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The Crystal Structure of a Molybdenum Acetyl: *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$

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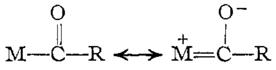
The crystal and molecular structure of *trans*-dicarbonyl-π-cyclopentadienyl(triphenylphosphine)molybdenum acetyl, *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$, has been determined by single-crystal X-ray diffraction techniques. The final discrepancy index is $R_F = 7.43\%$ for 2119 independent nonzero reflections collected with a 0.01°-incrementing Buerger automated diffractometer. The compound crystallizes in the centrosymmetric monoclinic space group C2/c (C_{2h}^6; no. 15) with $a = 26.13 \pm 0.03$ Å, $b = 11.91 \pm 0.02$ Å, $c = 17.81 \pm 0.03$ Å, $\beta = 121.91 \pm 0.03°$, $Z = 8$. Observed and calculated densities are, respectively, 1.50 ± 0.04 and 1.473 g cm^{-3}. The complex exists as a monomeric molecular species, the central molybdenum atom being formally heptacoordinate. The molybdenum–acyl linkage, Mo–C = 2.264 ± 0.014 Å, is significantly (in fact, 8.5σ) shorter than the molybdenum–alkyl distance of 2.383 ± 0.010 Å in $[C_{10}H_8Mo(CO)_3CH_3]_2$. This structural analysis thus provides the first direct evidence for d_π–p_π back-donation in transition metal acyls.

Introduction

Although there are no available data on transition metal–acyl bond lengths, it has been generally accepted that the metal–carbon σ bond is accompanied by some contribution from d_π–p_π metal-to-acyl back-donation. In simple valence-bond terms this has been illustrated[1] by canonical structures such as



$$M-\overset{\overset{O}{\|}}{C}-R \longleftrightarrow \overset{+}{M}=\overset{\overset{O^-}{|}}{C}-R$$

I II

Since it is well-established that molybdenum–carbon bond lengths are remarkably sensitive to changes in bond order[2] (extreme values for Mo–C bond distances being 2.41 Å for the Mo–CH_2 linkage in π-$C_5H_5Mo(CO)_3CH_2CO_2H$[3] and 1.94 Å for the Mo–CO bonds in $[NH_2(CH_2)_2NH(CH_2)_2NH_2]Mo(CO)_3$[2]), it was expected that measurement of a molybdenum–acyl bond length would provide direct evidence for the existence of d_π–p_π back-donation in transition metal acyls. Seeing that structural information on π-$C_5H_5Mo(CO)_3X$ and related species had been particularly well documented,[3-8] a study involving a member of the series π-$C_5H_5Mo(CO)_3COC_nH_{2n+1}$ was thought desirable. Unfortunately, none of these species is sufficiently stable[9,10] to allow a single-crystal X-ray diffraction study. However, both simple fluorinated acyls $[\pi$-$C_5H_5Mo(CO)_3COC_nF_{2n+1}]$[10] and monotriphenylphosphine derivatives of the nonfluorinated acyls $[\pi$-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_nH_{2n+1}]$[11] are rather more stable. This paper describes an X-ray structural analysis of π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$. [A crystallographic study of π-$C_5H_5Mo(CO)_3COCF_3$ has also been undertaken and will be reported at a later date.[12]]

Experimental Section

π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ was prepared in tetrahydrofuran following the method of Barnett and Treichel.[11] In contrast to previously reported results,[11] the infrared spectrum of the product (9 mg/ml in $CHCl_3$) was found to exhibit *two* ketonic stretching frquencies (1616 and 1591 cm^{-1}). Possibly, these bands are due to isomers of the complex with the triphenylphosphine ligand *cis* and *trans* (respectively) to the acetyl group. No attempt was made to separate isomers; the bright yellow crystals that were isolated from the reaction mixture appeared to have a single habit and (as shown later) are composed of *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$.

Unit Cell and Space Group

Optical examination and the observed reciprocal lattice symmetry of C_{2h} (2/m) indicated that the crystals belonged to the monoclinic system. Unit-cell parameters, obtained from a least-squares analysis of high-angle data (Cu Kα_2, λ 1.54433 Å) on $h0l$ and $hk0$ Weissenberg photographs, taken at 23 ± 2° and calibrated with aluminum ($a_{Al} = 4.049$ Å) are: $a = 26.13 \pm 0.03$ Å, $b = 11.91 \pm 0.02$ Å, $c = 17.81 \pm 0.03$ Å, $\beta = 121.91 \pm 0.03°$. The unit-cell volume is 4704 Å^3. The observed density, obtained by flotation in aqueous zinc iodide solution ($\rho_{obsd} = 1.50 \pm 0.04$ g cm^{-3}) is in satisfactory agreement with the value calculated for $M = 522$ and $Z = 8$ ($\rho_{calcd} = 1.473$ g cm^{-3}). A survey of $h0l$, $h1l$, $h2l$ Weissenberg photographs, and $0kl$, $1kl$, $2kl$, $hk0$, $hk1$, $hk2$ precession photographs (all taken with Mo Kα radiation), revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $h = 2n + 1$, $l = 2n + 1$, compatible with space groups Cc or C2/c. No piezoelectric test was performed, but the Patterson synthesis (*vide infra*) revealed a set of Mo···Mo vectors consistent with the centrosymmetric space group C2/c (C_{2h}^6; no. 15).

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Collection and Reduction of X-Ray Data

Two crystals were used for data collection. Crystal I, a parallelepiped with dimensions 0.44 × 0.20 × 0.30 mm, was mounted on its *b* axis; crystal II, an irregular octahedron with dimensions 0.54 × 0.10 × 0.10 mm, was mounted on its *c* axis.

Intensity data (Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01°-incrementing Buerger automated diffractometer using the customary "stationary background, ω scan, stationary background" counting sequence. The method and apparatus have been described in detail in a previous paper.[13] Specific details of the present analysis include: (i) The angle scanned (ω) is given by $\omega = [2.0 + (0.6/L)]°$ where $1/L$ is the Lorentz factor. (ii) The scan speed was 2°/min. (iii) Backgrounds (B_1 and B_2) were each counted for one-fourth the time of the main scan (C). (iv) Within a level, check reflections were remeasured after 20 reflections had been counted; also, at the end of each level the check reflection for the appropriate zero level, *i.e.*, $h0l$ or $hk0$, was remeasured. (No appreciable variations were detected in either case, indicating stability both of crystal and of electronics.) (v) The intensity of a reflection, $I(hkl)$, was calculated as: $I(hkl) = C - 2(B_1 + B_2)$.

Standard deviations assigned to reflections were: $I(hkl) \geqslant 1225$, $\sigma(hkl) = 0.1[I(hkl)]$; $1225 \geqslant I(hkl) \geqslant \delta$, $\sigma(hkl) = 3.5[I(hkl)]^{1/2}$; $I(hkl) < \delta$, reflection rejected. [$\delta = 3(C + B_1 + B_2)^{1/2}$—*i.e.*, the maximum probable error based on counting statistics.] Reflections were also rejected if B_1 and B_2 were asymmetric by more than 50%, since this had been found to be symptomatic of overlap of adjacent reflections.

Equiinclination geometry was used in collecting data for the zones hNl (N = 0–11) from crystal I. (This represents complete data out to $\sin\theta = 0.36$. No higher angle data were collected because long-exposure Weissenberg photographs had previously shown there to be little data beyond this limit.) In order to correlate these *b*-axis data, the zones hkM (M = 0–9) were collected from crystal II. Lorentz, polarization, and absorption corrections were applied to all data using a local modification of Burnham's GNABS.[14] (With μ = 6.57 cm^{-1}, transmission factors varied from 0.81 to 0.90 for crystal I and from 0.75 to 0.97 for crystal II.) All data were merged to a common scale by a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.[15] (The mean R factor for scaling was ~6%.) The resulting 2119 independent reflections were used in a Wilson plot, from which were obtained the approximate absolute scale and the over-all thermal parameter.

