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Synthesis, molecular structure and theoretical considerations on $Mo(PhC\equiv CCOOEt)_3(PMe_3)$

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Abstract

The reaction of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ with $PhC\equiv CCOOEt$ affords $(PhC\equiv CCOOEt)_3(PMe_3)$ (**1**). The molecular structure of **1** has been determined by means of X-ray analysis. NMR studies have shown that **1** undergoes a dynamic process in solution due to the alkyne rotation. The related energy barrier is experimentally determined to be 15.1 kcal mol^{-1}. The well established EHMO theoretical arguments, which uniquely explain the chemical bonding in these complexes, are extended to interpret the nature of the barrier and its dependence on the π-donor or π-acceptor capability of the axial ligand. The conceptual continuity between the chemical bonding of d^6 metal species coordinated by at least two alkyne molecules (e.g. $M(alkyne)_2L_4$, $M(alkyne)_2L_2$ and $M(alkyne)_3L$) is highlighted. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Alkyne complex; Molybdenum complex; EHMO calculations

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1. Introduction

In the course of our studies of molybdenum and tungsten bis(ethylene) complexes [1], we have investigated systematically the reactivity of the $M(C_2H_4)_2$ moiety toward a variety of reagents. For example, the interaction with carbon dioxide is shown to produce a unique example of ethylene carboxylation at the transition metal center [2]. As an extension of our research, the reactivity of the *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ complex toward the alkyne $PhC\equiv CCOOEt$ has been tested by us.

Although $W(alkyne)_3(CO)$ compounds were first reported in 1963–64 [3], there is a continuous interest in this chemistry, for example, because some of these compounds promote alkyne–alkyne coupling reactions as it has been recently described [4]. The tungsten derivatives have attracted the greatest attention [5] while those of the other Group 6 metals, chromium [6] and molybdenum [7], are scanty. We have now synthesized the molybdenum complex $Mo(PhC\equiv CCOOEt)_3(PMe_3)$ (**1**) and, in this paper, we present its molecular structure and behavior in solution. EHMO arguments, which uniquely describe the chemical bonding in this type of molecule and which have been developed by various authors [8], are adapted to interpret some aspects of the fluxionality process. Moreover we address qualitatively the conceptual continuity between d^6 metal complexes which contain at least two alkyne molecules coordinated.

2. Experimental section

Microanalyses were by the Microanalytical Service of the University of Sevilla. IR spectra were recorded on Perkin-Elmer Model 883 spectrophotometer. ^1H-, ^{13}C- and ^{31}P-NMR spectra were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C-

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NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The complex *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ was prepared as previously described ([1]a).

2.1. Synthesis of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**)

A solution of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ (0.22 g, 0.5 mmol) in 30 ml of Et_2O was reacted with $PhC{\equiv}CCOOEt$ (2.1 ml of a solution 0.9 M in THF). The mixture was stirred for 1 h at room temperature (r.t.) and the solvent removed under vacuum. The residue was extracted with Et_2O (10 ml), centrifuged and concentrated. Storage at -30°C gave complex **1** as pale orange crystals. Subsequent recrystallization from Et_2O affords white crystals of **1** (40% yield) which are suitable for the X-ray analysis. IR (Nujol): 1680 cm^{-1} (very br, υ_{CO}). Major isomer: ^1H-NMR (300 MHz, 250 K, CD_3COCD_3): δ 1.25 (t, 9H, 3 CH_2CH_3; $^3J_{HH} = 7.1$ Hz), 2.07 (d, 9H, $P(CH_3)_3$, $J_{P-H} = 9.2$ Hz), 4.29 (q, 6H, 3 CH_2CH_3; $^3J_{HH} = 7.1$ Hz), 7.33 (m, 6 H, Ph), 7.39 (m, 3 H, Ph), 7.54 (d, 6H, Ph; $^3J_{HH} = 6.9$ Hz). $^{31}P\{^1H\}$-NMR (202 MHz, 250 K, CD_3COCD_3): δ 9.41 (s). $^{13}C\{^1H\}$-NMR (75.5 MHz, 298 K, C_6D_6): δ 14.0 (s, CH_2CH_3), 16.8 (d, $P(CH_3)_3$, $^1J_{CP} = 24.7$ Hz), 60.4 (s, CH_2CH_3), 127.9 (s, Ph), 128.6 (s, Ph); 129.8 (s, Ph); 139.9 (s, Ph); 166.2 (d, $\equiv CCOO$, $^2J_{CP} = 17.9$ Hz), 174.5 (d, $PhC\equiv$, $^2J_{CP} = 9.0$ Hz), 196.2 (s, COO). Minor isomer: $^{31}P\{^1H\}$-NMR (202 MHz, 250 K, CD_3COCD_3): δ 8.60 (s). Anal. Found: C, 62.1; H, 5.4. Calc. for $C_{36}H_{39}PO_6Mo$: C, 62.2; H, 5.6%.

