no evidence for intermolecular oxidative addition of C–H bonds to $(\eta^5\text{-}C_5R_5)Fe(CO)R'$ species. The oxidative addition of any C–H bond to the photogenerated 16e $(\eta^5\text{-}C_5R_5)Fe(CO)R'$ species actually has little precedent,[10] but there is much literature showing that intramolecular C–H addition processes can be more facile than intermolecular processes.[6b] The photoreaction of $(\eta^5\text{-}C_5Me_4CH_2C_6H_4)Fe(CO)_2$ under H_2 shows that oxidative addition/reductive elimination processes are viable, and recent work[19] shows that $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ yields $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ when irradiated in the presence of Me_3SiH. Elaboration of the scope of photoinduced C–H addition processes in the $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ system will be attempted in this laboratory.

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Registry No. $(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2Me$, 100909-58-8; $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$, 100909-59-9; $(\eta^5\text{-}C_5H_4Bz)_2Fe_2(CO)_4$, 95585-27-6; $(\eta^5\text{-}C_5Me_4Bz)_2Fe_2(CO)_4$, 95420-99-8; $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2H$, 100909-60-2; $(\eta^5\text{-}C_5H_4CH_2C_6H_4)Fe(CO)_2$, 100909-61-3; $(\eta^5\text{-}C_5Me_4CH_2C_6H_4)Fe(CO)_2$, 100909-62-4; $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)(^{13}CO)Me$, 100909-63-5; $(\eta^5\text{-}C_5H_4Bz)Fe(CO)(PPh_3)Me$, 100909-64-6; $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)(PPh_3)Me$, 100909-65-7; $(\eta^5\text{-}C_5H_4CH_2C_6H_4)Fe(CO)(PPh_3)$, 100909-66-8; $(\eta^5\text{-}C_5Me_4CH_2C_6H_4)Fe(CO)(PPh_3)$, 100909-67-9.

Supplementary Material Available: Listings of thermal parameters and of structure factor amplitudes for $(\eta^5\text{-}C_5Me_4CH_2C_6H_4)Fe(CO)_2$ (13 pages). Ordering information is given on any current masthead page.

Structural Characterization of $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$. An Alternative Configuration for the Dinuclear Structure of Molybdenocene

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An X-ray structure determination of $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$ has been performed and confirms an alternative configuration which had been previously proposed for the dinuclear structure of molybdenocene. The two $(\eta^5\text{-}C_5H_4CH_3)MoH$ units are bridged symmetrically by a π-fulvalene ligand. Each Mo atom achieves a filled valence shell configuration by bonding through a long two-electron Mo–Mo single bond of 3.3623 (5) Å, to a single terminal hydride ligand (δ −9.22), and in an η^5-fashion to a methylcyclopentadienyl ring and to one ring of the fulvalene bridge. The compound crystallizes in a noncentrosymmetric orthorhombic unit cell of $Fdd2$ symmetry with refined lattice parameters of a = 35.781 (7) Å, b = 34.150 (6) Å, c = 6.382 (2) Å, V = 7798 (3) Å^3, Z = 16, and ρ_{calcd} = 1.732 g/cm^3. Full-matrix least-squares refinement (based on F_o^2) of 2463 diffractometry data converged with final discrepancy indices of $R(F_o^2)$ = 0.0252, $R(F_o^2)$ = 0.0369, and $R_w(F_o^2)$ = 0.0624 with σ_1 = 1.608.

Introduction

The stereochemistry and reactivity of molybdenocene represents a continually challenging area of research in early-transition-metal chemistry. Efforts undertaken by Green and his co-workers[1] during the past decade have led to the development of synthetic routes for the preparation of several dimeric forms of molybdenocene. Treatment of $[(\eta^5\text{-}C_5H_5)_2MoHLi]_4$ with N_2O in toluene[2a,b] produces two yellow molybdenocene isomers, *cis*- and *trans*-$[(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)_2][(\eta^5\text{-}C_5H_5)MoH]_2$ (**1** and **2**), which are analogous to structurally characterized tungstenocene compounds.[2c] These compounds have been shown independently by Smart,[3] Green,[1c] and their co-workers to undergo a reductive coupling in toluene at 50 °C to yield a green dimer, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)MoH]_2$ (**3**). Although the presence of a bridging fulvalene and terminal hydride ligands in **3** has been supported by NMR and infrared data, the molecular structure of **3** remains to be determined. In this paper we wish to report the isolation and structural characterization of a methylcyclopentadienyl analogue, $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$ (**4**). The results of our X-ray diffraction analysis of **4** have provided an opportunity to investigate the nature of the Mo–Mo and Mo–H interactions.

