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Preparation and Structural Characterization of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. An Investigation of the Stereochemical Influence of the Orbital Occupancy of the HOMO upon the Metal–Acetylene Interaction in $(\eta^5\text{-}C_5H_5)_2M(C_2R_2)$-Type Complexes

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$(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ has been prepared and characterized by spectroscopic and X-ray diffraction methods to examine the influence of the orbital occupancy of the HOMO upon the nature of the molybdenum–acetylene interaction. The principal structural feature of this complex is the central, three-membered metallacyclopropene ring. The hexafluoro-2-butyne molecule is symmetrically coordinated to the Mo atom via two equivalent Mo–C bonds of 2.128 (7) and 2.129 (7) Å. This mode of coordination is accompanied by a ca. 0.08 Å lengthening of the carbon–carbon multiple bond with a concomitant decrease in its stretching frequency to 1778 cm^{-1}. The bending of the perfluoro groups away from the Mo center reduces the C–C–CF_3 bond angles from 180° in the free acetylene to 138.3° (average) in this adduct and is consistent with the transformation of the acetylene's geometry toward that of a cis olefin. The nonbonding character of the HOMO is confirmed by a comparison of the corresponding structural parameters within the metallacyclopropene ring for $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2Me)_2)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. The molybdenacyclic derivative is prepared by the reduction of $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$ with Na/Hg amalgam in the presence of hexafluoro-2-butyne. The compound crystallizes in an orthorhombic space group, *Pbca*, with refined lattice parameters $a = 26.409$ (5) Å, $b = 15.194$ (3) Å, $c = 7.697$ (5) Å, $V = 3088$ (2) Å^3, and $Z = 8$. Full-matrix least-squares refinement of 1684 diffractometry data with $F_o^2 > \sigma(F_o^2)$ converged with final discrepancy indices of $R(F_o) = 0.050$, $R(F_o^2) = 0.068$, and $R_w(F_o^2) = 0.102$ with $\sigma_1 = 1.80$.

Introduction

Since the development of organotitanium complexes as homogeneous catalysts for olefin polymerization, early-transition-metal complexes have been extensively studied to examine their chemical reactivity toward olefins and acetylenes. For these systems the course of the reaction pathway is dictated by the nature of the interaction between the early-transition-metal center and the unsaturated organic substrate. Consequently, the stereochemistry and bonding properties associated with metal–acetylene or metal–olefin complexes constitute an area of continued chemical interest. Recently, we have undertaken a systematic effort using a combination of spectroscopic and structural techniques to evaluate the influence of the metal's electronic configuration upon its interaction with the multiple carbon–carbon bond. Dicyclopentadienyl transition-metal complexes are well suited for this purpose since olefin and acetylene derivatives of Ti,[1] V,[2] and Mo[3] are known. In particular, olefins and acetylenes add to vanadocene and molybdenocene to form the corresponding metallacyclopropane, $(\eta^5\text{-}C_5H_5)_2M(C_2R_4)$, and metallacyclopropene, $(\eta^5\text{-}C_5H_5)_2M(C_2R_2)$ derivatives. For the d^1 vanadocene adducts this structural arrangement has been confirmed independently by Floriani and co-workers[2c] and by our group[4] using X-ray diffraction methods, whereas for the molybdenocene derivatives the analogous structure has been proposed by Thomas[3] on the basis of ^{13}C NMR spectral data. To provide a structural basis for comparison of the acetylene adducts of vanadocene and molybdenocene, we have performed an X-ray diffraction analysis of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. Since the HOMO of $(\eta^5\text{-}C_5H_5)_2Mo(C_2R_2)$ contains one more electron than its vanadacyclic analogue, the outcome of this study has provided an opportunity to examine the stereochemical influence of this additional metal valence electron upon the nature of the metal–acetylene interaction.

Experimental Section

Reagents and Materials. All reactions and manipulations were carried out under an atmosphere of purified Ar or N_2 with use of flame-dried Schlenk glassware on a double-manifold vacuum line. All solvents (reagent grade) were purified and dried by refluxing with sodium benzophenone ketyl and saturated with Ar prior to use. Molybdenum pentachloride was purchased from Alfa Ventron and was used without further purification. Hexafluoro-2-butyne was purchased from PCR Research Chemicals, Inc.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Instrumentation. The ^1H and ^{13}C NMR spectra were recorded with a Varian CFT-20 NMR spectrometer operating in the FT mode. Deuteriobenzene and $CHCl_3$-d_1 were used as solvents with Me_4Si as the internal standard. Solution infrared spectra were measured on a Beckman IR-10 a Varian The spectra were calibrated relative to polystyrene film.

