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Theoretical analysis of bis(ethylene) complexes of molybdenum and tungsten

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Dedicated to Professor Pascual Royo

Abstract

Density functional calculations on the zero-valent bis(ethylene) *trans*-$[M(C_2H_4)_2(PH_3)_4]$ model complexes and the actual *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M = Mo, W) compounds were carried out at the BPW91 level of theory. The experimentally characterised molecular structures of both molybdenum and tungsten complexes were properly reproduced by the energy optimised geometries only when the trimethylphosphine ligands were used. The experimentally observed ruffling of the phosphine ligands was not detected when the simplified model was considered. This discrepancy was interpreted as a consequence of different steric interactions between the PH_3 and PMe_3 ligands. The theoretical analysis gives a good account of some chemical properties observed in these compounds. In particular, the low PMe_3 dissociation energies calculated for these compounds are in agreement with the experimental observation of free phosphine dissociation in the solutions of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ compounds. The comparison of energy data for PH_3 and PMe_3 complexes corroborates the experimental hypothesis that phosphine dissociation has a steric origin.

Keywords: Ethylene complexes; DFT calculations; Molybdenum; Tungsten

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1. Introduction

From an experimental point of view, Carmona and co-workers have developed the chemistry of zero-valent molybdenum and tungsten bis(ethylene)-complexes containing phosphine co-ligands [1]. They have investigated systematically the reactivity of the $[M(C_2H_4)_2]$ core toward a variety of reagents [2]. For example, the interaction with carbon dioxide was shown to produce a unique example of ethylene carboxylation at the transition metal centre [3]. Subsequently, this reaction has also been observed in related complexes containing phosphite ligands [4] and the research on the chemical reactivity of the *trans*-$[M(C_2H_4)_2]$ core enlarged to other substrates [5]. On the other hand, other groups have also contributed to increase the knowledge of the chemical properties of Group 6 bis(ethylene) [6] and bis(olefin) derivatives [7].

From a theoretical point of view, the relative orientation of two ethylene ligands in octahedral zero-valent Group 6 metal complexes was a topic studied by Veillard and co-workers in a paper published in 1978 [8]. The consideration of metal–ligand π interactions and competition for d_π orbitals (metal–ligand back donation in terms of the Dewar–Chatt–Duncanson, DCD, model [9]) dictate the classical *trans*-staggered-eclipsed stereochemistry of such type of complexes. Afterwards, Hoffmann et al. published some papers dedicated to ethylene derivatives [10]. More recently, theoretical studies devoted to ethylene [11,12], bis(ethylene) [13], or, in general, to olefin complexes [14] are an area of great interest due to the intense research in olefin polymerisation processes [15] and other homogeneous

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Table 1
Selected structural parameters of *trans*-[$M(C_2H_4)_2(PR_3)_4$] complexes

Selected structural data [a]	Calculated R = H		Calculated R = Me		Experimental R = Me [b]	
	M = Mo	M = W	M = Mo	M = W	M = Mo	M = W
M–P	2.42	2.41	2.53	2.52	2.485(2)–2.506(2)	2.472(3)–2.499(3)
M–C	2.29	2.28	2.29	2.28	2.265(7)–2.276(6)	2.24(1)–2.27(1)
P–M–P(*cis*)	90.2	90.2	91.0	91.2	90.47(7)–91.73(7)	90.4(1)–91.8(1)
P–M–P(*trans*)	173.2	172.5	164.8	163.5		
C–C	1.44	1.46	1.44	1.46		
H–C–C–H [c]	141.9	139.1	140.6	137.3	138.2	130.6

[a] Bond lengths in Å, angles and torsion angles in °.

[b] Range of values are shown for some entries.

[c] Average torsion angle between the *trans* H atoms of ethylene ligand.

organometallic reactions in which metal–olefin complexes are possible intermediates [16].

In the present work, we describe density functional calculations on the bis(ethylene) *trans*-[$M(C_2H_4)_2(PH_3)_4$] model compounds and the actual *trans*-[$M(C_2H_4)_2(PMe_3)_4$] (M = Mo, W) complexes. Our main goal was to investigate the applicability of the small PH_3 ligand as a model for larger phosphines. We were particularly interested in the *trans*-[$M(C_2H_4)_2(PMe_3)_4$] → [$M(C_2H_4)_2(PMe_3)_3$] + PMe_3 dissociation process, which is thought to be the rate determining step in various reactions of these complexes.

