Ab Initio Study of Stable Bis(carbon dioxide)molybdenum Complexes‡

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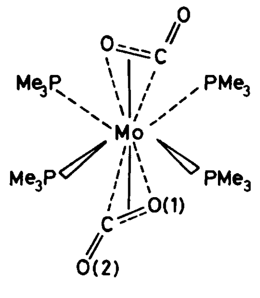
Ab initio valence calculations of double-ζ quality using atomic pseudo-potentials have been carried out for the bis(carbon dioxide) complexes, *trans*-$[Mo(CO_2)_2(PH_3)_4]$ and *trans,mer*-$[Mo(CO_2)_2(CNH)(PH_3)_3]$. The conformational preferences of the CO_2 ligands for the former complex have been investigated. The most stable conformation has the two carbon dioxide ligands mutually perpendicular and eclipsing the Mo–P bonds. The main carbon dioxide–metal interactions, as well as the effects of the substitution of a PH_3 ligand by a CNH ligand in the equatorial plane, are discussed.

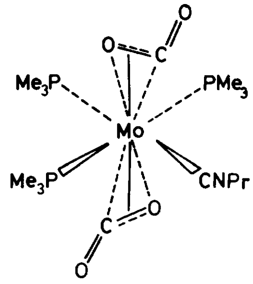
Interest in the chemistry of carbon dioxide has been stimulated by the search for alternative petrochemical feedstocks and the investigation of the water–gas shift reaction.[1] Carbon dioxide has some important functional properties which influence its co-ordination to metal centres. In general, co-ordination activates ligands and creates favourable steric conditions for ligand interactions and numerous catalytic processes.[2–5] Many reactions of transition metal–carbon dioxide complexes have been reported.[3,6,7] However, the co-ordination of carbon dioxide to transition metals in stable compounds has been restricted to a few cases[8–10] in which only one CO_2 molecule is attached.

Carmona and co-workers[11] have recently reported the synthesis of the first stable bis(carbon dioxide) adduct of a transition metal, *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ (**1**). However, efforts to obtain crystals of this compound suitable for *X*-ray analysis were unsuccessful. The interaction of (**1**) with various isocyanides afforded new carbon dioxide complexes of composition *trans,mer*-$[Mo(CO_2)_2(CNPr^i)(PMe_3)_3]$, (**2**), where substitution of only one PMe_3 ligand by $CNPr^i$ was observed.[12] The *X*-ray crystal structure of complex (**2**) is essentially octahedral with the CO_2 ligands bonded in a side-on co-ordination through one of the C=O bonds. The CO_2 ligands are mutually perpendicular and eclipse the *trans*-Mo–L bonds, *i.e.* a staggered–eclipsed structure (the term staggered indicates the relative orientation between the carbon dioxide molecules and eclipsed refers to their orientation with respect to the equatorial ligands). I.r. and n.m.r. spectroscopic data for complexes (**1**) and (**2**) suggest that they must be similar.[11,13] The relative orientation of the co-ordinated double bonds is similar to that found in *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$, (**3**), and *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$, (**4**).[14]

Theoretical studies of complexes containing CO_2 have been useful in forming a better understanding of the nature of the co-ordinate bond, its electron structure, and conformational preferences. Morokuma and co-workers[15] have carried out *ab initio* calculations for model organometallic compounds containing one CO_2 ligand in order to explain the different modes and nature of the co-ordinate bond. Hoffmann and co-workers,[16] by means of the EHMO (extended-Hückel molecular orbital) method, have investigated possible routes to the joining of a metal fragment and a linear triatomic molecule such as CX_2 (X = O or S).