2.2. X-ray structure determination of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**)

A summary of the crystal data, including the results of the structural refinement are given in Table 1. A white crystal was mounted on a Enraf-Nonius CAD4 diffractometer. The cell dimensions were refined by least-squares fitting of 25 reflections in the 2θ range of 10–12°. The intensity data were corrected for Lorentz and polarization effects. Atomic scattering factors are those reported by Cromer and Waber [9]. The structure was solved by combined Patterson and Fourier methods. An empirical absorption correction was applied via ψ-scan measurements and the transmission factors are in the range 93.73–99.90. All the computational work was carried out on a Digital DEC 2000 AXP workstation using the program SHELX96 [10]. The program ZORTEP was also used for molecular drawings [11]. Refinement was carried out by means of full matrix least-square calculations, initially attributing isotropic thermal parameters to all atoms. In the last L.S. cycles, anisotropic thermal parameters were used for all non-hydrogen atoms. Fractional atomic coordinates for **1** are given in Table 2. Hydrogen atoms were included

Table 1
Crystal data and structure refinement for 1

Empirical formula	$C_{36}H_{39}MoO_6P$
Molecular weight	694.62
Crystal system	Trigonal
Space group	R_3 (No 146)
a (Å)	10.3080(10)
b (Å)	10.308(5)
c (Å)	10.308(2)
α (°)	107.53(2)
β (°)	107.530(10)
γ (°)	107.53(2)
V (Å^3)	898.6(5)
Z	1
$D_{calc.}$ (g cm^{-3})	1.283
μ, (mm^{-1})	0.450
Temperature (K)	293(2)
Wavelength (Å)	0.71069
$F(000)$	360
Theta range for data collection (°)	3.36 to 24.97
Index ranges	$-12 \leq h \leq 11$, $-12 \leq k \leq 11$, $0 \leq l \leq 12$
Reflections collected	3348
Independent reflections	2030 [$R_{int} = 0.0286$]
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	2030/1/137
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0182$, $wR_2 = 0.0475$
R indices (all data)	$R_1 = 0.0183$, $wR_2 = 0.0476$
Absolute structure parameter	$-0.01(3)$
Largest difference peak and hole (e A^{-3})	0.167 and -0.108

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**)

	x	y	z	U(eq)[a]
Mo(1)	8829	8829	8829	31(1)
P(1)	6609(1)	6609(1)	6609(1)	44(1)
C(1)	10539(2)	8600(2)	10276(2)	39(1)
C(2)	9601(2)	7277(2)	9156(2)	40(1)
C(3)	9455(3)	5732(2)	8666(2)	48(1)
C(4)	8193(4)	3314(3)	8532(5)	83(1)
C(5)	6937(5)	2553(4)	8804(6)	109(2)
C(6)	5335(3)	7051(4)	5349(3)	69(1)
O(1)	10143(3)	5273(2)	8037(3)	75(1)
O(2)	8445(2)	4888(2)	8970(2)	63(1)
C(1,1)	11917(2)	9204(2)	11648(2)	44(1)
C(2,1)	12250(3)	10412(3)	12939(3)	63(1)
C(3,1)	13557(4)	10922(4)	14229(4)	89(1)
C(4,1)	14532(4)	10266(5)	14222(4)	93(1)
C(5,1)	14218(3)	9092(4)	12952(4)	85(1)
C(6,1)	12913(3)	8536(4)	11673(3)	64(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

with fixed isotropic contributions at the calculated positions. No unusual trend in ΔF versus F_o or $(\sin\theta)/\lambda$ was observed. A final difference synthesis showed no significant electron density residues. Listing of atomic coordinates of the hydrogen atoms, anisotropic thermal parameters of all and structure factors are provided as supplementary material.