2. Computational details

The electronic structure and optimised geometries of the *trans*-[$M(C_2H_4)_2(PR_3)_4$] (M = Mo, W; R = H, Me) complexes were computed within the framework of density functional theory using a generalised gradient-corrected functional. In particular we employed the Becke 1988 [17] exchange functional with Perdew and Wang's 1991 correlation functional [18] (referred to as BPW91). The Hay-Wadt Los Alamos National Laboratory 2 shell double-ζ (LANL2DZ) basis set with relativistic effective core potential was used for the Mo, W and P atoms [19]. The Dunning valence double-ζ basis set was used on hydrogen and first row atoms [20]. The basis set of P and C atoms were augmented with a set of d polarisation functions [21]. Bond energies (ΔE) and bond enthalpies at 298 K (ΔH) were calculated from the difference in the optimised energies of the ground states of the products and the reactants for the reaction sketched in Eq. (1) (see below). A collection of calculated energies and Cartesian coordinates for all optimised molecules are available from the authors upon request. All these calculations were performed using the GAUSSIAN98 package [22]. The molecular drawings of Figures have been made by using the program ORTEP-3 for WINDOWS [23] included in the graphic interface of WINGX [24].

A note of explanation is required concerning the optimisation process and the calculation of the bond energies. In the frequency calculations that follows the optimisation of the PH_3 models, using the default grid and convergence criteria in GAUSSIAN98, an imaginary frequency is obtained (Nimag = 1; $-44i$ cm^{-1} and $-29i$ cm^{-1} for Mo and W, respectively). Calculations were repeated using different starting geometries but they always converged to the same structure showing an imaginary frequency. Therefore, we decided to use tightened convergence criteria and a finer integration grid (Opt = Tight, Int = (Grid = Ultrafine) in GAUSSIAN98 keywords). The new optimised structures were found to be real local minima (Nimag = 0). The structural parameters of the new optimised structures are essentially the same. The values of bond distances and angles presented in Table 1 correspond to the optimised model using the tighter grid and convergence criteria. Nevertheless, as the values of the energy in DFT calculation depends on the integration grid used, and only these two complexes were calculated using this finer grid, the energy values discussed in the text correspond to the optimised geometries under the default convergence criteria. In the case of the PMe_3 compounds, default optimisation criteria and integration grid were used. A structure showing the PMe_3 ligands rotated 90° with respect to their positions in the X-ray structure was obtained. These structures were real minima (Nimag = 0) but they did not present the characteristic ruffling of the crystal structure. The optimisation was then repeated using a different starting geometry. A structure that reproduced the orientation of the PMe_3 ligands and the ruffling of the experimental structure was obtained, but the frequency calculation showed, again, an imaginary value (Nimag = 1; $-162i$ and $-30i$ cm^{-1} for Mo and W, respectively). The system is too large to repeat the calculation under tightened convergence criteria as in the case of the PH_3 model so in the light of the smallness of the changes involved in the case of PH_3, we have considered the latter obtained values to be valid in the discussion. No major differences are found in the structural parameters, with the exception of the P–M–P angles, and consequently we discuss only the data corresponding to the experimental structure. It should also be pointed out that in the case of PMe_3 the difference in energy between the two optimised structures is very small (less than 1 kcal mol^{-1}). In fact the energy of the structure with ruffling is slightly higher than the one without the ruffling. As it has been showed previously [25], systems with two or more moderately large ligands may present a potential energy surface (PES) which is flat around the energy minimum, probably due to a large number of competing long-range interactions.

As mentioned before, the total energies of relevant equilibrium structures were used to estimate the metal–ligand interaction energies. In particular, we were concerned with the energy of the $[M(C_2H_4)_2(PR_3)_4] \rightarrow [M(C_2H_4)_2(PR_3)_3] + PR_3$ dissociation process (see later) and we used another density functional methodology to analyse the M–PR_3 binding energies in terms of the energy partitioning scheme developed by Ziegler and Rauk [26]. These calculations were carried out at the BPW91 level as implemented in the ADF program (version 2000.02) [27]. The basis set we have chosen include the standard triple-ζ polarisation Slater-type orbital basis set for Mo and W (database IV in ADF) and the double-ζ polarisation set (database III) for the remaining atoms. The frozen core approximation was applied for the Mo(1s–3d), W(1s–4d) and P(1s–2p) inner shells and also for the 1s shells of the C and O atoms. First order relativistic corrections were included in the calculation of metal–ligand interaction energies.