Determination of the Crystal Structure

The coordinates of the molybdenum atom (x = 0.131, y = 0.087, z = 0.005) were quickly obtained from a three-dimensional Patterson synthesis[16] which had been sharpened such that the average intensity was independent of $\sin\theta$ and which had the origin peak reduced to the height of a single Mo···Mo vector.[17] A structure-factor calculation,[18] based on molybdenum contributions only (R_F = 0.50),[19] was used to phase an electron density map[16] from which the coordinates of the phosphorus atom were obtained. From this stage the structure was solved by a series of Fourier, structure-factor, Fourier sequences, each successive Fourier synthesis being phased by an increasing number of atoms until all 32 nonhydrogen atoms had been located. Refinement[20] of positional and individual isotropic thermal parameters for all 32 atoms converged at $R_F = 0.114$, $R_{wF^2} = 0.080$.[19] A difference-Fourier map was now calculated[20] and a search made for the 23 hydrogen atoms in the structure. Although there were no indications of the three hydrogen atoms associated with the acetyl group, peaks ranging from 0.3 to 0.8 e Å^{-3} were found in locations corresponding to those calculated for π-cyclopentadienyl and phenyl hydrogen atoms. (On an "observed" electron density synthesis at this stage, the average carbon atom peak height was ~5 e Å^{-3}.) However, since there were also a number of spurious peaks of comparable magnitude to those "due" to hydrogen atoms, it cannot be claimed that the hydrogen atoms were *unambiguously* located. Nevertheless, inclusion of the 20 phenyl and π-cyclopentadienyl hydrogen atoms (each with B = 6.0 Å^2) in a structure-factor calculation resulted in an immediate decrease in the discrepancy indices to $R_F = 0.107$, $R_{wF^2} = 0.073$. Since the difference-Fourier map had also shown asymmetric features around many of the atomic positions, refinement was continued using anisotropic thermal parameters[21] for each of the 32 nonhydrogen atoms; hydrogen atoms were placed in calculated positions[22] but were not allowed to refine. The 289 variables were partitioned into two submatrices so that all parameters could be refined in a single cycle. Matrix I (154 variables) included three positional parameters and six anisotropic thermal parameters for each of the π-cyclopentadienyl, acetyl, carbonyl, C_{21}, C_{31}, C_{41}, Mo, and P atoms, plus the scale factor. Matrix II (135 variables) consisted of positional and thermal parameters for the remaining 15 carbon atoms of the triphenyl-

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(13) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(14) GNABS is a general absorption program for the IBM 7094, by C. W. Burnham.

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

(16) Initial Patterson and Fourier syntheses were computed using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende.

(17) Sharpened Patterson coefficients were calculated using an updated version of PASHCO, an IBM 7094 program by B. R. Penfold; see also R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Cryst.*, **14**, 598 (1961).

(18) During the early stages of the structural analysis, structure factor calculations were carried out using ORFLS, a FORTRAN least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

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

(20) During the latter part of the structural investigation, all crystallographic computations were performed using CRYRM, an integrated set of crystallographic routines for the IBM 7094 written by R. E. Marsh and his co-workers at the California Institute of Technology.

(21) Anisotropic thermal parameters (T) are defined by: $T = \exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$.

(22) Hydrogen atom positions were recalculated at the end of each cycle and were defined such that the π-cyclopentadienyl and phenyl groups maintained their appropriate D_{5h} or pseudo-D_{6h} symmetry with d(C–H) = 1.080 Å.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS) FOR *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$[a]