2.3. Extended Hückel molecular orbital study

All the MO calculations were of the extended Hückel type [12] using a weighted-modified Wolfsberg–Helmholz formula [13]. The geometry of the starting model $Mo(HC{\equiv}CH)_3(PH_3)$ is based on that of the X-ray structure. The STO parameters for molybdenum are taken from literature [14], while those of the main group elements are the standard ones tabulated in the program CACAO [15]. The input files are available from the authors on request [16].

3. Results and discussion

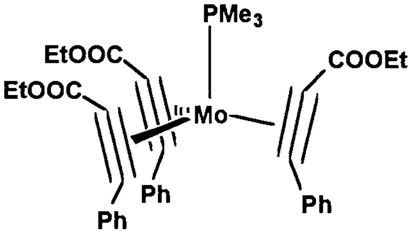
The reaction of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ complex with three equivalents of $PhC{\equiv}CCOOEt$ affords crystals of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**) after work up (Eq. 1) in good yields. The use of a large excess of alkyne produced intractable materials,

$$\textit{trans}\text{-}Mo(C_2H_4)_2(PMe_3)_4 + PhC{\equiv}CCOOEt \Rightarrow Mo(PhC{\equiv}CCOOEt)_3(PMe_3)\ (\mathbf{1})$$

probably due to the presence of alkyne polymerization products.

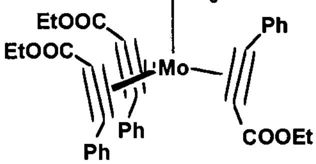
The presence of one PMe_3 ligand in **1** is clearly evident from NMR spectra. The three alkyne ligands give only one set of signals in the ^1H-and $^{13}C\{^1H\}$-NMR spectra. For example, in the $^{13}C\{^1H\}$-NMR spectrum two doublets at 174.5 and 166.2 ppm were assigned to $Ph\mathit{C}{\equiv}$ ($^2J_{CP} = 9$ Hz) and $\equiv\mathit{C}COO$ ($^2J_{CP} = 17.9$ Hz) carbon atoms, respectively. A close inspection of the NMR data at r.t. reveals, in addition to the resonances due to **1**, small signals in an approximate ratio 1:9 with respect to **1**. ^1H-NMR spectrum displays a small broad hump at 1.88 ppm close to the slightly broad doublet due to PMe_3 and, analogously, $^{31}P\{^1H\}$-NMR spectrum shows a small broad resonance at 7.6 ppm close to the singlet resonance for the PMe_3 ligand. Considering the results reported by Cooper and coworkers ([5]a,b) where some $W(alkyne)_3(L)$ complexes showed dynamic NMR behavior due to alkyne rotation, we have performed a variable temperature NMR study for **1**.

At 250 K, $^{31}P\{^1H\}$-NMR spectrum (CD_3COCD_3) shows two sharp singlets (9:1 ratio). After heating, both signals get wider and at 323 K only one broad band centered at 8.1 ppm was observed. This fact suggests the minor presence of a second isomer of **1**, probably with a different orientation of the alkyne ligands. The structural disposition of the alkyne ligands for the major isomer was supposed to be that found in the solid state (see ahead) and was schematically shown in **I**.

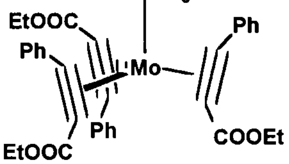


I

In order to establish the structure of the minor isomer the ^1H-NMR spectrum was recorded at low temperature. At 250 K, the minor isomer gives signals for the PMe_3 ligand at 1.85 ppm and for the Et groups at 4.18 and 1.07 ppm. Unfortunately the present NMR data are not clear enough to detect unequivocally the three possible structures **II**, **III** and **IV** as previously done by Cooper and coworkers for an analogous case ([5]a,b).