Synthesis of Compounds. The synthesis of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ was performed by using a method originally described by Thomas.[3a] The principal starting materials, $(\eta^5\text{-}C_5H_4CH_3)_2MoH_2$ and $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$, were prepared by modification of literature methods.[5]

Preparation of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. To a sodium/mercury amalgam containing 6.0 mmol of Na and 6 mL of Hg dispersed in 60 mL of toluene was added 0.5 g (1.54 mmol) of $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$. The reaction mixture was vigorously stirred for 15 h with 1 atm pressure of hexafluoro-2-butyne maintained within the reaction vessel. Filtration through dry Celite yielded a clear bright orange solution. Removal of solvent in vacuo followed by sublimation of the residue at 45–50 °C and 10^{-2} torr gave 0.46 g of the bright orange crystalline product (ca. 70% yield based upon $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$). Crystals suitable for the structural and chemical analyses were obtained by a second slow sublimation. The compound seems only slightly air sensitive as a solid, since no noticeable discoloration occurred after 30 min upon exposure to air. However, upon being heated, the compound decomposes in air within the range of 67–70 °C.

$(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ was identified by the following: IR (toluene) 1778 (C≡C), 1450 (C=C), 1250 (C—F), 1219 (C—F), 1105 cm^{-1} (C—CH_3); ^1H NMR (C_6D_6) δ 1.49 (s, 3, CH_3), 4.10 (m, 4, Cp); ^{13}C NMR (C_6D_6): δ 14.64 (C_A), 105.85 (C_B), 89.64 (C_C), 85.25 (C_D). The chemical shifts are downfield relative to Me_4Si. Anal. Calcd for $C_{16}H_{14}F_6Mo$: C, 46.17; H, 3.39; F, 27.40. Found: C, 46.51;

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(1) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398.

(2) (a) Tsumara, R.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 861. (b) deLiefde Meijer, H. J.; Jellinek, F. *Inorg. Chim. Acta* **1970**, *4*, 651. (c) Fachinetti, G.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282 and references cited therein.

(3) (a) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (b) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.

(4) Petersen, J. L.; Griffith, L. *Inorg. Chem.* **1980**, *19*, 1852.

(5) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854.

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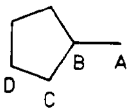
H, 3.44; F, 27.13. To date we have been unable to resolve the corresponding ^{13}C NMR resonances for the coordinated hexafluoro-2-butyne molecule. The ^{13}C NMR spectral assignments are based upon the NMR studies performed by Stucky and co-workers[6] on alkyl-substituted titanocene and zirconocene dichlorides. The atom labeling scheme for the methylcyclopentadienyl rings is shown below.



For purposes of comparison the corresponding ^{13}C NMR resonances of the methylcyclopentadienyl rings in $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$ are as follows: δ 15.62 (C_A), 121.79 (C_B), 102.42 (C_C), 94.37 (C_D). The methyl carbon NMR resonance remains relatively constant whereas the ring carbon resonances are shifted 10–15 ppm upfield for the hexafluoro-2-butyne adduct.

Collection of X-ray Diffraction Data for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. A parallelepiped-shaped, dark orange crystal with dimensions of 0.18 × 0.23 × 0.65 mm was mounted with the *c* axis nearly parallel to the spindle axis of the goniometer. The crystal was protected from air and moisture by a thin coating of quick-drying shellac. Preliminary oscillation and Weissenberg photographs taken with Cu Kα radiation indicated the Laue symmetry to be orthorhombic, D_{2h}-*mmm*. The systematic absences for $\{hk0\}$ of $h = 2n + 1$, $\{0kl\}$ of $k = 2n + 1$, and $\{h0l\}$ of $l = 2n + 1$ uniquely determine the space group as *Pbca* (D_{2h}^{15}, No. 61). The crystal was transferred to a Picker four-circle diffractometer under computer control by a Krisel control diffractometer automation system. The angular coordinates (ω, χ, 2θ) for 20 diffractometer peaks within a range of $25° < 2\theta < 30°$ were optimized by the automatic-centering routine.[7] Least-squares refinement yielded unit cell parameters with a = 26.409 (5) Å, b = 15.194 (3) Å, c = 7.697 (5) Å, and V = 3088 (2) Å^3. The calculated density of 1.79 g/cm^3 with $Z = 8$ compares well with the density measured by flotation methods of 1.80 g/cm^3.

Intensity data (*hkl*) were measured with Zr-filtered Mo Kα radiation within a detector range $5° \leq 2\theta \leq 45°$ with the takeoff angle set at 2.0°. The θ–2θ scan mode was employed with a fixed scan rate of 2°/min and variable scan width, w, calculated from the expression $(1.0 + 0.7 \tan\theta)°$ for each peak. Ten-second background counts were measured at the extremes of each scan. The pulse-height analyzer of the scintillation detector was adjusted to accept 90% of the diffraction peak. The intensities of three standard reflections were measured after every 120 min of crystal exposure time. Their combined intensities decreased by ca. 10% during data collection. The integrated intensity, I, and its standard deviation, $\sigma_c(I)$, for each reflection were calculated from the respective equations $I = w(S/t_s - B/t_b)$ and $\sigma_c(I) = w(S/t_s^2 + B/t_b^2)^{1/2}$. In these expressions S represents the total scan count measured in time t_s and B is the combined background count in time t_b. The intensity data for the 2034 measured peaks were corrected for intensity decay, absorption,[8] and Lorentz-polarization effects. The standard deviation of the square of each structure factor, $F_o^2 = I/Lp$, was calculated from $\sigma(F_o^2) = [(\sigma_c(F_o^2))^2 + (0.04F_o^2)^2]^{1/2}$ where $\sigma_c(F_o^2)$ is determined from counting statistics and 0.04 is an empirical factor that accounts for the variation of the integrated intensities of the reference reflections. Duplicate reflections were averaged to yield 1684 reflections with $F_o^2 > \sigma(F_o^2)$.

