DFT Analysis of Bis(ethylene) Complexes of Molybdenum and Tungsten: Substitution Reactions and Bond Dissociation Energies

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Received March 3, 2003

Theoretical calculations of DFT type on the molybdenum and tungsten zerovalent bis(ethylene) species *trans,mer*-$M(C_2H_4)_2(N_2)(PR_3)_3$ (**2**) and *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ ($M =$ Mo, W, $R =$ H, Me, $x = 1-4$; **3**−**6**) compounds were carried out. The study allowed the calculation of the relative energies (ΔE) corresponding to several substitution reactions of bis(ethylene) compounds. In particular, the solution behavior of *trans*-$M(C_2H_4)_2(PMe_3)_4$ (**1**) compounds and the formation of complexes **2** were investigated. Additionally, the subsequent CO substitution reactions, starting from the parent *trans*-$M(C_2H_4)_2(PR_3)_4$ (**1**) and resulting in *trans*-$M(C_2H_4)_2(CO)_4$ (**6**) derivatives, were also analyzed. The computed ΔE values for the bis(ethylene) compounds containing PMe_3 were in good agreement with the experimentally observed processes. In fact, the comparison of the reaction energies ΔE accounts well for the synthesis of *trans,mer*-$M(C_2H_4)_2(CO)(PMe_3)_3$ (**3**) and *trans,trans,trans*-$M(C_2H_4)_2(CO)_2(PMe_3)_2$ (**4**) starting from **1** and also for the fact that *trans*-$M(C_2H_4)_2(CO)_3(PMe_3)$ (**5**) type complexes are not formed from **4**. The effect of the substitution of PMe_3 by CO on the π-acceptor capabilities of ethylene ligands was also studied in the series of complexes *trans*-$M(C_2H_4)_2(CO)_x(PMe_3)_{4-x}$ ($x = 0-4$). In fact, the C−C ethylene distance diminishes and the Mo−C(C_2H_4) distance increases gradually and simultaneously with the incorporation of CO ligands. Furthermore, the energies and optimized geometries of the unsaturated complexes *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{3-x}$ ($M =$ Mo, W, $R =$ H, Me, $x = 1-3$) were computed. These calculations allow us to estimate the bond dissociation energies (BDEs) of CO and PR_3 groups in the saturated compounds.

Introduction

The chemistry of molybdenum and tungsten bis(ethylene) compounds containing PMe_3 coligands have been developed by Carmona's research group.[1,2] The most important chemical feature of *trans*-$M(C_2H_4)_2(PMe_3)_4$ ($M =$ Mo, W) complexes is their behavior in solution, where a straightforward dissociation of one PMe_3 ligand is easily detected. The availability of a vacant coordination site generates rich chemistry in this system. In fact, Carmona and co-workers[3,4] have investigated systematically the reactivity of these bis(ethylene) compounds toward a variety of reagents. From a theoretical point of view, we have recently studied, in collaboration with Papai and Schubert,[5] the *trans*-$M(C_2H_4)_2(PMe_3)_4$ ($M =$ Mo, W) complexes by making use of the DFT approach. The molecular structures and some experimental properties of these compounds were properly reproduced. In addition, the PMe_3 dissociation process was studied and the corresponding bonding dissociation energy was calculated. The computed value was atypically low (for instance, $\Delta E = 3.7$ kcal/mol for the Mo complex), and the energy decomposition data corroborated the experimental hypothesis that the dissociation process has a steric origin.[5]

In this paper, we have extended the studies on bis(ethylene) group 6 derivatives to *trans,mer*-$M(C_2H_4)_2(N_2)(PR_3)_3$ (**2**) and *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ ($M =$ Mo, W, $R =$ H, Me, $x = 1-4$, **3**−**6**) compounds. The optimized structures of these compounds are described, and the energies of several substitution reactions, starting from *trans*-$M(C_2H_4)_2(PR_3)_4$ (**1**) and resulting in *trans*-$M(C_2H_4)_2(CO)_4$ (**6**), are discussed. Bond dissociation energies (BDEs) in transition-metal compounds are not easy to determine by experimental procedures,[6] and DFT methods offer a possible alternative to overcome

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10.1021/om030147+ CCC: $25.00
Publication on Web 06/17/2003

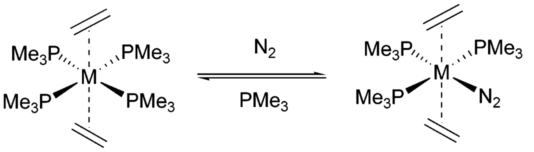
this difficulty. In this respect, calculations on the unsaturated complexes *trans*-M(C_2H_4)$_2$(CO)$_x$(PR$_3$)$_{3-x}$ (M = Mo, W, R = H, Me, x = 1−3) have permitted the estimation of the M−PMe$_3$ and M−CO bond dissociation energies in these bis(ethylene) compounds. While our work was in progress, DFT calculations on the complex *trans*-W(C_2H_4)$_2$(CO)$_4$ (**6b**) were reported.[7]

