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The Crystal and Molecular Structure of Acetylacetonato(cycloocta-2,4-dienyl)palladium

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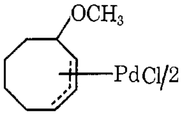
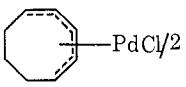
Acetylacetonato(cycloocta-2,4-dienyl)palladium, $C_8H_{11}Pd(CH_3COCHCOCH_3)$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.07 \pm 0.02$ A, $b = 9.92 \pm 0.02$ A, $c = 9.89 \pm 0.02$ A, $\alpha = 94.8 \pm 0.2°$, $\beta = 86.8 \pm 0.2°$, $\gamma = 109.8 \pm 0.2°$, $Z = 2$. A three-dimensional single-crystal X-ray structural analysis, based on 1758 independent, visually-estimated reflections, has led to the location of all atoms other than hydrogen. The complex is shown to be an α–β unsaturated π-allylpalladium derivative, only three atoms of the conjugated dienyl system being bonded to the metal. The three atoms constituting the π-allyl group are at an average distance of 2.11 A from the palladium whereas the remaining two atoms of the conjugated system are 2.91 and 3.93 A distant from the metal.

Introduction

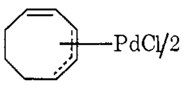
Although palladium forms some of its most stable organometallic complexes with such chelating olefins as dicyclopentadiene and cycloocta-1,5-diene,[1] the reaction of palladium salts with *conjugated* diolefins has been shown to result in the formation of π-allylpalladium species in preference to the expected 1,3-diene complexes.[2,3] Thus, the reaction of cycloocta-1,3-diene with sodium chloropalladite in methanol gives rise to the π-(methoxy)allyl complex (I). When this is heated, *in situ*, methanol is eliminated and a cyclooctadienyl complex is formed.[3] Of the structures (II and III) proposed for this product, the former was considered to be the more likely, since the infrared spectrum showed no absorption appropriate to an uncomplexed double bond, save for a very weak band at about 1660 cm^{-1}. The bonding to the palladium of all five carbon atoms of a dienyl ligand as in II would result in an 18-electron complex. However, unlike the majority of organo transition metal complexes, square-planar complexes of a d^8 Pd(II) ion have a preference for 16 electrons in their outermost bonding and nonbonding orbitals.[4] This requirement is met by the alternative structure (III).



I



II



III

An X-ray structural analysis of the monomeric acetylacetonato analog was therefore undertaken in order to ascertain whether the complex had a true palladium–dienyl linkage (as in II) or was, in fact, an α–β unsaturated π-allyl complex (III). A preliminary account of this work has been published.[5]

Experimental Section

The compound was recrystallized from 40–60° petroleum ether at −5°. A single crystal of dimensions 0.3 × 0.3 × 0.15 mm was used in collecting two zones of Weissenberg data (0*kl* and 1*kl*) and seven zones of precession data (*hKl*, *K* = 0–3; *hKL*, *L* = 0–2). Precession data were collected on Ilford Industrial G X-ray film, and Weissenberg data on tripacks consisting of G, B, and C film, Mo Kα radiation (λ 0.7107 A) being used throughout the analysis. No correction was applied for absorption ($\mu = 13.9$ cm^{-1}). A total of 1758 independent reflections were estimated visually using a calibrated wedge made from the crystal under investigation. The observed intensities were corrected for Lorentz and polarization effects and placed on a single scale by comparison of common reflections. Unobserved reflections were ignored. All data were initially placed on the absolute scale suggested by a Wilson plot, which also indicated the over-all temperature factor, $\bar{B} = 3.44$ A^2. During the refinement of positional and thermal parameters (*vide infra*), the scale of each of the nine zones was also allowed to refine, but the maximum deviation from the original scale was only about 4% at the conclusion of the analysis.

Unit Cell and Space Group

The compound appeared to crystallize in a triclinic form. Since a systematic survey of the reciprocal lattice failed to produce evidence for any symmetry other than that imposed by the Friedel condition, the crystals were assumed to be truly triclinic. The space group is therefore P1 (no. 1) or $P\bar{1}$ (no. 2). The latter was chosen since, statistically, it occurs with considerably greater frequency than P1 when $Z = 2$. The accurate solution of the structure confirmed this assignment.