H	K	FO	FC
L = 0			
8	0	216	199
12	0	105	99
14	0	95	88
16	0	93	87
18	0	179	178
20	0	67	39
22	0	121	116
7	1	38	17
9	1	94	91
11	1	168	171
13	1	69	49
15	1	139	139
17	1	39	4
19	1	57	51
21	1	26	1
4	2	163	162
6	2	134	128
8	2	15	8
10	2	62	56
12	2	149	144
14	2	94	91
16	2	146	146
18	2	51	36
20	2	69	64
22	2	19	12
1	3	268	244
3	3	72	61
5	3	69	61
7	3	24	29
9	3	43	26
11	3	63	57
13	3	97	97
15	3	79	69
17	3	49	45
19	3	33	27
21	3	50	49
2	4	59	56
4	4	170	171
6	4	188	178
8	4	139	145
10	4	37	32
12	4	146	150
14	4	84	83
16	4	125	136
18	4	21	10
20	4	77	77
1	5	258	259
3	5	177	176
5	5	243	237
7	5	135	139
9	5	159	155
11	5	79	82
13	5	65	66
15	5	94	83
17	5	34	34
19	5	126	122
0	6	226	237
2	6	28	26
4	6	226	230
8	6	173	177
10	6	65	63
12	6	64	62
16	6	73	69
18	6	73	65
1	7	43	34
3	7	51	46
5	7	66	45
7	7	125	110
9	7	58	47
11	7	98	100
13	7	81	76
15	7	59	57
17	7	51	52
0	8	54	5
2	8	55	52
6	8	22	10
10	8	18	6
12	8	15	11
1	9	33	36
3	9	16	12
5	9	23	9
7	9	66	66
9	9	43	27
11	9	110	111
13	9	49	52
0	10	209	210
2	10	12	13
4	10	127	123
6	10	56	58
8	10	120	117
10	10	44	39
12	10	82	72
3	11	71	67
[illegible]	11	68	66
9	11	70	66
0	12	61	30
2	12	39	32
L = 1			
5	1	49	53
7	1	173	175
-7	1	215	205
9	1	74	81
-9	1	155	150
11	1	33	18
-11	1	52	56
13	1	41	36
15	1	25	6
-15	1	32	34
17	1	45	46
-17	1	119	125
19	1	38	35
-19	1	40	25
21	1	49	55
-21	1	89	86
-23	1	26	11
6	2	241	250
-6	2	217	220
8	2	81	81
10	2	167	179
-10	2	125	137
-12	2	143	144
14	2	156	156
-14	2	173	177
16	2	72	67
-16	2	35	30
18	2	138	141
-18	2	76	78
20	2	36	22
-20	2	53	50
-22	2	49	41
1	3	58	37
-1	3	220	228
3	3	277	268
-3	3	176	177
5	3	274	274
-5	3	204	209
7	3	129	137
-7	3	101	101
9	3	161	275
-9	3	240	241
11	3	103	101
-11	3	41	45
13	3	223	226
-13	3	214	223
15	3	90	90
-15	3	34	33
17	3	103	101
-17	3	113	113
19	3	49	52
-19	3	73	79
-21	3	93	92
0	4	145	140
2	4	370	377
-2	4	156	168
-4	4	232	217
6	4	140	142
-6	4	100	112
8	4	14	4
-8	4	68	64
10	4	76	74
-10	4	121	119
12	4	66	16
14	4	28	11
-14	4	50	55
-16	4	95	99
18	4	58	35
-18	4	89	79
20	4	81	79
-20	4	76	78
1	5	100	98
-1	5	34	33
3	5	30	34
-3	5	111	112
7	5	61	63
-7	5	73	66
9	5	29	28
11	5	17	0
-11	5	48	48
13	5	18	14
15	5	12	1
17	5	21	15
-17	5	18	16
-19	5	35	22
-21	5	24	21
2	6	191	194
-2	6	108	108
-4	6	75	76
6	6	42	45
-6	6	128	130
-10	6	64	65
12	6	72	0
-12	6	46	47
14	6	23	18
-14	6	37	29
16	6	30	20
-16	6	66	71
18	6	13	12
-18	6	27	19
-20	6	71	74
1	7	35	36
-1	7	162	164
3	7	96	102
-3	7	84	86
5	7	145	145
-5	7	181	182
7	7	106	106
-7	7	154	154
9	7	128	130
-9	7	121	123
-11	7	52	50
13	7	117	123
-13	7	62	60
15	7	52	54
17	7	102	103
-17	7	56	54
2	8	66	68
-2	8	108	106
4	8	33	38
-4	8	161	160
6	8	120	123
8	8	79	74
-8	8	99	84
10	8	121	115
-10	8	141	135
12	8	39	40
-12	8	66	69
14	8	133	129
-14	8	128	128
16	8	68	62
1	9	136	141
-1	9	112	108
3	9	65	64
-3	9	103	105
5	9	104	109
-5	9	106	106
7	9	80	67
-7	9	56	44
9	9	95	93
-9	9	97	90
-11	9	61	58
13	9	82	82
-13	9	55	51
-15	9	14	10
0	10	36	38
2	10	89	91
-2	10	80	78
4	10	13	10
6	10	26	24
-6	10	21	24
-8	10	17	14
-10	10	41	4
-12	10	38	28
1	11	33	20
-1	11	13	0
3	11	38	42
-3	11	48	60
-5	11	42	38
-7	11	46	40
-2	12	75	77
L = 2			
4	0	428	403
8	0	282	267
-8	0	99	112
10	0	68	4
-10	0	70	58
12	0	170	177
-12	0	79	84
14	0	66	45
16	0	91	91
-16	0	148	151
18	0	86	87
-18	0	165	165
20	0	51	54
-20	0	136	131
-22	0	82	80
3	1	131	99
5	1	231	219
7	1	73	79
-7	1	181	175
9	1	164	171
-9	1	42	28
11	1	155	153
-11	1	96	107
13	1	80	70
-13	1	30	34
15	1	115	119
-15	1	122	125
17	1	27	3
19	1	62	64
-19	1	79	77
-21	1	15	3
-23	1	45	50
2	2	60	43
4	2	201	187
6	2	131	125
-6	2	125	113
8	2	153	148
10	2	47	46
-10	2	119	115
12	2	90	91
-12	2	131	125
14	2	33	34
16	2	76	72
-16	2	106	111
18	2	67	67
-18	2	44	44
20	2	59	62
-20	2	18	11
-22	2	26	24
1	3	57	55
-1	3	58	62
3	3	38	35
-3	3	213	208
5	3	56	49
-7	3	39	40
9	3	24	9
-9	3	145	134
11	3	95	94
-11	3	75	74
13	3	44	45
-13	3	94	88
15	3	49	48
-15	3	38	37
-17	3	37	37
19	3	15	9
-19	3	22	12
-21	3	20	12
0	4	185	184
2	4	44	38
-2	4	177	163
4	4	56	63
-4	4	252	255
6	4	91	88
-6	4	155	144
8	4	104	114
-8	4	187	192
10	4	87	83
-10	4	75	76
12	4	133	141
-12	4	146	154
14	4	76	76
-14	4	32	29
16	4	83	83
-16	4	95	98
18	4	18	20
-18	4	12	24
-20	4	45	38
-22	4	44	49
1	5	186	192
-1	5	108	116
3	5	124	134
5	5	93	101
-5	5	195	197
7	5	50	52
-7	5	61	67
9	5	129	139
-9	5	164	168
11	5	80	82
-11	5	68	70
13	5	27	28
-13	5	76	76
15	5	102	98
-15	5	117	120
-17	5	21	17
-19	5	137	138
-21	5	32	25
0	6	224	238
2	6	8	12
-2	6	36	39
4	6	238	242
-4	6	193	196
6	6	29	3
8	6	143	149
-8	6	196	200
10	6	33	23
-10	6	53	54
12	6	92	98
-12	6	103	103
14	6	21	10
-14	6	59	61
16	6	50	52
-16	6	57	56
-20	6	65	70
1	7	58	63
3	7	72	68
-3	7	91	91
7	7	117	118
-7	7	61	56
9	7	22	17
11	7	100	102
-11	7	142	144
13	7	47	53
-13	7	23	14
15	7	73	71
-15	7	73	73
-17	7	48	41
-19	7	41	38
0	8	19	20
2	8	9	5
-4	8	46	48
4	8	21	12
6	8	14	19
-6	8	35	30
8	8	32	0
-8	8	19	3
10	8	25	29
-10	8	24	0
12	8	22	26
-12	8	40	13
14	8	18	14
-16	8	22	24
1	9	13	14
-1	9	10	0
-3	9	47	48
-5	9	17	20
7	9	76	80
-7	9	92	97
9	9	11	4
11	9	97	95
-11	9	101	103
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-17	1	17	19
-19	1	46	42
-21	1	28	24
-4	2	30	20
-6	2	33	33
-8	2	64	53
-12	2	47	39
-14	2	15	4
-16	2	34	32
-18	2	27	24
-20	2	31	29
-6	4	48	36
-8	4	77	82
-12	4	82	87
-16	4	72	68
-18	4	25	3
-11	5	82	84
-15	5	43	43
L = 17			
-9	1	30	24
-13	1	27	23
-17	1	68	68
-19	1	14	11
-10	2	51	43
-14	2	61	55
-16	2	20	15
-18	2	61	55
-14	4	29	21

[a] Table gives h, k, $|F_o|$, $|F_c|$ in blocks of constant l.

phosphine ligand. Utilizing this "blocking" of the total matrix, the refinement process converged smoothly in four cycles to the values $R_F = 0.0743$, $R_{wF^2} = 0.0367$, at which stage refinement was judged to be complete since the final suggested shifts in positional and thermal parameters were each less than $^1/_{15}$ of the appropriate estimated standard deviation (esd). A final difference-Fourier synthesis was devoid of significant features, thus confirming the correctness of the structure. The standard deviation for an observation of unit weight (*i.e.*, the "goodness-of-fit"[23]) was 1.81.

Throughout the analysis the scattering factors for neutral phosphorus, oxygen, carbon, and hydrogen were

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(23) The "goodness-of-fit" is defined by $[\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - m)]^{1/2}$, where n = the number of observations (2119) and m = the number of variables (289).

used:[24a] the Thomas–Fermi–Dirac values for neutral molybdenum[24b] were corrected for the real part of the dispersion[24c] ($\Delta f' = -1.7$ electrons) but not for the imaginary component ($\Delta f'' = +0.9$ electron). The residual minimized was $\Sigma w\left||F_o|^2 - |F_c|^2\right|^2$.

Observed and calculated structure factors are shown in Table I, atomic positional and thermal parameters are collected in Table II, and the associated vibration ellipsoids for nonhydrogen atoms are defined in Table III.

