Reaction of Vinylacetylene with $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$. Reactivity of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}(\mu\text{-}HC{\equiv}CCH{=}CH_2)]$. Crystal Structures of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_3)][BF_4]$ and of $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]_2\text{-}\mu\text{-}(\mu\text{-}HC{\equiv}CCH_2CH_2)_2]$

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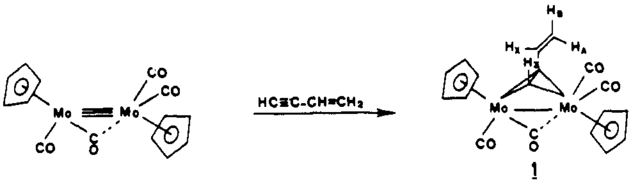
The reaction of vinylacetylene with $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$ affords the adduct $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CCH{=}CH_2)]$ (1). The electrophilic attack of HBF_4 gives the ionic allylic complex $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_3)][BF_4]$ (2). An unexpected reaction occurs with CPh_3PF_6 leading to $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_2CPh_3)][PF_6]$ (3). Complex **2** undergoes nucleophilic attack with $NaBH_4$ and $LiCH_3$ exclusively on the carbon atom bearing the methyl group, giving μ-alkyne complexes $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CCH_2CH_3)]$ (6) and $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CC(CH_3)_2)]$ (7), respectively. However, in the case of complex **3**, the delocalization of the positive charge allows $NaBH_4$ to react in two different ways to give the μ-alkyne species $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CCH_2CH_2CPh_3)]$ (9) and allylic $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\sigma,\eta^3\text{-}HC\text{⋯}CH\text{⋯}CHCH_2CPh_3)]$ (10). The reduction of **1** with sodium amalgam leads to the formation of the σ-η^3 allylic complex $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\sigma,\eta^3\text{-}HC\text{⋯}CH\text{⋯}CHCH_3)]$ (5) and tetrametallic $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]_2\text{-}\mu\text{-}(\mu\text{-}HC{\equiv}CCH_2CH_2)_2]$ (4). Another dimerization occurs in the reaction of **2** with sodium amalgam, leading to $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]_2\text{-}\mu\text{-}(\mu\text{-}HC{\equiv}CCH(CH_3)\text{–})_2]$ (8). This product exists as three isomers, the meso **8A** (*R*S**) and a racemic mixture of **8B** (*SS*) and **8C** (*RR*). The action of base (DBU) on **3** gives the μ-substituted vinylacetylene complex $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CCH{=}CHCPh_3)]$ (11E). The structures of **2** and **4** have been solved by single-crystal X-ray diffraction methods. Crystallographic data [space group, a/Å, b/Å, c/Å, β/deg, Z, number of observed reflections, R_w]: for **2**, $P2_1/n$, 12.924 (7), 18.339 (18), 8.431 (6), 95.36 (5), 4, 2239, 0.0568; for **4**, $P2_1/n$, 8.308 (6), 14.457 (4), 14.664 (9), 102.97 (3), 2, 1558, 0.046.

Introduction

Vinylacetylene is one of the constituents of the "C_4" cut of hydrocarbons, in which it exists together with but-1-yne, buta-1,3-diene, and buta-1,2-diene. In previous work we have reported that these alkynes are complexed selectively by monomeric complexes of tungsten and molybdenum, as four-electron donors in $[W(CO)(dtc)_2(\pi\text{-alkyne})]$ (dtc = diethyldithiocarbamato anion) or as two-electron donors in $[MoO(dtc)_2(\pi\text{-alkyne})]$, and so could be separated from the olefins.[1] However, apart from recent work concerning the use of vinylacetylene derivatives as precursors of (alkenylcarbene)ruthenium complexes,[2] few studies have been undertaken concerning the reactivity of vinylacetylene toward organometallic compounds, although the presence of a second unsaturated site, the vinyl group, in this molecule is very attractive.

The behavior of vinylacetylene toward mononuclear molybdenum and tungsten compounds shows that the alkyne function is preeminent in that molecule. So, a classical 1/1 adduct with the dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$ could be expected. Subsequent reactions leading to the saturation of the olefinic group and lengthening of the carbon chain by carbon–carbon coupling or giving rise to a change in the bonding of the organic ligand to the metal atoms can then be envisaged.

Scheme I



Results and Discussion

The reaction of an excess of vinylacetylene with $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$ in toluene solution gives rise to the classical formation of a 1/1 adduct (complex 1) containing the pseudotetrahedral core Mo_2C_2 (Scheme I).

In the ^1H NMR spectrum there appears an ABX set of resonances in the region of the vinylic protons. The presence of a $\nu(C{\equiv}O)$ band vibration at 1825 cm^{-1} suggests the presence of a semibridging carbonyl. In fact, all the complexes described in this paper contain the entity $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, and in many of them a semibridging carbonyl is reflected in a relatively low-frequency band in the 1830–1900-cm^{-1} range.[3]

The dynamic behavior of the complexes $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}R\text{-}C_2\text{-}R')]$ has been studied previously by NMR methods and can be interpreted on the following assumptions.[4,5] A low-energy process interconverts Mo(1)

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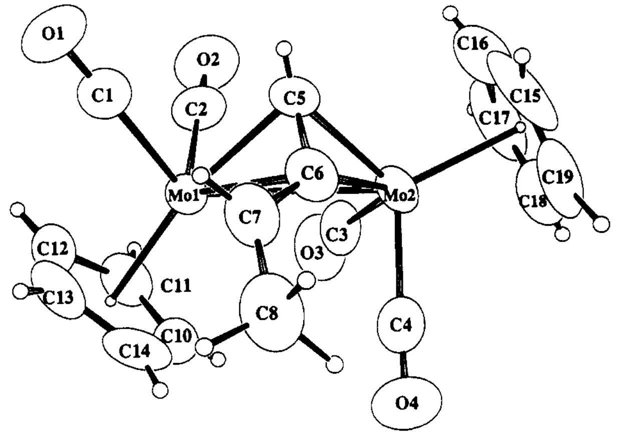

Figure 1. Molecular structure of the cation of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_3)][BF_4]$ (2).

Table I. Selected Bond Lengths (Å) and Angles (deg) in $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_3)][BF_4]$ (2)[a]

Cp(1)–Mo(1)	1.986	Cp(2)–Mo(2)	1.997 (1)
Mo(1)–Mo(2)	3.007	Mo(1)–C(1)	2.003 (7)
Mo(1)–C(2)	2.023 (7)	Mo(1)–C(3)	3.098 (7)
Mo(1)–C(5)	2.126 (7)	Mo(1)–C(6)	2.253 (6)
Mo(2)–C(3)	1.989 (7)	Mo(2)–C(4)	2.003 (9)
Mo(2)–C(5)	2.152 (7)	Mo(2)–C(6)	2.127 (6)
O(1)–C(1)	1.127 (8)	O(2)–C(2)	1.132 (8)
O(3)–C(3)	1.147 (8)	O(4)–C(4)	1.127 (9)
C(5)–C(6)	1.395 (10)	C(6)–C(7)	1.380 (9)
C(7)–C(8)	1.443 (12)	C(10)–C(11)	1.399 (12)
C(11)–C(12)	1.406 (11)	C(12)–C(13)	1.392 (12)
C(13)–C(14)	1.403 (12)	C(10)–C(14)	1.380 (13)
C(15)–C(16)	1.37 (2)	C(15)–C(19)	1.39 (2)
C(16)–C(17)	1.41 (2)	C(17)–C(18)	1.35 (2)
C(18)–C(19)	1.38 (2)		
Cp(1)–Mo(1)–C(1)	110.6 (2)	Cp(2)–Mo(2)–C(3)	111.9 (2)
Cp(1)–Mo(1)–C(2)	111.9 (2)	Cp(2)–Mo(2)–C(4)	117.4 (2)
C(1)–Mo(1)–C(2)	84.5 (3)	C(3)–Mo(2)–C(4)	88.0 (3)
C(1)–Mo(1)–C(5)	79.5 (3)	C(3)–Mo(2)–C(5)	107.1 (3)
C(1)–Mo(1)–C(6)	93.9 (3)	C(3)–Mo(2)–C(6)	121.2 (3)
C(5)–Mo(1)–C(6)	37.0 (3)	C(4)–Mo(2)–C(5)	117.8 (3)
Mo(1)–C(1)–O(1)	117.9 (7)	C(4)–Mo(2)–C(6)	82.1 (3)
Mo(1)–C(2)–O(2)	178.4 (7)	Mo(2)–C(3)–O(3)	172.4 (6)
C(5)–C(6)–C(7)	130.5 (7)	Mo(2)–C(4)–O(4)	177.4 (7)
		C(6)–C(7)–C(8)	127.0 (8)

