viously postulated for reaction 1 or with $\{CH_3COMn(CO)_4\}_B$, if rearrangement has occurred. In the first case *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ would be formed initially whereas $\{CH_3COMn(CO)_4\}_B$ would lead to the equilibrium mixture of the two isomers. The choice will depend on the energy required to rearrange $\{CH_3COMn(CO)_4\}_A$ relative to that required to form it. As mentioned earlier, this point could not be ascertained because of an unfavorable kinetic situation in benzene-d_6.

The proposed mechanism for reaction 2 is in agreement with the previously reported[6] experiment with (+)-$C_6H_5CH_2CH(CH_3)COMn(CO)_5$ showing retention of sign of rotation during its reaction with I^- in 2,2′-diethoxydiethyl ether. The alternative explanation[6] of a stereospecific slow preequilibrium of $RCOMn(CO)_5$ to $RMn(CO)_5$ must be ruled out on the basis of the present data.

No important isomerizations, with consequent statistical redistribution of ^{13}CO, were observed,[5] within the time of the experiment, during the reaction of $CH_3Mn(CO)_5$ with ^{13}CO, whereas isomerization occurs with $CH_3COMn(CO)_4P(C_6H_5)_3$. This can be explained on kinetic terms by considering that $CH_3COMn(CO)_5$ can exchange its CO groups with CO in the gas phase only *via* decarbonylation to $CH_3Mn(CO)_5$ or, in other words, through the intermediate $\{CH_3COMn(CO)_4\}_A$ (k ranging from 2.46×10^{-5} to 1.99×10^{-6} sec^{-1} at 30° depending on the solvent[7]). The decarbonylation of $CH_3COMn(CO)_5$ is therefore a slow process compared to its formation from $CH_3Mn(CO)_5$. On the other hand, the initially formed *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ reverts to the *trans* isomer at a rate which is relatively fast ($k = 2.5 \times 10^{-4}$ sec^{-1} at 30° in acetone).

We can conclude by saying that the experimental facts contained in this paper and probably most of those reported in previous papers[1–3,5–7] can be explained by assuming the *preliminary* formation of intermediates obtained from changes taking place at a position *cis* with respect to the alkyl or the acyl group.

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of Dimeric Azulenetricarbonylmethylmolybdenum

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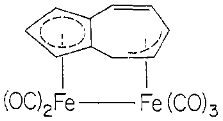
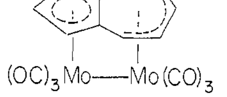
Dimeric azulenetricarbonylmethylmolybdenum, $[C_{10}H_8Mo(CO)_3CH_3]_2$, crystallizes in the triclinic space group $P\bar{1}$ (C_i^1; No. 2) with cell parameters $a = 10.02 \pm 0.02$ Å, $b = 8.36 \pm 0.02$ Å, $c = 8.19 \pm 0.02$ Å, $\alpha = 107.3 \pm 0.2°$, $\beta = 89.3 \pm 0.2°$, $\gamma = 100.4 \pm 0.2°$, $Z = 1$. Observed and calculated densities are, respectively, 1.68 ± 0.02 and 1.667 g cm^{-3}. A single-crystal X-ray structural analysis, based on complete three-dimensional data ($\sin\theta_{max} = 0.38$, Mo Kα radiation) collected with a Buerger automated diffractometer, has been completed. Patterson, Fourier, and least-squares refinement techniques have led to the accurate location of all atoms other than the methyl hydrogens. The final discrepancy index, R_F, is 5.82% for 1438 independent nonzero reflections. The crystal consists of discrete molecular units of $[C_{10}H_8Mo(CO)_3CH_3]_2$ separated by normal van der Waals forces. The molecule possesses a crystallographic center of symmetry, two azulene residues being linked *via ortho–ortho* (4,4′) carbon–carbon coupling. An $Mo(CO)_3CH_3$ moiety is bonded to each five-membered ring of the resulting diazulene ligand. The Mo–CH_3 bond length is 2.383 ± 0.010 Å and the mean Mo–CO distance is 1.996 ± 0.012 Å.

Introduction

Although azulene–metal–carbonyl complexes have been known for some time,[1–5] only recently have the structures of any of these complexes been unambiguously established. Crystallographic studies of azulenediiron pentacarbonyl[6,7] (I) and azulenedimolybdenum hexacarbonyl[8,9] (II) show them to have a metal atom associated with each ring. There are, however, some azulene–metal–carbonyl complexes in which the azulene-to-metal ratio is 1:1, *viz*, $[C_{10}H_8V(CO)_4]_2$,[4] $[C_{10}H_8$-



I



II

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[1] R. Burton and G. Wilkinson, *Chem. Ind.* (London), 1205 (1958).

[2] R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *ibid.*, 1592 (1958).

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[4] E. O. Fischer, Abstracts, Organometallic Chemical Symposium, Cincinnati, Ohio, June 1963, p 66.

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[7] M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

[8] M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).

[9] J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).

$Mn(CO)_3]_2$,[3] and $[C_{10}H_8Mo(CO)_3CH_3]_2$.[5] A number of different formulations for these species have been suggested[3,5,10] the most reasonable of which[5] requires that the five-membered rings behave as π-cyclopentadienyl systems in linking to the metal atoms and that dimerization occurs *via* a carbon–carbon bond between the seven-membered rings of two azulene systems.

A crystallographic analysis of $[C_{10}H_8Mo(CO)_3CH_3]_2$ has been undertaken in order to obtain unambiguous information on the nature of the azulene–molybdenum bonding and to determine the stereochemistry of the carbon–carbon coupling in this complex. A preliminary account of this work has been published.[11]

Collection and Reduction of X-Ray Diffraction Data

Crystals of $[C_{10}H_8Mo(CO)_3CH_3]_2$ were prepared from azulenedimolybdenum hexacarbonyl following the method of King and Bisnette.[5] Optical examination and preliminary X-ray diffraction photographs indicated that the crystals were triclinic. A careful survey of $0kl$ Weissenberg and $hk0$, $hk1$, $h0l$, $h1l$ precession photographs (all taken with Mo Kα radiation) revealed no systematic absences nor any diffraction symmetry higher than $C_i(\bar{1})$; the crystals were therefore assumed to be truly triclinic.