Table II

Final Atomic Coordinates and Anisotropic Thermal Parameters[21] ($\times 10^4$) for *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ (with Esd's)[a]

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
MO	-0.12965(4)	+0.09428(7)	+0.49693(6)	12.5(0.2)	48.1(0.9)	40.6(0.6)	4.0(0.5)	21.3(0.6)	5.5(0.9)
P	-0.09009(11)	+0.27998(20)	+0.49166(16)	9.2(0.5)	37.8(2.1)	27.1(1.5)	4.5(1.7)	15.2(1.6)	0.7(2.7)
O1	-0.0703(4)	+0.0315(7)	+0.3929(6)	26(2)	57(7)	87(7)	12(7)	73(7)	[illegible]
O2	-0.2498(4)	+0.2221(7)	+0.3816(5)	[illegible]	63(7)	56(6)	17(6)	17(5)	2(10)
O3	-0.1982(5)	-0.1240(7)	+0.4133(7)	37(3)	53(6)	99(8)	-31(7)	46(8)	-14(12)
C1	-0.0938(5)	+0.0608(8)	+0.4303(8)	10(2)	27(8)	51(7)	1(6)	17(5)	3(11)
C2	-0.2060(5)	+0.1753(8)	+0.4215(8)	15(3)	44(8)	40(7)	-16(9)	25(7)	-19(12)
C3	-0.1913(5)	-0.0304(11)	+0.2936(9)	12(3)	87(12)	69(9)	16(9)	27(8)	-28(17)
C4	-0.2216(6)	-0.0026(11)	+0.2939(10)	28(4)	84(11)	59(8)	-7(11)	11(9)	-39(16)
C11	-0.1463(6)	-0.0212(12)	+0.5898(7)	22(3)	103(14)	63(8)	[illegible]	46(9)	77(17)
C12	-0.1377(5)	+0.0872(10)	+0.6255(8)	18(3)	91(12)	48(7)	8(9)	40(8)	47(15)
C13	-0.0788(6)	+0.1217(11)	+0.6532(8)	25(4)	99(13)	28(7)	2(10)	34(8)	38(13)
C14	-0.0499(5)	-0.0350(11)	+0.6385(8)	16(3)	100(12)	53(7)	14(11)	11(7)	47(15)
C15	-0.0914(6)	+0.0540(10)	+0.5973(9)	32(4)	67(10)	65(9)	49(11)	55(11)	53(15)
C21	+0.1294(4)	+0.4070(8)	+0.4332(6)	6(2)	44(8)	16(5)	-4(6)	0(5)	-16(10)
C22	-0.1253(5)	+0.5263(9)	+0.4547(7)	22(3)	61(9)	38(6)	10(8)	44(7)	14(12)
C23	-0.1525(6)	+0.6027(9)	+0.4597(9)	31(4)	43(9)	54(9)	26(9)	-5(10)	29(12)
C24	-0.1841(5)	+0.5980(10)	+0.5019(9)	16(3)	71(11)	55(8)	5(9)	21(8)	-34(15)
C25	-0.1866(5)	+0.5029(10)	+0.5427(8)	24(3)	57(10)	61(8)	-1(9)	27(9)	-32(14)
C26	-0.1590(5)	+0.4077(8)	+0.5384(5)	17(3)	57(9)	42(7)	4(9)	25(7)	-9(12)
C31	-0.0884(4)	+0.2976(6)	+0.3922(7)	16(3)	42(8)	71(5)	4(7)	27(7)	-6(10)
C32	-0.1437(5)	+0.2935(8)	+0.3101(8)	20(3)	54(9)	42(7)	7(8)	33(6)	4(13)
C33	-0.1463(6)	+0.2917(10)	+0.2420(8)	26(4)	85(11)	22(7)	6(10)	30(8)	2(14)
C34	-0.0926(7)	-0.2892(12)	-0.2334(9)	44(5)	[illegible]	28(6)	[illegible]	[illegible]	22(16)
C35	-0.0378(6)	+0.2971(12)	+0.3113(9)	24(4)	166(17)	43(8)	[illegible]	45(10)	47(18)
C36	-0.0351(5)	+0.3005(10)	-0.3927(8)	16(3)	[illegible]	40(8)	20(9)	14(9)	28(14)
C41	-0.0120(4)	+0.3048(9)	-0.5624(8)	10(2)	46(8)	24(6)	-8(7)	17(6)	6(11)
C42	+0.0043(5)	+0.3973(9)	+0.6371([illegible])	12(3)	77(10)	31(6)	2(9)	1(7)	-18(13)
C43	+0.0648(6)	+0.4103(10)	+0.7068([illegible])	27(4)	79(11)	44(5)	-25(11)	27(9)	-35(14)
C44	+0.1060(5)	+0.3353(12)	+0.7184(8)	17(3)	104(13)	43(5)	14(11)	[illegible]	65(16)
C45	+0.0912(5)	+0.2419(10)	+0.6616(9)	17(3)	77(11)	56(6)	[illegible]	43(9)	55(15)
C46	+0.0322(5)	+0.2256(8)	+0.5972(7)	11(3)	69(9)	44(6)	[illegible]	[illegible]	[illegible]
H11	-0.1872	-0.0720	+0.5618	B(ISOTROPIC) = 6.0					
H12	-0.1707	+0.1354	+0.6310	B(ISOTROPIC) = 6.0					
H13	-0.0589	+0.2023	+0.6811	B(ISOTROPIC) = 6.0					
H14	-0.0035	-0.0366	+0.6566	B(ISOTROPIC) = 6.0					
H15	-0.0829	-0.1324	+0.5763	B(ISOTROPIC) = 6.0					
H22	-0.1011	-0.5086	+0.4209	B(ISOTROPIC) = 6.0					
H23	-0.1491	+0.6801	+0.4212	B(ISOTROPIC) = 6.0					
H24	-0.2077	+0.6718	+0.5030	B(ISOTROPIC) = 6.0					
H25	-0.2104	+0.5031	+0.5775	B(ISOTROPIC) = 6.0					
H26	-0.1605	+0.3323	+0.5709	B(ISOTROPIC) = 6.0					
H32	-0.1858	+0.2917	+0.3077	B(ISOTROPIC) = 6.0					
H33	-0.1896	+0.2922	+0.1707	B(ISOTROPIC) = 6.0					
H34	-0.0935	+0.2807	+0.1723	B(ISOTROPIC) = 6.0					
H35	+0.0023	-0.3007	+0.3080	B(ISOTROPIC) = 6.0					
H36	+0.0072	+0.3053	+0.4555	B(ISOTROPIC) = 6.0					
H42	+0.0296	+0.4583	+0.6260	B(ISOTROPIC) = 6.0					
H43	+0.0787	+0.4805	-0.7512	B(ISOTROPIC) = 6.0					
H44	+0.1539	+0.3590	+0.7723	B(ISOTROPIC) = 6.0					
H45	+0.1236	+0.1802	+0.6672	B(ISOTROPIC) = 6.0					
H46	+0.0205	+0.1505	+0.5574	B(ISOTROPIC) = 6.0					

[a] Esd's appear in parentheses after each parameter. They are right-adjusted to the last significant digit of the preceding number.