Computational Details

The electronic structure and optimized geometries of the compounds *trans,mer*-M(C_2H_4)$_2$(N_2)(PR$_3$)$_3$ (**2**), *trans*-M(C_2H_4)$_2$(CO)$_x$(PR$_3$)$_{4-x}$ (M = Mo, W, R = H, Me, x = 1−4; **3**−**6**), and the unsaturated complexes *trans*-M(C_2H_4)$_2$(CO)$_x$(PR$_3$)$_{3-x}$ (M = Mo, W; R = H, Me; x = 1−3) were computed within the framework of density functional theory using a generalized gradient-corrected functional. In particular, we employed the Becke 1988[8] exchange functional with Perdew and Wang's 1991 correlation functional[9] (referred to as BPW91). The Hay−Wadt Los Alamos National Laboratory two-shell double-ζ (LANL2DZ) basis set with relativistic effective core potential was used for the Mo, W, and P atoms.[10] The Dunning valence double-ζ basis set was used on hydrogen and first-row atoms.[11] The basis sets of P and C atoms were augmented with a set of d polarization functions.[12] This computational approach has been used for a similar system (*trans*-M(C_2H_4)$_2$(PR$_3$)$_4$) with good accuracy.[5] The optimized geometries were characterized as local energy minima by diagonalization of the analytically computed Hessian (vibrational frequency calculations). Relative reaction energies (ΔE) were calculated from the difference in the optimized energies of the ground states of the products and those of the reactants in a given reaction. Bond dissociation energies (BDE) were calculated from the difference in the optimized energies of the ground states of the unsaturated species and the dissociated ligands and those of the corresponding *trans*-M(C_2H_4)$_2$(CO)$_x$(PR$_3$)$_{4-x}$ compounds and included ZPE corrections. These values were computed without corrections for basis set superposition error, since we are concerned exclusively with relative energies and their trends and such errors can be assumed to be small at the DFT level.[13] A collection of calculated energies and Cartesian coordinates for all optimized molecules are available from the authors upon request. All these calculations were performed using the Gaussian98 package.[14] The molecular drawings of Figures 1−3 have been made by using the program ORTEP-3 for Windows[15] included in the graphic interface of WINGX.[16]

Results and Discussion

***trans,mer*-M(C_2H_4)$_2$(N_2)(PMe$_3$)$_3$ Compounds.** Petroleum ether solutions of *trans*-M(C_2H_4)$_2$(PMe$_3$)$_4$ (**1**) compounds, under nitrogen, show IR absorptions in the range of metal−dinitrogen derivatives due to the formation of *trans,mer*-M(C_2H_4)$_2$(N_2)(PMe$_3$)$_3$ (M = Mo (**2a**), W (**2b**)) complexes.[17] An equilibrium, such as that represented in eq 1, is established in solution.[2] As we stated before,[5] the formation of **2** occurs through a stepwise process in which the creation of a vacant coordination position is the first step: i.e., formation of the unsaturated *trans*-[M(C_2H_4)$_2$(PMe$_3$)$_3$] species (M = Mo, W).



(1)

1 **2**

With the aim of understanding the whole process and of completing the previous calculations on compounds **1**,[5] we have studied the *trans,mer*-M(C_2H_4)$_2$(N_2)(PR$_3$)$_3$ complexes at the DFT level of theory. The whole set of possible combinations (M = Mo, W, PR$_3$ = PH$_3$, PMe$_3$) was optimized without symmetry restrictions. Only the most stable trans-staggered configuration of the M(C_2H_4)$_2$ moiety was considered in our calculations.[18] Similar restriction was applied to all the rest of the calculations in this work. In agreement with other authors who pointed out the failure of the modelization of PMe$_3$ by PH$_3$ due to steric reasons,[19] we noticed[5] that the use of PH$_3$ as a model for the PMe$_3$ ligand had important consequences in this type of compound and this substitution is not adequate. Despite this fact, we have also calculated, for comparative purposes, the PH$_3$ model compounds, and the greater part of these results are included as Supporting Information. We will focus our attention, here and throughout the paper, on the discussion of the computed results for PMe$_3$ compounds.