[a] Cp(1) and Cp(2) denote the centroids of the C_5 rings. The numbers in parentheses are estimated standard deviations.

and Mo(2), Cp(1) and Cp(2) (Cp = η^5-C_5H_5), and the pairs of carbonyl ligands, and a higher energy process effects rotation about the Mo–Mo bond. At room temperature, in some complexes described in this work, the slow-exchange limit for the low-energy process is reached and the ^{13}CO spectrum shows four lines of equal intensity, while for other compounds the four lines coalesce to two lines as required for unsymetrical alkynes. Sometimes one of these peaks is broadened and not easy to detect in the background noise, but in this case, raising the temperature sharpens this broad peak, while four lines appear at lower temperatures. The most unsymmetrical molecules, such as those containing μ-σ,η^3 allylic ligands, exhibit four CO lines even at room temperature.

Reactivity of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CCH{=}CH_2)]$ (1). The reactions described in this paper are represented in Scheme II.

In solution in diethyl ether, complex 1 reacts with HBF_4 to give the orange ionic complex 2. Its ^1H NMR spectrum was not well resolved at room temperature and decomposition occurred before the complete ^{13}C NMR spectrum could be accumulated, so it was decided to determine the structure of 2 by X-ray diffraction. The result is shown in Figure 1. Selected bond lengths and angles are given in Table I, and final fractional coordinates, in Table II.

Table II. Final Fractional Coordinates and Estimated Standard Deviations for 2

atom	*x*	*y*	*z*	*B*,[a] Å^2
Cp(1)	0.0840	0.2658	0.3736	4*
Cp(2)	0.3803	0.0199	0.1205	4*
Mo(1)	0.13090 (5)	0.16279 (3)	0.39155 (8)	3.12 (1)
Mo(2)	0.27692 (5)	0.09431 (3)	0.17682 (8)	3.37 (1)
F(1)	0.2695 (8)	0.4458 (4)	–0.1528 (9)	12.3 (3)
F(2)	0.2731 (6)	0.3332 (4)	–0.2338 (9)	10.2 (2)
F(3)	0.2916 (5)	0.3586 (4)	0.0245 (7)	9.2 (2)
F(4)	0.1404 (5)	0.3675 (6)	–0.108 (1)	12.7 (3)
O(1)	0.0124 (5)	0.0802 (4)	0.6450 (8)	6.6 (2)
O(2)	0.3251 (5)	0.1421 (4)	0.6439 (8)	6.8 (2)
O(3)	0.3943 (5)	0.2350 (3)	0.3037 (8)	6.3 (2)
O(4)	0.1687 (6)	0.1858 (4)	–0.1055 (8)	7.0 (2)
C(1)	0.0540 (6)	0.1092 (4)	0.551 (1)	4.6 (2)
C(2)	0.2553 (7)	0.1506 (5)	0.554 (1)	4.6 (2)
C(3)	0.3454 (6)	0.1851 (4)	0.262 (1)	4.3 (2)
C(4)	0.2075 (7)	0.1542 (5)	–0.001 (1)	4.6 (2)
C(5)	0.1825 (6)	0.0545 (4)	0.3557 (9)	3.8 (2)
C(6)	0.1203 (6)	0.0700 (4)	0.215 (1)	3.8 (2)
C(7)	0.0148 (6)	0.0827 (4)	0.190 (1)	4.4 (2)
C(8)	–0.0426 (7)	0.1041 (6)	0.042 (1)	6.1 (2)
C(10)	0.1375 (7)	0.2784 (4)	0.270 (1)	4.9 (2)
C(11)	0.1665 (7)	0.2843 (4)	0.433 (1)	5.0 (2)
C(12)	0.0801 (7)	0.2661 (4)	0.515 (1)	5.0 (2)
C(13)	0.0004 (6)	0.2464 (4)	0.401 (1)	5.4 (2)
C(14)	0.0361 (8)	0.2543 (4)	0.249 (1)	5.9 (2)
C(15)	0.3168 (8)	–0.0254 (5)	0.122 (2)	8.0 (3)
C(16)	0.3837 (8)	–0.0062 (6)	0.250 (1)	7.7 (3)
C(17)	0.4465 (7)	0.0494 (6)	0.196 (2)	7.5 (3)
C(18)	0.4164 (8)	0.0642 (6)	0.040 (1)	6.8 (2)
C(19)	0.3359 (8)	0.0172 (6)	–0.008 (1)	7.8 (3)
B	0.2399 (9)	0.3761 (6)	–0.119 (1)	5.1 (2)
H(10)	0.169 (8)	0.280 (6)	0.21 (1)	6.5*
H(11)	0.234 (8)	0.291 (6)	0.50 (1)	6.5*
H(12)	0.078 (8)	0.261 (6)	0.61 (1)	6.5*
H(13)	–0.061 (8)	0.237 (6)	0.41 (1)	6.5*
H(14)	0.002 (8)	0.248 (6)	0.15 (1)	6.5*
H(15)	0.27 (1)	–0.061 (8)	0.13 (2)	9.8*
H(16)	0.39 (1)	–0.016 (7)	0.34 (2)	9.8*
H(17)	0.480 (9)	0.067 (8)	0.26 (1)	9.8*
H(18)	0.438 (9)	0.089 (7)	–0.03 (2)	9.8*
H(19)	0.30 (1)	0.012 (7)	–0.12 (2)	9.8*
H(5)	0.183 (6)	0.029 (4)	0.417 (9)	2.2*
H(7)	–0.021 (6)	0.071 (5)	0.27 (1)	3.7*
H(81)	–0.115 (9)	0.126 (7)	0.05 (1)	9.1*
H(82)	0.00 (1)	0.123 (8)	–0.06 (2)	10.8*
H(83)	–0.054 (9)	0.060 (7)	0.02 (2)	9.8*

[a] Starred *B* values are for atoms that were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[A^2B(1,1) + B^2B(2,2) + C^2B(3,3) + AB(\cos\gamma)B(1,2)\ AC(\cos\beta)B(1,3) + BC(\cos\alpha)B(2,3)$.

The molybdenum–carbon(CO) distances suggest that all the carbonyl ligands are terminal, as expected from the absence of $\nu(C{\equiv}O)$ frequencies lower than 1900 cm^{-1} in the infrared spectrum. The Mo(1)–Mo(2) single bond is longer than that usually observed in compounds $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}RC{\equiv}CR')]$ (2.956 (1) Å, R = R′ = C_6H_5; 2.977 (1) Å, R = R′ = C_2H_5; 2.980 (1) Å, R = R′ = H)[4] and could explain the nonexistence of a semibridging carbonyl. The Mo_2C_2 entity is almost tetrahedral; the C(5) and C(6) carbon atoms are each bonded to both Mo(1) and Mo(2), but C(7) interacts with Mo(1) exclusively (Mo(1)–C(7) = 2.613 Å; Mo(2)–C(7) = 3.410 Å). The C(5)–C(6) bond length (1.395 (10) Å), compared with that usually encountered in such Mo_2C_2 entities (1.337 Å with bridging