II



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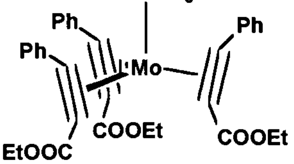


IV

Coalescence temperatures were determined from $^{31}P\{^1H\}$- and ^1H-NMR spectra and were used to calculate a $\Delta G^{\neq}$ value of 15.1 kcal mol^{-1}. This value is superior to that reported for $W(Me_3SiC{\equiv}CSiMe_3)_3(CO)$ (< 8 kcal mol^{-1}) ([8]a) and only slightly higher than

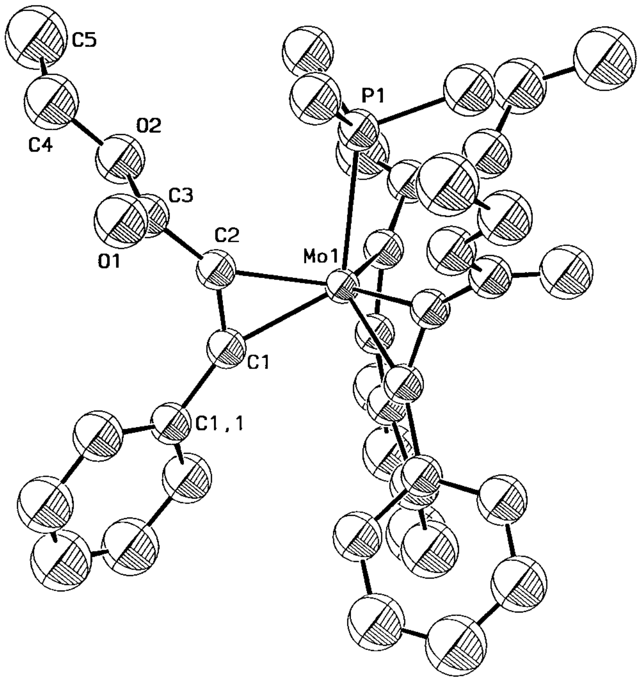


Fig. 1. Molecular structure of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**).

those of $W(PhC{\equiv}CPh)_3(SnMe_3)^-$ (12.7 kcal mol^{-1}) ([8]a), $Cr(PhC{\equiv}CPh)_3(CO)$ (13.1 kcal mol^{-1}) ([8]a) and $W(PhC{\equiv}CPh)_3(SnPh_3)^-$ (13.1 kcal mol^{-1}) ([5]b). Similar values have been determined for $W(PhC{\equiv}CPh)_3(CO)$ ([5]b) (17.2 kcal mol^{-1}) and $W(PhC{\equiv}CPh)_3(PMe_2Ph)$ (16.4 kcal mol^{-1}) ([8]a) compounds and for related d^6 rhenium compounds with general formula $Re(alkyne)_3(X)$ (14–15 kcal mol^{-1}) [17].

Table 3
Selected bond distances (Å) and angles (°) of $Mo(PhC{\equiv}CCOOEt)_3(PMe_3)$ (**1**)

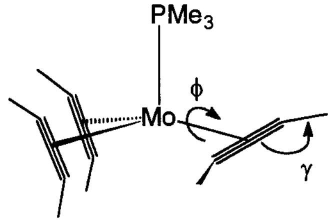
Bond distances (Å)	
Mo(1)–C(1)	2.066(2)
Mo(1)–C(2)	2.059(2)
Mo(1)–P(1)	2.500(2)
C(1)–C(2)	1.309(3)
C(2)–C(3)	1.463(3)
C(3)–O(1)	1.201(3)
C(3)–O(2)	1.324(3)
C(4)–O(2)	1.462(3)
C(4)–C(5)	1.453(5)
Bond angles (°)	
C(2)–Mo(1)–C(1)	37.00(9)
C(2)–Mo(1)–P(1)	85.25(6)
C(1)–Mo(1)–P(1)	122.13(6)
C(2)–C(1)–C(1,1)	136.6(2)
C(1)–C(2)–C(3)	137.6(2)
C(2)–C(1)–Mo(1)	71.20(12)
C(1)–C(2)–Mo(1)	71.79(12)
C(1,1)–C(1)–Mo(1)	152.2(2)
C(3)–C(2)–Mo(1)	150.6(2)
O(1)–C(3)–O(2)	124.0(2)
O(1)–C(3)–C(2)	124.2(2)
O(2)–C(3)–C(2)	111.7(2)
C(5)–C(4)–O(2)	108.2(3)
C(3)–O(2)–C(4)	117.0(2)

