpendicularly to the OMO plane.

However, while in the metal calix[4]arenes the phenyl rings are naturally kept together by the $-CH_2$ bridges, in the pyramidal tetraphenolates the ortho-hydrogen atoms of adjacent rings may give nonbonding interactions. This problem was avoided by allowing the phenyl rings to rotate around the O$-$C bonds, therefore reducing the titanium tetraphenolate symmetry to C_4. Indeed, a few single-point calculations on the square planar $Ti(OPh)_4$ with different orientation of the phenyl groups gave similar total energies (within 5 kcal mol^{-1}) and left unaffected the frontier orbital pattern, showing that the rotation of the four phenyl rings has a negligible effect on the electronic structure of these tetraphenolate complexes (at least as long as no steric interaction is involved).

A significant energy decrease has been observed, reducing the $\angle$OMO in the pyramidalization process until a minimum is reached around 160.0$-$165.0°. Finally a full optimization within C_4 symmetry was performed and the main geometrical parameters are reported in Table 2 together with those calculated for the Mo complex. It is worth noting that this value is close to the $\angle$OMO values observed for several metal calix[4]arene complexes with 4-fold symmetry. This shows that metal calixarene complexes assume the most stable pyramidalization angle, a kind of "magic angle", within 4-fold symmetry constraints. The pyramidal geometries for Ti and Mo have been calculated to be, respectively, 9.5 and 16.5 kcal mol^{-1} lower in energy than the square planar structure.

The variation in energy of the main frontier orbitals of $Ti(OPh)_4$ associated with the distortion from square planar to pyramidal geometry is illustrated on the right of Figure 2. All orbitals are slightly destabilized except the $b_2(d_{xy})$, which is no longer directly pointing toward the oxygen. This is essentially due to the symmetry descent, which allows small but significant σ interaction, to d_{xz}, d_{yz}, and d_{xy} orbitals and removes the nonbonding character of d_{z^2}.

Table 3. Electron Affinities (EA) and Mulliken Charges (Q) for Titanium and Molybdenum Tetraphenolates in Tetrahedral, Square Planar, and Pyramidal Coordination and for the Corresponding Calix[4]arene Complexes

	EA (kcal mol^{-1})		Q	
	Ti	Mo	Ti	Mo
tetrahedral	21.3	47.5	1.76	1.75
square planar	63.5	57.1	1.72	1.60
pyramidal	59.6	46.0	1.68	1.55
calixarene	53.1	45.7	1.84	1.71

The energetics of the three considered geometries of titanium and molybdenum tetraphenolates is illustrated in Figure 5. This figure shows that when titanium is bound to four monodentate phenolate ligands, the minimum energy structure corresponds to a tetrahedral coordination, and the energy increases strongly when the system is flattened to a square planar coordination. However, when the planar titanium tetraphenolate is distorted to a pyramidal geometry, the energy shows a slight decrease and a constrained geometry optimization within C_4 symmetry (which simulates the $-CH_2$ bridges in the calix[4]arene), leading to a local minimum with $\angle OMO = 160°$.

An analogous behavior is found for the molybdenum tetraphenolate. In the latter complex, however, the square planar coordination is much lower in energy and the C_4 optimized pyramidal geometry is only 5 kcal mol^{-1} above the tetrahedral structure (see Figure 5). This difference can be attributed to the occupation by two electrons of the $a_1(d_{z^2})$ orbital, which is strongly stabilized upon tetrahedral to square planar coordination (see discussion above).

Finally we considered the effect of the pseudotetrahedral to square planar and square planar to pyramidal distortions on the reactivity of the metal tetraphenolate. The main effect of this distortion is the significant energy lowering of three metal d orbitals (one of σ and two of π symmetry), which makes this species highly electrophilic. This is supported by the increase of electron affinity calculated for these metal tetraphenolates upon tetrahedral to square planar distortion (see Table 3). It is worth noting that this increased electrophilicity is due exclusively to orbital factors because the charge on the metal is slightly affected, or even decreased, by the distortion (see Table 3). Because of the similarity between the geometrical and electronic properties of pyramidal tetraphenolates and the corresponding calixarenes (see Tables 1$-$3), we can assert that they will show an analogous reactivity. Indeed, (i) the geometrical parameters of the computed calixarenes agree quite well with those of the pyramidal tetraphenolates, (ii) the lower metal d orbitals, the d_{z^2}, d_{xz}, and d_{yz}, one of σ and two of π symmetry, are in a 0.9 eV energy range, like in the corresponding $Ti(OPh)_4$ (0.985 eV), and (iii) $\{calix[4]O_4\ M\}$ and $M(OPh)_4$ have similar electron affinities much higher than those of pseudotetrahedral tetraphenolates. The metal center of these calixarene complexes therefore shows an increased electrophilicity compared to metal supported by four monomeric phenolate moieties; it can be easily coordinated by σ and π donor species, and calix[4]arene ligand is appropriate for the stabilization of M$-$C, M$-$N, and M$-$O multiple bonds. That is confirmed by the synthesis and characterization of calixarene tungsten alkylidenes and alkylidynes[4] and calixarene molybdenum imido complexes.[21]