Unit-cell dimensions were obtained from zero-layer photographs taken with Cu Kα radiation (λ 1.5418 A). The 0*kl* Weissenberg film was calibrated using aluminum powder ($a_{Al} = 4.049$ A); the *hk*0 and *h*0*l* precession photographs were calibrated with a single crystal of sodium chloride ($a_{NaCl} = 5.640$ A). The cell constants thus obtained are: $a = 7.07 \pm 0.02$ A, $b = 9.92 \pm 0.02$ A, $c = 9.89 \pm 0.02$ A, $\alpha = 94.8 \pm 0.2°$, $\beta = 86.6 \pm 0.2°$, $\gamma = 109.8 \pm 0.2°$. The unit-cell volume is 649.5 A^3; the observed density is 1.58 ± 0.05 g cm^{-3}, in satisfactory agreement with the calculated density (for $Z = 2$ and $M = 312.4$) of 1.60 g cm^{-3}. The total number of electrons per unit cell is 316; on the scale of Table III, $F_{000} = 1580$.

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[1] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

[2] S. D. Robinson and B. L. Shaw, *ibid.*, 4806 (1963).

[3] S. D. Robinson and B. L. Shaw, *ibid.*, 5002 (1964).

[4] L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory," Methuen and Co., London, p 149.

[5] M. R. Churchill, *Chem. Commun.*, 625 (1965).

TABLE I

$C_8H_{11}Pd(CH_3COCHCOCH_3)$: FINAL POSITIONAL PARAMETERS, WITH ESTIMATED STANDARD DEVIATIONS

Atom	X	$10^4\sigma(X)$	Y	$10^4\sigma(Y)$	Z	$10^4\sigma(Z)$
Pd	0.20288	0.8	0.16445	0.8	0.02534	0.6
O_1	0.2916	8.	0.0899	7.	0.1930	6.
O_2	0.0121	7.	0.2457	8.	0.1496	7.
C_1	0.2381	10.	0.1156	10.	0.3150	8.
C_2	0.1108	10.	0.1891	10.	0.3593	9.
C_3	0.0115	11.	0.2452	11.	0.2801	10.
C_4	0.3220	13.	0.0487	14.	0.4157	10.
C_5	−0.1278	16.	0.3244	13.	0.3494	13.
C_6	0.1751	10.	0.2439	12.	−0.1617	9.
C_7	0.2496	12.	0.1279	13.	−0.1844	9.
C_8	0.4214	10.	0.1337	8.	−0.1181	8.
C_9	0.6086	10.	0.2561	11.	−0.0954	9.
C_{10}	0.6904	11.	0.3518	12.	−0.1940	10.
C_{11}	0.5785	12.	0.3792	12.	−0.3009	10.
C_{12}	0.4397	12.	0.4600	11.	−0.2545	10.
C_{13}	0.2866	11.	0.4019	10.	−0.1489	10.

Structure Determination

The three-dimensional Patterson[6] synthesis P(UVW) contained large peaks corresponding to the palladium–palladium vectors $\pm(2x, 2y, 2z)$, leading to the unambiguous assignment of the palladium position to $X = 0.203$, $Y = 0.166$, $Z = 0.028$. A three-dimensional Fourier[6] map, phased only by the palladium atom, R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) $= 0.27$, led to the location of the two oxygen atoms and five carbon atoms of the acetylacetonate group, but a number of subsequent electron-density syntheses were required before all eight carbon atoms of the cyclooctadienyl group had been unambiguously located. The first structure-factor calculation,[7] phased by all atoms other than hydrogen, had a discrepancy index $R = 0.17$ which converged, after five cycles of least-squares refinement of positional and isotropic thermal parameters, to a value $R = 0.102$. The small standard deviations for the isotropic thermal parameters prompted continuation of the refinement using anisotropic thermal parameters (T) defined by