(**1**)



(**2**)

To our knowledge no bis(carbon dioxide) transition-metal complex has been theoretically studied. However, Veillard and co-workers[17] have investigated a relative problem concerning the stereochemistry of *trans*-$[Mo(C_2H_4)_2X_4]$ (**5**) [a model complex of (**3**)], where X = PH_3, CO, or Cl, on the basis of *ab initio* calculations, concluding that the staggered–eclipsed arrangement was the most stable conformation. This prediction was confirmed by the *X*-ray crystal structure reported later for complex (**3**).[14] More recently, this group has extended its studies on axial ligands to some metalloporphyrins.[18]

In this work, we study theoretically the conformational preference of *trans*-$[Mo(CO_2)_2(PH_3)_4]$, (**6**), as a model of compound (**1**). The result may support the experimental hypothesis of a stable arrangement similar to that of complex (**2**).[11] We examine the different carbon dioxide–metal fragment interactions, comparing them with those found in the study of complex (**5**).[17] In order to analyse the changes associated with the replacement of a PH_3 ligand by CNH, calculations on *trans*-$[Mo(CO_2)_2(CNH)(PH_3)_3]$, (**7**), have also been carried out, in its most stable conformation.

Calculations

Ab initio SCF-MO calculations were carried out by using the pseudo-potential method of Durand and Barthelat.[19,20] The basic program used was PSHONDO,[21] an adaptation of the HONDO program[22] to the use of pseudo-potentials. In this technique, the inner-shell core electrons for each atom are taken into account through a non-empirical pseudo-potential. The specific parameters used for molybdenum were the relativistic ones determined by Hay and Wadt.[23] For phosphorus, carbon, and oxygen the values obtained from standard calculations were used.[24]

The basis sets were essentially double-ζ for the valence

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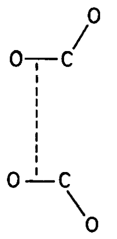
‡ *Non-S.I. units employed:* cal = 4.184 J, a.u. = 1.66×10^{-27} kg.

orbitals of molybdenum, carbon, and oxygen, and a minimal one for the ligand atoms in the equatorial plane. The (3*s*,3*p*,4*d*) primitive Gaussian functions were contracted to a [2*s*,2*p*,2*d*] set for Mo, and (4*s*,4*p*)/[2*s*,2*p*] for C and O.[24]

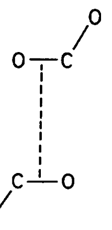
The geometrical parameters for the model complexes (**6**) and (**7**) were taken from the experimental values of complex (**2**),[12,13] without further optimization, assuming an average value for the Mo–P bond length (2.5 Å), the experimental values of the P–H and N–H bond lengths in PH_3 (1.42 Å)[25] and CNH (1.065 Å), and a tetrahedral angle for HPH in the PH_3 ligand. It should be noted that in these complexes the carbon dioxide has been found to have a bent geometry (OCO 133.4°), with two different CO bond lengths [C–O(1) 1.26, C–O(2) 1.22 Å].

Results and Discussion

The Six Main Conformations of $[Mo(CO_2)_2(PH_3)_4]$.—This complex has a quasi-octahedral structure where the relative orientation of the axial carbon dioxide ligands gives six main conformations. The side-on co-ordination of carbon dioxide to the metal fragment gives rise to two different structures when the two CO_2 molecules are eclipsed: a *cis* form (**I**), and a *trans* form (**II**), depending on whether the two outer oxygen atoms are on the same side of the plane perpendicular to the co-ordinated C–O bond, or on the opposite side. Thus, we may denote the different conformations in a classical way, adding *cis* or *trans* as appropriate to the conformations involving an eclipsed orientation of the two CO_2 molecules. The conformations are: ss, staggered–staggered, (**III**); se, staggered–eclipsed, (**IV**); *trans*-es, *trans*-eclipsed–staggered, (**V**); *cis*-es, *cis*-eclipsed–staggered (**VI**); *trans*-ee, *trans*-eclipsed–eclipsed, (**VII**); and *cis*-ee *cis*-eclipsed–eclipsed, (**VIII**).