The optimized geometry of the molybdenum complex **2a** is depicted in Figure 1; the geometry of the tungsten derivative **2b** is fully analogous to that of **2a**. Calculated bond distances and angles of *trans,mer*-M(C_2H_4)$_2$(N_2)(PR$_3$)$_3$ are collected in the Supporting Information. The M−P bond distances in **2** are ca. 0.1 Å shorter than those calculated for the parent *trans*-M(C_2H_4)$_2$(PMe$_3$)$_4$ compounds.[5] Conversely, the bond lengths around the

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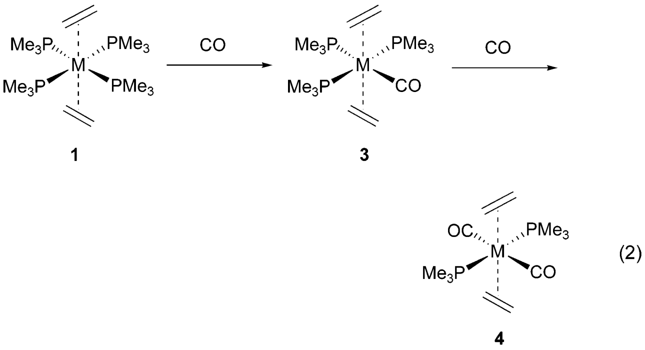
$M(C_2H_4)_2$ moiety do not show any major variation. The computed trans P−M−P angles are around 170°, a value greater than the 165° computed for the complexes containing four PMe_3 ligands. These data suggest yet again the importance of the steric effects in the structural distortions found in *trans*-$M(C_2H_4)_2(PMe_3)_4$ ("ruffling"). The substitution of one PMe_3 by N_2 alleviates the congestion around the metal center, and consequently, the ruffling roughly disappears. The reaction energies corresponding to eq 1 are around −21 kcal/mol for both Mo and W species. Thus, the substitution of one phosphine ligand by the dinitrogen molecule is clearly favored energetically, which is in line with the experimental evidence.[2] There are two reasons for the shifting of the equilibrium displayed in eq 1 to the *trans,mer*-$M(C_2H_4)_2(N_2)(PMe_3)_3$ compounds. One is related to the diminution of the steric congestion around the metal center, as stated above. The second is connected with the MO distribution of a d^6-$M(C_2H_4)_2$ metal fragment.[20] Considering the z axis along the vector that joins the two midpoints of the ethylene ligands ($M(C_2H_4)_2$ moiety), the HOMO of *trans*-$M(C_2H_4)_2(PMe_3)_4$ is mostly the d_{xy} metal orbital. The other d_{xz} and d_{yz} pseudo-t_{2g} orbitals participate in the interaction with the π^* component of each ethylene. The substitution of PMe_3 by a ligand possessing some π-acceptor character, such as the N_2 ligand, produces the stabilization of the HOMO through a $M(d_{xy}) \rightarrow NN(\pi^*_{xy})$ back-donation. The second π^* component of the dinitrogen ligand, for example π^*_{xz}, takes part in the $M(d_{xz})-C_2H_4(\pi^*)$ interaction, being the origin of the slight asymmetry in the bonding of one ethylene, which lies parallel to the M−N vector (for example, 2.303 and 2.321 Å for the Mo−C distances in **2a**).

Optimized Structures of *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ Compounds ($x = 1-4$). From an experimental viewpoint, the reaction of *trans*-$M(C_2H_4)_2(PMe_3)_4$ with CO proceeds smoothly, at low temperature, affording *trans,mer*-$M(C_2H_4)_2(CO)(PMe_3)_3$ (M = Mo (**3a**), W (**3b**)) compounds.[2] More forcing conditions (2−3 atm of CO) are required for the substitution of a second phosphine ligand and formation of complexes $M(C_2H_4)_2(CO)_2(PMe_3)_2$ (**4**) with an all-trans configuration (see eq 2).[2b]



(2)

The compounds *trans*-$M(C_2H_4)_2(CO)_3(PMe_3)$ (**5**) and *trans*-$M(C_2H_4)_2(CO)_4$ (**6**) are not experimentally accessible through the additional PMe_3 substitution by CO ligands (eq 3). Indeed, complexes **6** are prepared using