Experimental Section

General Considerations. All manipulations were performed by using a combination of glovebox and high vacuum line tech-

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niques. Nitrogen or argon was purified by passage through successive columns containing activated BTS catalyst (R-11) and Linde 4A molecular sieves. Solvents were dried by using standard methods and vacuum distilled into storage flasks containing $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$. Benzene-$d_6$ and toluene-d_8 were dried over $LiAlD_4$ and Na/K alloy, respectively, and vacuum distilled prior to use. $Mo_2(O_2CCH_3)_4$[4] and $KC_5H_4CH_3$[5] were prepared and purified by using previously published methods. Triphenylphosphine (Aldrich) was purified by sublimation before use. The NMR spectra were recorded on a JEOL GX-270 NMR spectrometer operating in the FT mode at 270 MHz (^1H) and 67.5 MHz (^{13}C). For the NMR spectra the residual ^1H resonance (δ 7.24[6a] relative to Me_4Si) for benzene-d_6 and ^{13}C resonance (δ 20.4[6b] relative to Me_4Si) for the methyl carbon of toluene-d_8 were used as the internal references. The visible absorption spectrum within the range 400–700 nm was recorded by using a Varian Cary-219 spectrometer with a rectangular quartz cell (path length = 1.000 cm) equipped with a high-vacuum Teflon stopcock. The elemental analysis was performed by Dornis and Kolbe Microanalytical Laboratories, Mulheim, West Germany.

Preparation of $(\eta^5:\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$. An alternative procedure that has been developed by Green and co-workers[2a] for the synthesis of molybdenocene dichloride was modified accordingly to prepare bis(methylcyclopentadienyl)molybdenocene dichloride. The first step of the reaction sequence leads to the formation of the corresponding green molybdenocene intermediate, which in the latter case is $(\eta^5:\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$. The reaction is initiated by placing 1.7 g (14.2 mmol) of $KC_5H_4CH_3$, 1.5 g (3.5 mmol) of $Mo_2(O_2CCH_3)_4$, and 1.9 g (7.25 mmol) of $P(C_6H_5)_3$ in a 250-mL round-bottom flask. Approximately 125 mL of THF was added by vacuum distillation, and the reaction mixture was stirred at room temperature for 24 h. The resultant black reaction mixture was concentrated and filtered. The collected solid was washed twice with 15-mL portions of THF, and the washings were combined with the filtrate. Removal of the solvent left a black residue that was rinsed several times with pentane until the washings, which contain unreacted $P(C_6H_5)_3$ and $(\eta^5\text{-}C_5H_4CH_3)_2MoH_2$, were colorless. The remaining green solid on the frit was washed twice with 10 mL of ether (0 °C) and recrystallized from DME. Analytically pure compound was obtained by solvent extraction with pentane followed by slow cooling of a DME solution saturated at 70 °C. An overall yield of 30% for 4 was obtained.

Anal. Calcd for $C_{24}H_{28}Mo_2$: C, 56.47; H, 5.93. Found: C, 56.29; H, 5.95.

Visible spectrum (benzene): λ_{max} 603 nm.

^1H NMR spectrum (benzene-d_6): methylcyclopentadienyl ring protons, δ 4.71, 4.58, 4.54, 4.13 (pseudoquartet, J_{H-H} (resolved) = 2.9, 2.6, 1.8 Hz); fulvalene ring protons, 3.78 (pseudotriplet, J_{H-H} = 2.9 and 1.8 Hz), 3.36 (pseudotriplet, J_{H-H} = 2.9 and 1.5 Hz), 3.11 (pseudotriplet, J_{H-H} = 1.8 and 1.5 Hz); 1.92 (CH_3, s), 1.84 (CH_3, s), −9.22 (Mo–H, singlet); ratio of peak areas 1:1:1:1:1:1:1:3:3:1. The values for J_{H-H} were determined by selective homonuclear decoupling experiments and thereby made it possible to distinguish the resonances of the methylcyclopentadienyl ring protons from those for the ring protons of the fulvalene ligand. The solution ^1H NMR spectrum of 4 gave no evidence of the presence of any other isomeric species. Variable-temperature measurements indicated the ^1H NMR spectrum of 4 remains unchanged from −90 to 25 °C.