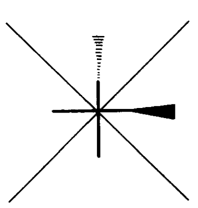


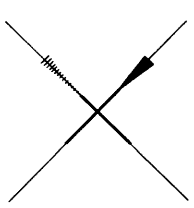
(**I**)

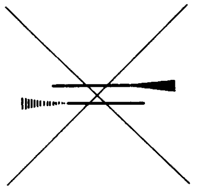


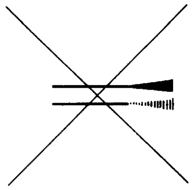
(**II**)

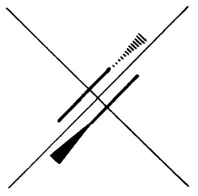
The relative energies of these six conformations are reported in Table 1. These results classify the structures into two groups differing by *ca.* 70 kcal mol^{-1}. The most stable group is formed by structures where the CO_2 ligands are mutually perpendicular [(**III**) and (**IV**)], and the other group by the conformations where the CO_2 ligands are eclipsed [(**V**)—(**VIII**)]. It is worth noting that a secondary interaction gives differential behaviour within each group. When the carbon dioxide ligands are staggered, the most favourable orientation with respect to the Mo–P bonds is eclipsed [se, (**IV**), is more stable than ss, (**III**)]. On the other hand, when the CO_2 ligands are eclipsed, a staggered orientation is preferred [*cis*-es, (**VI**), is more stable than *cis*-ee, (**VIII**), and *trans*-es, (**V**), more stable than *trans*-ee, (**VII**)]. The most stable conformation is se, in good agreement with the experimental hypothesis for complex (**1**).[11,13] A comparison of these results with those of the conformational study on $[Mo(C_2H_4)_2(PH_3)_4]$[17] shows that the se structure is the most stable conformation in both cases. However, the sequence for the other structures is not the same. In addition, the energy gap for complexes containing olefin ligands is closer than those containing CO_2. The large energy gap between the conformation sets suggests a synchronous rotation of the two CO_2 ligands around the carbon dioxide–metal direction rather than their independent rotation.


(**III**)


(**IV**)


(**V**)


(**VI**)


(**VII**)

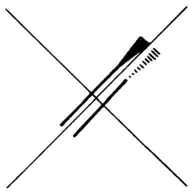

(**VIII**)

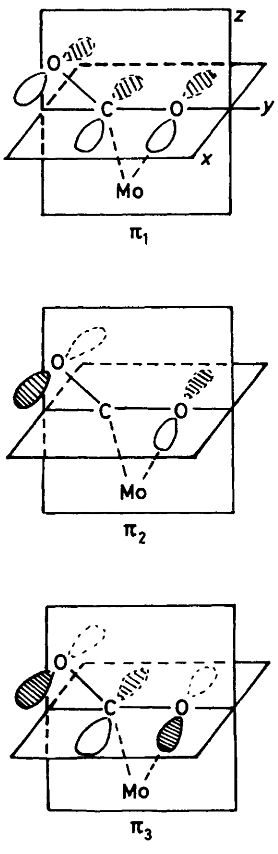
Table 1. Relative energies (E_{rel}) of the six main conformations of complex (**6**)

Conformation	E_{rel}/kcal mol^{-1}
ss (**III**)	3.8
se (**IV**)	0.0
trans-es (**V**)	75.1
cis-es (**VI**)	70.1
trans-ee (**VII**)	77.0
cis-ee (**VIII**)	74.1

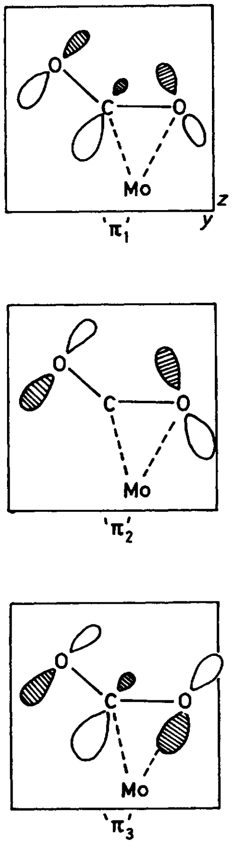
Since, in complex (**6**) the CO_2 molecules are distorted from their linear structure, their degenerated π systems split into two sets, *i.e.* the genuine π system built from the *p* atomic orbitals perpendicular to the OCO plane, (**IX**), and a pseudo-π system oriented along the OCO plane, (**X**). The latter will be referred to as 'π'.