Unit-cell parameters, obtained from calibrated ($a_{NaCl} = 5.640$ Å) precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 24 ± 2°, are: $a = 10.02 \pm 0.02$ Å, $b = 8.36 \pm 0.02$ Å, $c = 8.19 \pm 0.02$ Å, $\alpha = 107.3 \pm 0.2°$, $\beta = 89.3 \pm 0.2°$, $\gamma = 100.4 \pm 0.2°$. [These "experimental" cell constants are used throughout this paper. The corresponding reduced cell, obtained by a Delaunay reduction, is defined by $a' = a = 10.02 \pm 0.02$ Å, $b' = [011] = 9.81 \pm 0.02$ Å, $c' = -c = 8.19 \pm 0.02$ Å, $\alpha' = 125.6 \pm 0.2°$, $\beta' = 90.7 \pm 0.2°$, $\gamma = 98.2 \pm 0.2°$.] The unit-cell volume is 643.9 Å^3. The observed density ($\rho_{obsd} = 1.68 \pm 0.02$ g cm^{-3}, by flotation in aqueous zinc iodide solution) is in satisfactory agreement with the value calculated for $M = 646.36$ and $Z = 1$ ($\rho_{calcd} = 1.667$ g cm^{-3}). Of the possible space groups P1 and P$\bar{1}$, the latter was considered the more likely owing to its greater frequency of occurrence[12] and the high probability that the molecule possessed a center of symmetry. The successful solution of the structure proved that the true space group was, indeed, P$\bar{1}$ (C_i^1; No. 2).

The crystal used initially in this analysis (crystal I), an approximately rectangular parallelepiped of dimensions 0.20 × 0.09 × 0.04 mm, was mounted along its extended direction (a) and inserted into a 0.2-mm diameter thin-walled capillary tube.

Data were collected on a 0.01°-incrementing Buerger automated diffractometer, used in conjunction with a fully stabilized Phillips X-ray generator (operated at 47 kV, 17 mA), a Phillips No. 52572 transistorized scintillation counter, and a Phillips No. 12206 electronic circuit panel. The scintillation counter was adjusted to receive Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å), the Kβ component being virtually eliminated by the use of 0.003-in. zirconium foil at the X-ray source.

The diffractometer was programmed to collect all data in a given Weissenberg zone, using a "stationary-background, ω-scan, stationary-background" counting sequence. Within a given zone, the stability of the entire system was monitored by remeasuring a carefully preselected check reflection after each batch of 20 reflections had been collected. No significant variations were detected. Throughout the analysis a chart recorder was used to allow inspection of peak profile and centering of the reflection in ϕ and to guard against possible errors that might result from overlap of adjacent reflections.

Previous photographic studies had indicated that the crystal had a normal mosaicity, and the scan range $\omega = (2.0 + (0.8/L))°$ was selected [where $1/L$ is the Lorentz factor[13]].

$I(hkl)$, the intensity of a reflection hkl, having Weissenberg coordinates[14] $\Upsilon_0(hkl)$ and $\Phi_0(hkl)$, was recorded by the following sequence: (i) the counter was positioned to $\Upsilon_0(hkl)$ where it remained during subsequent steps; (ii) the crystal was rotated to the angle ϕ_1, given by $\phi_1 = \Phi_0(hkl) - (\omega(hkl)/2)$, and the first background (B_1) counted for t seconds; (iii) the crystal was slowly rotated by $\omega(hkl)$ degrees at a rate of 2°/min until it reached the angle ϕ_2, given by $\phi_2 = \Phi_0(hkl) + (\omega(hkl)/2)$. This ω scan took $4t$ seconds, the associated count being C; (iv) the second background (B_2) was counted for t seconds at ϕ_2; (v) the integrated intensity was calculated as $I(hkl) = C - 2(B_1 + B_2)$.

Equiinclination geometry was used in collecting a total of 1721 reflections (in the zones $0kl$ through $10kl$) from crystal I. [This represents complete data to $\sin\theta = 0.38$. Beyond this limit there are a *few* isolated reflections, but extending the limit beyond the present value would result in a very low percentage of additional significant (count/$3\sigma > 1$) reflections.] To correlate these a-axis data, the zones $h0l$ through $h4l$ were collected from crystal II, a somewhat smaller parallelepiped of dimensions 0.08 × 0.07 × 0.03 mm, which was mounted along its b axis. Data were weighted by the following scheme, where δ is the maximum probable error in a count ($= 3\sigma$ based on counting statistics): $I(hkl) > 625$, $\sigma = 0.1[I(hkl)]$; $625 > I(hkl) > \delta$, $\sigma = 2.5[I(hkl)]^{1/2}$; $I(hkl) < \delta$, reflection rejected. The linear absorption coefficient μ is 16.6 cm^{-1} for Mo Kα radiation. Since variations in transmission factor were estimated to be less than 5%, no absorption corrections were applied. After adjustment for Lorentz and polarization factors [$(LP)^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)$, where $\bar{\mu}$ is the equiinclination angle], data were placed on a common scale using a least-squares procedure which minimizes a sum of

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[10] M. A. Bennett, *Advan. Organometal Chem.*, **4**, 366 (1966).

[11] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 705 (1967).

[12] W. Nowacki, T. Matsumoto, and A. Edenharter, *Acta Cryst.*, **22**, 935 (1967); (b) J. D. H. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, "Crystal Data, Determinative Tables," American Crystallographic Association, Monograph No. 5, 2nd ed, 1963.

[13] The term involving the Lorentz factor is included to allow for the divergence of the X-ray beam which results in extended low-order reflections on upper-level data: D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

[14] C. T. Prewitt, *Z. Krist.*, **13**, 355 (1960).

residuals linear in the logarithms of the individual scale factors.[15] From the resulting 1438 independent reflections, a Wilson plot was calculated to determine the approximate absolute scale and the over-all thermal parameter (the value $\bar{B}$ = 2.73 Å^2 was obtained by this technique).

Solution and Refinement of Structure

The position of the molybdenum atom (x = 0.290, y = 0.177, z = 0.195) was obtained quickly and unambiguously from a three-dimensional Patterson[16] map from which the origin peak had been removed and which had been sharpened so that the average intensity was independent of sin θ. A three-dimensional "difference" Fourier synthesis phased only by the molybdenum atom (R_F = 0.29)[17] revealed immediately the positions of all nonhydrogen atoms, indicating that the molecule possessed a center of symmetry at $x = 0$, $y = 0$, $z = 1/2$ and justifying the choice of the centrosymmetric space group P$\bar{1}$. Five cycles of least-squares refinement, in which positional and individual isotropic thermal parameters were allowed to vary, resulted in the discrepancy index, R_F, converging from an initial value of 0.247 to a final value of 0.089. [The weighted R factor, R_{wF^2},[17] had a value of 0.119 at the termination of isotropic refinement.] A difference Fourier synthesis at this stage revealed evidence of anisotropic thermal motion for most atoms and also indicated unambiguously the positions of all hydrogen atoms associated with the diazulene ligand, individual peak heights for these hydrogen atoms varying from 0.5 to 0.8 e Å^{-3}. [There were no other peaks of comparable height except those representing residual electron density at the known atomic positions of molybdenum, carbon, and oxygen atoms. A complete electron density map showed that peak heights for carbon atoms ranged from 5.1 to 5.7 e Å^{-3}, and those for oxygen varied from 6.9 to 7.4 e Å^{-3}.]