Structural Analysis of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. The structure of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ was solved by heavy-atom techniques. An analysis of the Harker vectors for a three-dimensional Patterson map provided the approximate fractional coordinates of the molybdenum atom. Subsequent Fourier syntheses yielded the positions of the remaining 22 nonhydrogen atoms. The positions of 14 hydrogen atoms were located by difference Fourier techniques. Full-matrix least-squares refinement was performed with anisotropic temperature factors assigned to the nonhydrogen atoms and isotropic temperature factors for the ring hydrogens. Isotropic temperature factors for the methyl hydrogens were included as fixed contributions. The final refinement converged with $R(F_o) = 0.050$, $R(F_o^2) = 0.068$, and $R_w(F_o^2) = 0.102$. The standard deviation of an observation of unit weight, σ_1, was 1.80 for the 1684 reflections.[9–13] A final difference map revealed four residuals located ca. 1.0 Å from the Mo atom, with electron density values of ca. 1.0 e$^-$/Å^3. Presumably these features arise from the inadequacy of the structural model to account for the electron delocalization about the Mo atom. The final positional and thermal parameters for all of the atoms are provided in Table I. Interatomic distances and bond angles with their esd's calculated from the errors in the fractional atomic coordinates are provided in Table II. Least-squares planes of interest have been calculated[14] and are available with a table of the observed and calculated structure factors.[15]

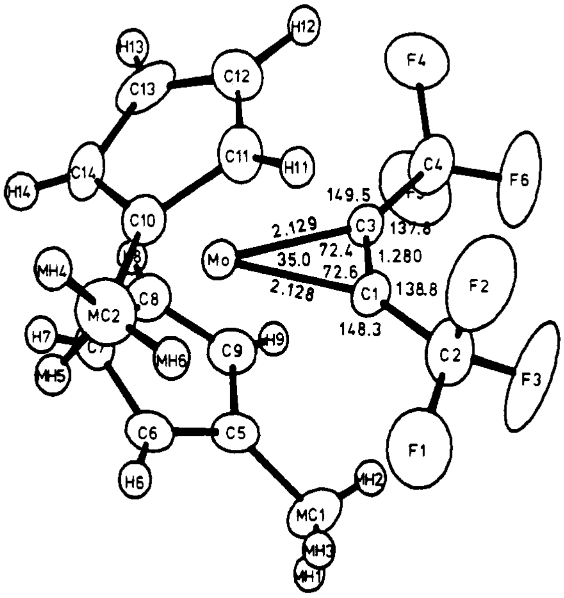


Figure 1. Perspective view of the molecular configuration for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ with the atom numbering scheme. Bond distances and bond angles within the metallacyclopropene ring are provided. The thermal ellipsoids are scaled to enclose 30% probability.

Results and Discussion

Molecular Configuration of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. The reaction of hexafluoro-2-butyne with molybdenocene, as reported by Thomas,[3a] leads to the formation of a monomeric metal–acetylene adduct, $(\eta^5\text{-}C_5H_5)_2Mo(C_2(CF_3)_2)$. Spectroscopic studies of this and other acetylene derivatives by IR,[3b]

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(6) Davis, J. H.; Sun, H.; Redfield, D.; Stucky, G. D. *J. Magn. Reson.* **1980**, *37*, 444.

(7) The automatic peaking centering algorithm is similar to that described by Busing: Busing, W. R. "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 319. The ω, χ, and 2θ angles are optimized with respect to the K_{α_1} peak.

(8) The absorption correction was performed with use of the general polyhedral-shape routine of the program DTALIB. The distance from the crystal center to each face and the corresponding orientation angles (ϕ and χ) needed to place each face in diffracting position were used to define the crystal's shape, size, and orientation with respect to the diffractometer's coordinate system. The range of transmission coefficients was 0.82–0.86 for μ = 9.0 cm^{-1}.

(9) The least-squares refinement[8] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|$, where the individual weights, w_i, equal $1/\sigma^2(F_o^2)$ and S is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_iF_o^4]^{1/2}$. The final goodness-of-fit parameter is $\sigma_1 = [\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$ where n is the number of observations and p is the number of parameters (viz., 258) varied. Final data-to-parameter ratio is 6.5:1.

(10) The scattering factors utilized in all calculations were those of Cromer and Waber[11] for the nonhydrogen atoms and those of Stewart et al.[12] for the hydrogen atoms with corrections included for anomalous dispersion.[13]

(11) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(14) The computer programs used to perform the necessary calculations are described in: Petersen, J. L. *J. Organomet. Chem.* **1979**, *155*, 179.

(15) Supplementary material.