First, the main interactions giving rise to the large energy gap between the two conformation sets are investigated. Figure 1 shows a simplified interaction diagram with two possibilities for attachment of the CO_2 ligands. There is a donation from the CO_2 'π_1' orbitals to the metal d_{z^2} orbital. Given the axial symmetry of this *d* orbital, this interaction must be nearly constant for all conformations. The h.o.m.o. (highest occupied molecular orbital) of the CO_2 molecule, the non-bonding 'π_2' orbital, plays a minor role in this interaction, owing to the very small density charge in the O–C bonding region. Another primary interaction is the back donation which appears to be important in stabilizing the conformations where the CO_2 ligands are perpendicular, as shown in Table 2. This interaction is due to the overlap between the occupied d_π orbitals and the virtual 'π_3^*' orbitals of the carbon dioxide ligands. The population analysis for the d_π orbitals indicates a larger back donation for (III) and (IV) than for the others. Likewise, the net-charge analysis points to the greatest charge transfer from metal to carbon dioxide for (III) and (IV). Thus, the $d_\pi \longrightarrow$ 'π_3^*' interactions are the origin of the separation of the six structures into two groups. This analysis has already been proposed by Veillard and co-workers[17] for the case of bis(olefin) complexes. In fact, when the two CO_2 ligands are staggered the d_π orbitals may both combine with the CO_2 'π_3^*' orbitals. In the case where both CO_2 ligands eclipse the Mo–P bonds, it is clear that each d_π orbital, d_{xz} and d_{yz}, combines with the 'π_3^*' orbital of the CO_2 located in its plane, xz and yz. When both CO_2 ligands are staggered with respect to Mo–P bonds, adapted symmetry combinations of d_π orbitals lead to similar interactions. On the contrary, if the CO_2 are eclipsed only one effective $d_\pi \longrightarrow$ 'π_3^*' interaction takes place.

Secondly, the small energy gap between the se and ss structures is examined. There are two weak interactions that may justify the order of stability obtained. As shown in (XI), the se structure has a stabilizing interaction between an occupied d orbital on the square plane, d_{xy}, and virtual π_3^* orbitals of the CO_2 ligands. This interaction is not found for the ss structure due to the nodal properties, (XII). On the other hand, as Veillard and co-workers[17] have already pointed out, the occupied 'π_1' orbitals of the CO_2 ligands have destabilizing interactions with the metal d_{xy} orbital in the ss structure, whereas in the se orientation the 'π_1' orbitals have stabilizing interactions with



(IX)



(X)

Table 2. Results of population analysis for the different conformations of complex (6) and the most stable conformation of complex (7)

Conformation	d_π (d_{xz}, d_{yz})	Mo, net charge	CO_2, net charge
$[Mo(CO_2)_2(PH_3)_4]$			
ss (III)	1.91	+1.32	−0.57
se (IV)	1.90	+1.31	−0.57
trans-es (V)	2.65	+1.06	−0.35
cis-es (VI)	2.77	+1.15	−0.42
trans-ee (VII)	2.68	+1.05	−0.35
cis-ee (VIII)	2.68	+1.04	−0.36
$[Mo(CO_2)_2(CNH)(PH_3)_3]$			
se	1.98	+1.68	−0.42