Gated nondecoupled ^{13}C NMR spectrum (toluene-d_8): methylcyclopentadienyl ring carbons (C–H), δ 83.23 (d, $^1J_{^{13}C-H}$ = 173 Hz), 80.20 (d, $^1J_{^{13}C-H}$ = 172 Hz), 79.46 (d, $^1J_{^{13}C-H}$ = 177 Hz), 79.35 (d, $^1J_{^{13}C-H}$ = 177 Hz); fulvalene carbons (C–H), 76.37 (d, $^1J_{^{13}C-H}$ = 172 Hz), 73.86 (d, $^1J_{^{13}C-H}$ = 172 Hz); 64.17 (d, $^1J_{^{13}C-H}$ = 179 Hz; t, $^3J_{^{13}C-H}$ = 7 Hz); quaternary carbons (C), 90.87 (s), 83.61 (s), 81.24 (s); methyl carbons (CH_3), 15.96 (q, $^1J_{^{13}C-H}$ = 127 Hz), 15.45 (q, $^1J_{^{13}C-H}$ = 127 Hz). The assignments of the methylcyclopentadienyl ring and fulvalene carbons were made by comparison with the corresponding $^{13}C\{^1H\}$ and selective heteronuclear decoupled ^{13}C NMR spectra.

Table I. Data for X-ray Diffraction Analysis of $(\eta^5:\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$

A. Crystal Data	
crystal system	orthorhombic
space group	*Fdd*2 (no. 43, C_{2v}^{19})
a, Å	35.781 (7)
b, Å	34.150 (6)
c, Å	6.382 (2)
V, Å^3	7798 (3)
fw, amu	508.40
d(calcd), g/cm^3	1.732
Z	16
μ, cm^{-1}	12.6
B. Data Collection and Analysis Summary	
crystal dimens, mm	0.35 × 0.425 × 0.600
reflctns sampled	*hkl* ($5 \le 2\theta \le 55°$)
2θ range for centered reflctns	35–40°
scan rate	2°/min
scan width, deg	$1.1 + 0.8 \tan \theta$
no. of std reflctns	3
% cryst decay	1%
total no. of measd reflctns	2463
no. of unique data used	2463
transmission coeff	0.613–0.665
p	0.03
discrepancy indices for 2393 data with $F_o^2 > \sigma(F_o^2)$	
$R(F_o)$	0.0252
$R(F_o^2)$	0.0369
$R_w(F_o^2)$	0.0624
σ_1	1.608
no. of variables	298
data to parameter ratio	8.27:1

X-ray Data Collection and Structural Analysis of $(\eta^5:\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$. A dark green crystal was sealed in a glass capillary tube under a prepurified N_2 atmosphere in a locally constructed drybox. The sample was optically aligned on a Picker goniostat that is controlled by a Krisel Control diffractometer automation system. Analogous procedures to those described previously[7] were carried out to determine the lattice parameters for the orthorhombic unit cell and to collect the X-ray diffraction data for the structural analysis. The intensity data were measured at room temperature with Zr-filtered Mo Kα radiation with a fixed scan rate and a variable scan width. The integrated intensity, I, and the standard deviation, $\sigma_c(I)$, were calculated from the respective expressions $I = w(S/t_s - B/t_b)$ and $\sigma_c(I) = w(S/t_s^2 + B/t_b^2)^{1/2}$, where S represents the total scan count in time t_s and B is the combined background count in time t_b. The raw intensity data for the 2463 unique reflections ($F_o^2 \ge 0$) were corrected for absorption[8] and Lorentz–polarization effects. The standard deviation of the square of each structure factor, F_o^2, was calculated from $\sigma(F_o^2) = [(\sigma_c(F_o^2))^2 + (pF_o^2)^2]^{1/2}$ where $\sigma_c(F_o^2)$ is based on counting statistics. Specific details with regard to the lattice parameters and the data collection procedure are summarized in Table I.