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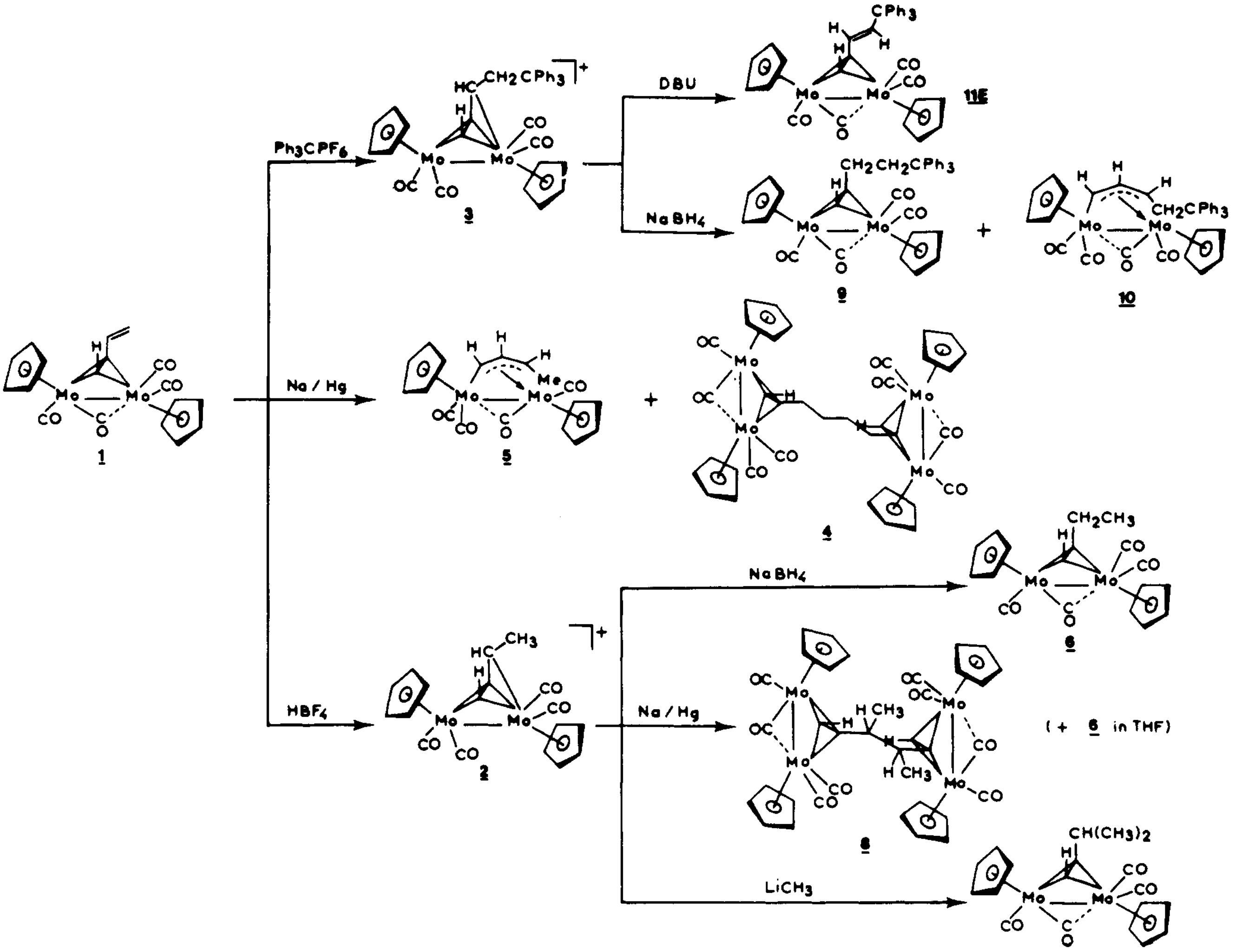
Scheme II



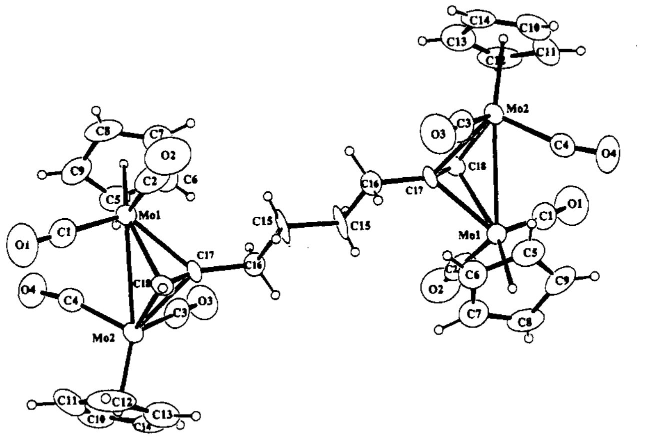
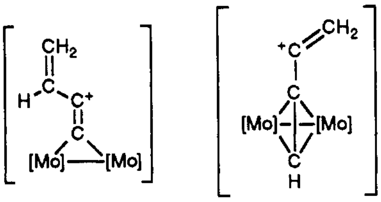


Figure 2. Molecular structure of [[{Mo(η^5-C$_5$H$_5$)(CO)$_2$}$_2$]$_2$-μ-(μ-HC≡CCH$_2$CH$_2$-)$_2$] (4).

acetylene, 1.335 Å with hex-3-yne, and 1.329 Å with diphenylacetylene) and in association with the C(6)–C(7) (1.380 (9) Å) and C(7)–C(8) (1.443 (12) Å) bond lengths, denotes an important electronic delocalization over the bridging organic ligand. The structure of 2 can then be compared with that of the cations in [{W(η^5-C$_5$H$_5$)(CO)$_2$}$_2$(μ-HC≡CC(CH$_3$)$_2$)][BF$_4$][6] and [{Mo(η^5-C$_5$H$_4$Me)(CO)$_2$}$_2$(μ-η^2,η^3-HC≡CCH$_2$][BF$_4$][3] in which Curtis et al. propose that the bridging organic entity can be regarded as a μ-η^2,η^3-allenyl group.

CPh$_3$$^+PF_6$$^-$ is well-known to effect hydride abstraction from a carbon atom in an α or β position relative to a metallic center.[7-11] Intermediate species such as those represented as



(probably unstable but able to rearrange) were possible products from complex 1. Instead, however complex 1 undergoes electrophilic attack by CPh$_3$$^+PF_6$$^-$, leading to

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Table III. Selected Bond Lengths (Å) and Angles (deg) in $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]_2\text{-}\mu\text{-}(\mu\text{-}HC{\equiv}CCH_2CH_2\text{-})_2]$ (4)[a]

Mo(1)–Mo(2)	2.964 (2)	Mo(2)–C(18)	2.12 (34)
Mo(1)–Cp(1)	2.008 (15)	C(17)–C(18)	1.34 (10)
Mo(1)–C(1)	1.96 (2)	C(16)–C(17)	1.532 (14)
Mo(1)–C(2)	1.98 (2)	C(15)–C(16)	1.56 (4)
Mo(1)–C(4)	2.875	C(15)–C(15)	1.493
Mo(2)–Cp(2)	2.03 (3)	C(5)–C(6)	1.43 (3)
Mo(2)–C(3)	1.938 (3)	C(5)–C(9)	1.37 (3)
Mo(2)–C(4)	1.93 (2)	C(6)–C(7)	1.38 (4)
C(1)–O(1)	1.17 (2)	C(7)–C(8)	1.38 (2)
C(2)–O(2)	1.13 (2)	C(8)–C(9)	1.43 (5)
C(3)–O(3)	1.16 (2)	C(10)–C(11)	1.40 (4)
C(4)–O(4)	1.17 (2)	C(10)–C(14)	1.38 (2)
Mo(1)–C(17)	2.186 (14)	C(11)–C(12)	1.39 (4)
Mo(1)–C(18)	2.21 (19)	C(12)–C(13)	1.41 (3)
Mo(2)–C(17)	2.23 (2)	C(13)–C(14)	1.35 (4)

Cp(1)–Mo(1)–C(1)	125.6 (6)	Mo(2)–C(4)–O(4)	167 (2)
Cp(1)–Mo(1)–C(2)	112 (1)	C(18)–C(17)–C(16)	137
Mo(1)–C(1)–O(1)	179 (1)	C(17)–C(16)–C(15)	111 (1)
Mo(1)–C(2)–O(2)	179 (4)	Mo(1)–C(17)–Mo(2)	84.3
Mo(2)–C(3)–O(3)	179 (1)	Mo(1)–C(18)–Mo(2)	86.4

[a] Cp(1) and Cp(2) denote the centroids of the C_5 rings. The numbers in parentheses are estimated standard deviations.

the complex 3 in which the CPh_3^+ entity is attached to the organic ligand.