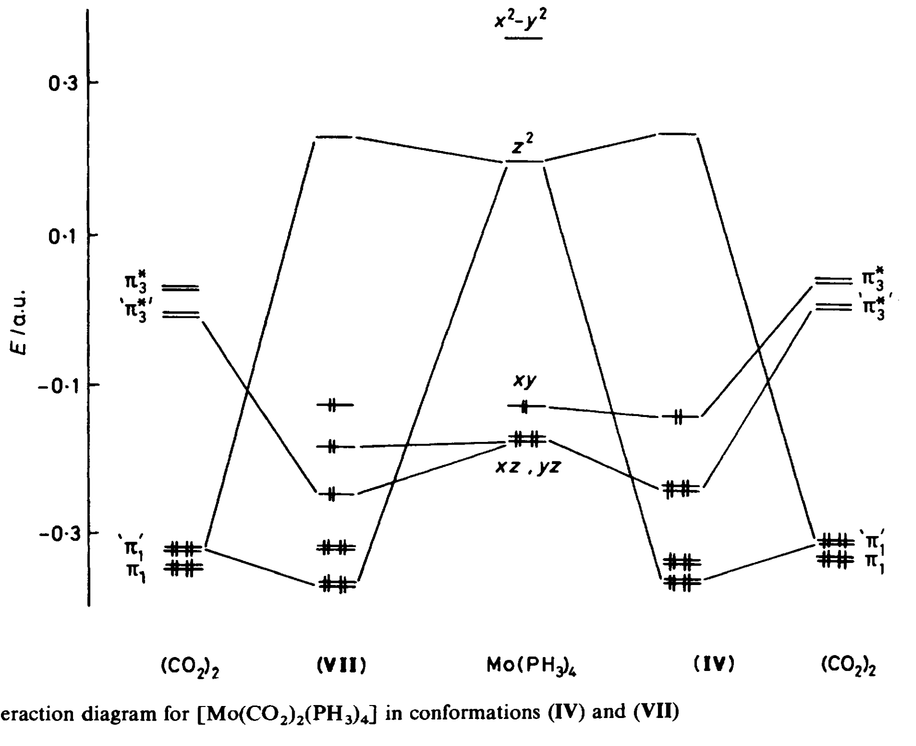
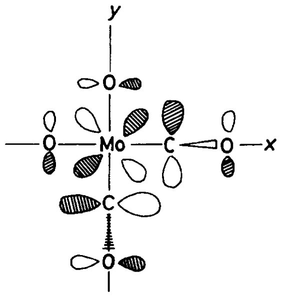
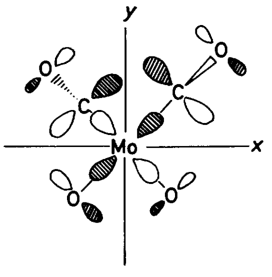


Figure 1. Simplified interaction diagram for $[Mo(CO_2)_2(PH_3)_4]$ in conformations (IV) and (VII)



(XI)



(XII)

the virtual $d_{x^2-y^2}$ orbital. The large energy gap between the orbitals involved in these interactions implies only small changes in the total energies of conformations (**III**) and (**IV**). This explains the energy difference of *ca.* 4 kcal mol^{-1}. Veillard and co-workers[17] found a larger energy gap between the abovementioned conformations (18.8 kcal mol^{-1}). This is explained essentially by steric repulsions between the olefin and phosphine protons where the distance between them is shorter than the sum of the van der Waals radii of the hydrogen atoms. In the case of the CO_2 ligands, this repulsion does not take place, but we do not exclude the possibility of slightly destabilizing interactions between the σ m.o.s on the Mo–P axis and the π m.o.s of the CO_2.

Thirdly, the differential behaviour in the second group of conformations is analysed. When the CO_2 ligands are eclipsed, the plane containing them has a significant electron density. Thus, if the P–Mo bonds are localized within this plane, the electron repulsion must increase strongly, favouring staggered orientations where the equatorial bonds are placed out of this plane. In fact, Table 1 shows that the es structures are more stable than the corresponding ee structures. However, since no geometric optimizations were performed for the conformations, it is difficult to deal with the small energy gap obtained. Nevertheless, the secondary interactions found in the fragment analysis of the wavefunctions suggest that the energy order of these conformations holds true, even though the numerical values are rough approximations.