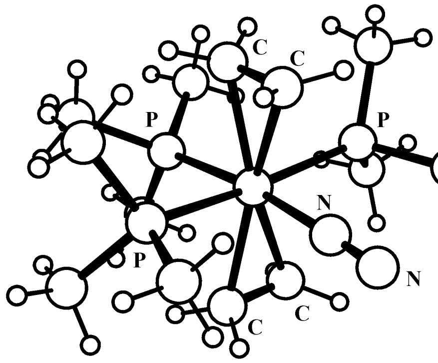
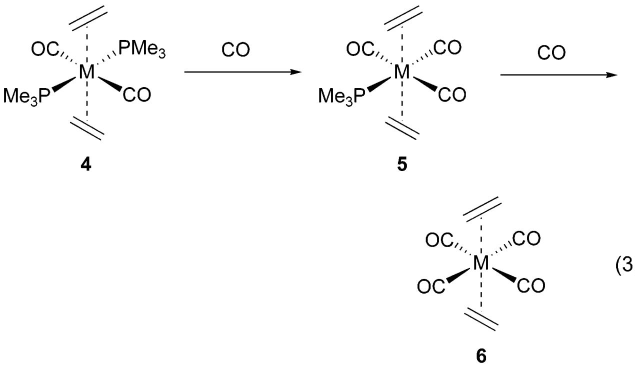


Figure 1. Optimized structure of the compound *trans,-mer*-$Mo(C_2H_4)_2(N_2)(PMe_3)_3$.



(3)

different synthetic routes.[21]

The structures of compounds *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ (M = Mo, W, R = H, Me, $x = 1-4$; **3**−**6**) have been optimized at the DFT level of theory, and Figure 2 displays the resulting structures of some of these complexes, namely **3a**, **4a**, and **6b**. Tables 1 and 2 show selected structural data (experimental and calculated) corresponding to the complexes *trans,mer*-$Mo(C_2H_4)_2(CO)(PMe_3)_3$ (**3a**) and *trans*-$W(C_2H_4)_2(CO)_4$ (**6b**), respectively. Selected bond distances and angles of the remaining calculated compounds are collected in the Supporting Information, including the isomers *trans,-cis*-$M(C_2H_4)_2(CO)_2(PR_3)_2$, which are not known experimentally.

Concerning Tables 1 and 2, a quite satisfactory agreement between the calculated and experimental values of geometrical parameters was found for both **3a** and **6b**. The M−P bonds are less overestimated than in the calculation of *trans*-$M(C_2H_4)_2(PMe_3)_4$, and in general, all bond distances agree within 0.04 Å. The largest deviation of bond angles appears to be about 4°. On the other hand, the calculated values for the tungsten compound *trans*-$W(C_2H_4)_2(CO)_4$ are completely equivalent to those previously reported (included for comparison in Table 2), which were computed with similar basis sets.[7] The same arguments about the MO distributions outlined for **2** are valid for complexes **3**. Actually, the same small asymmetry in the bonding of the ethylene

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[20] See for example: (a) Bachmann, C.; Demuynck, J.; Veillard, A. *J. Am. Chem. Soc.* **1978**, *100*, 2366. (b) Branchadell, V.; Dedieu, A. *Inorg. Chem.* **1987**, *26*, 3966.

[21] See for example: (a) Szymańska-Buzar, T.; Kern, K.; Downs, A. J.; Greene, T. M.; Morris, L. J.; Parsons, S. *New J. Chem.* **1999**, *23*, 407. (b) Szymańska-Buzar, T.; Kern, K. *J. Organomet. Chem.* **1999**, *592*, 212. (c) Szymańska-Buzar, T.; Kern, K.; Stufkens, D. J. *New J. Chem.* **1998**, *22*, 1539.

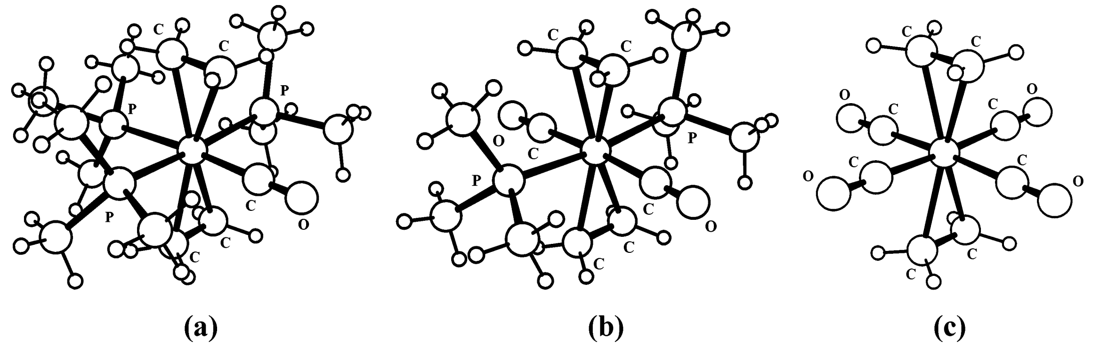

Figure 2. Optimized structures of the compounds (a) *trans,mer*-Mo$(C_2H_4)_2(CO)(PMe_3)_3$, (b) *trans,trans,trans*-Mo$(C_2H_4)_2(CO)_2(PMe_3)_2$, and (c) *trans*-W$(C_2H_4)_2(CO)_4$.