Initial coordinates for the two independent molybdenum atoms were interpolated from an E map calculated on the basis of phases determined by MULTAN78.[9] The statistical distribution of the intensities was consistent with a noncentrosymmetric space group. Approximate coordinates for the remaining non-hydrogen atoms were provided by subsequent Fourier summations. Ideal coordinates for the hydrogens of the methylcyclopentadienyl and

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(8) The absorption correction was performed with the 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 provided to define the crystal's shape, size, and orientation with respect to the diffractometer's coordinate system.

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Table II. Positional Parameters for $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$[a]

atom	x	y	z
Mo1	0.14087 (7)	0.46292 (1)	0.50000
Mo2	0.21248 (1)	0.39918 (1)	0.49402 (9)
C1	0.0883 (2)	0.4717 (2)	0.6875 (10)
C2	0.1088 (2)	0.4412 (2)	0.7901 (10)
C3	0.1094 (2)	0.4101 (2)	0.6504 (12)
C4	0.0905 (1)	0.4203 (2)	0.4679 (12)
C5	0.0770 (1)	0.4598 (2)	0.4839 (14)
C6	0.0518 (2)	0.4810 (2)	0.3363 (15)
C7	0.1476 (1)	0.5271 (1)	0.5564 (9)
C8	0.1778 (2)	0.5079 (2)	0.6541 (11)
C9	0.1996 (1)	0.4905 (1)	0.4936 (9)
C10	0.1813 (2)	0.4987 (1)	0.2997 (8)
C11	0.1493 (1)	0.5217 (1)	0.3354 (9)
C12	0.1263 (2)	0.5415 (2)	0.1717 (11)
C13	0.2299 (2)	0.3467 (1)	0.3063 (9)
C14	0.1993 (2)	0.3645 (2)	0.1951 (9)
C15	0.1678 (2)	0.3612 (2)	0.3206 (10)
C16	0.1782 (1)	0.3422 (1)	0.5094 (13)
C17	0.2166 (1)	0.3324 (1)	0.5006 (14)
C18	0.2369 (2)	0.3076 (2)	0.6557 (13)
C19	0.2730 (1)	0.4156 (2)	0.4520 (9)
C20	0.2505 (1)	0.4451 (2)	0.3586 (9)
C21	0.2300 (1)	0.4635 (1)	0.5234 (9)
C22	0.2393 (1)	0.4440 (1)	0.7141 (8)
C23	0.2660 (1)	0.4146 (2)	0.6731 (9)
C24	0.2876 (2)	0.3914 (2)	0.8338 (11)
H1	0.148 (1)	0.445 (1)	0.284 (10)
H2	0.194 (2)	0.401 (1)	0.714 (12)
H3	0.082 (2)	0.493 (2)	0.758 (14)
H4	0.120 (2)	0.435 (2)	0.932 (11)
H5	0.120 (2)	0.387 (2)	0.684 (12)
H6	0.089 (2)	0.406 (2)	0.356 (13)
H7	0.0536	0.4690	0.2015
H8	0.0578	0.5081	0.3280
H9	0.0263	0.4782	0.3867
H10	0.132 (2)	0.542 (2)	0.639 (10)
H11	0.182 (2)	0.504 (2)	0.808 (11)
H12	0.191 (2)	0.489 (2)	0.156 (10)
H13	0.1078	0.5573	0.2395
H14	0.1151	0.5227	0.0840
H15	0.1424	0.5586	0.0893
H16	0.256 (2)	0.342 (2)	0.248 (14)
H17	0.202 (2)	0.373 (2)	0.066 (11)
H18	0.147 (2)	0.373 (2)	0.295 (12)
H19	0.163 (2)	0.341 (2)	0.619 (12)
H20	0.2281	0.3127	0.7941
H21	0.2635	0.3125	0.6492
H22	0.2329	0.2799	0.6245
H23	0.290 (2)	0.397 (2)	0.375 (12)
H24	0.251 (2)	0.452 (2)	0.236 (13)
H25	0.227 (2)	0.450 (2)	0.858 (10)
H26	0.3062	0.3756	0.7628
H27	0.2712	0.3748	0.9107
H28	0.3002	0.4090	0.9278

[a] The estimated standard deviations in parentheses for this and subsequent tables refer to the least significant figures.