Few examples of such an "alkylation" are described in the literature. The complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2S(R)\text{-}CPh_3][PF_6]$ was formed from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2SR)]$, in which the sulfur atom may be considered as an obvious site of alkylation.[12] A second example arises with the alkylidene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)({=}CHCH_2CPh_3)][PF_6]$, obtained from $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH{=}CH_2)]$, in which delocalization of the vinylic bond may confer to the C_β carbon atom a significant nucleophilic character.[13]

The reactivity of 3 will be discussed later in this paper. However, in the absence of crystallographic data for this compound, some spectroscopic features merit noting. The ^{13}C chemical shifts of the C_α, C_β, and C_γ carbon atoms and the $J_{C_\gamma\text{-}H}$ coupling constant values lie in the range found in π-allyl complexes[14] and could indicate sp^2 hybridization of the C_γ atom. On the other hand, the δ_{C_α} and $J_{C_\alpha\text{-}H}$ values are also comparable with those observed in μ-alkyne complexes (see complex 1 and $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}HC{\equiv}CH)]$; J_{CH} = 216 Hz[4]), in which the carbon atoms possess weak sp^2 character. Similar discussion of the spectroscopic data for 2 was not possible because of the decomposition of that product in solution.

Complexes 4 and 5 were formed in the reaction of 1 with sodium amalgam. Their presence was verified by NMR spectroscopy on the crude product before chromatography. ^1H and ^{13}C NMR resonances indicate a bridging $HC{\equiv}C\text{-}CH_2CH_2$ entity for complex 4, suggesting the formation of a tetranuclear compound. The molecular structure determined by X-ray diffraction, and shown in Figure 2, confirms the presence of the octa-1,7-diyne ligand, in which the two acetylenic bonds are complexed by two $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ groups. The tetranuclear molecule is centrosymetric. The Mo(1)–Mo(2) (2.964 (2) Å) bond is shorter than that found in complex 2, and one of the CO ligands is semibridging (Mo(1)–C(4) = 2.875 Å). A consequence of this interaction is the 167° value of the Mo(2)–C(4)–O(4) angle, whereas the other Mo—C≡O bonds are linear. The values for the C(18)–C(17) bond length and the C(18)–C(17)–C(16) angles correspond to those found usually in $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}RC{\equiv}CR')]$ entities.[4] The other bond length and angle values for the carbon chain are as expected for saturated carbon atoms. Selected bond lengths and angles are given in Table III, and final fractional coordinates, in Table IV.

Table IV. Final Fractional Coordinates and Estimated Standard Deviations for 4

atom	*x*	*y*	*z*	*B*,[a] Å^2
Mo(1)	0.5602 (1)	0.09679 (7)	0.26458 (7)	2.38 (2)
Mo(2)	0.5453 (1)	0.25941 (7)	0.38553 (7)	2.39 (2)
O(1)	0.181 (1)	0.0817 (9)	0.2534 (8)	7.2 (4)
O(2)	0.546 (2)	−0.1062 (7)	0.3329 (8)	7.0 (3)
O(3)	0.892 (1)	0.3137 (7)	0.3582 (7)	5.1 (3)
O(4)	0.372 (1)	0.3146 (7)	0.1843 (7)	5.7 (3)
C(1)	0.323 (2)	0.0866 (9)	0.2578 (9)	4.0 (4)
C(2)	0.551 (2)	−0.032 (1)	0.3090 (9)	4.6 (4)
C(3)	0.761 (2)	0.2937 (9)	0.3673 (8)	3.3 (3)
C(4)	0.443 (2)	0.2843 (9)	0.2559 (9)	4.1 (4)
C(5)	0.666 (2)	0.187 (1)	0.1582 (8)	3.8 (3)
C(6)	0.799 (2)	0.127 (1)	0.2019 (9)	4.0 (4)
C(7)	0.741 (2)	0.038 (1)	0.1817 (9)	4.2 (4)
C(8)	0.587 (2)	0.041 (1)	0.1215 (9)	4.7 (4)
C(9)	0.537 (2)	0.135 (1)	0.1092 (9)	4.6 (4)
C(10)	0.425 (2)	0.393 (1)	0.4254 (9)	5.0 (4)
C(11)	0.302 (2)	0.325 (1)	0.418 (1)	6.2 (4)
C(12)	0.360 (2)	0.260 (1)	0.4875 (9)	5.4 (3)
C(13)	0.515 (2)	0.290 (1)	0.5389 (9)	4.4 (4)
C(14)	0.551 (2)	0.371 (1)	0.501 (1)	5.4 (4)
C(15)	0.914 (1)	0.009 (1)	0.473 (1)	4.0 (4)
C(16)	0.887 (2)	0.1147 (8)	0.4533 (9)	3.3 (3)
C(17)	0.708 (1)	0.1350 (8)	0.4023 (8)	2.4 (3)
C(18)	0.556 (2)	0.1153 (9)	0.4136 (8)	2.8 (3)
H(5)	0.68 (2)	0.24 (1)	0.17 (1)	4.9*
H(6)	0.88 (2)	0.15 (1)	0.241 (9)	4.9*
H(7)	0.82 (2)	−0.00 (1)	0.21 (1)	4.9*
H(8)	0.55 (2)	0.00 (1)	0.11 (1)	4.9*
H(9)	0.44 (2)	0.15 (1)	0.08 (1)	4.9*
H(10)	0.42 (2)	0.43 (1)	0.39 (1)	6.3*
H(11)	0.20 (2)	0.34 (1)	0.38 (1)	6.3*
H(12)	0.30 (2)	0.22 (1)	0.50 (1)	6.3*
H(13)	0.57 (2)	0.25 (1)	0.59 (1)	6.3*
H(14)	0.67 (2)	0.39 (1)	0.52 (1)	6.3*
H(18)	0.49 (2)	0.064 (9)	0.452 (8)	3.8*
H(151)	0.83 (2)	−0.02 (1)	0.508 (9)	5.3*
H(152)	0.89 (2)	−0.02 (1)	0.42 (1)	5.3*
H(161)	0.92 (2)	0.13 (1)	0.409 (9)	4.0*
H(162)	0.93 (2)	0.15 (1)	0.509 (9)	4.0*

[a] See footnote *a* of Table II.

The ^1H NMR spectrum of 5 is characterized by a resonance at low field (9.38 ppm). The chemical shifts of the other protons and of the carbon atoms correspond to a σ,η^3 allylic arrangement of the organic ligand.[15] The $^1J_{CH}$ coupling constants agree with a cis arrangement of the protons. The existence of two resonances for the $\eta^5\text{-}C_5H_5$ ligands in the ^1H and ^{13}C NMR spectra, and of four lines assigned to the CO groups, confirm the asymmetry of the molecule.