Table III

Atomic Vibrations Ellipsoids[a,b] for *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$

ATOM	B MAX (D. C.'S MAJOR AXIS)	B MED (D. C.'S MEDIAN AXIS)	B MIN (D. C.'S MINOR AXIS)
MO	4.06 (-0.4298,+0.0986,+0.9891)	2.82 (-0.4526,-0.8836,+0.1376)	2.34 (-0.7813,+0.4577,+0.0528)
P	2.58 (-0.4096,-0.1966,+0.9727)	2.27 (+0.3674,+0.8583,+0.1099)	1.66 (-0.8350,+0.4740,+0.2042)
O1	8.10 (+0.1689,-0.0594,+0.7459)	4.75 (-0.6533,-0.7542,+0.4019)	2.57 (-0.7380,+0.6540,+0.5312)
O2	7.48 (-0.5058,+0.0426,+0.9988)	4.87 (-0.2100,-0.9748,+0.0473)	1.84 (-0.8367,+0.2189,+0.0161)
O3	10.92 (-0.7278,+0.1315,+0.9560)	7.70 (+0.6108,-0.3217,+0.2912)	2.32 (-0.3116,-0.9377,+0.0341)
C1	5.59 (-0.4967,+0.0308,+0.9988)	1.88 (-0.8670,-0.0634,+0.0387)	1.56 (+0.0397,-0.9975,+0.0284)
C2	3.86 (-0.0761,-0.3304,+0.8388)	3.55 (-0.8668,+0.4882,+0.5441)	1.89 (+0.4927,+0.8078,+0.0142)
C3	7.88 (-0.4327,-0.4491,+0.8923)	4.24 (+0.2085,+0.7937,+0.3748)	1.68 (-0.8771,+0.4102,+0.2515)
C4	8.61 (-0.8167,-0.3319,+0.8324)	5.18 (+0.5597,-0.6546,+0.1355)	3.44 (+0.1404,+0.6792,+0.5373)
C11	8.83 (-0.2226,+0.7289,+0.6673)	4.40 (+0.7587,-0.2875,+0.0952)	2.13 (-0.6122,-0.6214,-0.7387)
C12	6.52 (-0.0518,+0.7882,+0.5479)	3.56 (+0.6306,-0.4503,+0.2033)	2.20 (-0.7744,-0.4194,+0.8115)
C13	6.39 (-0.6060,+0.7631,+0.5110)	5.22 (-0.7799,-0.5144,+0.1095)	1.95 (-0.1566,-0.3912,+0.8526)
C14	6.62 (-0.2540,+0.8506,+0.5250)	4.57 (-0.9200,-0.3593,+0.6190)	1.96 (-0.2983,-0.3838,-0.5841)
C15	7.78 (+0.4988,+0.4918,+0.3412)	5.08 (-0.8375,+0.0618,+0.9035)	2.53 (+0.2229,-0.8685,+0.2580)
C21	3.01 (-0.4753,-0.7334,+0.6638)	2.05 (-0.7278,+0.6381,+0.5980)	0.83 (+0.4944,+0.2343,+0.4492)
C22	4.56 (+0.6378,+0.3301,+0.2537)	2.77 (-0.4949,+0.8679,+0.2972)	2.40 (-0.5902,-0.3712,+0.9205)
C23	6.71 (+0.6123,+0.3179,+0.2908)	4.17 (-0.7590,-0.0200,+0.9536)	1.99 (+0.2214,-0.9479,+0.0774)
C24	7.44 (-0.5879,-0.5190,+0.8374)	3.51 (+0.4218,+0.4577,+0.4414)	2.46 (-0.6902,+0.7219,+0.3222)
C25	6.07 (+0.1104,-0.3531,+0.7303)	4.17 (-0.8708,-0.4850,+0.3916)	2.31 (-0.4791,+0.8001,+0.5597)
C26	3.94 (+0.0843,-0.2650,+0.7708)	3.27 (-0.7206,-0.6819,+0.2748)	2.28 (-0.6882,+0.6817,+0.5747)
C31	3.48 (-0.8967,-0.4222,+0.3610)	2.48 (+0.2523,-0.7345,+0.4014)	1.55 (-0.3638,+0.5313,+0.8418)
C32	4.11 (+0.6282,+0.3166,+0.2712)	3.58 (-0.6445,-0.2999,+0.9377)	2.91 (-0.4359,+0.8999,+0.2171)
C33	5.43 (-0.9692,-0.1247,+0.3322)	4.89 (-0.1327,+0.9909,+0.0901)	2.76 (-0.2074,-0.0510,+0.9389)
C34	11.19 (-0.6884,-0.6320,+0.0619)	4.88 (+0.4051,-0.7420,+0.2393)	1.16 (-0.6016,+0.2236,+0.9690)
C35	10.16 (+0.1930,-0.9371,+0.1448)	4.19 (-0.6811,-0.3413,+0.1898)	2.60 (-0.7063,-0.0730,+0.9711)
C36	6.71 (+0.1710,+0.9156,+0.2184)	3.61 (-0.2162,-0.3951,+0.6436)	1.83 (-0.9613,+0.0740,+0.7335)
C41	2.90 (-0.5972,+0.6232,+0.7443)	2.42 (-0.5687,-0.7729,+0.5394)	1.88 (+0.5656,-0.1192,+0.3937)
C42	5.15 (-0.5271,-0.7274,+0.6515)	3.57 (-0.6462,+0.6788,+0.6376)	2.03 (+0.5519,+0.1001,+0.4111)
C43	7.27 (-0.9186,-0.3907,+0.5352)	5.39 (-0.2357,-0.6608,+0.7295)	2.50 (+0.3170,-0.6408,+0.4259)
C44	7.85 (-0.3602,+0.7521,+0.6589)	4.60 (-0.8786,-0.4724,+0.5241)	2.20 (+0.3136,-0.4596,+0.5396)
C45	6.40 (-0.3040,+0.5902,+0.7955)	3.56 (+0.4045,-0.6307,+0.3484)	2.86 (-0.8625,-0.5038,+0.4958)
C46	3.81 (-0.6552,+0.1923,+0.9665)	3.43 (-0.2358,-0.9708,-0.1620)	2.06 (+0.7177,-0.1434,+0.1990)

[a] Direction cosines are referred to the monoclinic axes. [b] Atom vibration ellipsoids are presented in terms of the isotropic thermal parameter B. The transformation to root-mean-square displacment, $(\overline{U^2})^{1/2}$ is: $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$.

The Molecular Structure

Figure 1 depicts the molecule projected down a. The numbering scheme is such that the digit in the tens column designates the ring to which an atom belongs and a hydrogen atom is identified by the number of the carbon atoms to which it is bonded. Bond lengths and intramolecular contacts (with esd's) are shown in Table IV; bond angles (with esd's) are collected in Table V.

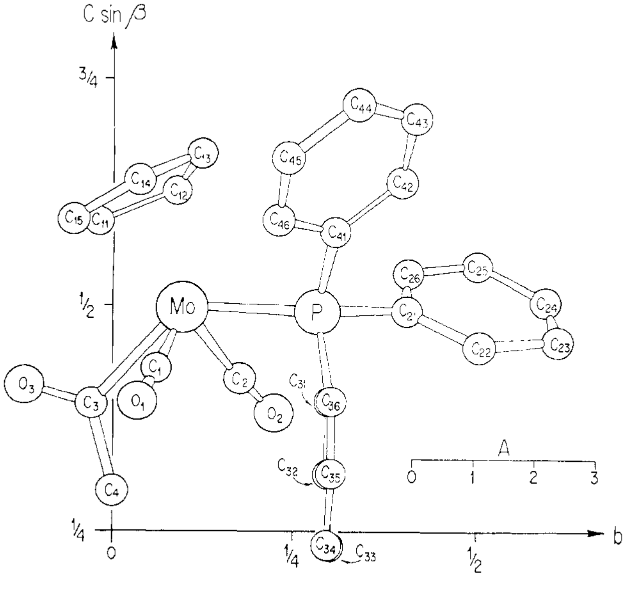

Figure 1.—The molecule viewed along a.