Table III. Interatomic Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms and Hydride Ligands in $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$[a,b]

A. Interatomic Distances

Mo1–H1	1.53 (6)	Mo2–H2	1.55 (7)
Mo1–Cp(1)	1.961 (8)	Mo2–Cp(2)	1.952 (7)
Mo1–Fv(1)	1.927 (7)	Mo2–Fv(2)	1.926 (7)
Mo1–C1	2.250 (6)	Mo2–C13	2.245 (5)
Mo1–C2	2.302 (6)	Mo2–C14	2.295 (6)
Mo1–C3	2.331 (7)	Mo2–C15	2.338 (6)
Mo1–C4	2.327 (6)	Mo2–C16	2.303 (5)
Mo1–C5	2.291 (5)	Mo2–C17	2.286 (4)
Mo1–C7	2.234 (5)	Mo2–C19	2.253 (5)
Mo1–C8	2.251 (6)	Mo2–C20	2.248 (5)
Mo1–C9	2.304 (4)	Mo2–C21	2.293 (4)
Mo1–C10	2.284 (5)	Mo2–C22	2.288 (5)
Mo1–C11	2.286 (5)	Mo2–C23	2.292 (5)
Mo1···Mo2	3.3623 (5)	C9–C21	1.438 (6)
C1–C2	1.433 (9)	C13–C14	1.438 (8)
C2–C3	1.386 (10)	C14–C15	1.390 (9)
C3–C4	1.392 (10)	C15–C16	1.418 (10)
C4–C5	1.436 (8)	C16–C17	1.416 (7)
C5–C1	1.421 (11)	C17–C13	1.414 (10)
C5–C6	1.491 (11)	C17–C18	1.492 (10)
C7–C8	1.411 (8)	C19–C20	1.420 (8)
C8–C9	1.419 (8)	C20–C21	1.427 (7)
C9–C10	1.429 (8)	C21–C22	1.427 (7)
C10–C11	1.406 (8)	C22–C23	1.411 (7)
C11–C7	1.424 (8)	C23–C19	1.434 (8)
C11–C12	1.493 (9)	C23–C24	1.510 (9)

B. Bond Angles

H1–Mo1–Mo2	67 (2)	H2–Mo2–Mo1	69 (2)
Cp(1)–Mo1–Fv(1)	146.3 (3)	Cp(2)–Mo2–Fv(2)	146.7 (3)
C2–C1–C5	110.7 (6)	C14–C13–C17	108.9 (5)
C1–C2–C3	105.8 (6)	C13–C14–C15	107.4 (5)
C2–C3–C4	109.8 (6)	C14–C15–C16	108.3 (5)
C3–C4–C5	109.8 (7)	C15–C16–C17	109.2 (6)
C4–C5–C1	103.8 (6)	C16–C17–C13	106.2 (6)
C4–C5–C6	127.9 (7)	C16–C17–C18	125.6 (7)
C1–C5–C6	127.6 (6)	C13–C17–C18	127.8 (5)
C8–C7–C11	110.1 (5)	C20–C19–C23	109.4 (5)
C7–C8–C9	107.4 (5)	C19–C20–C21	107.1 (5)
C8–C9–C10	106.8 (4)	C20–C21–C22	107.7 (4)
C9–C10–C11	110.1 (5)	C21–C22–C23	109.4 (4)
C10–C11–C7	105.6 (5)	C22–C23–C19	106.5 (5)
C10–C11–C12	126.1 (5)	C22–C23–C24	126.5 (5)
C7–C11–C12	127.6 (5)	C19–C23–C24	126.3 (5)
C8–C9–C21	126.1 (5)	C20–C21–C9	124.9 (5)
C10–C9–C21	126.0 (5)	C22–C21–C9	126.0 (5)

[a] Cp(n) and Fv(n) denote the centroids of the cyclopentadienyl rings for the methylcyclopentadienyl and dimethylfulvalene ligands, respectively. [b] The esd's given in parentheses for the interatomic distances and bond angles were calculated from the standard errors in the functional coordinates of the corresponding atomic positions.