Possible mechanisms for the formation of complexes 4 and 5 are illustrated in Scheme III. Two kinds of reduction may be envisaged, the first one involving one electron from the sodium atom to the dimetallic species. An alternative pathway for the formation of 4 could be the addition of a proton to the anionic dimetallic species, giving rise to neutral radicals followed by their dimerization. Concerning the formation of 5, the addition of one proton provides a neutral radical. Transition-metal radicals are

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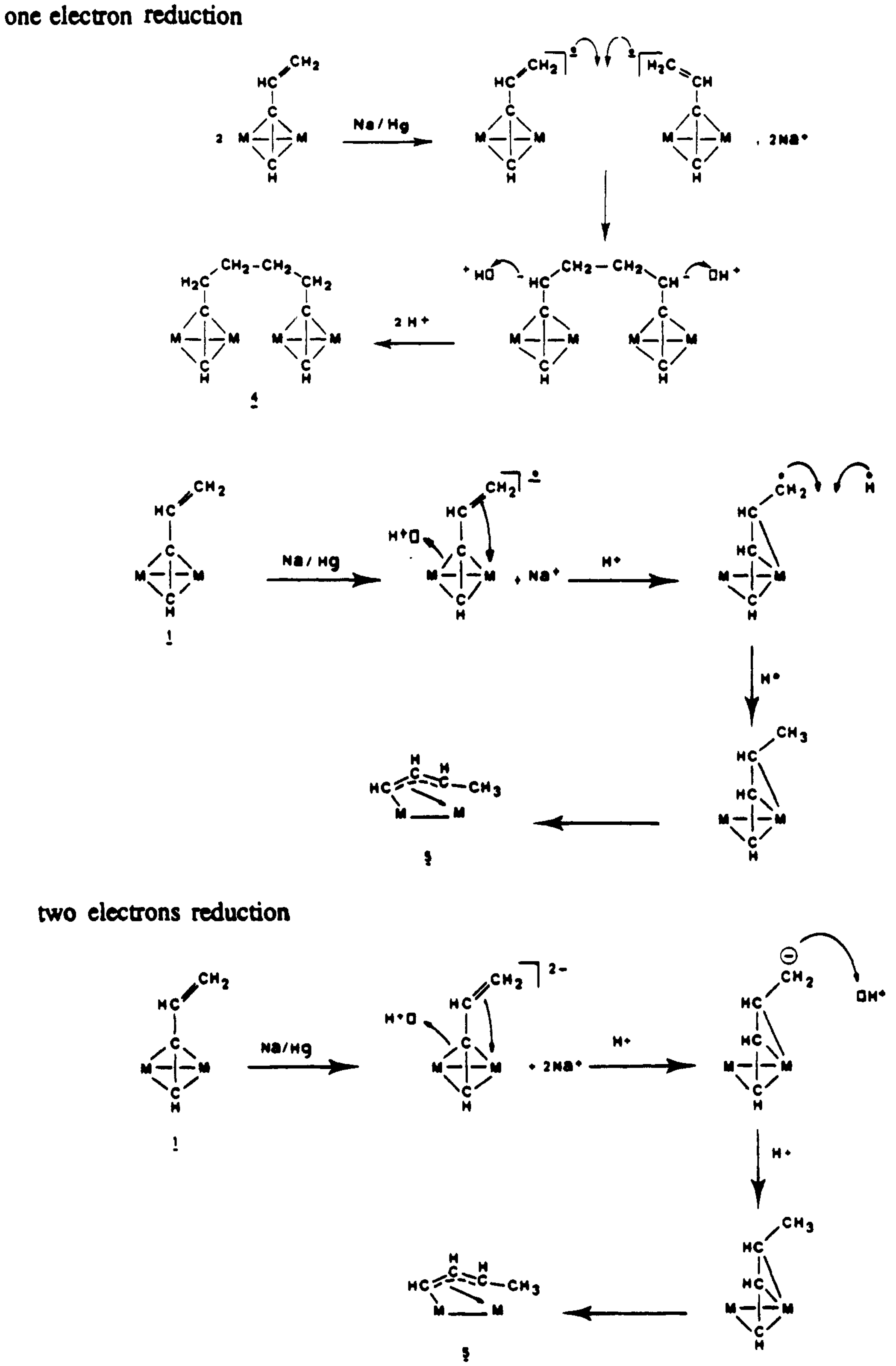
(12) Guerchais, V.; Thêpot, J. Y.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1554.

(13) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heach, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

(14) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

(15) Barker, G. K.; Carroll, W. E.; Green, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1071.

Scheme III



well-known to abstract H atoms from THF.[16] Such an intervention of H atoms should occur in the reduction of 2 by sodium amalgam to lead to small amounts of 6 in THF (see Experimental Section).

Dianions of 1 may be formed by reduction with two electrons. In this case compound 4 should result from the coupling of that dianion with the neutral species 1 and compound 5 from the addition of two protons. Electrochemical studies will be performed in order to check on these possibilities.

Reactivity of Complex 2. The ^{1}H NMR spectrum of 2 was not well resolved at room temperature. At 213 K the different peaks sharpened; the methyl proton peak was resolved as a doublet, and the acetylenic proton signal, as a quartet, while two signals corresponding to the η^5-C_5H_5

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(16) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471 and references therein.

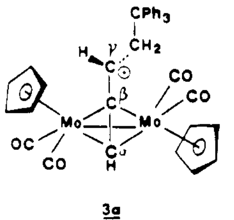
ligands appeared. A fluxional equilibrium similar to that proposed by Curtis for $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$ may be retained.[3]

As discussed above, the crystal structure of **2** suggests a delocalization of the positive charge over the whole carbon chain, corresponding to a $\mu\text{-}\eta^2,\eta^3$-allenyl arrangement. However, the reaction of nucleophilic agents such as $NaBH_4$ and $LiCH_3$ leads exclusively to the molecular μ-alkyne complexes **6** and **7**, respectively, by attack on the carbon atom bearing the methyl group.

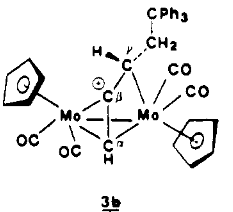
The reduction of **2** with sodium amalgam in THF leads to the formation of complexes **6** and **8**. When the reaction was performed in toluene, complex **8** was obtained exclusively. The ^1H and ^{13}C NMR spectra of **8** consist of two sets of resonances of nearly equal intensity. The shielding of the non-acetylenic CH proton in **8** compared with that observed in **2**, and the position of the corresponding carbon peak (J_{CH} = 40 ppm), suggest that this carbon atom possesses an unequivocal sp^3 character, consistent with a carbon–carbon coupling leading to a tetrametallic compound. Such a dimerization has been observed previously with $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$ in the same experimental conditions.[3] However, it may be noted that with $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}C(CH_3)_2)][BF_4]$ the action of sodium amalgam leads only to the formation of the monomeric **7**, which shows the influence of the substitution degree on the C_γ carbon atom on the evolution of the reaction.[17] Moreover the formation of a new carbon–carbon bond induces the creation of two centers of chirality in the molecule. That means that three conformations may be envisaged for complex **8**: a meso compound *R*S** **8A**, which gives one NMR spectrum, and a racemic mixture **8B** (*SS*) and **8C** (*RR*) providing the second spectrum. A radical mechanism illustrated in Scheme IV may be proposed for the formation of **8**. Depending to the disposition of the two radicals before coupling, the three conformations are formed.

The formation of the meso compound and of the racemic mixture in almost equal intensities is quite fortuitous, indicating that the reaction is not stereospecific.