Hydrogen atom contributions were not immediately included but refinement of nonhydrogen atoms was continued using anisotropic temperature factors (T) of the form: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. The discrepancy index converged to a value R_F = 0.0630. The eight observed hydrogen atoms were now included in the calculation and both their positions and isotropic thermal parameters were allowed to refine. The result was neither very encouraging, nor was it disastrous; resulting carbon–hydrogen distances varied from 0.7 to 1.3 Å, isotropic thermal parameters varied from 3 to 12 Å^2, and the discrepancy index decreased to R_F = 0.0598. It was decided, however, to reposition all hydrogen atoms in calculated positions (using d(C–H) = 1.08 Å and the appropriate idealized trigonal or tetrahedral geometry). Hydrogen atoms were included with B = 6.0 Å^2 and were not allowed to refine while positional and anisotropic thermal parameters for all other atoms were varied. At the end of each cycle of refinement, hydrogen atoms were replaced in their newly calculated positions. [The effective "shifts" at this stage of the refinement process were, however, small.] After three such cycles, no parameter was varying by more than $1/20$ of its standard deviation, and refinement was judged to be complete. A difference Fourier synthesis revealed no unexpected features but failed to locate the three hydrogen atoms associated with each methyl group. Since the other hydrogen atoms are so well defined, it is assumed that this is due to rotation of the methyl group about the Mo–CH$_3$ axis.

Final discrepancy indices are R_F = 0.0582 and R_{wF^2} = 0.0461. The standard deviation for an observation of unit weight is 1.55. Throughout the analysis the scattering factors for neutral molybdenum, oxygen, carbon, and hydrogen were used.[18] Dispersion corrections[19] are small and were ignored. The residual minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$.

Observed and calculated structure factors are shown in Table I; atomic positions are collected in Table II. Anisotropic thermal parameters and their associated vibration ellipsoids are given in Tables III and IV, respectively.

The Molecular Structure

Figure 1 shows the asymmetric unit viewed along b; bond distances (with esd's) are collected in Table V and bond angles (with esd's) are shown in Table VI.

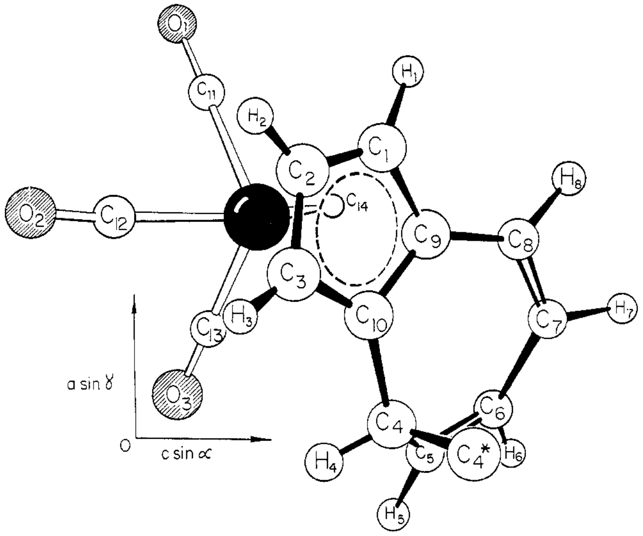

Figure 1.—The asymmetric unit of $[C_{10}H_8Mo(CO)_3CH_3]_2$ projected down b. The symmetry-related C$_4$ ($-x$, $-y$, $1 - z$) is shown as C$_4$*.

This crystallographic analysis confirms the proposal of King and Bisnette[5] that the molecule contains a π-cyclopentadienyl–molybdenum linkage and that dimerization involves carbon–carbon coupling between seven-membered rings. Further, it is seen that this coupling involves carbon atoms *ortho* to the five mem-

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(15) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(16) All crystallographic calculations including Fourier syntheses, structure factors calculations, least-squares refinement, geometry calculations, and atomic vibration ellipsoids were performed using CRYRM—an integrated set of crystallographic programs for the IBM 7094 written by R. E. Marsh and his co-workers at the California Institute of Technology.

(17) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

(18) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, pp 202, 211.

(19) $\Delta f' = -1.7$ electrons, $\Delta f'' = +0.9$ electron; see ref 18, p 216.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[C_{10}H_8Mo(CO)_3CH_3]_2$[a]