fulvalene ligands were calculated. The positions for the two hydrides were located in a difference Fourier summation that was calculated by using only low-angle data with $(\sin\theta)/\lambda < 0.40$ Å^{-1}. Full-matrix least-squares refinement[10–14] with anisotropic temperature factors for the 26 non-hydrogen atoms and isotropic temperature factors for the 28 hydrogen atoms[15] converged with final discrepancy indices of $R(F_o) = 0.0252$, $R(F_o^2) = 0.0369$, and $R_w(F_o^2) = 0.0624$ with $\sigma_1 = 1.608$ for the 2393 data with $F_o^2 > \sigma(F_o^2)$. The values for these indices were slightly higher for the other enantiomorph, whose coordinates were determined by changing the signs of the fractional coordinates for all of the atoms. A final difference Fourier map did not reveal any residuals of significant magnitude in the vicinity of the molybdenum atoms.

The positional parameters from the last least-squares refinement cycle are provided in Table II for all of the atoms. The interatomic distances and bond angles and their esd's are given in Table III. Tables of the refined thermal parameters, the carbon–hydrogen distances and angles, the pertinent least-squares planes, and the observed and calculated structure factors for

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(10) The least-squares refinement[11] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|^2$, where w_i is the individual weighting factor 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 standard deviation of an observation of unit weight, σ_1, equals $[\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied during the last refinement cycle.

(11) The scattering factors employed in all of the structure factor calculations were those of Cromer and Mann[12] for the non-hydrogen atoms and those of Stewart et al.[13] for the hydrogen atoms with corrections included for anomalous dispersion.[14]

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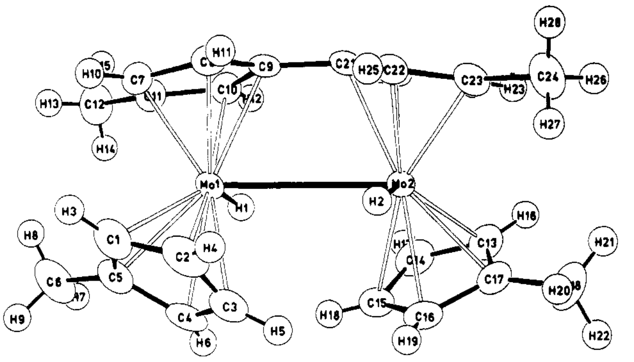

Figure 1. Perspective view of the molecular structure of $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability. For clarity the radii of the spheres for the hydrogens were reduced arbitrarily. Atoms C19, C20, and H24 are hidden behind atoms C23, C22, and H25, respectively.

$(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)MoH]_2$ are available with the supplementary material.[16]

Discussion of Results

Description of the Molecular Structure. The dinuclear structure of $(\eta^5{:}\eta^5\text{-}C_{10}H_6(CH_3)_2)[(\eta^5\text{-}C_5H_4CH_3)\text{-}MoH]_2$ is illustrated in Figure 1 with the atom numbering scheme. The structure of 4 is consistent with Green's proposed structure[1a] for $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)MoH]_2$ (3) and closely resembles the structure suggested by Davison and Wreford[17] for $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2$,[18] with the exception that the two hydrides of 4 occupy terminal rather than μ_2-bridging coordination sites. The two $(\eta^5\text{-}C_5H_4CH_3)MoH$ units of 4 are bridged symmetrically by a π-fulvalene ligand. Each Mo atom achieves a filled-valence-shell configuration by bonding through a rather long two-electron Mo–Mo single bond of 3.3623 (5) Å (vide infra), to a single terminal hydride ligand, and in an η^5-fashion to a methylcyclopentadienyl ring and to one ring of the fulvalene bridge. The two planar five-membered rings of the nonplanar fulvalene ligand are connected by a C–C bond of 1.438 (6) Å and exhibit a dihedral angle of 20.2°. The corresponding values for these parameters in related dinuclear molybdenum complexes are 1.45 (1) Å and 17.5° in $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)_2Mo_2H_3]PF_6$ (5)[2a] and 1.42 (1) Å and 18.1° in $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}H)(\mu\text{-}OH)[(\eta^5\text{-}C_5H_5)Mo]_2(PF_6)_2$ (6).[1c] The rotation of these two rings about the C9–C21 bond in 4 is accompanied by a commensurate distortion of the central Mo_2H_2 moiety, as demonstrated by a dihedral angle of 27.4° between the planes passing through H1, Mo1, Mo2 and H2, Mo1, Mo2. The small range observed for the C–C bonds in the fulvalene ligand of 1.406–1.434 Å reflects a substantial degree of π-electron delocalization.