Reactivity of Complex 3. The two cationic complexes resulting from the protonation (complex **2**) or from the alkylation (complex **3**) of the organic chain in **1** seem similar structurally. However, as discussed above, the spectroscopic data for the C_α atom are comparable with those observed in μ-alkyne complexes. It may therefore be suggested that the positive charge is concentrated on the C_β and C_γ atoms:



3a

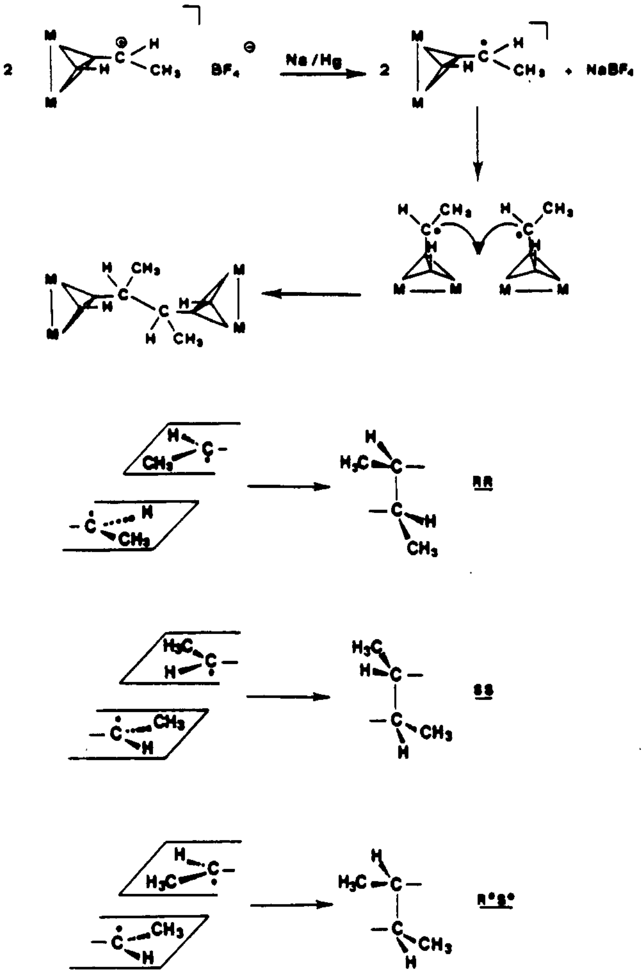


3b

In effect, the action of $NaBH_4$ gives rise to the formation of two new compounds **9** and **10**, resulting from two different sites of nucleophilic attack on complex **3**.

The NMR spectra of complex **9** are consistent with a bridging substituted vinylacetylene, obtained by an attack of hydride on the C_γ carbon atom of form **3a**, whereas the formation of complex **10** may arise from an unprecedented attack on the C_β carbon (form **3b**). The deshielding of the H_α proton (9.09 ppm) and the existence of three doublets in the ^{13}C NMR spectrum is consistent with a $\mu\text{-}\sigma,\eta^3$ allylic carbon chain substituted with CH_2CPh_3.

Scheme IV



The action of a base such as DBU or NaH on complex **3** leads to the neutral **11E** by abstraction of a proton from the CH_2 group. The value of the coupling constant (J_{HH} = 15.3 Hz) agrees with the presence of the **11E** isomer, whereas the forms *E* and *Z* were generated in $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(C(H){=}C(H)R)]$, in various proportions according to the nature of R, from the cationic $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)({=}C(H)CH_2(R)]$.[13] In our case, we suggest that the bulky triphenylmethyl group does not favor the formation of the *Z* isomer.

Experimental Section

General Considerations. All the reactions and purifications were performed under nitrogen using Schlenk techniques.

The solvents were freshly distilled under nitrogen from drying agents as follows: sodium/benzophenone for THF and toluene; CaH_2 for dichloromethane, hexane, and diethyl ether. The deuterated solvents were dried over activated molecular sieves prior to use.

Infrared spectra were obtained with a Perkin-Elmer 1430 spectrometer, using solutions in CH_2Cl_2 or KBr pellets. Infrared frequencies are reported in wavenumber units (cm^{-1}).

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 (^1H, 300.13 MHz; ^{13}C, 75.47 MHz) instrument. Chemical shifts are reported as δ in units of parts per million (ppm) relative to an internal reference of tetramethylsilane. Coupling constants are reported in hertz (Hz).

Analyses were performed at the Service Central d'Analyses du CNRS.

Materials. $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$ was obtained by a published method.[18] Vinylacetylene was prepared by the reaction of

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[17] Unpublished results.

Table V. Crystal Data and Details of Measurements for 2 and 4

	2	4
formula	$C_{18}H_{15}BF_4Mo_2O_4$	$C_{36}H_{30}Mo_4O_8$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	12.924 (7)	8.308 (6)
b, Å	18.339 (18)	14.457 (4)
c, Å	8.431 (6)	14.664 (9)
β, deg	95.36 (5)	102.97 (3)
V, Å³	1985.3	1716.4
Z	4	2
d_{calcd} g cm⁻³	1.92	1.885
cryst dimens, mm	0.2 × 0.21 × 0.12	0.15 × 0.075 × 0.042
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
abs coeff, cm⁻¹	12.9	14.44
no. of data collcd	3762	3248
no. of unique data >3σ	2239	1558
no. of params varied	308	263
R	0.0447	0.038
R_w	0.0568	0.046
GOF	1.54	1.12

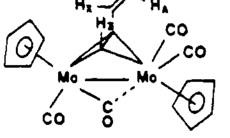
trans-1,4-dichloro-2-butene (Aldrich) and $NaNH_2$.[19] All other chemicals used were obtained from commercial sources.

Crystallography. Single crystals grown from dichloromethane/diethyl ether were mounted on an Enraf-Nonius CAD-4 four-circle automatic diffractometer. The unit cells were determined and refined from 25 randomly selected reflections obtained by use of the CAD-4 automatic routines. The intensities were measured in an ω–2θ scan (θ_{min} 1°, θ_{max} 25°), and reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structures.

All calculations were carried out by use of the Enraf-Nonius SDP package.[20] The structures were solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were determined in a difference map (organic ligands in 2 and 4) or calculated by the "hydro" program of SDP (cyclopentadienyl rings). Apart from the hydrogen atoms of the organic ligand in 2, which were refined directly, all these atoms were included in the final calculations with *B*(iso)(H) = 1.3*B*(iso)(C) (C is the carbon atom bearing the hydrogen atom or the average of the carbon atoms of the rings).

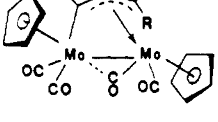
Because of the small size of the crystal, no correction for absorption was carried out for 4. The weighting scheme employed was $w^{-1} = {}^1/_4[\sigma(I)/I + 0.06(I)^2]$. Pertinent crystallographic information is summarized in Table V. The final atomic coordinates, selected bond distances, and selected bond angles are listed in Tables I–IV.

Synthesis. For NMR discussion of some compounds, hydrogen atoms are numbered in the following manner:



1

11E (H_B replaced by CPh_3)



5 (R = CH_3)

10 (R = CH_2CPh_3)