According to the extended transition state scheme [26], the total binding energy (ΔE) is first separated into two terms: $\Delta E = \Delta E_{prep} + \Delta E_{int}$, where ΔE_{prep} (preparation energy) is the energy required for distortion of the fragments ($[M(C_2H_4)_2(PR_3)_3]$ and PR_3 in the present case) from their equilibrium structure to the geometry they have in the saturated $[M(C_2H_4)_2(PR_3)_4]$ complex, and ΔE_{int} (interaction energy) includes the following components: $\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$. Here, ΔE_{elstat} is the classical electrostatic interaction between the two unperturbed fragments charge distributions, ΔE_{Pauli} gives the Pauli repulsion between the occupied fragment orbitals, and finally, ΔE_{orb} corresponds to the orbital interaction energy.

We note that we have optimised the geometries of all complexes and fragments with the ADF code as well and for the equilibrium structural data we found a very good agreement with those given in Table 1. For example, the equilibrium bond lengths obtained with the two methods typically differ only by 0.01 Å, but not more than 0.03 Å, and the angles are equal to within 1°. Having this level of agreement, we did not feel important to report the ADF equilibrium structures here.

3. Results and discussion

Taking into account both theoretical [28] and experimental [29] data on zero-valent Group 6 bis(ethylene) compounds, only the *trans* configuration (staggered between both ethylene ligands and eclipsing the P–M–P vectors) was considered in our calculations. Initially, only the model compounds *trans*-$[M(C_2H_4)_2(PH_3)_4]$ (M = Mo, W) were considered with the aim to speed the calculations. However, as the optimised geometries of the model complexes did not reproduce well the geometries of the actual compounds and also as a recent theoretical work [30] showed that adequate modelling of the phosphine ligand has great impact on the structural predictions, the actual complexes, *trans*-$[M(C_2H_4)_2(PMe_3)_4]$, were considered as well. The whole set of possible combinations (M = Mo, W; $PR_3 = PH_3$, PMe_3) was optimised without symmetry restrictions. Selected calculated parameters and, for comparison, the corresponding experimental data from X-ray crystallography are collected in Table 1. The optimised geometries of the *trans*-$[M(C_2H_4)_2(PH_3)_4]$ and *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ complexes are depicted in Fig. 1.

The X-ray molecular structures of bis(ethylene) compounds have a distorted octahedral geometry characterised by the presence of two P–M–P angles lower than 180° (around 164°) for the *trans*-PMe_3 ligands ('ruffling'). Parkin et al. [31] have shown, in theoretical calculations of related *trans*-$[MX_2(PMe_3)_4]$ (M = Mo, W, X = F, Cl, Br, I) compounds, that the use of PH_3 as a substitute of PMe_3 ligands gave a poor description of the system, due precisely to absence of the experimentally observed 'ruffling' when PH_3 model was considered. This discrepancy was interpreted as a consequence of the steric differences between PH_3 and PMe_3. The structural data of Table 1 agree with this observation. For the model with R = H, it is evident that the M–P lengths are underestimated by more than 0.06 Å in the models. But, the major discrepancy found in the calculated structures with respect to the experimental values concerns the P–M–P angles. Optimised struc-

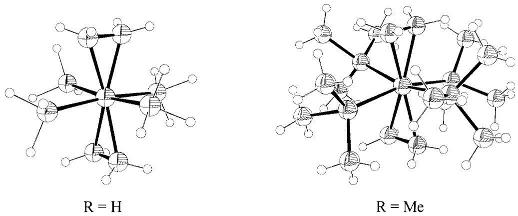

R = H R = Me

Fig. 1. Optimised structures of model compounds *trans*-$[M(C_2H_4)_2(PH_3)_4]$ and complexes *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M = Mo and W).