Table I. Positional Parameters and Temperature Factors for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)^{a,b}$

A. Positional Parameters and Isotropic Temperature Factors

atom	*x*	*y*	*z*	*U*, Å^2
Mo	0.39403 (2)	0.54043 (3)	0.09958 (7)	
F1	0.2666 (2)	0.4333 (5)	0.2097 (10)	
F2	0.2935 (3)	0.4453 (5)	0.4534 (10)	
F3	0.3005 (2)	0.3270 (4)	0.3252 (12)	
F4	0.4653 (2)	0.3966 (4)	0.4462 (8)	
F5	0.4629 (3)	0.3164 (4)	0.2359 (10)	
F6	0.4092 (2)	0.3009 (5)	0.4295 (12)	
C1	0.3535 (3)	0.4412 (4)	0.2363 (10)	
C2	0.3051 (3)	0.4082 (6)	0.3003 (15)	
C3	0.4008 (3)	0.4240 (4)	0.2517 (9)	
C4	0.4328 (3)	0.3602 (6)	0.3443 (15)	
C5	0.3677 (3)	0.4523 (5)	−0.1414 (9)	
C6	0.3591 (3)	0.5417 (6)	−0.1739 (11)	
C7	0.4077 (4)	0.5824 (7)	−0.1771 (10)	
C8	0.4444 (3)	0.5205 (6)	−0.1376 (10)	
C9	0.4189 (3)	0.4394 (6)	−0.1169 (11)	
MC1	0.3288 (5)	0.3806 (7)	−0.1391 (15)	
C10	0.3567 (3)	0.6689 (4)	0.1949 (10)	
C11	0.3658 (4)	0.6168 (5)	0.3446 (10)	
C12	0.4176 (4)	0.6018 (6)	0.3655 (12)	
C13	0.4422 (3)	0.6450 (6)	0.2331 (15)	
C14	0.4059 (3)	0.6877 (5)	0.1287 (11)	
MC2	0.3079 (3)	0.7060 (6)	0.1374 (13)	
H6	0.328 (3)	0.565 (4)	−0.188 (9)	0.058 (22)
H7	0.409 (2)	0.634 (4)	−0.197 (8)	0.034 (20)
H8	0.479 (3)	0.521 (4)	−0.152 (9)	0.060 (23)
H9	0.436 (3)	0.385 (5)	−0.102 (9)	0.072 (25)
H11	0.340 (3)	0.597 (4)	0.414 (8)	0.059 (23)
H12	0.434 (3)	0.555 (4)	0.462 (9)	0.075 (23)
H13	0.472 (3)	0.646 (4)	0.231 (9)	0.050 (23)
H14	0.411 (2)	0.725 (4)	0.040 (8)	0.041 (19)
MH1	0.323 (4)	0.351 (5)	−0.246 (11)	0.101
MH2	0.337 (4)	0.340 (6)	−0.054 (11)	0.101
MH3	0.294 (3)	0.407 (6)	−0.109 (11)	0.101
MH4	0.301 (3)	0.773 (5)	0.189 (10)	0.101
MH5	0.308 (3)	0.715 (5)	0.003 (11)	0.101
MH6	0.276 (3)	0.671 (5)	0.182 (11)	0.101

B. Anisotropic Temperature Factors

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	343 (3)	350 (4)	446 (4)	2 (3)	−18 (3)	−9 (3)
F1	420 (32)	1993 (63)	1779 (67)	−40 (36)	33 (37)	696 (56)
F2	1293 (59)	1994 (79)	1459 (63)	−610 (52)	751 (53)	−147 (58)
F3	875 (41)	759 (38)	3348 (101)	−145 (31)	619 (51)	640 (55)
F4	1119 (47)	1232 (50)	1414 (57)	93 (40)	−748 (43)	189 (41)
F5	1544 (59)	1189 (47)	1666 (64)	904 (49)	−267 (51)	−42 (46)
F6	951 (44)	1444 (57)	3069 (109)	−198 (43)	−338 (53)	1632 (68)
C1	384 (43)	451 (39)	613 (51)	−49 (34)	−11 (34)	21 (37)
C2	617 (65)	791 (66)	955 (75)	35 (48)	159 (59)	135 (58)
C3	457 (52)	398 (36)	581 (50)	−39 (33)	−50 (38)	41 (34)
C4	634 (55)	462 (49)	1285 (86)	112 (46)	−174 (61)	181 (55)
C5	589 (51)	688 (56)	504 (51)	35 (43)	−117 (38)	−172 (42)
C6	568 (52)	683 (56)	563 (49)	81 (48)	−176 (41)	−69 (45)
C7	833 (72)	705 (60)	397 (47)	−130 (55)	−51 (42)	111 (46)
C8	473 (51)	788 (62)	599 (56)	1 (45)	99 (44)	−84 (43)
C9	605 (53)	734 (62)	565 (53)	103 (47)	24 (44)	−197 (47)
MC1	1033 (78)	768 (68)	981 (90)	−306 (64)	−214 (70)	−268 (55)
C10	568 (49)	389 (38)	588 (50)	82 (35)	−29 (42)	−50 (37)
C11	753 (63)	526 (47)	422 (49)	−1 (45)	181 (44)	−82 (39)
C12	823 (66)	617 (56)	588 (60)	106 (50)	−122 (50)	−102 (45)
C13	408 (56)	581 (54)	1281 (96)	−26 (45)	−106 (62)	−345 (59)
C14	653 (58)	390 (42)	721 (60)	−71 (38)	88 (47)	76 (40)
MC2	682 (58)	742 (58)	954 (72)	257 (47)	−53 (55)	−57 (57)

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures. [b] The form of the anisotropic temperature factors ($\times 10^4$) is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. The isotropic temperature factor is given by $[-8\pi^2U(\sin^2\theta)/\lambda^2]$, with *U* fixed at 0.101 Å^2 for all of the methyl H atoms.