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-HC≡CCH=CH$_2$)] (1). In a typical experiment, a cold solution (–40 °C) of vinylacetylene (2.2 g, 42 mmol) in toluene (100 mL) was added to a cold solution (–40 °C) of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$ (10 g, 23 mmol) in toluene (100 mL). The mixture was allowed to reach room temperature and stirred for 18 h. The solution turned from brown to deep red. The solvent was evaporated in vacuo, and complex 1 was extracted with 150-mL portions of hexane. Removal of solvent from the combined hexane solutions yielded dark red crystals (yield 80%). ¹H NMR ($CDCl_3$ solution): 6.72 (H_X (ddd, $^4J_{XZ}$ = 0.6, $^3J_{BX}$ = 10.0, $^3J_{AX}$ = 16.6), 5.47 H_Z (d, $^4J_{ZX}$ = 0.6), 5.30 C_5H_5 (s), 5.06 H_A (dd, $^3J_{AX}$ = 16.6, $^2J_{AB}$ = 1.9), 4.96 H_B (dd, $^3J_{BX}$ = 10.0, $^2J_{AB}$ = 1.9). $^{13}C\{^1H\}$ NMR (C_6D_6 solution): 231.8, 223.3 CO, 141.1 CH_X (d, $^1J_{CH}$ = 156.9), 113.4 CH_2 (t, $^1J_{CH}$ = 156.1), 91.5 C_5H_5, 76.7 CH_Z (d, $^1J_{CH}$ = 210.3), 61.5 ≡C (s). IR (CH_2Cl_2): 1980 (s), 1910 (s), 1825 (s), ν(C≡O). Anal. Calcd for $C_{18}H_{14}Mo_2O_4$: C, 44.47; H, 2.90; Mo, 39.47. Found: C, 44.50; H, 2.85; Mo, 40.11.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-η^2,η^3-HC≡CCHCH$_3$)][BF$_4$] (2). To a stirred solution of 500 mg (1.03 mmol) of 1 in 30 mL of diethyl ether was added dropwise 1 mL of a solution of HBF_4 in diethyl ether. The orange precipitate produced was separated off, washed with diethyl ether (2 × 5 mL), and then recrystallized from a CH_2Cl_2/Et_2O solvent mixture to give single crystals of 2 (yield quantitative). ¹H NMR ($(CD_3)_2CO$ solution, room temperature): 6.70 CH (q, broad), 6.50 ≡CH (s), 5.93 C_5H_5 (s), 1.94 CH_3 (d, broad). ¹³C NMR: decomposition. IR (CH_2Cl_2): 2060 (s), 2000 (s), 1900 (s), ν(C≡O); 1100 (s), ν(B-F). Anal. Calcd for $C_{18}H_{15}BF_4Mo_2O_4$: C, 37.66; H, 2.63; Mo, 33.43. Found: C, 37.68; H, 2.64; Mo, 32.14.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-η^2,η^3-HC≡CCHCH$_2$C(C$_6$H$_5$)$_3$][PF$_6$] (3). A solution of 500 mg (1.03 mmol) of complex 1 in dichloromethane was transferred at –20 °C to a solution of CPh_3PF_6 (400 mg, 1.03 mmol) in the same solvent. The mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo, and the residue was chromatographed on Florisil. Complex 3 was eluted as an orange band with a 50/50 CH_2Cl_2/THF mixture (yield 65%). ¹H NMR $(CD_3)_2CO$ solution (unresolved spectrum): 7.36–7.25 C_6H_5 (multiplets), 6.08 CH (t), 5.42 C_5H_5 (s). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$ solution): 217.7 CO (s), 145.9–129.3, 128.7–127.0 C_6H_5 (multiplets), 116.6 C≡ (s), 99.6 CH (d, $^1J_{CH}$ = 159.8), 93.1 C_5H_5, 78.0 ≡CH (d, $^1J_{CH}$ = 224.3), 58.5 CPh_3 (s), 46.0 CH_2CPh_3 (t, $^1J_{CH}$ = 132.0). IR (CH_2Cl_2): 2060 (s), 2010 (s), 1905 (s), ν(C≡O); 845 (s), ν(P–F). Anal. Calcd for $C_{37}H_{29}F_6Mo_2O_4P$: C, 50.82; H, 3.34; Mo, 21.94; P, 3.54. Found: C, 49.72; H, 3.25; Mo, 20.63; P, 3.33.

Synthesis of [[{Mo(η^5-C_5H_5)(CO)$_2$}$_2$]$_2$-μ-(μ-HC≡CCH$_2$CH$_2$)$_2$] (4) and [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-η^2,η^3-HC⋯CH⋯CHCH$_3$)] (5). Complex 1 (500 mg, 1.03 mmol) was dissolved in 60 mL of THF. The resulting solution was transferred onto 15 g of 2% sodium amalgam. The mixture was stirred for 18 h at room temperature, the solution was filtered, and the solvent was removed in vacuo. The crude solid was chromatographed on silica gel. A red band was eluted with a dichloromethane/hexane mixture (1/2 in volume). Concentration of the solution gave small single crystals of 4 (yield 20%). A second band containing the orange complex 5 was eluted with 50/50 hexane/dichloromethane (yield 20%).

Data for 4 are as follows. ¹H NMR (C_6D_6 solution): 5.76 ≡CH (s), 4.90 C_5H_5 (s), 2.71 CH_2 (t, broad), 1.27 CH_2 (td broad). ¹³C NMR (C_6D_6 solution): 233.5 CO (s), 91.4 C_5H_5, 86.1 HC≡, 58.3 *C*≡, 35.6 *C*H$_2$, 32.8 *C*H$_2$. IR (KBr pellet): 1970 (s), 1915 (s), 1905 (s), 1890 (s), 1880 (sh), 1825 (s), ν(C≡O). Anal. Calcd for $C_{36}H_{30}Mo_4O_8$: C, 44.37; H, 3.10; Mo, 39.38. Found: C, 44.41; H, 3.06; Mo, 38.85.

Data for 5 are as follows. ¹H NMR (C_6D_6 solution): 9.38 H_a (dd, $^3J_{ab}$ = 9.8, $^4J_{ac}$ = 0.9), 5.11 H_b (dd, $^3J_{ab}$ = 9.8, $^3J_{bc}$ = 9.1), 4.85 C_5H_5 (s), 4.27 C_5H_5 (s), 1.91 H_c (qdd, $^3J_{bc}$ = 9.1, $^4J_{ac}$ = 0.9), 1.37 CH_3 (d). $^{13}C\{^1H\}$ NMR (C_6D_6 solution): 250.4 (s), 243.9 (s), 238.8 (s), 238.0 (s) CO, 166.3 CH_a (d, $^1J_{CH}$ = 146.4), 94.1 C_5H_5, 90.3 C_5H_5, 79.7 CH_b (d, $^1J_{CH}$ = 159.0), 37.6 CH_c (d, $^1J_{CH}$ = 123.5), 19.0 CH_3 (q). IR (KBr pellet): 1935 (s), 1895 (s), 1765 (s), 1725 (s), ν(C≡O). Anal. Calcd for $C_{18}H_{16}Mo_2O_4$: C, 44.28; H, 3.30; Mo, 39.30. Found: C, 44.07; H, 3.23; Mo, 39.23.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-HC≡CCH$_2$CH$_3$)] (6). A solution of complex 2 (400 mg, 0.7 mmol) in 50 mL of THF was poured onto 40 mg (1.06 mmol) of sodium tetrahydroborate. The heterogeneous mixture was stirred for 18 h at room temperature, and the red solution formed was filtered off. The solvent was removed in vacuo, and the solid residue was chromatographed on silica gel. A red band was eluted with a hexane/dichlormethane

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mixture (2/1 in volume). Removal of solvent and recrystallization from dichloromethane/hexane gave red crystals of **6** (yield 50%). ^{1}H NMR ($CDCl_3$ solution): 5.95 $\equiv$CH (s), 5.28 C_5H_5 (s), 2.58 CH_2 (q), 0.87 CH_3 (t). ^{13}C NMR ($CDCl_3$ solution): 233.7, 228.2 CO, 91.3 C_5H_5, 85.7 $\equiv$CH, 61.8 C$\equiv$, 29.5 CH_2, 17.4 CH_3. IR (CH_2Cl_2): 2055 (s), 2000 (s), 1900 (s), ν(C$\equiv$O). Anal. Calcd for $C_{18}H_{16}Mo_2O_4$: C, 44.28; H, 3.30; Mo, 39.30. Found: C, 44.22; H, 3.24; Mo, 39.48.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-HC$\equiv$CCH(CH_3)$_2$)] (7). A 1.2-mL volume of $LiCH_3$ (1.6 M in diethyl ether) was added dropwise to a cold solution (−60 °C) of 1 g (1.8 mmol) of **2** in 100 mL of dichloromethane. The mixture was stirred for 2 h while it was to room temperature. The solution was filtered, and the solvent was removed in vacuo. The residue was chromatographed on silica gel using a mixture of hexane and dichloromethane (5/1 in volume) as eluent. After removal of solvent, complex **7** was obtained as a red powder (yield 40%). ^{1}H NMR (C_6D_6 solution): 5.55 $\equiv$CH (s), 4.85 C_5H_5 (s), 2.58 CH (h), 0.85 CH_3 (d). ^{13}C{^{1}H} NMR (C_6D_6 solution): 234.1 CO (s), 91.4 C_5H_5, 86.0 $\equiv$CH (d, $^1J_{CH}$ = 209.8), 65.3 C$\equiv$ (s), 32.5 CH (d, $^1J_{CH}$ = 132.4), 26.3 CH_3 (q, $^1J_{CH}$ = 132.4). IR (KBr pellet): 1972 (s), 1900 (s), 1887 (s), 1822 (s), ν(C$\equiv$O). Anal. Calcd for $C_{19}H_{18}Mo_2O_4$: C, 45.44; H, 3.61; Mo, 38.20. Found: C, 45.45; H, 3.54; Mo, 38.19.