Substituting a PH_3 *Ligand by a* CNH *Ligand in the Equatorial Plane.*—The substitution of a phosphine ligand by an isocyanide ligand implies a large modification of the molybdenum–ligand bonding. The existence of π orbitals in the CNH ligand introduces back donation, d–π^*, interactions in the $[Mo(PH_3)_3(CNH)]$ complex. These interactions cannot be found for the $[Mo(PH_3)_4]$ complex. Thus, the electron population of metal d orbitals decreases from 5.41 for the $[Mo(PH_3)_4]$ complex to 5.10 for the $[Mo(PH_3)_3(CNH)]$ complex.

In the most stable conformation, se, of bis(carbon dioxide) complexes (**6**) and (**7**), the molybdenum net charge increases from +1.31 to +1.68, although the carbon dioxide net charge diminishes from −0.57 to −0.42 (Table 2). Thus, the back donation in complex (**7**) is due not only to the interactions between metal d_π and CO_2 'π^*_3' orbitals, but also to the metal d–CNH π^* interactions.

Figure 2 shows the energy differences between the two square-planar complexes $[Mo(PH_3)_4]$ and $[Mo(CNH)(PH_3)_3]$, and the corresponding bis(carbon dioxide) complexes (se conformation). The CO_2, CNH, and PH_3 molecules have been considered in their equilibrium geometries. As can be seen in this Figure, the substitution of an isocyanide ligand by a phosphine ligand strongly stabilizes the square-planar complex, as would be expected from the electron delocalization caused by the isocyanide ligand. The bonding energy of the two CO_2 ligands to the metal fragment decreases in going from complex (**6**) to (**7**). This is a consequence of the minor d_π–'π^*' interaction, since one of the d_π orbitals has already been involved in a strong bond with a CNH π^* orbital.

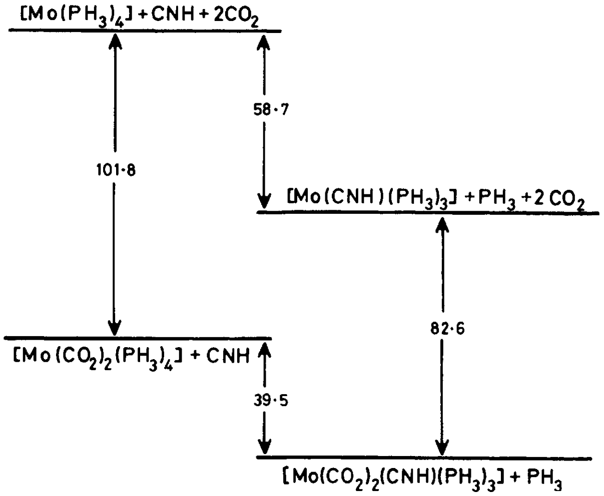


Figure 2. Relative energies (kcal mol^{-1}) for complexes (**6**) and (**7**) and their fragments

The bonding energy to link CO_2 to the metal fragment is in qualitative agreement with the observed behaviour of these complexes, which show no appreciable tendency towards CO_2 dissociation.[13] The relatively high thermal stability observed for complexes derived from (**2**) with respect to those derived from (**1**) agrees quite well with the relative energy calculated for (**6**) and (**7**), although this stability is not due to a stronger carbon dioxide–metal fragment bonding, but rather to the back donation established with the isocyanide ligand.

In conclusion, the study of carbon dioxide co-ordination to the metal fragment indicates that the relative stability of the complex cannot be derived from the strength of the carbon dioxide–metal bonding. Thus, the complex containing one isocyanide dissociates by losing the equatorial ligand less easily than that containing four phosphine ligands, although in the latter there are stronger carbon dioxide–metal bonds. The electron delocalization supplied by the back donation to the CO_2 ligands is a factor that strengthens the bonds. However, the tendency of the complex to decompose by dissociation is averted by replacing one ligand which also diminishes the high electron density by means of a back-bonding interaction. These structural studies may be a good starting point to investigate the reactivity of the CO_2 ligands in these complexes. Work is in progress in order to obtain a deeper insight into the thermodynamic and kinetic aspects of bis(carbon dioxide) complexes formed from other square-planar complexes.

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