$$T = \exp\{-[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl]\}$$

TABLE II

$C_8H_{11}Pd(CH_3COCHCOCH_3)$: FINAL ANISOTROPIC THERMAL PARAMETERS

	10^4b_{11} (σ)	10^4b_{22} (σ)	10^4b_{33} (σ)	10^4b_{12} (σ)	10^4b_{13} (σ)	10^4b_{23} (σ)	B,[a] A^2
Pd	221.3 (1.3)	117.6 (1.1)	101.6 (0.8)	60.8 (0.7)	21.7 (0.5)	18.3 (0.7)	3.97
O_1	311 (13.)	165 (10.)	123 (7.)	108 (10.)	25 (7.)	39 (9.)	5.03
O_2	273 (11.)	151 (9.)	149 (8.)	105 (9.)	71 (7.)	66 (9.)	5.28
C_1	227 (15.)	97 (11.)	105 (9.)	14 (12.)	7 (9.)	3 (11.)	3.81
C_2	248 (15.)	120 (11.)	113 (9.)	27 (12.)	29 (10.)	−9 (12.)	4.31
C_3	233 (16.)	109 (12.)	149 (11.)	32 (12.)	59 (11.)	19 (13.)	4.89
C_4	359 (21.)	212 (17.)	124 (11.)	105 (16.)	−7 (11.)	58 (15.)	6.17
C_5	426 (21.)	189 (16.)	217 (15.)	154 (17.)	149 (15.)	−3 (16.)	7.49
C_6	214 (15.)	202 (17.)	100 (9.)	31 (13.)	−30 (9.)	24 (14.)	4.88
C_7	326 (20.)	153 (14.)	94 (9.)	91 (17.)	30 (10.)	10 (13.)	4.90
C_8	280 (17.)	84 (9.)	116 (9.)	64 (10.)	27 (10.)	−13 (11.)	4.12
C_9	225 (15.)	169 (14.)	136 (10.)	67 (12.)	30 (10.)	48 (14.)	5.04
C_{10}	248 (18.)	184 (17.)	142 (18.)	64 (14.)	−32 (14.)	44 (19.)	5.52
C_{11}	323 (20.)	152 (15.)	131 (11.)	46 (14.)	64 (12.)	29 (14.)	5.35
C_{12}	328 (21.)	140 (13.)	150 (20.)	85 (15.)	94 (17.)	43 (19.)	5.48
C_{13}	315 (18.)	114 (10.)	135 (11.)	77 (12.)	−12 (11.)	17 (13.)	4.92

[a] B, the equivalent isotropic temperature factor, is obtained by averaging $4b_{11}/a^{*2}$, $4b_{22}/b^{*2}$, and $4b_{33}/c^{*2}$.

Three cycles of refinement led to a reduction in the discrepancy index to the final value $R = 7.08\%$, at which stage refinement was discontinued. Weighting factors used in the least-squares treatment were derived from the following estimated errors in intensities: $\sigma(I) = 0.1I$ if $I > 20I_{\min}$, $\sigma(I) = 2I_{\min}$ if $I \leq 20I_{\min}$, where $I_{\min}$ is the minimum observable intensity for the zone under consideration.

During the analysis the scattering factors for neutral palladium, oxygen, and carbon were used;[8] contributions from the hydrogen atoms were not included in the calculation. Dispersion corrections are small and were ignored.[9]

Final atomic coordinates are shown in Table I, and anisotropic thermal parameters in Table II. The standard deviations $\sigma(j)$ in each of these tables were estimated by the least-squares program ORFLS[7] from the diagonal element (a_{jj}) of the matrix inverse to the normal equation matrix.[10] Observed and calculated structure factors are collected in Table III.

The Molecular Structure

The over-all molecular stereochemistry and the numbering of atoms in the complex are illustrated in Figure 1. Intramolecular distances and angles are listed in Table IV, along with their average estimated standard deviations (esd values).[11]

The palladium atom is within bonding distance of

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[6] 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.

[7] Structure-factor calculations and full-matrix least-squares refinement of positional and thermal parameters were performed using ORFLS, a Fortran least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

[8] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England. Values for palladium are taken from p 211; those for oxygen and carbon are from p 202.

[9] The corrected scattering factor for palladium $f_\theta = f_{0,\theta} + \Delta f' + i\Delta f''$, where $\Delta f' = -1.0$ electron and $\Delta f'' = +1.3$ electrons: ref 8, p 216.

[10] $\sigma(j) = [a_{jj}(\Sigma w\Delta^2)/(m - n)]^{1/2}$, where m is the number of observations, n the number of variables in the refinement, and $\Sigma w\Delta^2$ the summed, weighted, discrepancy between observed and calculated structure factors.

[11] Since the esd values are calculated using only the diagonal elements of the inverted normal equation matrix,[10] it is probable that these represent a slight underestimate of the true errors. The slow photodecomposition of the crystal by X-rays during the course of the analysis may also have led to some systematic errors that will tend to increase the esd values. Fortunately, a comparison of chemically equivalent bond lengths and angles (Table IV) shows only one such set (C_1–C_4 and C_3–C_5) where the difference (0.062 A) is greater than 3σ (0.054 A).