	H 0 -8	
2	168	147
3	79	-92
	H 1 -8	
0	173	-164
1	165	151
2	83	36
3	205	-194
	H 2 -8	
0	80	-5
1	202	178
2	114	-102
3	89	-98
4	88	79
	H 3 -8	
0	160	155
1	82	52
2	165	-159
	H 4 -8	
0	163	151
1	162	-143
2	67	-17
3	152	119
	H 5 -8	
1	136	-109
2	145	130
	H 0 -7	
1	125	130
2	79	54
3	240	-244
4	74	85
5	219	235
6	91	-78
	H 1 -7	
0	113	110
1	169	166
2	131	-127
4	253	262
5	82	22
6	197	-201
	H 2 -7	
0	304	322
1	63	-24
2	227	-229
3	203	205
4	138	134
5	176	-160
	H 3 -7	
0	164	174
1	323	-307
3	259	270
4	97	-73
5	164	-153
	H 4 -7	
0	152	-165
1	192	-177
2	204	196
4	219	-223
5	97	35
	H 5 -7	
0	242	-234
1	81	62
2	148	124
3	97	-96
4	141	-128
	H 6 -7	
0	120	-120
1	250	218
2	80	62
3	167	-132
	H 7 -7	
0	105	82
	H 0 -6	
1	125	132
2	264	-266
4	257	257
5	200	-200
6	135	-105
7	177	186
	H 1 -6	
0	212	232
1	155	-180
2	192	-177
3	308	309
4	112	101
5	243	-241
7	199	205
	H 2 -6	
0	110	122
1	344	-343
3	327	316
4	287	-307
	330	-307
J	243	-260
6	143	123
	H 3 -6	
0	219	-204
1	298	-277
2	253	238
3	89	-90
4	326	-335
5	105	55
6	199	190
7	183	-185
	H 4 -6	
0	232	-228
1	101	96
2	246	226
3	159	-154
5	291	311
	H 5 -6	
1	341	317
3	241	-221
4	130	105
5	175	171
	H 6 -6	
0	248	244
1	80	68
2	290	-270
3	75	-84
4	214	198
	H 7 -6	
0	216	205
1	129	-128
2	107	-97
	H 0 -5	
1	72	-81
2	283	-278
3	293	301
4	188	177
5	253	-266
6	115	110
7	163	158
8	131	-128
	H 1 -5	
0	339	349
1	279	-283
2	72	73
3	327	334
4	228	-227
5	161	-171
6	222	218
7	113	99
8	269	-274
	H 2 -5	
0	206	-208
1	195	-194
2	444	428
4	299	-298
5	235	231
6	221	239
7	149	-155
	H 3 -5	
0	391	-401
1	242	248
2	318	254
3	373	-370
4	106	90
5	244	258
7	126	-120
8	169	165
	H 4 -5	
0	100	-115
1	251	247
2	159	-157
3	243	-232
4	248	245
5	139	144
6	230	-248
	H 5 -5	
0	142	128
1	126	101
2	258	-233
3	112	106
4	290	279
5	167	-155
6	156	-144
	H 6 -5	
0	188	202
1	136	-143
3	163	154
5	204	-194
	H 7 -5	
1	192	-177
3	135	116
	H 8 -5	
0	164	-157
	H 0 -4	
1	500	-494
2	115	111
3	436	434
4	85	-87
5	140	-117
6	334	344
7	92	-69
8	227	-218
9	173	161
	H 1 -4	
0	258	-264
1	118	-113
5	202	203
6	122	125
7	271	-277
8	56	-76
9	275	278
	H 2 -4	
0	623	-634
1	332	347
3	629	-634
4	206	-192
5	201	200
6	138	-132
7	273	-285
8	164	162
	H 3 -4	
0	332	-325
1	326	332
2	215	-205
3	305	-307
4	255	270
5	69	42
6	175	-178
7	98	-44
8	167	145
	H 4 -4	
0	261	224
1	377	371
2	246	-238
3	135	146
4	177	196
5	151	-150
6	169	-182
7	194	200
	H 5 -4	
0	286	288
1	218	-210
2	210	-194
3	313	298
5	310	-315
6	132	144
7	98	105
	H 6 -4	
0	141	-136
1	358	-331
2	228	218
3	148	137
4	245	-249
6	194	205
	H 7 -4	
0	276	-261
2	216	214
3	72	-75
4	245	-245
	H 8 -4	
0	211	-203
1	128	120
2	68	77
	H 0 -3	
1	137	-142
2	676	660
3	157	-74
4	532	-505
5	249	250
6	198	185
7	308	-330
9	212	197
	H 1 -3	
0	337	-356
1	324	332
2	423	404
3	596	-592
4	148	-169
4	189	-169
5	562	558
6	302	-288
7	211	-218
8	282	282
9	89	67
	H 2 -3	
0	307	261
1	696	686
2	279	-286
3	301	-305
4	402	408
5	133	130
6	217	-231
7	118	116
8	288	303
9	198	-207
	H 3 -3	
0	730	733
1	93	-83
2	462	-472
3	178	152
4	357	349
5	154	-158
6	63	-30
7	278	294
8	68	-45
9	175	-175
	H 4 -3	
0	467	-492
1	501	-508
3	566	578
4	171	-173
5	196	-203
6	217	225
7	149	177
8	240	-261
	H 5 -3	
1	293	-278
2	403	411
3	77	66
4	400	-409
5	67	31
6	329	342
7	158	-182
	H 6 -3	
0	269	-257
2	271	253
3	234	-217
4	159	-150
5	231	241
6	119	106
	H 7 -3	
1	259	263
3	151	-128
	H 8 -3	
0	92	88
1	202	205
2	120	-122
	H 0 -2	
1	585	588
2	1001	915
3	384	-388
4	313	290
5	481	480
6	281	-267
7	55	-52
8	274	262
10	185	-181
	H 1 -2	
0	565	526
1	382	380
2	483	-443
3	259	-264
4	478	454
5	124	-125
6	392	-407
7	278	295
8	66	46
9	256	-258
	H 2 -2	
1	873	-790
2	675	-669
3	282	297
4	265	247
5	498	-502
6	56	28
7	211	213
8	123	-142
9	167	-164
	H 3 -2	
0	123	148
1	595	-605
3	531	535
4	96	-86
5	310	-314
6	218	220
7	95	93
8	285	-309
9	61	53
	H 4 -2	
0	58	-56
1	457	-463
2	326	338
3	257	253
4	403	-411
6	147	163
7	204	-229
8	138	-151
	H 5 -2	
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-4	84	-76
-3	167	139
-1	222	-208
0	136	138
	H -8 6	
1	153	156
2	76	-79
	H -7 6	
2	254	-242
4	76	77
5	141	-131
	H -6 6	
1	260	-262
2	182	-181
3	183	172
4	126	-115
5	126	-136
6	141	131
	H -5 6	
1	217	-234
2	138	165
3	120	115
4	177	-178
6	174	182
7	135	-135
	H -4 6	
1	80	46
2	252	248
3	163	-171
4	205	-199
5	188	189
7	209	-205
	H -3 6	
1	267	289
3	358	-370
5	209	213
6	187	-167
	H -2 6	
1	191	196
2	264	-279
3	118	-131
4	310	311
5	89	-55
6	142	-143
7	111	98
	H -1 6	
2	292	-294
3	92	66
4	151	148
5	234	-234
7	110	104
	H 0 6	
0	98	85
1	218	-224
2	121	-141
3	262	257
4	69	-55
5	146	-156
6	136	116
	H 1 6	
-6	240	-246
-5	96	104
-4	105	106
-3	272	-294
-1	265	229
0	166	-108
1	142	-165
2	251	256
3	77	67
4	143	-143
6	139	122
	H 2 6	
-5	170	147
-4	152	-183
-4	201	-185
-3	182	-181
-2	282	280
-1	67	-10
0	246	-257
1	88	85
2	144	136
3	176	-190
4	93	-47
5	151	134
	H 3 6	
-4	220	-223
-3	113	82
-2	204	206
-1	170	-169
0	183	-187
1	196	196
2	103	-82
3	120	-120
	H 4 6	
-3	181	182
-1	186	-190
0	119	104
1	105	99
	H -7 7	
1	248	-226
3	175	171
	H -6 7	
1	156	-164
2	231	230
3	89	71
4	133	-110
5	94	86
	H -5 7	
2	185	178
3	119	-119
5	158	155
6	65	-17
1	220	214
3	188	-179
4	127	117
5	103	108
6	199	-186
	H -3 7	
1	222	230
2	249	-243
4	207	204
5	113	-76
6	137	-144
	H -2 7	
1	74	-64
2	173	-183
3	197	202
4	147	147
5	148	-134
6	92	71
	H -1 7	
1	170	-170
2	109	98
3	282	286
4	113	-118
5	71	-69
6	157	159
	H 0 7	
0	180	-191
2	239	243
3	65	-39
4	280	-271
5	137	124
	H 1 7	
-5	188	169
-4	246	-243
-3	80	-77
-2	258	241
-1	141	-110
0	176	-175
1	158	159
2	141	145
3	237	-223
4	66	-18
	H 2 7	
-4	163	-130
-3	193	173
-2	169	169
-1	184	-176
0	82	-1
1	233	238
	H 3 7	
-1	133	-126
	H -5 8	
1	200	210
	H -4 8	
1	95	104
2	179	-168
4	119	85
	H -3 8	
1	135	-152
2	86	-69
3	135	136
	H -2 8	
1	169	-175
2	116	95
4	141	-133
	H -1 8	
1	100	-102
2	121	119
3	88	-83
	H 0 8	
0	164	-153
1	80	103
2	93	90
	H 1 8	
-1	102	-92

[a] Table shows $10|F_o|$ and $10F_c$.

bered ring. Since King and Bisnette,[5] Paul,[20] and ourselves each obtained a single crystalline product, it appears that the reaction is specific in producing the 4,4′-diazulene derivative.