As expected, the central molybdenum atom is bonded directly to two carbonyls, a triphenylphosphine, an acetyl, and a π-cyclopentadienyl ligand: the triphenylphosphine ligand lies opposite the acetyl group, so the complex is *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$-$COCH_3$. The molecule may be regarded as a heptacoordinate d^4 Mo(II) complex.[25] Most previously investigated π-$C_5H_5Mo(CO)_3X$ (and related) species[4-8] have the Mo–X bond lying immediately below one carbon atom of the π-cyclopentadienyl system. However, in the present molecule, as in π-$C_5H_5Mo(CO)_3$–$Sn[\pi$-$C_5H_5Fe(CO)_2]_2Cl$,[26] the substituent lies below the center of the bond between two carbon atoms of the five-membered ring ($C_3 \cdots C_{11} = 3.043$ Å, $C_o \cdots C_{15} = 3.168$ Å). Despite this anomaly, the arrangement of monodentate ligands around the molybdenum atom is

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(24) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England: (a) p 202; (b) p 211; (c) p 216.

(25) Assuming that (i) the π-cyclopentadienyl ligand is regarded as a formally tridentate, six-electron donor, *i.e.*, π-$C_5H_5^-$, and (ii) the acetyl ligand is regarded as the CH_3CO^- anion.

(26) J. E. O'Connor and E. R. Corey, *J. Am. Chem. Soc.*, **89**, 3930 (1967).

TABLE IV

BOND DISTANCES AND INTRAMOLECULAR CONTACTS WITHIN THE *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ MOLECULE

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum Atom			
Mo–P	2.473 (3)	Mo–C$_{11}$	2.332 (15)
Mo···O$_1$	3.102 (11)	Mo–C$_{12}$	2.376 (14)
Mo···O$_2$	3.099 (10)	Mo–C$_{13}$	2.358 (11)
Mo···O$_3$	3.068 (10)	Mo–C$_{14}$	2.357 (12)
Mo–C$_1$	1.934 (13)	Mo–C$_{15}$	2.310 (13)
Mo–C$_2$	1.976 (13)		
Mo–C$_3$	2.264 (14)		
(ii) Distances within Carbonyl Groups			
C$_1$–O$_1$	1.172 (17)	C$_2$–O$_2$	1.124 (17)
(iii) Distances within the Acetyl Group			
C$_3$–O$_3$	1.211 (16)	C$_3$–C$_4$	1.550 (20)
(iv) Distances within the π-Cyclopentadienyl Ring			
C$_{11}$–C$_{12}$	1.405 (19)	C$_{14}$–C$_{15}$	1.415 (20)
C$_{12}$–C$_{13}$	1.408 (22)	C$_{15}$–C$_{11}$	1.422 (25)
C$_{13}$–C$_{14}$	1.380 (20)		
(v) Distances in the Triphenylphosphine Ligand			
P–C$_{21}$	1.836 (10)	P–C$_{41}$	1.836 (11)
P–C$_{31}$	1.831 (11)		
C$_{21}$–C$_{22}$	1.399 (14)	C$_{31}$–C$_{32}$	1.403 (17)
C$_{22}$–C$_{23}$	1.376 (18)	C$_{32}$–C$_{33}$	1.356 (19)
C$_{23}$–C$_{24}$	1.380 (23)	C$_{33}$–C$_{34}$	1.388 (27)
C$_{24}$–C$_{25}$	1.368 (18)	C$_{34}$–C$_{35}$	1.370 (22)
C$_{25}$–C$_{26}$	1.371 (18)	C$_{35}$–C$_{36}$	1.417 (20)
C$_{26}$–C$_{21}$	1.380 (17)	C$_{36}$–C$_{31}$	1.378 (20)
C$_{41}$–C$_{42}$	1.381 (14)	C$_{44}$–C$_{45}$	1.421 (19)
C$_{42}$–C$_{43}$	1.408 (20)	C$_{45}$–C$_{46}$	1.362 (19)
C$_{43}$–C$_{44}$	1.361 (22)	C$_{46}$–C$_{41}$	1.404 (16)
(vi) Intramolecular Contacts from the π-Cyclopentadienyl Group to Other Ligands (Cyclically)			
C$_1$···C$_{14}$	3.271	C$_2$···C$_{11}$	3.457
C$_1$···C$_{15}$	3.244	C$_2$···C$_{12}$	3.262
C$_3$···C$_{15}$	3.168	P···C$_{13}$	3.316
C$_3$···C$_{11}$	3.043		

TABLE V

BOND ANGLES IN *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ (IN DEGREES)

(i) Around Molybdenum Atom			
P–Mo–C$_1$	78.3 (3)	P–Mo···O$_1$	80.1 (2)
P–Mo–C$_2$	79.8 (4)	P–Mo···O$_2$	80.1 (2)
P–Mo–C$_3$	132.7 (4)		
C$_1$–Mo–C$_2$	107.9 (5)	O$_1$···Mo···O$_2$	111.2 (3)
C$_1$–Mo–C$_3$	73.2 (5)	O$_1$···Mo–C$_3$	72.7 (4)
C$_2$–Mo–C$_3$	74.2 (5)	O$_2$···Mo–C$_3$	74.9 (4)
P–Mo–c.o.g.[a]	116.5		
C$_1$-Mo–c.o.g.[a]	125.2	O$_1$···Mo–c.o.g.[a]	123.1
C$_2$–Mo–c.o.g.[a]	126.2	O$_2$···Mo–c.o.g.[a]	124.7
C$_3$–Mo–c.o.g.[a]	110.8		
C$_{11}$–Mo–C$_{12}$	34.7 (5)	C$_{14}$–Mo–C$_{15}$	35.3 (5)
C$_{12}$–Mo–C$_{13}$	34.6 (5)	C$_{15}$–Mo–C$_{11}$	35.7 .5)
C$_{13}$–Mo–C$_{14}$	34.0 (5)		
(ii) In Carbonyl Groups			
Mo–C$_1$–O$_1$	173.9 (9)	Mo–C$_2$–O$_2$	175.9 (12)
(iii) In Acetyl Ligand			
Mo–C$_3$–C$_4$	121.2 (9)	C$_4$–C$_3$–O$_3$	117.7 (12)
Mo–C$_3$–O$_3$	120.9 (10)		
(iv) In π-Cyclopentadienyl Ring			
C$_{15}$–C$_{11}$–C$_{12}$	107.5 (13)	C$_{13}$–C$_{14}$–C$_{15}$	108.4 (14)
C$_{11}$–C$_{12}$–C$_{13}$	108.0 (13)	C$_{14}$–C$_{15}$–C$_{11}$	107.3 (12)
C$_{12}$–C$_{13}$–C$_{14}$	108.7 (12)		
(v) In Triphenylphosphine Ligand			
Mo–P–C$_{21}$	119.0 (4)	C$_{21}$–P–C$_{31}$	102.8 (4)
Mo–P–C$_{31}$	112.3 (3)	C$_{21}$–P–C$_{41}$	103.0 (4)
Mo–P–C$_{41}$	113.6 (3)	C$_{31}$–P–C$_{41}$	104.5 (5)
C$_{26}$–C$_{21}$–C$_{22}$	119.5 (10)	C$_{36}$–C$_{31}$–C$_{32}$	120.2 (11)
C$_{21}$–C$_{22}$–C$_{23}$	119.9 (12)	C$_{31}$–C$_{32}$–C$_{33}$	121.4 (14)
C$_{22}$–C$_{23}$–C$_{24}$	118.6 (11)	C$_{32}$–C$_{33}$–C$_{34}$	118.6 (13)
C$_{23}$–C$_{24}$–C$_{25}$	122.5 (12)	C$_{33}$–C$_{34}$–C$_{35}$	121.5 (15)
C$_{24}$–C$_{25}$–C$_{26}$	118.5 (14)	C$_{34}$–C$_{35}$–C$_{36}$	119.8 (16)
C$_{25}$–C$_{26}$–C$_{21}$	120.9 (10)	C$_{35}$–C$_{36}$–C$_{31}$	118.3 (12)
C$_{46}$–C$_{41}$–C$_{42}$	119.2 (10)	C$_{43}$–C$_{44}$–C$_{45}$	119.0 (13)
C$_{41}$–C$_{42}$–C$_{43}$	119.3 (12)	C$_{44}$–C$_{45}$–C$_{46}$	119.7 (13)
C$_{42}$–C$_{43}$–C$_{44}$	121.5 (12)	C$_{45}$–C$_{46}$–C$_{41}$	121.2 (10)