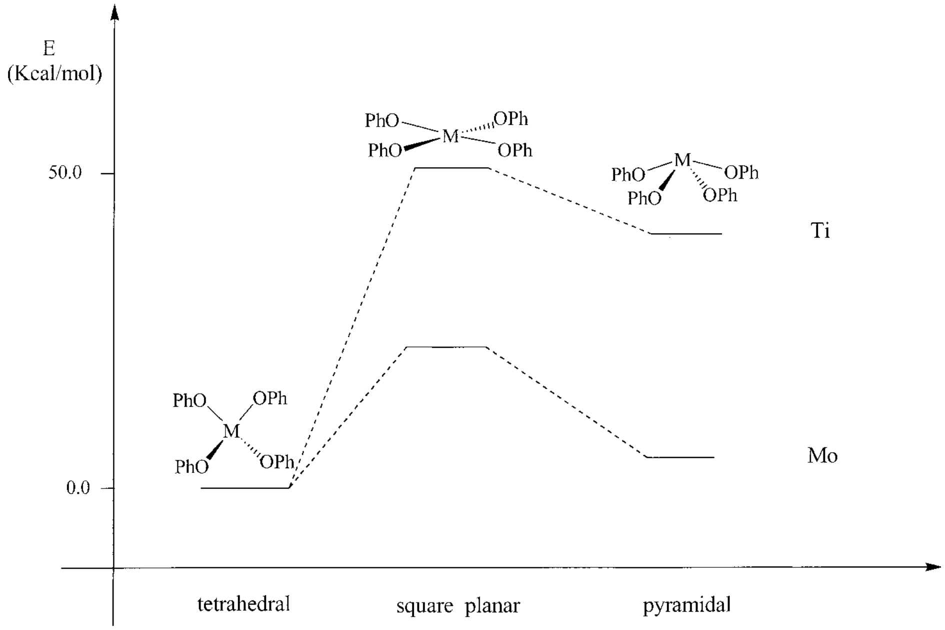


Figure 5. Energy minima of $M(OPh)_4$ (M = Ti, Mo) corresponding to tetrahedral, square planar, and pyramidal coordination.

4. Conclusions

In this paper density functional calculations have been performed on d^0 and d^2 calix[4]arenes of Ti and Mo. These complexes have been compared to another class of compounds, the Ti and Mo tetraphenolates, in which the central metal is bound to four phenolate groups. When the phenolate ligands are free, like in tetraphenolate, they arrange around the metal in a pseudotetrahedral coordination while in the calix[4]arene the metal has a nearly planar coordination with the four oxygens in the same hemisphere.

One of the main goals of this work has been to elucidate the effects on the electronic structure of the geometry constraints imposed by the macrocyclic structure of calix[4]arenes on the four phenolate ligands. This has been achieved by applying a tetrahedral to square planar to pyramidal distortion to the tetraphenolate complexes. The study of the energy pathways associated with these processes has revealed that the tetrahedral geometry is the more stable one; the energy increases during the tetrahedral to square planar distortion but slightly decreases during the square planar to pyramidal distortion, reaching a minimum for $\angle$OTiO of 160.0°, which is very close to the values observed in metal calix[4]arene complexes. The main effect of this distortions on frontier orbitals is the energy lowering of three metal d orbitals, one of σ and two of π symmetry, which makes this species highly electrophilic. This is established by the increase of electron affinities from tetrahedral to pyramidal metal tetraphenolates.

We have found that pyramidal $Ti(OPh)_4$ and {calix[4]-O_4-Ti} show the same metal d orbital sequence, confirming that the latter has essentially the same electronic properties of a tetraphenolate constrained by symmetry to have the four ligands in the same hemisphere. Therefore, the metal supported by calix[4]arene can bond to σ and π donor species and the ligand has the effect of stabilizing M−C, M−N, and M−O multiple bonds, as confirmed by the synthesis and characterization of several alkylidyne, alkylidene, imido, and oxo complexes.[4,21]

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