The coordination sphere of the molybdenum atom is similar to that already found in π-$C_5H_5Mo(CO)_3$-C_3F_7,[21,22] π-$C_5H_5Mo(CO)_3C_2H_5$,[23,24] π-$C_5H_5Mo(CO)_2$-

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(20) Professor I. C. Paul (University of Illinois) informs us that his group had taken preliminary crystallographic data on this complex. Their unit-cell dimensions are in substantial agreement with our own.

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(22) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(23) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

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TABLE II

FINAL ATOMIC COORDINATES,[a] INCLUDING CALCULATED HYDROGEN POSITIONS, FOR $[C_{10}H_8Mo(CO)_3CH_3]_2$

Atom	x	y	z
Mo	0.29349 (9)	0.17462 (12)	0.19580 (12)
O_1	0.5536 (9)	0.3528 (10)	0.0612 (11)
O_2	0.2851 (9)	−0.0409 (12)	−0.1908 (11)
O_3	0.0454 (9)	0.2851 (13)	0.0596 (11)
C_1	0.3981 (10)	0.1042 (14)	0.4149 (14)
C_2	0.3616 (10)	−0.0392 (13)	0.2752 (13)
C_3	0.2184 (10)	−0.0771 (11)	0.2604 (12)
C_4	0.0182 (9)	0.0449 (12)	0.4295 (12)
C_5	−0.0177 (9)	0.2205 (13)	0.4860 (13)
C_6	0.0468 (11)	0.3597 (13)	0.6062 (13)
C_7	0.1743 (11)	0.3825 (13)	0.6974 (13)
C_8	0.2798 (11)	0.3012 (14)	0.6470 (13)
C_9	0.2808 (9)	0.1618 (12)	0.4892 (12)
C_{10}	0.1660 (9)	0.0477 (12)	0.3889 (12)
C_{11}	0.4594 (12)	0.2904 (14)	0.1083 (14)
C_{12}	0.2862 (10)	0.0369 (15)	−0.0502 (16)
C_{13}	0.1372 (12)	0.2482 (15)	0.1102 (14)
C_{14}	0.3143 (11)	0.4736 (13)	0.3298 (14)
H_1	0.5017	0.1621	0.4589
H_2	0.4311	−0.1082	0.1937
H_3	0.1586	−0.1844	0.1659
H_4	−0.0391	−0.0223	0.3104
H_5	−0.1035	0.2515	0.4313
H_6	−0.0091	0.4631	0.6321
H_7	0.1938	0.4747	0.8228
H_8	0.3667	0.3495	0.7363

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and are right-adjusted to the last significant digit of the preceding number.

TABLE III

FINAL ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^4$) FOR $[C_{10}H_8Mo(CO)_3CH_3]_2$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mo	79.3 (1.0)	147.3 (1.8)	143.3 (1.7)	8.1 (1.8)	23.9 (1.8)	88.8 (2.5)
O_1	135 (11)	207 (19)	263 (20)	−86 (23)	182 (25)	53 (31)
O_2	150 (12)	332 (24)	154 (18)	36 (26)	14 (24)	4 (34)
O_3	137 (12)	378 (26)	253 (21)	201 (29)	−11 (25)	240 (37)
C_1	77 (12)	168 (23)	201 (24)	25 (26)	−45 (27)	126 (39)
C_2	105 (13)	130 (21)	170 (22)	82 (27)	86 (27)	89 (36)
C_3	122 (14)	74 (18)	137 (19)	21 (25)	29 (26)	64 (30)
C_4	68 (11)	106 (19)	135 (19)	7 (22)	5 (23)	60 (29)
C_5	79 (12)	161 (23)	150 (21)	66 (27)	64 (25)	161 (36)
C_6	101 (13)	123 (21)	164 (22)	42 (27)	75 (28)	91 (35)
C_7	126 (15)	123 (21)	123 (20)	−10 (28)	58 (28)	40 (32)
C_8	101 (13)	174 (23)	137 (21)	−13 (28)	24 (27)	101 (37)
C_9	60 (11)	130 (19)	129 (19)	10 (23)	−3 (23)	101 (33)
C_{10}	85 (12)	111 (18)	117 (18)	20 (23)	11 (23)	116 (30)
C_{11}	117 (15)	149 (23)	157 (22)	−9 (30)	40 (30)	34 (36)
C_{12}	79 (13)	204 (26)	210 (28)	12 (28)	30 (30)	191 (45)
C_{13}	120 (16)	199 (26)	145 (22)	39 (32)	73 (30)	104 (38)
C_{14}	108 (14)	148 (22)	186 (23)	34 (27)	92 (28)	106 (36)

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

$[P(C_6H_5)_3]COCH_3$,[25] π-$C_5H_5Mo(CO)_3COCF_3$,[26] π-$C_5H_5Mo(CO)_3CH_2CO_2H$,[27] $[\pi$-$C_5H_5Mo(CO)_3]_2$,[28] and $[\pi$-$C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$.[29] The relative orientations of the $Mo(CO)_3CH_3$ moiety and the five-membered ring of the $[C_{10}H_8Mo(CO)_3CH_3]_2$ molecule are shown in Figure 2, which depicts a projection of the molecule in the plane of the five-membered ring. It can be seen that the methyl group lies approximately below C_9. The molybdenum–carbon distances vary systematically around the five-membered ring, ranging from 2.439 ± 0.009 Å for the Mo–C_9 distance to 2.286 ± 0.010 Å for the Mo–C_2 distance. This variation is definitely statistically significant (the difference between the Mo–C_9 and Mo–C_2 distances represents $\sim 14\sigma$) and does not affect the planarity of the π-cyclopentadienyl system (the rms deviation is only 0.008 Å). A "tilting" of the π-cyclopentadienyl system in π-$C_5H_5Mo(CO)_3C_3F_7$ was related previously[22] to similar features in other π-$C_5H_5Mo(CO)_3R$ systems, it being noted that in each case the longest molybdenum–π-cyclopentadienyl distance involved a carbon atom immediately above the noncarbonyl ligand. Since the shorter Mo–C distances are *trans* to the substituent (R) and the longer Mo–C distances are *trans* to strongly π-bonding carbonyl groups, it seems probable that an Mo–C distance for an atom in a π-cyclopentadienyl ring reflects the π character in the bond (or bonds) *trans* to it. However, this effect may sometimes be complicated by steric effects due to bulky ligands (*e.g.*, when a carbonyl group is replaced by a triphenylphosphine ligand[25]).