[a] c.o.g. is center of gravity of the π-cyclopentadienyl ring.

scarcely different from that in other molecules. For example, the angle P–Mo–$COCH_3$ is 132.7 ± 0.4° and may be compared to the corresponding *trans*-(OC–Mo–X) angles: 131.6° in $[C_{10}H_8Mo(CO)_3CH_3]_2$,[7] 131.8° in π-$C_5H_5Mo(CO)_3C_2H_5$,[4] and 131.9° in π-$C_5H_5Mo(CO)_3C_3F_7$.[5] Similarly, the angles *trans*-(OC–Mo–CO) (107.9 ± 0.5°) and *cis*-(OC–Mo–$COCH_3$) (73.2 ± 0.5°, 74.2 ± 0.5°) are in good agreement with angles found in other complexes.[27]

The π-Cyclopentadienyl Ligand.—The π-cyclopentadienyl ligand is planar (rms deviation = 0.014 Å). Individual carbon–carbon distances around the five-membered ring range from 1.380 ± 0.020 to 1.422 ± 0.025 Å and average 1.406 Å; intra-ring angles range from 107.3 ± 1.2 to 108.7 ± 1.2°, averaging 108.0°. However, variations from the mean values are not significant, and the π-cyclopentadienyl ligand has strict D_{5h} symmetry within the limits of experimental error.

Individual molybdenum–carbon distances range from 2.310 ± 0.013 to 2.376 ± 0.014 Å; this difference *is* significant (0.066 Å $\cong 3.3\sigma$) and there appears to be a pattern to the Mo–C distances, although it is not as clear-cut as that found in π-$C_5H_5Mo(CO)_3C_3F_7$[5] or $[C_{10}H_8Mo(CO)_3CH_3]_2$.[7b] The two shortest distances (Mo–C_{11} = 2.332 ± 0.015 Å; Mo–C_{15} = 2.310 ± 0.013 Å) are for the atoms lying above the acetyl group and *trans* to the triphenylphosphine ligand (see Figure 2); other distances (Mo–C_{12} = 2.376 ± 0.014 Å; Mo–C_{13} = 2.358 ± 0.011 Å; Mo–C_{14} = 2.357 ± 0.012 Å) are greater, possibly as a result of (i) the greater π character in the Mo–CO bonds *trans* to C_{12} and C_{14} and (ii) the fact that there is steric repulsion between C_{13} and the phosphorus atom (the distance of 3.316 Å for $C_{13}\cdots P$ is considerably less than the sum of the appropriate[28,29] van der Waals radii).

The Triphenylphosphine Ligand.—The over-all conformation of the triphenylphosphine ligand is shown in Figure 3. The molybdenum–phosphorus distance (2.473 ± 0.003 Å) is somewhat longer than that observed in $[\pi\text{-}C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$[8] ($Mo^{II}$–P =

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(27) See Table VI of ref 5b.

(28) Appropriate van der Waals radii are 1.9 Å for phosphorus and ~1.7 Å for the half-thickness of an aromatic ring system.[29]

(29) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

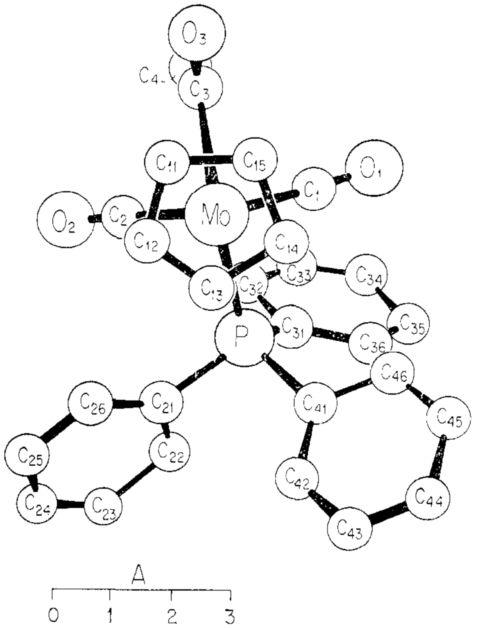

Figure 2.—The molecule projected in the plane of the π-cyclopentadienyl ring.

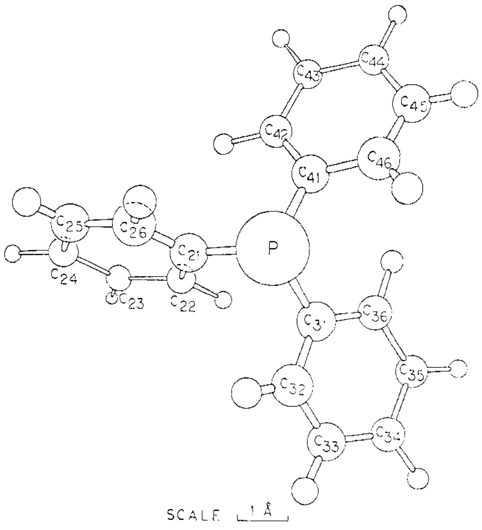

Figure 3.—The triphenylphosphine ligand projected in the plane defined by C_{21}, C_{31}, C_{41}.

2.416 ± 0.006, 2.426 ± 0.006 Å) but is shorter than that found in $[(C_2H_5)_3P_3]Mo(CO)_3$[30] (Mo^0–P = 2.52 ± 0.02 Å). Each of these bond lengths is considerably less than the "σ-only" value of 2.71 Å predicted from r(Mo) = 1.61 Å[31] and r(P) = 1.10 Å.[32] This may be taken as evidence for d_π–d_π metal→phosphorus back-donation in each case.

Phosphorus–carbon bond lengths in the present study are 1.836 ± 0.010, 1.831 ± 0.011, and 1.836 ± 0.011 Å; the C–P–C angles are 102.8 ± 0.4, 103.0 ± 0.4, and 104.5 ± 0.5°. These figures do not provide any additional evidence for Mo→P (d_π–d_π) back-donation, since a crystallographic study of triphenylphosphine[33] shows similar molecular features [P–C = 1.828 Å (av); C–P–C = 103.0° (av)]. The 18 independent carbon–carbon bond lengths within the triphenylphosphine ligand of the present complex have values ranging from 1.356 ± 0.019 to 1.421 ± 0.109 Å, averaging 1.385 Å (*cf.* the accepted[34a] value of 1.392 Å for the carbon–carbon bond length in an aromatic system). Root-mean-square deviations from planarity of the three phenyl rings are 0.014, 0.015, and 0.013 Å (see Table VI). The values should, of course, be regarded as an independent assessment of the accuracy of the crystallographic analysis, rather than as indicative of any real distortion of the phenyl rings from D_{6h} symmetry.