The molecular structure of **1** (Fig. 1 and Table 3 for selected bond lengths and angles) is typical of $M(alkyne)_3L$ complexes ($M = d^6$ metal, Cr(0) [6], Mo(0) ([7]a,b), W(0) ([5]a,b,d,e) or Re(I) [17] and L = two electron σ donor). The coordination geometry can be described as either a distorted tetrahedron or a tapered trigonal prism. The complex has a crystallographic C_3 symmetry axis along the Mo–P vector. The higher C_{3v} symmetry is not attainable mainly because steric factors prevent each COOEt substituent from being coplanar with the C≡C linkage. The latter is almost symmetrically coordinated to the molybdenum atom with Mo–C distances of 2.066(2) and 2.059(2) Å, respectively. The C≡C bonds are elongated to 1.309(3) Å with respect to the 1.18 Å average value for uncoordinated alkynes [18]. Also the carbon atoms linked to the C≡C bond are not linearly arranged, the C≡C–C angles being equal to 136.6(2) and 137.6(2)°, for the phenyl and carboxy substituent, respectively. The angles P(1)–Mo(1)–C(1) [122.13(6)] and P(1)–Mo(1)–C(2) [85.25(6)°] are in the ranges found for the structurally characterized $M(alkyne)_3(L)$ complexes (117–127 and 80–90°, respectively) [19].

The interpretation of the chemical bonding for complexes of the type $M(alkyne)_3(L)$ is one of the most successful applications of MO theory in organometallic chemistry. It is worth mentioning that Tate and coworkers, after obtaining the first specimen $W(alkyne)_3(CO)$, were able to predict its structure by using qualitative MO arguments [3] and their hypothesis was later confirmed by X-ray crystallography ([5]e). Further studies are due to King ([8]b) and more recently, Wink and coworkers ([8]a) have presented a comprehensive analysis of the bonding with implications for the fluxional behavior of coordinated alkynes. The basic MO arguments may be summarized as follows. In structures of type **I**, the coordinated d^6 metal atom receives one electron pair from the axial σ-donor and three more from the $\pi_{\|}$ MOs of the alkynes. Another four electrons are needed for the metal to reach saturation which can be in principle taken from the filled $\pi_{\perp}$ MOs of the alkynes. The latter are subdivided by the C_{3v} symmetry in a_2 and e combinations. Since the metal atom has no orbitals of a_2 symmetry, it accepts only the electrons of e symmetry, i.e. just those needed for saturation.

Our present theoretical interest is to understand better the origin of the alkyne rotation barrier in our complex **I**. In fact, we wish not only to verify the consistency of the calculated value with that derived from NMR experiments but also to evaluate the effects associated with both the bulkyness of the alkyl substituents and the electronic nature of the axial ligand.

The models $Mo(RC{\equiv}CR')_3L$, ($R = H$, Ph and $R' = H$, COOMe, $L = PH_3$, Cl^-, CO) have been used in the present calculations. As schematized in **V**, only one alkyne molecule is allowed a ϕ rotation while the other two alkyne ligands remain fixed in the planes containing the axis $M{-}L_{ax}$. While the observed $C{\equiv}C{-}X$ angles (γ) are ca. 137° in **1**, we have initially fixed them to the same 150° value used in the calculations of Wink and Creagan ([8]a). However, it may be anticipated that the parameter γ is to be critical even for X=H, i.e. when the steric problem is minimized.



V

The calculated barrier of ca. 14 kcal mol^{-1} is relatively close to the experimental value of 15.1 kcal mol^{-1}. As already pointed out by Wink and Creagan ([8]a), the HOMO is closely correlated with the barrier as it is most destabilized at $\phi = 90°$ (structure **V**). Interestingly, the barrier decreases to ca. 11 kcal mol^{-1} by closing γ to the experimental 137° value. Such an angular variation affects the $\pi_{\|}$ alkyne frontier orbitals (their energetics and hybridization) as it has been previously discussed by Hoffmann et al. [20]. In particular, the $\pi_{\|}^{*}$ combination is lowered and the backdonation from the appropriate metal d_{π} orbital improves. For smaller γ angles, the HOMO (largely centered on the metal) is relatively more stable over the whole range of ϕ rotations. Then, we have tried to evaluate the barrier for a model closer to **1**, namely with Ph and COOMe substituents. In particular, the carboxylate and the C≡C groupings are fixed in orthogonal planes. Only for the $C{\equiv}C{-}C$ angles of 137° does the barrier match that calculated for three simpler HC≡CH ligands but, in this case, even a small angular increase raises the total energy dramatically (by several eVs). In other words, the short contacts between the ligands determine a very high steric hindrance which affects the barrier itself.