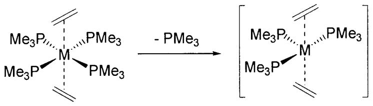
tures have only a minor distortion from octahedral geometry (absence of ruffling) and the computed *trans* P–M–P angles are around 173°, which is a large deviation with respect to the experimental values.

For the actual complexes, one can observe a satisfactory agreement between the calculated and experimental values of geometrical parameters for both metals. The M–P bonds are only slightly overestimated and, in general, bond distances agree within 0.05 Å. The largest deviation of bond angles appears to be about 3°. The description of the characteristic ruffling in these molecules is satisfactorily adequate when the actual PMe_3 ligand was considered. Calculated *trans*-P–M–P angles deviated less than 1° from those found in the X-ray structure. Bond lengths and angles around the metal-ethylene moiety agree well with experimental data, being the distances overestimated by around 0.02 Å whatever the R group is. Similar overestimation was found in the calculation of *trans*-$[W(C_2H_4)_2(CO)_4]$ [13b,13c]. The computed C–C and W–C bond lengths in *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (1.46 and 2.28 Å, respectively) are of the same order of magnitude than other calculated values in tungsten(0) complexes. For example, those reported by Frenking and Pidun [12a,12b], 1.402 and 2.372 Å in $[W(C_2H_4)(CO)_5]$, and those calculated for *trans*-$[W(C_2H_4)_2(CO)_4]$ (1.436 and 2.360 Å [13b]; 1.418 and 2.349 Å [13c]). The computed C–C distances are larger than those reported in a recent study of $[Cr(C_2X_4)(CO)_5]$ complexes [32] (1.385, 1.414 and 1.425 Å for X = H, F and Cl, respectively), but compares well with that calculated for calyx[4]arene W(IV) complexes [12c] (1.452 and 1.450 Å).

The H–C–C–H torsion angle about the carbon–carbon bond (usually represented by γ) has been used as a measure of the non-planarity of the bound olefin [33], which manifests in the bending back of substituent groups away from the metal. Low γ values would imply smaller sp^2 character for the bound carbon atoms and, in terms of the DCD model, an increase in the metal-ethylene back-bonding. With the exception of a report [34] in which the existence of a metalla-cyclopropane structure was shown to have a low propeller rotation barrier, generally the free ethylene rotation is favoured in species where the metal-ethylene acceptor component is small [10a,35]. The computed H–C–C–H torsion angle between the *trans* H atoms of ethylene ligand is higher in the molybdenum compound than in the tungsten one. On the basis of these data, the effect on changing from Mo to W would produce an increase in the $M(d_\pi)–C_2H_4(\pi^*)$ back-bonding and, thus, in terms of the DCD model the metalla-cyclopropane contribution is higher in the tungsten complex than in the molybdenum one, in which the π-component is superior. These facts are in agreement with the experimental observation [2,3] of a more rapid fluxional process for the Mo derivative than for the W complex, at the same temperature.

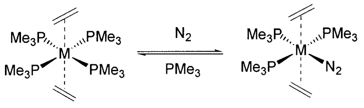
The fluxional processes mentioned above are observed in solution at room temperature and are due to a conrotatory metal-ethylene rotation mechanism [2,5b]. The coordination sphere around the metal is quite crowded and, as we have shown before [5b], the ethylene rotation must be concerted with a PMe_3 rotation around the M–P vector in order to avoid the steric pressure of the phosphine methyl arms. Our calculations have shown (see Computational details) that a second structure with the orientation of the PMe_3 ligands rotated by ca. 90° is energetically accessible and consequently the ethylene rotation is feasible in spite of the steric congestion around the metal centre. These results are in line with the presence of a fluxional process at room temperature.

Furthermore, the chemical reactivity of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ complexes is dominated by a solution behaviour characterised by the straightforward dissociation of one PMe_3 ligand (Eq. (1)) [2–5]. The availability of a vacant coordination site generates rich chemistry in this system.