NMR,[3b] and photoelectron spectroscopy[16] provide strong evidence for a metallacyclopropene structure associated with these complexes. The outcome of our X-ray structural analysis of the methylcyclopentadienyl analogue, $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, is consistent with this representation.

The molecular configuration of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, as depicted in Figure 1 with the corresponding atom labeling scheme, resembles that typically observed for $(\eta^5\text{-}C_5H_5)_2ML_2$-type complexes.[17] The structural parameters

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(16) Green, J. C.; Jackson, S. E. *J. Chem. Soc., Dalton Trans.* **1975**, 403.

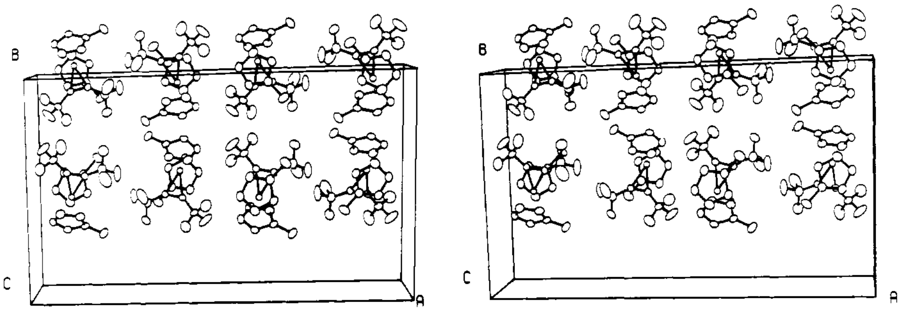

Figure 2. Stereoscopic view of the molecular arrangement of the eight $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ molecules in the orthorhombic unit cell.

associated with the bis(methylcyclopentadienyl)molybdenum moiety of this acetylene adduct and $(\eta^5\text{-}C_5H_5)_2MoCl_2$[17] are comparable in magnitude. The Mo–Cp (plane) distances range from 2.17 to 2.18 Å, and the angle between the two normals of the planar cyclopentadienyl rings is 134.6° for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ compared to 130.2° for $(\eta^5\text{-}C_5H_5)_2MoCl_2$. The bond distances and angles associated with the molybdenum–acetylene interaction indicate that the hexafluoro-2-butyne molecule is symmetrically attached to the Mo atom via two σ-type Mo–C bonds of 2.128 (7) and 2.129(7) Å. This structural arrangement for the central metallacyclopropene ring is analogous to that observed for the bis(methylcarboxy)acetylene derivative of vanadocene, $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$.[2c,5] This mode of acetylene coordination is accompanied similarly by a ca. 0.08 Å lengthening of the multiple carbon–carbon bond in both the 17-electron vanadium and 18-electron molybdenum adducts. This structural feature presumably reflects the reduction of the carbon–carbon bond order due to back-donation of the electron density from the metal to an empty π*-antibonding acetylene orbital. The appreciable bending of the C–C–CF₃ bond angle accompanies the concomitant alteration of the acetylene's geometry toward a cis olefin.

The molecular arrangement of the eight discrete $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ molecules in the orthorhombic unit cell is illustrated stereographically in Figure 2. The molecular packing is primarily dictated by van der Waals forces since the shortest intermolecular separations do not suggest the presence of any unusual interactions. The wide variations observed for the C–F bond distances (1.255 (11)–1.342 (13) Å) and F–C–F bond angles (110.7 (8)–118.4 (8)°) of the coordinated hexafluoro-2-butyne molecule indicate the presence of a substantial amount of thermal motion associated with the perfluoro substituents in the crystal lattice.

Comparison of Available Structural Data for Molybdenum–Acetylene Complexes. Although the chemical reactivity of alkynes toward cyclopentadienylmolybdenum complexes has been examined by several groups.[3,18-20] detailed structural information about the nature of the molybdenum–acetylene interaction is rather sparse. However, Stone and co-workers[20] have found that treatment of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ (M = Mo, W) with hexafluoro-2-butyne affords an unusual 16-electron complex, $(\eta^5\text{-}C_5H_5)M(C_2(CF_3)_2)_2Cl$. An X-ray structural determination of the tungsten species[19] has shown that the hexafluoro-2-butyne molecules occupy two coordination sites about the distorted-octahedral environment of the central W atom. The mode of acetylene coordination is similar to that observed for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ with multiple C–C bond distances of 1.28 (4) and 1.23 (4) Å and an average C–C–CF₃ bond angle of 140.3 (3)° for the two coordinated acetylenes. Since the chloride ligand is substitutionally labile,

Table II. Interatomic Distances (Å) and Bond Angles (Deg) for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)^a$