Table 1. Selected Structural Parameters (Bond Lengths in Å, Angles in deg) of the Compound *trans,mer*-Mo$(C_2H_4)_2(CO)(PMe_3)_3$

param	calcd	exptl
M−P	2.520	2.489(2)
	2.587	2.561(1)
	2.520	2.484(2)
M−CO	1.962	1.952(6)
M−C (ethylene)	2.291	2.267(5)
	2.291	2.280(5)
	2.321	2.325(5)
	2.307	2.297(5)
C−C	1.441	1.417(8)
	1.435	1.404(9)
P−M−P (trans)	170.3	168.45(6)
P−M−P (cis)	93.1	92.04(5)
	93.1	94.55(6)
P−M−CO (trans)	174.8	173.6(2)
P−M−CO (cis)	87.2	87.4(2)
	87.2	87.0(2)

Table 2. Selected Structural Parameters (Bond Lengths in Å, Angles in deg) of the Compound *trans*-W$(C_2H_4)_2(CO)_4$

param	calcd	exptl[21]	calcd[7b]	calcd[7a]
M−CO	2.043	2.033(10) 2.045(9)	2.050	2.032
M−C (ethylene)	2.338	2.299(9) 2.315(9)	2.349	2.360
C−C	1.428	1.413(13)	1.418	1.436
CO−M−CO (cis)	90.1	87.0(9) 90.9(3) 92.3(9)	n. r.	90.1
CO−M−CO (trans)	175.7	171.8(7)	174.2	174.9

molecule parallel to the M−CO vector is again evident (i.e. 2.307 and 2.321 Å, Mo−C distances for **3a**).

The computed trans P−M−P angles in *trans,mer*-M$(C_2H_4)_2(CO)(PMe_3)_3$ (**3**) and *trans,trans,trans*-M$(C_2H_4)_2(CO)_2(PMe_3)_2$ (**4**) are larger than the 165° found in **1** derivatives. The reasons are the same as those given in the case of complex **2**: that is, the attenuation of the steric pressure around the metal center by the substitution of PMe_3 by the CO ligand. All the trans OC-M−CO angles are close to 175°. Another effect produced by the replacement of one PMe_3 or dinitrogen ligand by CO in complexes **1** and **2**, respectively, is the noticeable elongation of the trans M−PMe_3 distance (about 0.6 Å larger than the other M−PMe_3 lengths in **3**), according to the known great trans influence of this ligand.[22] The same trans influence of CO is again evident in the increasing of the M−CO length when passing from *trans,mer*-M$(C_2H_4)_2(CO)(PMe_3)_3$ (1.962 Å for **3a**) to *trans,trans,trans*-M$(C_2H_4)_2(CO)_2(PMe_3)_2$ derivatives (2.026 Å for **4a**).

The series of computed complexes *trans*-M$(C_2H_4)_2(CO)_x(PMe_3)_{4-x}$ (M = Mo, W, $x = 0-4$, **1** and **3**−**6**) has allowed the accumulation of a sufficient body of information on the calculated structural parameters of coordinated ethylene ligands. We have employed these data to study the effect of the substitution of PMe_3 by CO on the π-acceptor capabilities of the ethylene ligands. We center our interest on the computed M−C and C−C distances of metal−ethylene fragments. The distance from the metal to ethylene centroid correlates well with the ethylene bond length ($R = 0.999$ and 0.993 for Mo and W, respectively) and with ^{13}C NMR of the ethylene carbons[23] ($R = 0.998$ and 0.990 for Mo and W, respectively), in accordance with the Dewar, Chatt, and Duncanson model[24] (see graphs in the Supporting Information).

Relative Reaction Energies (Δ*E*) of the Substitution of PR_3 by CO in Bis(ethylene) Compounds. The energies of the optimized compounds *trans*-M$(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ (M = Mo, W, R = H, Me, $x = 1-4$; **3**−**6**) and those of the CO and PR_3 ligands have been calculated in order to obtain the relative energies of several reactions in which a PR_3 ligand is substituted by CO (eqs 2 and 3). Schemes 1 and 2 summarize the calculated relative reaction energies (ΔE) for these processes in the compounds containing PMe_3. Similar schemes for PH_3 compounds are collected as Supporting Information.