(1)

For example, petroleum ether solutions of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$, under nitrogen, show IR absorptions in the range of metal-dinitrogen derivatives due to the formation of complexes $[M(C_2H_4)_2(N_2)(PMe_3)_3]$. An equilibrium, such as represented in Eq. (2) is set up in solution [2a,2b]. The formation of $[M(C_2H_4)_2(N_2)(PMe_3)_3]$ occurs, in our opinion, through a stepwise process in which the creation of a vacant coordination position, i.e. formation of the unsaturated $[M(C_2H_4)_2(PMe_3)_3]$ species, is the rate determining step. An alternative concerted mechanism is not feasible due to the steric hindrance caused by the ligands.



(2)

In order to gain a better comprehension of this dissociative process, we have theoretically studied the unsaturated $[M(C_2H_4)_2(PR_3)_3]$ species (M = Mo, W; R = H, Me). The geometry of these complexes was fully optimised at the same level of theory as the saturated systems. Selected calculated parameters of the final computed structures have been collected in Table 2. The optimised structures of the $[M(C_2H_4)_2(PH_3)_3]$ and $[M(C_2H_4)_2(PMe_3)_3]$ species are displayed in Fig. 2.

For a comparison between the saturated and unsaturated species we have centred our attention on the complexes containing the actual PMe_3 ligands. The

Table 2
Selected bond lengths (Å), angles and torsion angles (°) of calculated unsaturated $[M(C_2H_4)_2(PR_3)_3]$ complexes

Selected structural data	R = H		R = Me	
	M = Mo	M = W	M = Mo	M = W
M–P [a]	2.33/2.41	2.33/2.41	2.37/2.48	2.37/2.47
M–C(I)	2.26	2.24	2.26	2.24
M–C(II) [a]	2.24/2.31	2.22/2.30	2.23/2.31	2.21/2.29
P–M–P(*cis*)	91.0	91.0	96.2	96.1
P–M–P(*trans*)	169.7	169.7	163.7	163.1
C–C [a]	1.45/1.45	1.46/1.46	1.45/1.45	1.46/1.47

[a] The values separated by slashes correspond to two unequivalent fragments (the symmetry of the complexes reduce upon PR_3 dissociation).

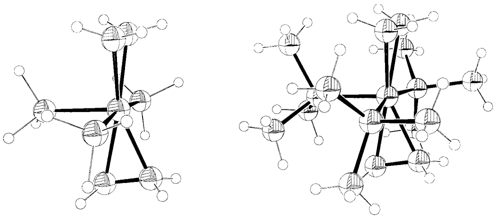

R = H R = Me

Fig. 2. Optimised structures of unsaturated $[M(C_2H_4)_2(PH_3)_3]$ and $[M(C_2H_4)_2(PMe_3)_3]$ species (M = Mo and W).

geometry distortion of the complexes when a PMe_3 ligand is dissociated merits some comments. First of all, we see a notable decrease in the M–P bond lengths. In particular, the M–P bonds in the *trans* position to the dissociating PMe_3 ligand shorten significantly for both Mo and W cases, which can be interpreted in the terms of the removal of the *trans* influence [36]. The C–C distances are barely altered, but the relative positions of the ethylene ligands change. The two ligands are displaced slightly to the vacant position and move from the perfectly *trans* disposition, with D1–M–D2 angles (D1 and D2 are the midpoints of the ethylene molecules) very close to 180°, to lower values of this angle (167 and 164° for the Mo and W complex, respectively). Furthermore, the M–C bonds for one C_2H_4 ligand remain almost unchanged (a slight drop off of about 0.02 Å for one ethylene molecule, C(I) in Table 2), but the bonding of the second ethylene molecule (C(II) in Table 2) changes appreciably. For this molecule, the bonding is asymmetric with a M–C distance longer than the other (for example: 2.24 and 2.31 Å in the Mo complex). These structural changes are related to the reduction of Pauli repulsion between the C_2H_4 and PR_3 ligands upon PR_3 dissociation, which allows a more efficient metal-ethylene backbonding.

The dissociation energies corresponding to the reaction displayed in Eq. (1) are summarised in Table 3. The inspection of this Table confirms some features concerning the dissociation process. The results suggest that a simple model (R = H) could not be suitable enough to describe the chemical properties of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ complexes. The reason is that the spontaneous dissociation process observed at room temperature does not fit well with the calculated ΔH_{298} value for the PH_3 model. On the other hand, the ΔH_{298} value for the actual W compounds is higher than the Mo one in accordance with the observation that the equilibrium shown in Eq. (2) is more shifted to the side of $[M(C_2H_4)_2(N_2)(PMe_3)_3]$ for the molybdenum complex than for the W analogue [2b].