	A. Interatomic Distances		
Mo–C1	2.128 (7)	Mo–C3	2.129 (7)
Mo–C5	2.391 (8)	Mo–C10	2.306 (7)
Mo–C6	2.298 (8)	Mo–C11	2.336 (8)
Mo–C7	2.252 (8)	Mo–C12	2.334 (9)
Mo–C8	2.278 (8)	Mo–C13	2.280 (10)
Mo–C9	2.359 (9)	Mo–C14	2.271 (7)
C1–C2	1.458 (12)	C3–C4	1.471 (12)
C2-F1	1.290 (12)	C4-F4	1.287 (12)
C2-F2	1.342 (13)	C4-F5	1.330 (12)
C2-F3	1.255 (11)	C4-F6	1.277 (12)
C1–C3	1.280 (10)		
C5-MC1	1.497 (14)	C10–MC2	1.474 (12)
C5–C6	1.400 (12)	C10–C11	1.418 (11)
C6–C7	1.426 (13)	C11-C12	1.396 (14)
C7–C8	1.382 (13)	C12-C13	1.375 (14)
C8–C9	1.413 (12)	C13–C14	1.411 (13)
C9–C5	1.378 (12)	C14–C10	1.424 (11)
C6-H6	0.90 (7)	C11-H11	0.93 (7)
C7-H7	0.81 (6)	C12-H12	1.11 (7)
C8-H8	0.91 (7)	C13-H13	0.80 (7)
C9-H9	0.95 (7)	C14-H14	0.90 (6)
MC1-MH1	0.95 (8)	MC2-MH4	1.11 (8)
MC1-MH2	0.92 (9)	MC2-MH5	1.04 (8)
MC1-MH3	1.02 (9)	MC2-MH6	1.05 (8)
	B. Bond Angles		
C1-Mo–C3	35.0 (3)		
Mo–C1–C3	72.6 (4)	Mo–C3–C1	72.4 (4)
Mo–C1–C2	148.3 (6)	Mo–C3–C4	149.5 (6)
C3–C1–C2	138.8 (7)	C1–C3–C4	137.8 (7)
C1-C2-F1	114.0 (8)	C3–C4-F4	113.3 (7)
C1-C2-F2	110.7 (8)	C3–C4-F5	111.7 (9)
C1-C2-F3	118.4 (8)	C3–C4-F6	115.6 (8)
MC1–C5–C6	126.6 (8)	MC2–C10–C11	127.3 (7)
MC1–C5–C9	124.6 (8)	MC2–C10–C14	127.7 (7)
C6–C5–C9	108.8 (7)	C11–C10–C14	104.3 (7)
C5–C6–C7	106.1 (8)	C10–C11–C12	110.6 (7)
C6–C7–C8	109.3 (8)	C11–C12–C13	107.4 (8)
C7–C8–C9	106.5 (8)	C12–C13–C14	108.7 (8)
C8–C9–C5	109.1 (8)	C13–C14–C10	108.9 (7)
H6–C6–C5	124 (4)	H11–C11–C10	122 (4)
H6–C6–C7	130 (4)	H11–C11–C12	127 (4)
H7–C7–C6	118 (4)	H12-C12–C11	124 (4)
H7–C7–C8	132 (4)	H12–C12–C13	128 (4)
H8–C8–C7	132 (4)	H13–C13–C12	120 (5)
H8–C8–C9	120 (4)	H13–C13–C14	131 (5)
H9–C9–C8	123 (5)	H14–C14–C13	128 (4)
H9–C9–C5	128 (5)	H14–C14–C10	123 (4)
C5-MC1-MH1	116 (5)	C10–MC2-MH4	113 (4)
C5-MC1-MH2	110 (6)	C10–MC2-MH5	110 (4)
C5-MC1-MH3	110 (5)	C10–MC2-MH6	114 (5)
MH1-MC1-MH2	110 (7)	MH4–MC2-MH5	104 (6)
MH1-MC1-MH3	104 (7)	MH4–MC2-MH6	102 (6)
MH2-MC1-MH3	108 (8)	MH5-MC2-MH6	113 (6)

[a] The esd's in parentheses for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

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subsequent addition of TlC_5H_5 has led to the isolation of $(\eta^5\text{-}C_5H_5)Mo(C_2(CF_3)_2)[(F_3C)C{=}C(CF_3)(C_5H_5)]$. The structural analysis of this complex[20] reveals that the two hexafluoro-2-butyne molecules interact quite differently with the central molybdenum atom. One of the acetylene molecules is bonded to a C_5H_5 ring; the resultant olefinic substrate interacts with the $(\eta^5\text{-}C_5H_5)Mo$ moiety via a long σ-type Mo–C bond of 2.25 (2) Å and a π interaction with the remaining diene structure of the attached cyclopentadienyl ring. The other hexafluoro-2-butyne molecule is symmetrically bonded to the Mo atom by two substantially shorter Mo–C bonds of 2.15 (1) and 2.13 (2) Å. The multiple C–C bond of 1.25 (2) Å and C–C–CF_3 angles of 138 (1) and 142 (1)° are comparable to their corresponding values in $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$. Thus, two entirely different modes of interaction have been observed for the molybdenum–acetylene interactions in these complexes.