Regarding the molybdenum complex **1a**, the first CO substitution reaction is characterized by a ΔE value of −42.2 kcal/mol. These data agree well with the experimental observation of the reaction of **1a** with CO, at low temperature, to give *trans,mer*-Mo$(C_2H_4)_2(CO)(PMe_3)_3$ (**3a**) (first part of eq 2). Starting from the latter compound, we have analyzed a second CO substitution. The ΔE value for obtaining the experimentally observed *trans,trans,trans*-Mo$(C_2H_4)_2(CO)_2(PMe_3)_2$ compound (**4a**; see its optimized structure in Figure 2) is −24.6 kcal/mol. This value is also in agreement with the experimental synthesis of this complex. The same ΔE value

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(22) See for example the recent article: Anderson, K. M.; Orpen, A. G. *Chem. Commun.* **2001**, 2682.

(23) Relationships between the metal−olefin back-donation and the olefin NMR chemical shift parameter have been previously highlighted: (a) Grevels, F.-W.; Jacke, J.; Betz, P.; Krüger, C.; Tsay, Y.-H. *Organometallics* **1989**, *8*, 293. (b) Angermund, H.; Grevels, F.-W.; Moser, R.; Benn, R.; Krüger, C.; Romão, M. *Organometallics* **1988**, *7*, 1994. (c) Reference 3d.

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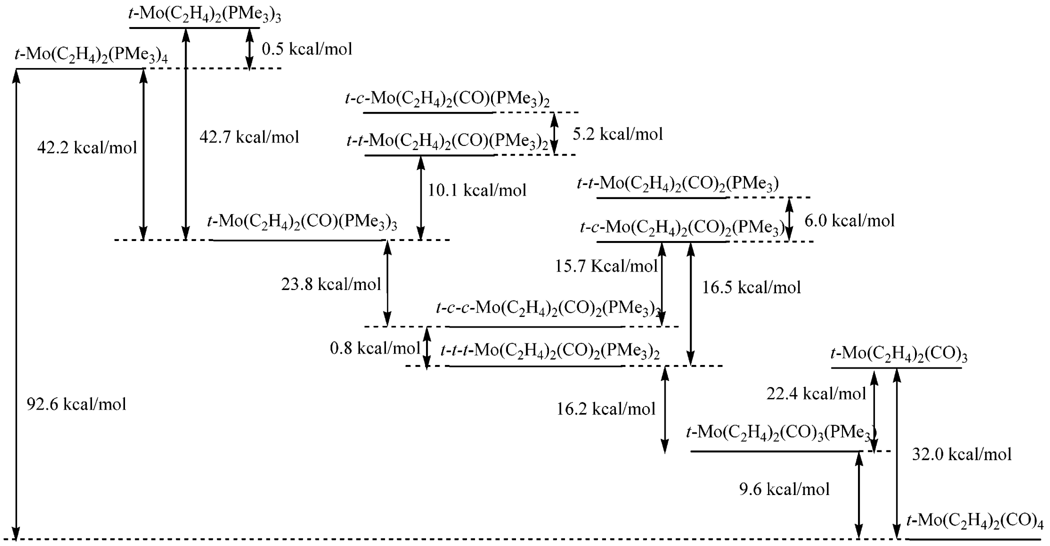
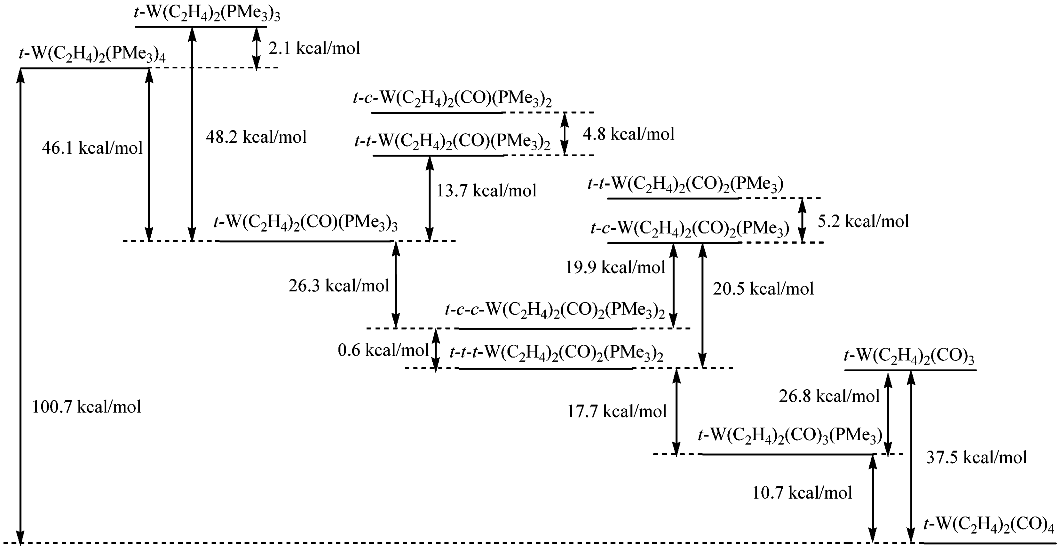
Scheme 1. Relative Energies Corresponding to Substitution Reactions of Compounds *trans*-$Mo(C_2H_4)_2(CO)_x(PMe_3)_{4-x}$ ($x = 0-4$) and Dissociation Energies (CO and PMe_3) To Yield the Unsaturated Species *trans*-$Mo(C_2H_4)_2(CO)_x(PMe_3)_{3-x}$ ($x = 0-3$)[a]



[a] The graph is not scaled, and only organometallic substrates are shown. t = trans, and c = cis.