The overall symmetry of 4 nearly conforms to C_2—2 symmetry with an imaginary twofold axis passing through the midpoints of the Mo1–Mo2 and C9–C21 vectors. The number of ^1H and ^{13}C resonances in the corresponding solution NMR spectra of 4 are consistent with its symmetrical solid structure. The terminal hydrides (δ -9.22) are disposed in a trans orientation and are situated in the open space provided by the canted five-membered rings. This trans configuration is also demonstrated by the methyl substituents of the fulvalene and cyclopentadienyl ligands. To relieve interring repulsions the methylcyclopentadienyl rings are rotated away from each other until the methyl groups are directed in an antiparallel fashion. Similar arrangements for the methyl groups have been observed in the solid-state structures of $[(\eta^5\text{-}C_5H_4CH_3)_2Ti(\mu\text{-}X)]_2$,[19] where X = Cl and Br, and $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$.[7] The methyl substituents of the bridging fulvalene ligand are located in the 3 and 3′ positions and reside directly above the methyl groups of the $C_5H_4CH_3$ ligands. The methyl carbons attached to the planar five-membered rings are similarly displaced by ca. 0.2 Å out of the plane in the direction away from the corresponding molybdenum atom.[20]

The pseudotetrahedral ligand arrangement about each Mo center in 4 closely resembles that found in $(\eta^5\text{-}C_5H_5)_2MoH_2$ (7).[21] The average Mo–Cp(n) and Mo–Fv(n) distances, where Cp(n) and Fv(n) are the centroids of the five-membered carbon rings of the methylcyclopentadienyl and fulvalene ligands, respectively, in 4 of 1.957 and 1.927 Å, respectively, are comparable to the Mo–Cp distance of 1.94 Å in 7. The similar canting of the planar cyclopentadienyl rings, as reflected by the average Cp(n)–Mo–Fv(n) angle in 4 of 146.5° and Cp–Mo–Cp′ angle in 7 of 145.8°, shows that the hydride ligand(s) allow the rings to adopt a more parallel configuration than that found in $(\eta^5\text{-}C_5H_5)_2MoCl_2$ and related derivatives.[22] In terms of the central Mo_2H_2 unit of 4, the two X-ray determined Mo–H bond distances of 1.53 (6) and 1.55 (7) Å are, as expected, inherently shorter than the neutron-determined Mo-H distances of 1.685 (3) Å for 7. The average H–Mo–Mo angle of 68° in 4 is comparable to the H–Mo–H′ bond angle of 75.5 (3) Å in 7. This structural feature is consistent with the fact the metal orbital that is used to form the second Mo–H bond in 7 is properly oriented about each Mo center to form the Mo–Mo bond in 4.

Comments Regarding the Mo–Mo Interaction. The diamagnetic behavior of 4 as demonstrated by its ^1H and ^{13}C NMR spectra is consistent with the presence of a formal Mo–Mo single bond. Depending upon the ancillary ligands and the Mo oxidation state, the Mo–Mo distance in dinuclear organomolybdenum complexes that contain a Mo–Mo single bond varies within a relatively wide range from 3.053 (1) Å in 6[1c] to 3.235 (1) Å in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.[23] By comparison, the substantially longer Mo–Mo distance of 3.3623 (5) Å in 4 reflects a weaker metal–metal bonding interaction in this case. Since the two metal orbitals that participate in metal–metal bond formation are properly directed toward each other, the observed elongation of this Mo–Mo bond probably arises from unfavorable intramolecular contacts that reduce the degree of orbital overlap.