Table 3
Energetics of the dissociation reaction of *trans*-$[M(C_2H_4)_2(PR_3)_4]$ complexes (kcal mol^{-1})

R	R = H		R = Me	
M	Mo	W	Mo	W
ΔE	25.7	29.9	3.7	6.5
$\Delta(E+ZPE)$	22.8	26.8	0.5	2.9
ΔH_{298}	23.9	28.8	1.6	3.9

The enthalpy data of Eq. (1) are the calculated bond dissociation enthalpies of PH_3 and PMe_3 and they are related with the bond strength of the M–P bond. From experimental calorimetric measurements, Nolan et al. [37] estimated the bond strength of Mo–P bond for different phosphine ligands. The values cover the range 35–43 kcal mol^{-1} and depend on the electronic and steric nature of the phosphine. From a theoretical point of view, Poli and co-workers have studied the PH_3 dissociation in $CpMoX(PH_3)_2$ model complexes and the computed bond dissociation energies are influenced by the electronic and steric properties of the metal centre, which are modulated by the nature of X co-ligand [38]. For a dissociation, without spin state change and without substantial π-donation stabilisation, the calculated values are between 13.4 and 25.3 kcal mol^{-1}. Our computed values for the PH_3 complexes are in consonance with the above data but those of PMe_3 are substantially lower.

In order to understand the role of electronic and steric factors in the variation of dissociation energies, we analysed the M–PR_3 binding energies using the extended transition state scheme [26]. The calculated energy components for the $[M(C_2H_4)_2(PR_3)_4] \rightarrow [M(C_2H_4)_2(PR_3)_3] + PR_3$ dissociation reactions (Eq. (1)) are collected in Table 4.

Note first that the ADF binding energies obtained for the small models are very similar to those in the GAUSSIAN98 calculations, which would one expect provided we employ the same functional and reasonably large basis sets in the two methodologies. Surprisingly enough, we find notable deviations in the binding energies of the $[M(C_2H_4)_2(PMe_3)_4]$ complexes (11.2 vs.

Table 4
Energy decomposition of $[M(C_2H_4)_2(PR_3)_3]+PR_3$ (kcal mol^{-1}) [a]

Energy terms	M = Mo		M = W	
	R = H	R = Me	R = H	R = Me
$\Delta E = \Delta E_{prep} + \Delta E_{int}$ [b]	25.8 (25.7)	11.2 (3.7)	30.8 (29.9)	13.6 (6.5)
ΔE_{prep} [c]	−3.6	−17.4	−4.9	−21.5
ΔE_{prep}(A)	−3.4	−16.8	−4.7	−20.7
ΔE_{prep}(B)	−0.2	−0.6	−0.2	−0.8
ΔE_{int}	29.4	28.6	35.7	35.1
ΔE_{Pauli}	−112.4	−116.5	−136.0	−140.3
ΔE_{elstat}	84.0	88.8	103.7	109.3
ΔE_{orb}	57.8	56.3	68.0	66.1

[a] Positive (negative) sign refers to stabilisation (destabilisation).

[b] GAUSSIAN results are shown in parentheses.

[c] A and B denote the $M(C_2H_4)_2(PR_3)_3$ and PR_3 fragments, respectively.

3.7 kcal mol^{-1} for M = Mo and 13.6 vs. 6.5 kcal mol^{-1} for M = W). These results suggest that the steric PR_3–PR_3 interactions are not described at the same level of accuracy by the two DFT methods. The steric repulsion energy of the six ligands in the $[Mo(C_2H_4)_2(PMe_3)_4]$ complex was estimated by simply disregarding the metal atom and computing the total energy of the $(C_2H_4)_2(PR_3)_4$ moiety for the arrangement they have in the *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ complex. In line with the calculated Mo–PMe_3 binding energies, the destabilisation is predicted to be significantly more important with GAUSSIAN98 (63 kcal mol^{-1}) than in the ADF calculations (47 kcal mol^{-1}) (the two energy values correspond to the same geometry, i.e. the one described in Table 1). It would be quite interesting to examine the reason why the two widely used DFT implementations provide so different energetics for the above repulsive interactions [39], but here we will rather focus on the trends we found for the PR_3 binding energies.