Scheme 2. Relative Energies Corresponding to Substitution Reactions of Compounds *trans*-$W(C_2H_4)_2(CO)_x(PMe_3)_{4-x}$ ($x = 0-4$) and Dissociation Energies (CO and PMe_3) To Yield the Unsaturated Species *trans*-$W(C_2H_4)_2(CO)_x(PMe_3)_{3-x}$ ($x = 0-3$)[a]



[a] The graph is not scaled, and only organometallic substrates are shown. t = trans, and c = cis.

for the formation of the possible isomer *trans,cis,cis*-$Mo(C_2H_4)_2(CO)_2(PMe_3)_2$ is calculated to be −23.8 kcal/mol. Although this value is practically equivalent to that of the trans,trans,trans distribution, no evidence of the presence of this trans,cis,cis isomer was experimentally found. Consequently, the nonexistence of such types of isomers in the reaction of formation of **4** is probably not due to thermodynamic factors but, rather, to kinetic arguments. The calculated BDE parameters are in agreement with this fact (vide infra).

The hypothetical third and fourth CO substitution reactions starting from the complexes *trans,trans,trans*-$M(C_2H_4)_2(CO)_2(PMe_3)_2$ (**4**) were also analyzed (eq 3). The energies corresponding to these substitution processes, in the Mo compounds, are −16.2 and −9.6 kcal/mol, respectively, significantly lower than the first and second substitution reactions. As it is evident in Scheme 1, the ΔE values for these reactions gradually diminish as a function of the number of coordinated CO ligands. The two ultimate substitution reactions are thus less energetically favored, in agreement with the lack of reaction of complexes **4** with CO. An analogous argument can be made for the results obtained with $W-PMe_3$ complexes, with somewhat higher values for all the ΔE parameters (see Scheme 2).

Dissociation Energies (BDE) of $M-PR_3$ and $M-CO$ Bonds in *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ Compounds. As we stated before, bond dissociation energies in transition-metal compounds are not easy to measure[6] and the number of experimental studies devoted to determine these parameters are still scarce. In particular, for the metal−phosphorus bond we can cite the work

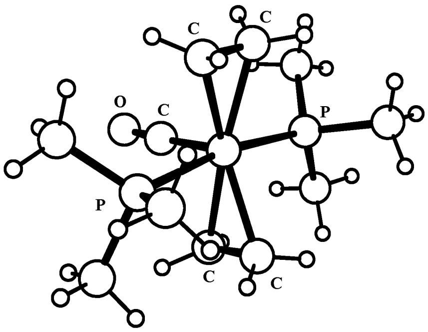


Figure 3. Optimized structure of the unsaturated complex *trans*-Mo$(C_2H_4)_2(CO)(PMe_3)_2$.

of Nolan and co-workers, in which they estimated the strength of the Mo−P bond for different phosphine ligands through experimental calorimetric measurements.[25] An alternative to overcome the inherent difficulties associated with experimental measurements is the use of the available theoretical tools. For example, Poli and co-workers studied the dissociation of PH_3 in $CpMoX(PH_3)_2$ model complexes[26] and found that the computed bond energies of PH_3 are influenced by the electronic and steric properties of the metal center. More recently, Frenking and co-workers have analyzed in detail the nature of the M−P bond in group 6 pentacarbonyl complexes.[27]

We have previously calculated the dissociation energy of the M−PMe_3 bond in the parent complexes **1** and rationalized the magnitude of such values.[5] With the purpose of obtaining the BDEs of CO and PR_3 groups in the related *trans*-M$(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ compounds (**3**−**6**), the geometries of the unsaturated complexes *trans*-M$(C_2H_4)_2(CO)_x(PR_3)_{3-x}$ (M = Mo, W, R = H, Me, $x = 1-3$) have been optimized at the same theoretical level than those of the saturated derivatives. Figure 3 displays the resulting structure of one of these unsaturated complexes. The other optimized structures and selected bond distances and angles for the unsaturated species are collected in the Supporting Information. Schemes 1 and 2 include the calculated relative bond dissociation energies (BDE) in the compounds containing PMe_3. As is evident in these schemes, the energy for the M−PMe_3 bond increases progressively with the number of coordinated CO ligands. For complexes **3**, two different BDE values were obtained, depending on whether the PMe_3 ligand occupies a trans position with respect to CO (10.1 kcal/mol for **3a**) or not (15.3 kcal/mol for **3a**). The former values are in agreement with the known trans effect of the CO ligand. Moreover, these data may explain the isolation of the all-trans isomer of **4**, instead of the trans,cis,cis isomer, in the reaction of complexes **3** with CO, because the dissociation of the PMe_3 ligand, trans with respect to CO, is favored due to the lower BDE value.