Although the reaction of hexafluoro-2-butyne with $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$ and Na/Hg amalgam produces the metallacyclopropene complex, $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, the same reaction when repeated with bis(methylcarboxy)acetylene provides an unexpected result. An X-ray structural determination[21] of an isolated product indicates that the red-orange compound is a molybdenum(IV)–oxo complex, $(\eta^5\text{-}C_5H_4CH_3)Mo({=}O)[(MeO_2C)C{=}C(CO_2Me)(C_5H_4CH_3)]$. Its molecular configuration is characterized by the reduction of the acetylene to an olefin with the formation of a C–C single bond of 1.49 Å to one of the methylcyclopentadienyl rings. This structural arrangement is similar to that observed by Stone and co-workers[20] for $(\eta^5\text{-}C_5H_5)Mo(C_2(CF_3)_2)[(F_3C)C{=}C(CF_3)(C_5H_5)]$ with the exception that the methylcyclopentadienyl ring attached to the bis(methylcarboxy)acetylene molecule interacts as an η^2 ring rather than as a η^4 ring. The corresponding Mo–C separations to the η^2 ring of Mo–C8 (2.22 Å), Mo–C9 (2.24 Å), Mo–C10 (2.98 Å), Mo–C11 (3.36 Å), and Mo–C7 (3.05 Å) and the carbon–carbon bond distances within this ring for C7–C8 (1.53 Å), C8–C9 (1.44 Å), C9–C10 (1.45 Å), C10–C11 (1.33 Å), and C7–C11 (1.51 Å) are consistent with this representation. Consequently, these preliminary structural data suggest that the acetylene chemistry of molybdenocene is more complex than originally thought and likely involves the formation of one or more electron-deficient species.

Influence of the Orbital Occupancy on the Metal–Acetylene Interaction. Structural and theoretical studies performed by a number of investigators on numerous $(\eta^5\text{-}C_5H_5)_2ML_2$-type complexes have shown collectively that the electronic configuration of the metal has a predictable stereochemical influence upon the L–M–L bond angle and the M–L bond distance. In general, as the number of nonbonding electrons on the metal atom increases from 0 to 1 to 2, the L–M–L bond angle decreases accordingly with a noticeable increase in the M–L bond distance.[22] Dilute single-crystal EPR studies performed on the corresponding d^1 V[23] and Nb[24] complexes have shown that the unpaired electron resides in a hybridized metal orbital of a_1 symmetry, which is directed primarily normal to the plane bisecting the ML_2 bond angle. On the basis of the structural similarities between $(\eta^5\text{-}C_5H_5)_2VL_2$ and $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$ complexes, one would expect the spatial distributions of the unpaired electrons in these 17-electron systems to be comparable. This premise was borne out by frozen-glass EPR measurements on a variety of acetylene adducts of vanadocene, $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$.[4] Consequently, the outcome of our structural analysis of $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ provides us with a similar opportunity to examine the stereochemical effect of the orbital occupancy of the HOMO upon the nature of the metal–acetylene interaction in $(\eta^5\text{-}C_5H_5)_2M(C_2R_2)$ complexes.

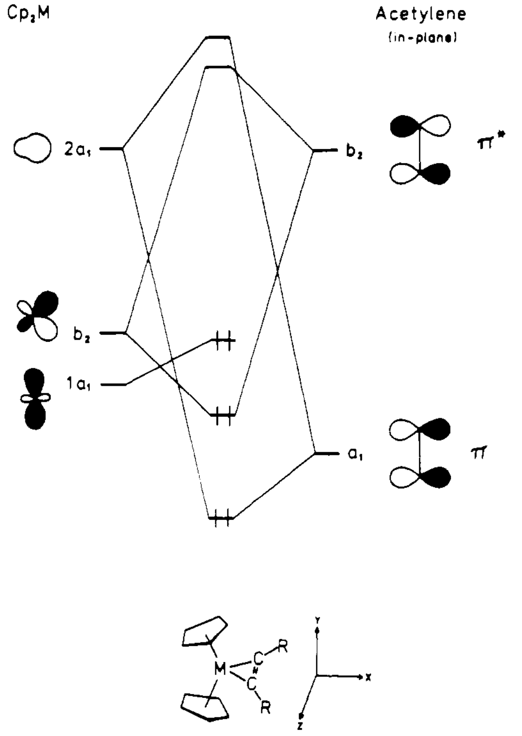

Figure 3. Qualitative molecular orbital energy level diagram representing the metal–acetylene interaction in $(\eta^5\text{-}C_5H_5)_2Mo(C_2R_2)$-type complexes.

The principal structural parameters within the metallacyclic ring of interest are the M–C and C–C bond distances and the C–M–C bond angle. The average Mo–C bond distance of 2.13 Å in $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ is ca. 0.04 Å longer than the corresponding average V–C bond distance of 2.09 Å in $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$. This difference is consistent with the larger covalent radius of Mo (viz., 1.296 Å) compared to that for vanadium (viz., 1.224 Å).[25] An examination of the C–M–C bond angles and the multiple C–C bond lengths of these two systems clearly shows that the additional metal valence electron of the Mo atom does not exhibit a pronounced effect upon the magnitude of either of these parameters. The C–M–C bond angle and C–C bond distance of 35.0 (3)° and 1.280 (10) Å for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ are equivalent within experimental error to their respective values of 35.58 (8)° and 1.276 (3) Å for $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$.[4] On the basis of this structural data the HOMO, which is fully occupied in $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, effectively behaves as a nonbonding orbital.