As the next step we have substituted the axial PH_3 group for either the CO or Cl^- ligands in the model $Mo(HC{\equiv}CH)_3(L)$. In this manner, we expected to estimate the changes in the barrier when either the π-donor (halides) or the π-acceptor (carbon monoxide) capabilities of the axial ligand are modified. The trends follow in the direction that emerges from other experimental works. Namely, a CO ligand increases the barrier (17 kcal mol^{-1}) while a halide decreases it (9 kcal mol^{-1}).

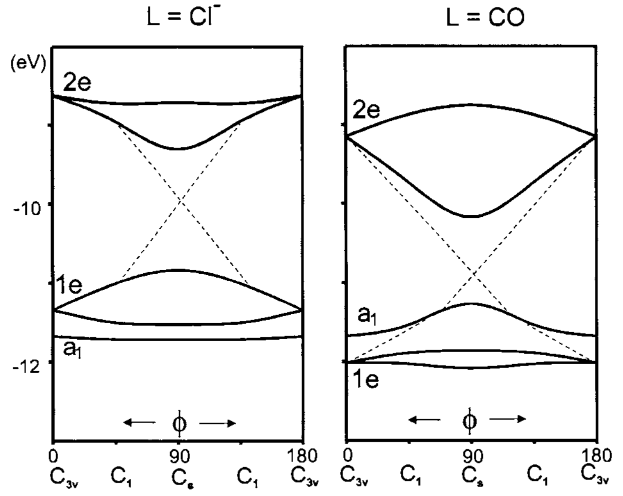
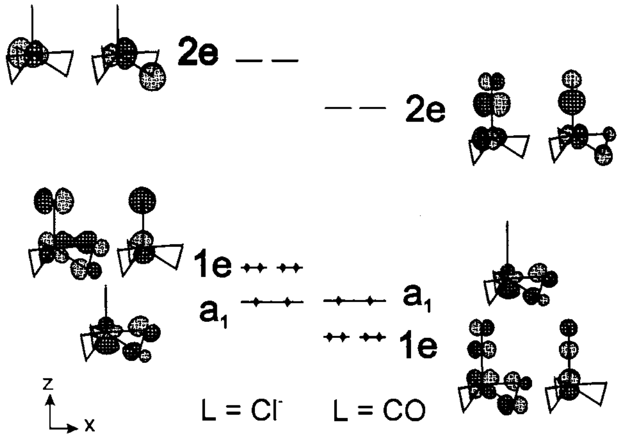


Fig. 2. Evolution of the d metal centered MOs upon the 180° alkyne rotation in the models $[Mo(HC{\equiv}CH)_3Cl]^-$ and $Mo(HC{\equiv}CH)_3(CO)$.

It is possible to point out the electronic underpinnings of the latter result in a manner not totally highlighted before ([8]a). In **VI**, we compared the frontier MOs (centered on the metal d orbitals) of the two alternative C_{3v} structures with one axial Cl and CO ligand, respectively. For clarity, only the orbital contribution of the alkyne ligand in the plane of the drawing is shown.



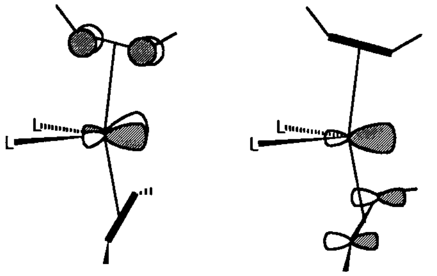
VI

In both cases, the lower and filled a_1 and 1e levels (z^2, xz and yz) are stabilized by the combinations of the empty $\pi_{\|}^{*}$ levels of the alkynes. Also shown is the higher set (2e) of the empty xy and x^2-y^2 orbitals which are antibonding with the $\pi_{\perp}$ orbitals of the alkyne. Recall that two out of three combinations of the second alkyne π bonding MOs act as donors. Importantly, the order $a_1 < 1e$ is inverted in going from the π donor to π acceptor axial ligand. Namely, the related ΔE passes from -0.3 to $+0.4$ eV when the axial ligand stabilizes the degenerate xz and yz metal orbitals. As shown by the Walsh diagrams of Fig. 2, the rotation of one alkyne ligand (the one featuring orbital contributions in

VI) causes one member of the degenerate 1e level (*xz*) to rise in energy because the stabilizing interaction with the alkyne $\pi_{\parallel}^{*}$ orbital vanishes. At the same time, the higher *xy* orbital of 2e, stabilizes because of the loss of the antibonding interaction with alkyne $\pi_{\perp}$ orbital.