The highest Mo−PMe_3 BDEs are those of compounds **4a** and **5a (**22.5 and 22.4 kcal/mol, respectively), while in all of the cases the BDEs computed for the tungsten derivatives are to some extent higher than those of molybdenum (for example, 25.7 and 26.8 kcal/mol for complexes **4b** and **5b**, respectively). In general, the computed dissociation energies for M−PMe_3 bonds are lower than the experimental value of 38.4 kcal/mol (average) found in $Mo(CO)_3(PR_3)_3$ compounds[25a] and also lower than the computed values of 36.5 and 42.4 kcal/mol for $Mo(CO)_5(PMe_3)$ and $W(CO)_5(PMe_3)$, respectively.[27] However, at the level of theory employed in our calculations no precise comparisons with experimental data or more accurate theoretical work can be satisfactorily made.

The dissociation energies for the M−CO bonds are always significantly higher than those of M−PMe_3 (see Schemes 1 and 2). The values range from 32.0 to 42.7 kcal/mol in the molybdenum compounds, whereas the data for the tungsten derivatives are always approximately 5−6 kcal/mol higher. Our computed dissociation energies are of the same order of magnitude as those found for $M(CO)_6$ complexes (for instance, 40.1 and 44.8 kcal/mol (B3LYP) for $Mo(CO)_6$ and $W(CO)_6$, respectively).[28] The BDE value for CO generally increases when the number of CO ligands diminishes in the corresponding *trans*-M$(C_2H_4)_2(CO)_x(PMe_3)_{4-x}$ complex. The highest value was found in *trans,mer*-M$(C_2H_4)_2(CO)(PMe_3)_3$ (**3**), where the M−CO bond strength is higher due to the stabilization of the HOMO through the back-donation of the d_{xy} metal orbital to the XY π^*-acceptor component of the single CO. An increase in the number of the coordinated CO ligands causes a redistribution of the back-donation between all of them with a subsequent attenuation of the BDE. In fact, the lowest value corresponds to complexes **6** with four CO ligands. Another consideration that affects the BDE magnitude concerns the nature of the ligand trans to CO. The BDEs increase ca. 6 kcal/mol (see the two values calculated for complexes **5**) when the trans ligand changes from CO to PMe_3, in agreement with the trans effect and analogous to that found in the BDEs of PMe_3.

Frenking and co-workers have recently pointed out[27] that there is no correlation between the bond lengths and the bond dissociation energies of the M−P bonds. Additionally, other authors have been shown that the M−L bond separation is not a good indicator of bond strength for donor/acceptor complexes.[29] Our results agree with these findings, and no trends were found between the BDEs for M−PMe_3 or M−PH_3 bonds and the equivalent M−P distances. However, a good correlation is evident between M−CO distances and the energy for the M−CO dissociation ($R = 0.996$ in the Mo−PMe_3 compounds). Similar relationships were observed for W−PMe_3 and M−PH_3 complexes (with R values always higher than 0.975). For this series of compounds, as we discussed above, the electron richness of the common M$(C_2H_4)_2$ entity is entirely modulated by the acceptor properties of the coordinated CO coligands and, accordingly, the BDE−distance relationship

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for the CO ligand is reasonably good for these specific compounds. Notwithstanding this fact, no general trends can be made for a common correlation between M−CO lengths and CO dissociation energies.

Acknowledgment. We thank Professor Imre Papai for fruitful discussions. Financial support from the Ministerio de Ciencia y Tecnología (Grant No. BQU2001-3715), the Ministerio de Educación, Cultura y Deporte (research studentship, D.d.R.) and the Junta de Andalucía are gratefully acknowledged.

Supporting Information Available: Qualitative schemes including ΔE and BDE values for calculated PH_3 compounds (Schemes S1 and S2), selected calculated structural parameters of *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{4-x}$ ($x = 0-4$) and *trans*-$M(C_2H_4)_2(CO)_x(PR_3)_{3-x}$ ($x = 0-3$) compounds and optimized structures of the molybdenum compounds (Tables S1−S11), and figures showing several linear relationships discussed in the text (Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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