Synthesis of [[{Mo(η^5-C_5H_5)(CO)$_2$}$_2$]$_2$-μ-(μ-HC$\equiv$CCH(CH_3)−)$_2$] (8). A solution of complex **2** (500 mg, 0.9 mmol) in 100 mL of toluene was poured onto 15 g of 2% sodium amalgam. After stirring (22 h) and filtration, the solvent was removed in vacuo and the residue was chromatographed on silica gel using a mixture of hexane and dichloromethane (1/1) as eluent. After removal of solvent, a red microcrystalline powder of **8** was formed (yield 30%). When this reaction was performed in THF, small amounts of **6** (yield <5%) were recovered (eluent hexane/dichloromethane, 2/1) together with compound **8**. ^{1}H and ^{13}C NMR spectra consist of two sets of peaks of about equal intensity, one set corresponding to **8A** (*R*S**) and the other to a mixture of **8B** (*SS*) and **8C** (*RR*). It was impossible to assign the sets. ^{1}H NMR (C_6D_6 solution): 5.94 $\equiv$CH (s, 1 H), 5.90 $\equiv$CH (s, 1 H), 5.10 C_5H_5 (s, 5 H), 5.01 C_5H_5 (s, 5 H), 4.94 C_5H_5 (s, 5 H), 4.90 C_5H_5 (s, 5 H), 2.93 CH (q, 1 H) 2.25 CH (q, 1 H), 1.25 CH_3 (d, 3 H) 0.30 CH_3 (d, 3 H). ^{13}C NMR (C_6D_6 solution): 234.5 (s), 234.4 (s), 233.9 (s), 232.9 (s), 232.4 (s), 224.8 (s), 224.4 (s) CO, 97.1, 92.1, 91.7, 91.2 C_5H_5, 89.3 $\equiv$CH (d), 88.9 $\equiv$CH (d), 63.0 C$\equiv$ (s), 62.0 C$\equiv$ (s), 42.1 CH (d), 40.2 CH (d), 18.0 CH_3 (q), 16.2 CH_3 (q). IR (KBr pellet): 1980 (s), 1930 (sh), 1895 (s), 1840 (sh), 1820 (s), ν(C$\equiv$O). Anal. Calcd for $C_{36}H_{30}Mo_4O_8$: C, 44.37; H, 3.00; Mo, 39.38. Found: C, 44.31; H, 2.98; Mo, 40.13.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-HC$\equiv$CCH$_2$CH$_2$CPh$_3$)] (9) and of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-σ,η^3-HC$\cdots$CH$\cdots$CHCH$_2$CPh$_3$)] (10). A 550-mg (0.6-mmol) amount of the ionic complex **3** was dissolved in 60 mL of THF in the presence of a large excess of $NaBH_4$. The color of the solution changed rapidly from orange to red. The reaction mixture was stirred at room temperature for about 4 h, and then the solution was filtered off and the solvent was removed in vacuo. Chromatography on silica gel separated two compounds. Complex **9** was obtained as a red band with hexane/dichloromethane (2/1) as eluent (yield 20%). Complex **10** (eluent dichloromethane) formed an orange microcrystalline powder after removal of solvent (yield 20%).

Data for **9** are as follows. ^{1}H NMR (C_6D_6 solution): 7.43 (d, 6 H), 7.17 (dd, 6 H), 7.00 (t, 3 H) C_6H_5, 5.63 $\equiv$CH (s, 1 H), 4.83 C_5H_5 (s, 10 H), 2.57 CH_2–CH_2 (m, 4 H). ^{13}C{^{1}H} NMR (C_6D_6 solution): 233.8 (s), 230.5 (s) CO, 147.8, 129.5, 128.3, 126.4 C_6H_5, 91.3 C_5H_5, 86.4 $\equiv$CH (d, $^1J_{CH}$ = 209.4)), 58.5 *C*Ph$_3$ (s), 56.9 C$\equiv$ (s), 44.7 CH_2 (t, $^1J_{CH}$ = 129.0), 32.3 CH_2 (t, $^1J_{CH}$ = 130.4). IR (KBr pellet): 1980 (s), 1895 (s), 1885 (sh), 1830 (sh); 1810 (s), ν(C$\equiv$O). Anal. Calcd for $C_{37}H_{30}Mo_2O_4$: C, 60.83; H, 4.14; Mo, 26.27. Found: C, 60.80; H, 4.00; Mo, 26.20.

Data for **10** are as follows. ^{1}H NMR (C_6D_6 solution): 9.09 H_a (d, 1 H), 7.60 (6 H), 7.27 (6 H), 7.05 (3 H) C_6H_5, 4.73 C_5H_5 (s, 5 H), 4.63 H_b (dd, 1 H), 4.23 C_5H_5 (s, 5 H), 4.19 H_c (td, 1 H), 2.19 CH_2 (m, 2 H). ^{13}C{^{1}H} NMR (C_6D_6 solution): 251.1 (s), 244.5 (s), 240.9 (s), 239.0 (s) CO, 165.6 *C*H$_a$ (d, $^1J_{CH}$ = 136.9), 147.0–126.6 C_6H_5 (3 m), 97.3 *C*H$_b$ (d, $^1J_{CH}$ = 151.2), 95.3 C_5H_5, 91.0 C_5H_5, 81.4 *C*H$_c$ (d, $^1J_{CH}$ = 139.6), 59.3 *C*Ph$_3$ (s), 46.2 *C*H$_2$ (t, $^1J_{CH}$ = 129.0). Anal. Calcd for $C_{37}H_{30}Mo_2O_4$: C, 60.83; H, 4.14; Mo, 26.27. Found: C, 60.65; H, 4.05; Mo, 24.00.

Synthesis of [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-HC$\equiv$CCH=CHCPh$_3$)] (11E). Complex **3** (850 mg, 0.97 mmol) was dissolved in 100 mL of dichloromethane at −20 °C, and then DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) (2.2 mL) was added dropwise. The orange solution turned rapidly to red as it was stirred for 1 h. Solvent was removed in vacuo, and elution of the crude solid on silica gel (hexane/dichloromethane (3/1)) gave complex **11E** (yield 40%). ^{1}H NMR (C_6D_6 solution): 7.38–7.00 C_6H_5 (m, 15 H), 6.80 H_x (d, $^3J_{AX}$ = 15.3), 6.44 H_A (d, $^3J_{AX}$ = 15.3), 5.08 $\equiv$CH (s), 4.83 C_5H_5 (s, 10 H). ^{13}C{^{1}H} NMR (C_6D_6 solution): 231.5 (s), 229.7 (s) CO, 147.0 C_6H_5 (s), 138.1 *C*H$_x$ (d, $^1J_{CH}$ = 154.0), 135.3 *C*H$_A$ (d, $^1J_{CH}$ = 157.0), 129.5–126.7 C_6H_5, 91.4 C_5H_5, 74.0 $\equiv$CH (d, $^1J_{CH}$ = 210.0), 65.3 *C*Ph$_3$ (s), 61.4 C$\equiv$ (s). IR (KBr pellet): 1970 (s), 1900 (s), 1835 (sh), 1817 (s), ν(C$\equiv$O). Anal. Calcd for $C_{37}H_{28}Mo_2O_4$: C, 61.00; H, 3.87; Mo, 26.34. Found: C, 60.96; H, 3.88; Mo, 26.16.

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Registry No. **1**, 137966-85-9; **2**, 137966-87-1; **3**, 137966-89-3; **4**, 137966-90-6; **5**, 137966-91-7; **6**, 88702-98-1; **7**, 87654-07-7; **8A**, 137966-92-8; **8B**, 138125-78-7; **8C**, 138125-79-8; **9**, 137966-93-9; **10**, 137966-94-0; **11E**, 137966-95-1; [Mo(η^5-C_5H_5)(CO)$_2$]$_2$, 56200-27-2; CPh_3PF_6, 437-17-2.

Supplementary Material Available: Complete tables of bond lengths and angles and anisotropic temperature factors (8 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.