At $\phi = 90°$, the inversion of the roles between *xz* and *xy* must have occurred (with respect to the alkyne, *xz* is now acceptor and *xy* is back-donor). Such an inversion implies an avoided crossing mechanism that is evident in both diagrams of Fig. 2. Even though there is no symmetry along the pathways (pointgroup C_1), the rising of the *xz* orbital starts from deeper energy in the CO ligand case due to the stabilization of π^*. In other words, the inversion of the roles between *xz* and *xy* orbitals, at the transition state, has a higher energy cost. Although presented in a very qualitative way, the substantial difference between the two cases is clear.

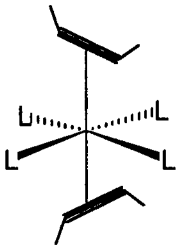
Wink and Creagan ([8]a) pointed out a continuity in the interpretation of the bonding by passing from $M(alkyne)_2L_2$to $M(alkyne)_3L$ complexes (M is a d^6 metal in both cases). In the former species (e.g. $Cr(PhC{\equiv}CPh)_2(dmpe)$ [21]) the quasi-orthogonal orientations of the alkynes (a slight bending away from the equatorial L ligands is also observed) allows the greatest involvement of both the two second pairs [22] as donors toward two empty d-p metal hybrids (see **VII**).



VII

Conversely, it is easly seen that d_{π}-π four electron repulsions would be triggered for different orientations of the alkynes. If the species $M(alkyne)_3L$ is thought of as derived from $M(alkyne)_2L_2$ upon the replacement of one σ-donor ligand with an alkyne, hardly the second π electron pair of the newly introduced ligand is used for metal bonding. If the orthogonal disposition of the first two alkynes is maintained as in the ideal precursor $M(alkyne)_2L_2$, the structure **V** should be adopted by the complexes $M(alkyne)_3L$. By contrast, the conformation **V** corresponds to a destabilized transition state and, we know that the uninvolvement of one of the second pairs in the C_{3v} geometry is to be ascribed to the unique unmatched symmetry of the combination a_2. For this reason, the chemical bonding in the molecule is highly delocalized and can be uniquely rationalized in terms of MO theory.

In conclusion, upto three types of d^6 complexes containing at least two alkynes, namely $M(alkyne)_2L_4$ [23], $M(alkyne)_2L_2$ ([8]a), [21] and $M(alkyne)_3L$, can be correlated. In the octahedral *trans*-bis(alkyne) complexes **VIII**, both the second π-bonding alkyne pair remain extraneous to metal bonding.



VIII

The two *trans* alkyne ligands are staggered to maximize metal backdonation from different metal orbitals (*xz* and *yz*) and also the four electron repulsions between second pairs and the filled t_{2g} metal orbitals are minimized. The point has been previously discussed by other authors [24]. The loss of two L ligands implies a slight reorientation of the alkynes but not a major deviation from the basic staggered disposition (for example in the complex $Cr(PhC{\equiv}CPh)_2(dmpe)$ [21] the dihedral angle between the two planes $CrC{\equiv}C$ increases only from 90 to 105°). Nonetheless this and other minor geometric rearrangements are sufficient for a full involvement of the second pair in bonding, as detailled by Wink and Creagan ([8]a). Finally, the ultimate substitution of one L ligand for a third alkyne is not limited to a simple replacement of the two electron donor functionality, but induces an overall geometrical rearrangement to the unique and highly symmetric structure (C_{3v}).

4. Addendum

When this manuscript was ready to be submitted, a mechanistic study of Yeh and coworkers [25] appeared on the substitution reactions of $W(PhC{\equiv}CPh)_3(CO)$. In this work a semi-empirical MO calculation of $W(PhC{\equiv}CPh)_2(CO)(PMe_3)_2$, with a bipyramid trigonal geometry, is also briefly discussed. Such a compound would fall inside the conceptual limits of the chemical bonding in d^6 metal complexes coordinated by at least two alkyne molecules as discussed by us.

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