This result can be reasonably rationalized by consideration of a qualitative molecular orbital representation for dicyclopentadienyl–early transition metal–acetylene complexes and

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(21) Petersen, J. L.; Egan, J. W., Jr., unpublished results. The molybdenum(IV)–oxo complex $(\eta^5\text{-}C_5H_5)Mo({=}O)[(MeO_2C)C{=}C(CO_2Me)(C_5H_4CH_3)]$, crystallizes in the monoclinic crystal system, $P2_1/c$, with refined lattice parameters of a = 8.914 (4) Å, b = 10.025 (4) Å, 19.806 (10) Å, β = 97.03 (4)°, and V = 1756 (1) Å^3. Full-matrix least-squares refinement of the positional parameters and anisotropic temperature factors for the 24 nonhydrogen atoms converged with discrepancy indices of $R(F_o) = 0.078$ and $R(F_o^2) = 0.155$ for the 2737 diffractometry-measured reflections with $F_o^2 > \sigma(F_o^2)$.

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the outcome of earlier EPR studies of the paramagnetic vanadium analogues. Lauher and Hoffmann[26] have shown that as the angle between two parallel cyclopentadienyl rings decreases from 180 to 135° for the canted ring systems, three frontier metal orbitals become available for bonding with the unsaturated organic substrate. For the acetylene adducts (as depicted in Figure 3) the filled in-plane π orbital of the acetylene behaves as a donor orbital by interaction with the empty metal $2a_1$ orbital. Two additional electrons are back-donated from the filled metal b_2 orbital to the empty in-plane π^* orbital of the acetylene. These interactions collectively reduce the bond order of the multiple C–C bond and stabilize the metal b_2 orbital so that it now lies below the doubly occupied, nonbonding metal a_1 orbital. This bonding representation is further supported by an interpretation of the frozen-glass EPR spectra for $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$ complexes.[4] The observed anisotropy of the ^{51}V hyperfine interaction arises from an admixture of $3d_{z^2}$ and $3d_{x^2-y^2}$ character in the a_1 HOMO. In terms of the assumed local-coordinate system at the metal atom (Figure 3), however, the relative contributions from these AO's are widely different. For $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$ the ratio of mixing coefficients, $(a(d_{z^2}))^2/b(d_{x^2-y^2}))^2$, is $-0.995^2/0.100^2 = 99/1$, whereas for $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$ it is 20/1.[23c] This difference is consistent with the much smaller C–V–C bond angle in the former complex. As the L–V–L bond angle decreases from 87.09 (9)° for $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$[23c] to ca. 36° for the acetylene adduct, the spatial distribution of the unpaired electron is redistributed to alleviate the increase in electron–electron repulsion that accompanies the large bond angle reduction. Since the HOMO contains contributions from both the $3d_{z^2}$ and $3d_{x^2-y^2}$ AO's, the relative metal character is adjusted by the shifting of electron density from the $3d_{x^2-y^2}$ AO to the $3d_{z^2}$ AO, which is directed away from the metal–acetylene interaction. Thus, on the basis of the spatial orientation of this nonbonding orbital with respect to the metallacyclic ring, one would expect that an increase in the orbital occupancy of the HOMO from 1 for $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$ to 2 for $(\eta^5\text{-}C_5H_5)_2Mo(C_2R_2)$ should have little effect on the structure of the metallacyclopropene ring. This premise is supported by the X-ray structural data.

The remaining two structural parameters to be examined are the C–C–R bond angle and the R–C–C–R torsional angle. In these complexes the coordination of the acetylene to the dicyclopentadienylmetal center is characterized by a substantial reduction of the C–C–R bond angle from 180° for the free acetylene. The average C–C–R bond angle for $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ of 138.3° is noticeably smaller than that for $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$ of 143.5°.[4] Whether or not this difference is due to electronic effects related to the orbital occupancy of the HOMO is unclear. However, one plausible explanation is that the higher orbital occupancy and larger spatial size of the HOMO for the Mo adduct may introduce a sufficient amount of through-space electron pair repulsion to produce a greater bending of the C–C–R bond angle. The orientations of the acetylene substituents with respect to the plane of the metallacyclic ring are also noticeably different for these two complexes. For $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, C2 and C4 are displaced equally by ca. 0.09 (1) Å to the same side of the MoC_2 plane, whereas for $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$ the corresponding carbon atoms are located on opposite sides of the VC_2 plane. Consequently, the R–C–C–R torsional angle is 0 (2)° in the former compared to 14.3 (5)° in the latter complex. For proper evaluation of the possible significance of these variations observed for the C–C–R bond angle and the R–C–C–R torsional angle and their relationship (if any) with the orbital occupancy of the HOMO additional structural data will be needed.

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Registry No. $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$, 77944-59-3; $(\eta^5\text{-}C_5H_4CH_3)_2MoCl_2$, 63374-10-7.

Supplementary Material Available: Listings of least-squares planes and calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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