Further insight into the primary stereochemical factors that limit the length of the Mo–Mo distance in 4 is obtained from a comparison of the corresponding Mo–Mo distances and Fv(n)–Mo–Cp(n) angles for a related series of dinuclear molybdenocene species. For 5[2a] and 6,[1c] reasonably normal Mo–Mo distances of 3.227 (1) and 3.053

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Organometallics 1986, 5, 910-917

(1) Å, respectively, are observed. However, the greater number or larger size of the σ-donor ligands attached to each Mo atom in these compounds as compared to 4 requires a greater canting of the corresponding pairs of five-membered rings. In turn, the resultant smaller average Fv(n)–Mo–Cp(n) angles in 5 and 6 of 140.4° and 134.8°, respectively, provide additional space to accommodate a shorter Mo–Mo separation. In contrast, the more parallel orientation of the corresponding pairs of rings in 4 introduces a greater degree of interring repulsion (between the two methylcyclopentadienyl rings) that can only be relieved by a longer Mo–Mo distance. The closest inter-ring contacts (calculated on the basis of an idealized C–H bond distance of 1.09 Å) are 1.97 and 2.11 Å for H5···H19 and H6···H18, respectively. Weak metal–metal single bonds are not that uncommon in sterically crowded dinuclear organometallic compounds. Similar arguments have been presented by Cotton, Muetterties, and their co-workers to rationalize the elongated Cr–Cr bonds of 3.281 (1) Å in $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[24] and of 3.341 (1) Å in $[(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3]_2$.[25]

Since the methyl substituents do not play a significant steric role in the structure of **4**, one would expect a similarly elongated Mo–Mo bond in **3**. This structural feature presumably explains the relative ease by which the Mo–Mo bond in **3** can be ruptured by CO as well as accounts for the compound's apparent fluxional behavior in solution.[3]

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Registry No. 4, 101033-26-5; $KC_5H_4CH_3$, 41066-45-9; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Mo, 7439-98-7.

Supplementary Material Available: Tables of refined thermal parameters, hydrogen bond distances and angles, least-squares planes of interest, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Group 14 Metalloles. 2.[†] Functional 2,5-Diphenylsilacyclopentadienes[‡] and Their Use as η^4-Ligands

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The reactions of 1,4-dilithio-1,4-diphenylbutadiene with several di- and trichloro- (or trimethoxy-) silanes lead to the formation of the corresponding silicon-substituted 2,5-diphenylsilacyclopentadienes. The compounds thus obtained are **1** (H, Cl), **2** (Me, H), **3** (Me, Me_3Si), **4** (Me, vinyl), **5** (Me, MeO), **6** (vinyl, MeO), **7** (allyl, MeO), **8** (Me_3Si, MeO), **9** (H, H), **10** (Me, Cl), **11** (Me, allyl), **12** (vinyl, H), **13** (allyl, H), and **14** (Me_3Si, H). The use of siloles **2**, **3**, **11**, and **15** as ligands was studied, and η^4-silole complexes with iron, cobalt, and nickel are described. Reaction of monosubstituted cobalt complexes with an excess of the ligand gives the corresponding disubstituted ones. The cobalt–cobalt bonds are cleaved with sodium amalgam, and the anions thus formed are trapped with triphenyltin chloride. The crystal structure of bis(η^4-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel (**16**) shows that nickel is tetrahedral and that the quasi-planar free ligand is bent (dihedral angle between the dienic plane and the C(2)–Si–C(5) one $\approx 20°$). This complex crystallizes with one molecule of cyclohexane per three molecules of **16**.

Introduction

Transition-metal complexes of siloles are well-known,[3] and in all complexes reported thus far the silole functions as an η^4-ligand. The earliest studies focused on the readily available 2,3,4,5-tetraphenylsilacyclopentadiene complexes and later on the 2,5-diphenylsilacyclopentadiene system. Since the most recent summary of silole derivative chemistry,[3] metal carbonyl complexes of C-unsubstituted siloles[1,4] as well as of 3,4-dimethylsilacyclopentadiene[5] have been reported.

Still unreported, however, is the generation or detection of an (η^5-silacyclopentadienyl)metal complex. A complex of η^5-silole could, in principle, be formed from reaction of an ionic silole with a metal derivative or by reaction of a coordinated η^4-silole. In either approach, silicon functional

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[†] Part 1, see ref 1.

[‡] For a preliminary communication see ref 2.

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