The Molybdenum–Methyl Linkage

The molybdenum–methyl distance of 2.383 ± 0.010 Å represents the most precise determination of a molybdenum–alkyl bond length yet reported. [Previous values are 2.397 ± 0.019 Å for the Mo–C_2H_5 bond in π-$C_5H_5Mo(CO)_3C_2H_5$[24] and 2.41 ± 0.02 Å for the Mo–CH_2CO_2H bond in π-$C_5H_5Mo(CO)_3CH_2CO_2H$.[27]] This crystallographic study confirms the Mo–C single bond length which has been used as a basis for obtaining direct evidence for metal→ligand back-donation in molybdenum perfluoroalkyls[21,22] and acyls.[25,26] The greater rigidity of the diazulene *vis á vis* the π-cyclopentadienyl ligand makes it apparent that crystallographic studies on complexes of the type $[C_{10}H_8Mo$-

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[25] M. R. Churchill and J. P. Fennessey, submitted for publication.

[26] M. R. Churchill and J. P. Fennessey, to be published.

[27] M. L. H. Green, J. K. P. Ariyante, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).

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TABLE IV

DIRECTION COSINES[a] FOR THE ATOMIC VIBRATION ELLIPSOIDS[b] IN $[C_{10}H_8Mo(CO)_3CH_3]_2$

Atom	B_{max} (dc's major axis)	B_{med} (dc's median axis)	B_{min} (dc's minor axis)
Mo	4.13 (0.622, −0.866, 0.392)	3.53 (0.091, 0.254, 0.832)	2.73 (−0.778, −0.431, 0.394)
O_1	11.23 (0.655, −0.644, 0.678)	4.88 (−0.148, 0.619, 0.566)	2.37 (−0.741, 0.450, 0.470)
O_2	9.92 (0.295, −0.975, 0.463)	5.76 (−0.955, −0.116, 0.114)	3.54 (−0.017, 0.190, 0.879)
O_3	9.70 (−0.275, −0.864, 0.040)	6.36 (−0.439, −0.026, 0.878)	3.62 (0.855, −0.503, 0.478)
C_1	5.32 (−0.390, 0.148, 0.847)	4.01 (0.015, −0.982, 0.388)	2.67 (0.921, −0.117, 0.365)
C_2	5.21 (0.669, −0.067, 0.701)	3.41 (−0.360, −0.771, 0.618)	2.59 (−0.653, 0.634, 0.356)
C_3	4.93 (0.974, −0.226, 0.238)	3.30 (−0.225, −0.090, 0.958)	1.77 (−0.020, −0.970, 0.162)
C_4	3.44 (0.282, −0.508, 0.945)	3.06 (−0.732, 0.589, 0.327)	2.30 (−0.622, −0.629, 0.017)
C_5	4.66 (0.326, 0.511, 0.543)	3.02 (0.714, −0.787, 0.407)	2.34 (−0.620, −0.347, 0.735)
C_6	5.02 (0.692, −0.233, 0.723)	3.05 (−0.437, 0.791, 0.287)	2.87 (−0.575, −0.566, 0.629)
C_7	6.00 (0.872, −0.536, 0.416)	2.87 (−0.472, −0.728, 0.536)	2.69 (−0.133, 0.429, 0.735)
C_8	5.38 (0.722, −0.811, 0.202)	3.57 (0.415, 0.333, 0.655)	2.93 (−0.554, −0.481, −0.730)
C_9	3.58 (−0.376, 0.687, 0.455)	2.81 (0.228, −0.679, 0.890)	2.26 (−0.898, −0.259, 0.022)
C_{10}	3.50 (−0.851, 0.493, 0.264)	3.15 (0.518, 0.326, 0.586)	1.95 (−0.087, −0.807, 0.766)
C_{11}	6.06 (0.731, −0.684, 0.547)	3.68 (−0.635, −0.232, 0.753)	3.13 (0.249, 0.691, 0.365)
C_{12}	5.77 (−0.172, 0.631, 0.552)	4.36 (0.522, −0.694, 0.759)	2.77 (−0.836, −0.347, 0.345)
C_{13}	5.60 (0.760, −0.712, 0.455)	4.70 (0.416, 0.685, 0.229)	2.90 (−0.499, −0.152, 0.860)
C_{14}	5.76 (0.678, −0.317, 0.743)	3.73 (−0.278, 0.860, 0.222)	2.95 (−0.680, −0.401, 0.632)

[a] Direction cosines are referred to triclinic axes. [b] Root-mean-square displacements along the ellipsoid axes are presented in terms of isotropic thermal parameters, B, since most readers probably have more feeling for these than for the equivalent root-mean-square displacement $(\overline{u^2})^{1/2}$. The transformation is trivial: $(\overline{u^2})^{1/2} = (B/8\pi^2)^{1/2}$.

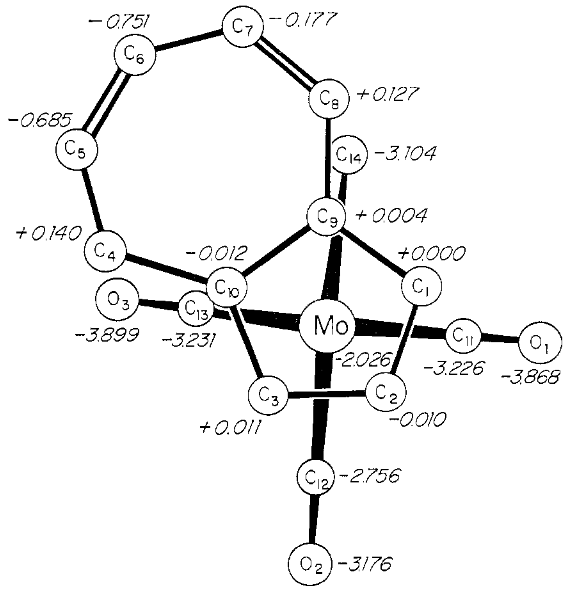


Figure 2.—The molybdenum coordination sphere. The molecule is projected onto the least-squares plane through the π-cyclopentadienyl system; numbers represent the distances (in angstroms) of the atoms from this plane.

$(CO)_3R]_2$ (R = alkyl, fluoroalkyl, acyl, fluoroacyl, aryl, perhaloaryl) will result in more precise determinations of molybdenum–carbon bond lengths than has previously been possible with other systems. [The π-C_5H_5 group in π-$C_5H_5Mo(CO)_3R$ systems is prone to give problems due to libration.]