Table 4 reveals that for a given metal, the ΔE_{int} contributions to the binding energies, which include all electronic M–PR_3 interactions between the frozen $[M(C_2H_4)_2(PR_3)_3]$ and PR_3 fragments, are nearly identical for the R = H and R = CH_3 complexes. On the contrary, the preparation energies are very different for the two models, which is due to the large distortion energy of the $[M(C_2H_4)_2(PMe_3)_3]$ fragment as compared with $[M(C_2H_4)_2(PH_3)_3]$. Additionally, one can also understand the variation of the M–PR_3 bond strength when going from M = Mo to M = W. Table 4 shows that the absolute values of the ΔE_{int} interaction energies are 6–7 kcal mol^{-1} larger for the tungsten complexes, which can be traced back to the variation of the three components of ΔE_{int}. Both types of attractive interactions (ΔE_{elstat} and ΔE_{Pauli}) become stronger in the tungsten complexes—particularly, the electrostatic contributions are more important in the $[W(C_2H_4)_2(PR_3)_4]$ complexes—however, they are partially compensated by the increase in the Pauli repulsion. The ΔE_{prep} contributions provide further compensation to the above energy differences and as a result, the tungsten complexes are only a few kcal mol^{-1} more stable with respect to phosphine dissociation.

Our energy decomposition analysis thus corroborates the experimental hypothesis [3b,4] that phosphine dissociation has steric origin, rather than electronic. The presence of two *trans* staggered ethylene induces a precise orientation for the Me arms of PMe_3 ligands in terms of steric repulsions. Not all the four PMe_3 molecules in the equatorial plane can be accommodated in the best way in order to alleviate the overcrowding and this fact causes severe conflicts between the in-plane co-ligands. The congestion around the metal centre is larger than other related *trans*-$[MX_2(PR_3)_4]$ systems where X is a symmetric ligand with respect to a free rotation around the M–X vector.

Our calculated energies for PMe_3 dissociation reflect a relatively weak M–P bond strength in agreement with several experimental facts. However, these data do not represent a general trend for the dissociation of PMe_3 in Group 6-ethylene complexes [42] and must be only ascribed to the *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ system. For example, a diminution of the steric hindrance can be accomplished by the substitution of two PMe_3 by $Me_2PCH_2CH_2PMe_2$ (dmpe) maintaining approximately constant the electronic characteristics of the metal. When passing from *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ to *trans*-$[M(C_2H_4)_2(dmpe)(PMe_3)_2]$ complexes [3b] two experimental facts are remarkable: (i) no PMe_3 dissociation is observable; and (ii) the chemical reactivity is diminished. These properties are consistent with a reinforcement of the Mo–P strength due to the absence of steric repulsions. Work is in progress in order to study related bis(ethylene)-Group 6 complexes and verify the bond strength of the metal–phosphine interaction.

4. Conclusions

In this paper, we have studied the *trans*-[M(C_2H_4)$_2$(PMe_3)$_4$] (M = Mo, W) complexes by making use of two of the most widely used Density Functional Theory programs (GAUSSIAN and ADF). The experimental molecular structures of both complexes were properly reproduced only when the trimethylphosphine ligands were used in the calculations. In this system, where the metal surroundings are overcrowded, the use of the PH_3 as a model for PMe_3 ligand is not adequate as the former do not properly describe the steric interactions between the phosphine ligands. The *trans*-[M(C_2H_4)$_2$(PMe_3)$_4$] → [M(C_2H_4)$_2$(PMe_3)$_3$] + PMe_3 dissociation process, which is thought to be the rate determining step in various reactions of these complexes, was also studied. The atypical low PMe_3 dissociation energies calculated for these compounds are in agreement with the experimental observation of phosphine dissociation in the solutions of *trans*-[M(C_2H_4)$_2$(PMe_3)$_4$] compounds. The comparison of energy decomposition data for PH_3 and PMe_3 complexes corroborates the experimental hypothesis that phosphine dissociation has a steric origin.

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