Table VI

Important Least-Squares Planes[a,b] in *trans*-π-$C_5H_5Mo(CO)_2$-$[P(C_6H_5)_3]COCH_3$

Atom	Distance, Å	Atom	Distance, Å
(a) π-Cyclopentadienyl Ring: $-0.1912X - 0.3861Y + 0.9023Z = 9.9358$			
C_{11}*	−0.001 (15)	O_1	−3.66 (1)
C_{12}*	+0.011 (13)	O_2	−3.82 (1)
C_{13}*	−0.017 (14)	C_1	−3.10 (1)
C_{14}*	+0.016 (13)	C_2	−3.21 (1)
C_{15}*	−0.009 (15)	C_3	−2.76 (1)
Mo	−2.018 (2)	O_3	−1.99 (1)
P	−3.179 (3)	C_4	−4.28 (2)
(b) $0.4595X + 0.2555Y + 0.8505Z = 3.9115$			
C_{21}*	−0.018 (10)	C_{24}*	−0.019 (14)
C_{22}*	+0.004 (12)	C_{25}*	+0.006 (13)
C_{23}*	+0.014 (14)	C_{26}*	+0.013 (13)
(c) $0.0105X - 0.9990Y + 0.0462Z = -3.3654$			
C_{31}*	+0.012 (11)	C_{34}*	+0.026 (16)
C_{32}*	+0.001 (12)	C_{35}*	−0.012 (15)
C_{33}*	−0.020 (14)	C_{36}*	−0.007 (13)
(d) $-0.5885X - 0.5162Y + 0.6222Z = 7.0192$			
C_{41}*	−0.007 (10)	C_{44}*	−0.000 (14)
C_{42}*	−0.010 (12)	C_{45}*	−0.017 (13)
C_{43}*	+0.013 (14)	C_{46}*	+0.019 (12)

[a] All planes are expressed in Cartesian coordinates. The transformations are: $X = xa + zc \cos \beta$, $Y = yb$, $Z = zc \sin \beta$. [b] A plane is derived using unit weights for atoms with asterisks.

The Acetyl Group.—Bond angles around the ketonic carbon atom (Mo–C_3–O_3 = 120.9 ± 1.0°, Mo–C_3–C_4 = 121.2 ± 0.9°, O_3–C_3–C_4 = 117.7 ± 1.2°) are not distinguishable from the expected sp^2 bond angle of 120°. The C_3–O_3 distance of 1.211 ± 0.016 Å is in good agreement with the value of 1.215 ± 0.005 Å accepted[34b] for a "ketonic-carbonyl" bond distance, and the C_3–C_4 distance of 1.550 ± 0.020 Å is within two esd's of the ideal C(sp^2)–C(sp^3) value of 1.51 Å

Perhaps the most important piece of information resulting from this structural analysis is the molybdenum–acetyl bond distance of 2.264 ± 0.014 Å. This represents a contraction of 0.119 Å (*i.e.*, 8.5σ) relative

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[30] M. A. Bush, V. R. Cook, and P. Woodward, *Chem. Commun.*, 630 (1967).

[31] From half the Mo–Mo distance of 3.222 Å in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$.[6]

[32] See ref 29, p 246.

[33] J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

[34] "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965: (a) p M127s; (b) p S21s.

to the "best"[35] molybdenum–alkyl bond length of 2.383 ± 0.010 Å for $[C_{10}H_8Mo(CO)_3CH_3]_2$.[7] It should be remembered, however, that there is a difference of approximately 0.03 Å in the covalent radii of sp^2- and sp^3-hybridized carbon atoms. The present molybdenum–acetyl bond length is thus reduced by ~0.09 Å (*i.e.*, $\sim 6.5\sigma$) from the idealized Mo–C(sp^2) single-bond distance and corresponds to a bond order of ~1.12.[2] Since changes in σ-bond strength in going from a molybdenum alkyl to a molybdenum acetyl are likely to be small,[36] we believe the observed Mo–$COCH_3$ distance to provide a direct qualitative and quantitative measure of d_π–p_π back-donation from a transition metal to an acyl group.

Infrared studies[1] on π-$C_5H_5Fe(CO)_2COCH_3$ and π-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ reveal ketonic stretching frequencies at 1640 and 1595 cm^{-1} (respectively), indicating that the triphenylphosphine ligand is not as good a π acceptor as a carbonyl group. This indicates that the bond order of the molybdenum–acetyl linkage in the present complex may be greater than that in the nonsubstituted complex π-$C_5H_5Mo(CO)_3COCH_3$.

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(35) This particular value is selected since it has the lowest esd of the measurements available. Other measured bond lengths are 2.397 ± 0.019 Å for the Mo–C_2H_5 linkage in π-$C_5H_5Mo(CO)_3C_2H_5$[4b] and 2.41 ± 0.02 Å for the Mo–CH_2 linkage in π-$C_5H_5Mo(CO)_3CH_2CO_2H$.[3] The molybdenum–alkyl bond length predicted from appropriate covalent radii is 2.38 Å (using half the Mo–Mo distance of 3.22 Å in $[\pi$-$C_5H_5Mo(CO)_3]_2$[6] and the C(sp^3) radius of 0.77 Å).

(36) Since carbon–carbon single-bond distances are 1.510 ± 0.005 Å for C—C=C and 1.506 ± 0.005 Å for C—C=O (see ref 34, p S15s).

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Infrared Intensities of the Carbonyl Stretching Modes and Electronic Spectra of Substituted Molybdenum Carbonyls[1]

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Intensity and frequency data for the CO stretching motion in substituted metal carbonyls are presented for compounds of the types $Mo(CO)_5L$, *trans*-$Mo(CO)_4L_2$, and *cis*-$Mo(CO)_3L_3$. The coupling between the two A_1 modes in the monosubstituted complexes has been found not to depend significantly on whether the M–C stretching force constant and various associated interaction constants are included in the vibrational analysis. The L matrix elements are used to calculate θ, the angle between axial and radial CO groups, assuming equal MCO group dipole moment derivatives for the two A_1 modes. Dipole moment derivatives have been calculated assuming characteristic moments for the A_1 and E modes. The electronic spectra for these complexes in the ultraviolet and visible regions are reported. The infrared and electronic spectral results indicate that substitution of CO by a ligand capable of π bonding does not necessarily result in any increase in π bonding to the remaining CO groups.

Introduction

In interpreting the infrared intensities of the CO stretching modes in substituted metal carbonyls some assumption must usually be made regarding the number of different characteristic localized MCO group moment derivatives for the various CO groups in a given complex.[3-9]

It may be assumed that there is but one characteristic moment derivative, that there is a different derivative for each of the chemically different CO groups, or that there is a different one for each symmetry mode. In this paper we discuss intensity results for several substituted molybdenum carbonyls. The results can be satisfactorily interpreted in terms of the assumption that each carbonyl stretching symmetry mode exhibits a characteristic MCO group moment derivative.

Coupling of the A_1 Symmetry Coordinates in the A_1 Modes

It is important to establish that the calculated coupling between the two CO stretching modes of A_1 symmetry is not sensitive to the assumptions made regarding the nature of the force field. The coupling between the two A_1 modes in a few select $Mo(CO)_5L$ molecules was computed using the simplest possible model, the Cotton–Kraihanzel approximations that $2k_c = k_t$ and $k_{c'} = k_c$.[10] The L matrix elements obtained are shown

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(1) This research was supported by a grant from the National Science Foundation.

(2) National Institutes of Health Predoctoral Fellow, 1967–1968.

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(7) T. L. Brown and D. J. Darensbourg, *ibid.*, **6**, 971 (1967). In order to bring our labeling into accord with the more general practice, we have in the present paper reversed the numbering of the A_1 modes. The higher frequency A_1 mode is now labeled 2, and its intensity I_2. Thus $|L_{11}| > |L_{12}|$, and $|L_{22}| > |L_{21}|$.

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