The Diazulene Ligand

The diazulene ligand possesses a crystallographic center of symmetry. Within the limits of experimental error, the carbon atoms of the five-membered ring are coplanar and possess D_{5h} symmetry. [Individual bond lengths range from 1.385 ± 0.015 to 1.439 ± 0.013 Å, averaging 1.412 Å; bond angles range from 106.7 to 110.1° averaging 108.0°.] The seven-membered ring is distinctly nonplanar, owing to the tetrahedral nature of C_4. Individual deviations with respect to the plane of the five-membered ring are shown in Figure 2. Bond distances within the seven-membered ring are each in agreement with accepted values. The $C(sp^3)$–$C(sp^2)$ bonds C_4–C_{10} and C_4–C_5 are, respectively, 1.510 ± 0.013 and 1.509 ± 0.013 Å in length, indis-

TABLE V

BOND LENGTHS AND INTRAMOLECULAR CONTACTS FOR $[C_{10}H_8Mo(CO)_3CH_3]_2$

Atoms	Distance, Å	Atoms	Distance, Å
(a) Distances from Molybdenum Atom			
Mo–C_1	2.359 ± 0.011	Mo–C_{12}	1.996 ± 0.012
Mo–C_2	2.286 ± 0.010	Mo–C_{13}	1.988 ± 0.012
Mo–C_3	2.313 ± 0.010	Mo–C_{14}	2.383 ± 0.010
Mo–C_9	2.439 ± 0.009	Mo···O_1	3.119 ± 0.008
Mo–C_{10}	2.391 ± 0.009	Mo···O_2	3.137 ± 0.009
Mo–C_{11}	2.003 ± 0.011	Mo···O_3	3.128 ± 0.009
(b) Distances within Diazulene Ligand			
C_1–C_2	1.385 ± 0.015	C_{10}–C_4	1.510 ± 0.013
C_2–C_3	1.410 ± 0.014	C_4–C_5	1.509 ± 0.013
C_3–C_{10}	1.415 ± 0.013	C_5–C_6	1.344 ± 0.014
C_{10}–C_9	1.439 ± 0.013	C_6–C_7	1.441 ± 0.015
C_9–C_1	1.412 ± 0.014	C_7–C_8	1.353 ± 0.015
C_4–C_4*	1.561 ± 0.018	C_8–C_9	1.462 ± 0.014
(c) Carbonyl Bond Lengths			
C_{11}–O_1	1.115 ± 0.014	C_{13}–O_3	1.140 ± 0.015
C_{12}–O_2	1.141 ± 0.015		
(d) Contacts within the $Mo(CO)_3CH_3$ Moiety			
O_1···O_2	3.903 ± 0.012	C_{11}···C_{12}	2.506 ± 0.016
O_1···O_3	5.020 ± 0.013	C_{11}···C_{13}	3.184 ± 0.016
O_1···C_{14}	3.321 ± 0.014	C_{11}···C_{14}	2.614 ± 0.015
O_2···O_3	4.038 ± 0.013	C_{12}···C_{13}	2.567 ± 0.017
O_2···C_{14}	5.043 ± 0.014	C_{12}···C_{14}	3.325 ± 0.016
O_3···C_{14}	3.345 ± 0.014	C_{13}···C_{14}	2.607 ± 0.016
(e) Contacts Involving π-Cyclopentadienyl Group (Cyclically)			
C_1···C_{14}	3.598 ± 0.015	C_3···O_2	3.838 ± 0.013
C_1···C_{11}	3.323 ± 0.016	C_3···C_{13}	3.518 ± 0.015
C_1···O_1	4.176 ± 0.014	C_3···O_3	4.450 ± 0.014
C_2···C_{11}	3.413 ± 0.015	C_{10}···C_{13}	3.251 ± 0.015
C_2···O_1	4.309 ± 0.013	C_{10}···O_3	4.100 ± 0.013
C_2···C_{12}	3.052 ± 0.016	C_{10}···C_{14}	3.770 ± 0.014
C_2···O_2	3.899 ± 0.014	C_9···C_{14}	3.211 ± 0.014
C_3···C_{12}	3.001 ± 0.015		

TABLE VI

BOND ANGLES WITHIN THE $[C_{10}H_8Mo(CO)_3CH_3]_2$ MOLECULE

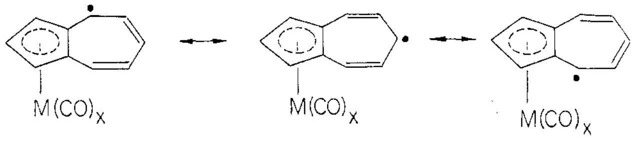
Atoms	Angle, deg	Atoms	Angle, deg
(a) Around the Molybdenum Atom			
C_{11}–Mo–C_{12}	77.6 ± 0.5	O_1···Mo···O_2	77.2 ± 0.2
C_{11}–Mo–C_{13}	105.8 ± 0.5	O_1···Mo···O_3	106.9 ± 0.2
C_{11}–Mo–C_{14}	72.6 ± 0.4	O_1···Mo···C_{14}	72.9 ± 0.3
C_{12}–Mo–C_{13}	80.2 ± 0.5	O_2···Mo···O_3	80.3 ± 0.2
C_{12}–Mo–C_{14}	131.6 ± 0.4	O_2···Mo···C_{14}	131.5 ± 0.3
C_{13}–Mo–C_{14}	72.6 ± 0.4	O_3···Mo···C_{14}	73.3 ± 0.3
C_1–Mo–C_2	34.7 ± 0.4	C_{10}–Mo–C_9	34.6 ± 0.3
C_2–Mo–C_3	35.7 ± 0.4	C_9–Mo–C_1	34.2 ± 0.3
C_3–Mo–C_{10}	35.0 ± 0.3		
(b) Carbonyl Groups			
Mo–C_{11}–O_1	178.3 ± 1.0	Mo–C_{13}–O_3	177.8 ± 1.1
Mo–C_{12}–O_2	178.5 ± 1.1		
(c) Angles within the Diazulene Ligand			
C_9–C_1–C_2	110.1 ± 0.9	C_{10}–C_4–C_5	112.9 ± 0.8
C_1–C_2–C_3	107.3 ± 0.9	C_4–C_5–C_6	127.9 ± 0.9
C_2–C_3–C_{10}	109.1 ± 0.9	C_5–C_6–C_7	128.3 ± 1.0
C_3–C_{10}–C_9	106.7 ± 0.8	C_6–C_7–C_8	128.4 ± 1.0
C_{10}–C_9–C_1	106.7 ± 0.9	C_7–C_8–C_9	125.1 ± 1.0
		C_8–C_9–C_{10}	127.8 ± 0.9
C_1–C_9–C_8	125.3 ± 0.9	C_9–C_{10}–C_4	126.5 ± 0.8
C_3–C_{10}–C_4	126.2 ± 0.9		
C_5–C_4–C_4*	109.7 ± 1.0		
C_{10}–C_4–C_4*	109.8 ± 1.0		

tinguishable from the anticipated value of 1.51 Å; bond lengths within the "butadiene" system C_5–C_6–C_7–C_8 (1.344 ± 0.014, 1.441 ± 0.015, 1.352 ± 0.015 Å) may be compared with distances obtained from an electron diffraction study of *trans*-buta-1,3-diene[30] (1.337 ± 0.005, 1.483 ± 0.01, 1.337 ± 0.005 Å); the C_8–C_9 linkage (1.462 ± 0.014 Å) is in the range expected for a single $C(sp)^2$–$C(sp^2)$ bond. Angles within the seven-membered rings are uniformly greater than the appropriate ideal sp^2 or sp^3 value. The angle C_{10}–C_4–C_5 (112.9 ± 0.8°) is 4.4σ above the ideal tetrahedral value of 109° 28′; other (sp^2) angles range from 125.1 to 128.4°. These systematic increases in bond angle are presumably due to the angular requirements for a seven-membered ring system, since the internal angle required for a regular, planar heptagon is 128.6°. [Although the crystal structure of azulene is disordered,[31] angles within the seven-membered rings of the azulene system in the azulene-1,3,5-trinitrobenzene molecular complex[32] and in azulene-1,3-dipropionic acid[33] are found to vary from 127.15 to 129.47° and from 125.9 to 130.2°, respectively.]

Discussion

The results of this present study, combined with evidence obtained from previous crystallographic analyses of azulenediiron pentacarbonyl,[6–7] azulenedimolybdenum hexacarbonyl[8–9] and guaiazulenedimolybdenum hexacarbonyl,[8] help to put the chemistry of azulene–metal–carbonyl complexes on a more systematic basis. The reaction of a transition metal carbonyl with azulene under the usual, rather drastic, conditions (*i.e.*, prolonged refluxing in solvent at ~140°) may be thought of as involving the following steps.

(i) The initial step in the reaction is the utilization of the five-membered ring to give a pseudo-π-cyclopentadienyl complex (III–V).



III IV V

(ii) If the metal has already attained an 18-electron configuration (*i.e.*, if the analogous π-$C_5H_5M(CO)_x$ is a stable, diamagnetic monomer), no metal–metal bond can be formed, and subsequent processes must affect the seven-membered ring. There would appear to be two main reaction pathways: (a) The radical may dimerize *via* a carbon–carbon bond (as in the structure here reported). The stereochemistry of dimerization

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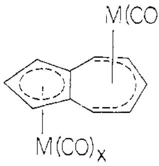
[30] A. Almenningen, O. Bastiansen, and M. Traettenberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

[31] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

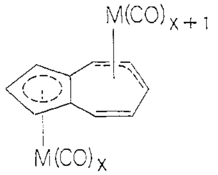
[32] A. W. Hanson, *ibid.*, **19**, 19 (1965).

[33] H. L. Ammon and M. Sundaralingam, *J. Am. Chem. Soc.*, **88**, 4794 (1966).

will depend on the relative energies for localization of an electron on the *ortho* and *para* positions. Qualitatively, localization at the *ortho* position would seem to be the more probable, since it conserves a conjugated butadiene system. [Although the stereochemistry of the $[C_{10}H_8Mo(CO)_3CH_3]_2$ molecule is established as involving *ortho-ortho* coupling, no definitive information is yet available on $[C_{10}H_8V(CO)_4]_2$[4] or $[C_{10}H_8Mn(CO)_3]_2$.[3]] (b) The five available carbon atoms in the seven-membered ring may combine with a further metal carbonyl residue, to form a *trans* product such as VI[34] or VII. [A *cis* product is unlikely since it would require the metal atoms to be within bonding distance.]

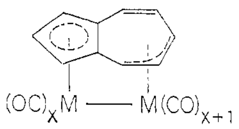


VI

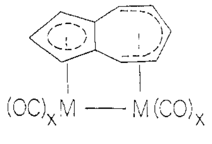


VII

(iii) If the metal atom in the pseudo-π-cyclopentadienyl complex (III–V) has only a 17-electron configuration, a metal–metal bond will be formed and a second metal carbonyl residue will be linked to the seven-membered ring *via* a π-allyl (VIII) or π-pentadienyl (IX) linkage. The reason why azulenediiron (I) contains a π-allyl–metal linkage whereas azulenedimolybdenum hexacarbonyl (II) has a π-pentadienyl–metal bond is not fully understood. It may be due to the 3d orbitals of the iron atom being too small to overlap effectively with all five atoms in the prospective π-pentadienyl system, or to the intrinsic stability of the $Fe(CO)_3$ system *per se*. It is hoped that current experiments involving the isoelectronic azulene–ruthenium–carbonyl system may clarify this problem.



VIII



IX

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(34) We have recently prepared a complex which mass spectrometric analysis indicates to be $C_{10}H_8Mn_2(CO)_6$. We expect this to have structure VI. NOTE ADDED IN PROOF.—This has now been confirmed (P. H. Bird and M. R. Churchill, *Chem. Commun.*, in press).

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY AND MATERIALS RESEARCH LABORATORY,
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Crystal Structure of a Binuclear Vanadyl(IV) Anion. Tetrasodium Divanadyl(IV) *d*-Tartrate *l*-Tartrate Dodecahydrate[1]

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The crystal structure of the sodium salt of divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate ($Na_4[VO\text{-}dl\text{-}C_4H_2O_6]_2 \cdot 12H_2O$) has been determined by Fourier methods, and the positional and anisotropic thermal parameters of the atoms were refined by least-squares methods on three-dimensional photographic data. The crystals are orthorhombic, space group Pbca, with $a = 19.85$, $b = 10.76$, and $c = 12.28$ A. The measured density is 1.85 g/cm^3 while that calculated for eight formula units of $Na_2[VOC_4H_2O_6] \cdot 6H_2O$ is 1.858 g/cm^3. The tetranegative dimeric anions contain two VO^{2+} ions bridged by a *d*-tartrate and an *l*-tartrate group which have lost all of the carboxyl and hydroxyl hydrogen atoms to give tetranegative tartrate ions. The vanadium atoms are situated in a normal square-pyramidal coordination site in contrast to the distorted trigonal-bipyramidal coordination found in $(NH_4)_4[VO\text{-}d\text{-}C_4H_2O_6]_2 \cdot 2H_2O$. The vanadium–vanadium distance is 4.082 A. The final R factor is 0.10 for 2629 nonzero reflections.

Introduction

Recently, we reported[2] the characterization and comparison of the two different complexes of vanadyl(IV) obtained with *d*-tartaric and racemic tartaric acids. Arguing purely from aqueous solution evidence and molecular models, we postulated structures for these two isomers consisting of two vanadyl(IV) ions bridged by two tartrate anions which have lost the protons from

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(2) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).