TABLE III

$C_8H_{11}Pd(CH_3COCHCOCH_3)$: OBSERVED AND CALCULATED STRUCTURE FACTORS (k, l, $5F_o$, AND $5F_c$)

K	L	FO	FC
H = 0			
0	2	62.	66.
0	3	197.	199.
0	4	106.	122.
0	5	199.	190.
0	6	207.	192.
0	7	109.	108.
0	8	14.	19.
0	9	15.	3.
0	10	16.	5.
0	11	-16.	-4.
0	12	-16.	-13.
0	13	-28.	-20.
1	2	390.	337.
1	-2	120.	123.
1	3	8.	7.
1	-3	217.	245.
1	4	-97.	-115.
1	-4	267.	274.
1	5	-11.	-9.
1	-5	268.	282.
1	6	-98.	-91.
1	-6	200.	244.
1	7	-115.	-107.
1	-7	158.	176.
1	8	-109.	-110.
1	-8	121.	120.
1	9	-87.	-88.
1	-9	125.	126.
1	10	-67.	-60.
1	-10	96.	94.
1	11	-61.	-54.
1	-11	51.	49.
1	12	-49.	-44.
1	-12	43.	30.
1	13	-35.	-34.
2	0	-368.	-350.
2	2	-194.	-182.
2	-2	-95.	-76.
2	3	-214.	-185.
2	-3	-57.	-46.
2	4	-185.	-165.
2	-4	110.	115.
2	5	-175.	-186.
2	-5	114.	116.
2	6	-225.	-228.
2	-6	50.	55.
2	7	-182.	-183.
2	-7	116.	123.
2	8	-136.	-139.
2	-8	97.	102.
2	9	-74.	-72.
2	-9	93.	84.
2	10	-60.	-59.
2	-10	101.	89.
2	11	-59.	-51.
3	0	-410.	-383.
3	1	-287.	-288.
3	-1	-448.	-459.
3	2	-256.	-252.
3	-2	-322.	-312.
3	3	-252.	-276.
3	-3	-210.	-208.
3	4	-178.	-178.
3	-4	-233.	-228.
3	5	-175.	-157.
3	-5	-122.	-116.
3	6	-149.	-137.
3	-6	-86.	-72.
3	7	-70.	-73.
3	-7	-52.	-54.
3	-8	-57.	-73.
4	0	-204.	-206.
4	1	-179.	-178.
4	-1	-106.	-119.
4	2	-47.	-38.
4	-2	-166.	-170.
4	3	-32.	-15.
4	-3	-237.	-247.
4	4	32.	40.
4	-4	-256.	-263.
4	5	35.	29.
4	-5	-221.	-220.
4	6	39.	31.
4	-6	-220.	-226.
4	7	50.	68.
4	-7	-134.	-128.
4	8	59.	72.
4	-8	-76.	-76.
4	9	65.	51.
4	-9	-124.	-113.
4	-10	-76.	-81.
5	0	94.	83.
5	1	96.	80.
5	-1	107.	110.
5	2	149.	136.
5	-2	94.	93.
5	3	186.	176.
5	-3	32.	8.
5	4	180.	177.
5	-4	-111.	-106.
5	5	147.	139.
5	-5	-91.	-90.
5	6	126.	132.
5	-6	-98.	-86.
5	7	115.	106.
5	8	79.	82.
6	0	118.	133.
6	1	153.	147.
6	-1	148.	163.
6	2	190.	185.
6	-2	221.	227.
6	3	162.	166.
6	-3	230.	237.
6	4	147.	137.
6	-4	125.	127.
6	5	120.	95.
6	-5	117.	123.
6	-6	69.	63.
7	0	94.	86.
7	1	91.	84.
7	-1	122.	125.
7	2	38.	51.
7	-2	124.	138.
7	-3	179.	179.
7	-4	130.	129.
7	-5	72.	91.
7	-6	118.	114.
7	-7	107.	95.
7	-8	82.	83.
8	0	-18.	-5.
8	1	-30.	-18.
8	-1	-38.	-21.
8	2	-81.	-82.
8	-2	-62.	-50.
8	3	-107.	-90.
8	4	-70.	-77.
8	5	-109.	-103.
9	0	-79.	-81.
9	1	-66.	-72.
9	-1	-110.	-109.
9	2	-68.	-86.
9	-2	-117.	-111.
9	3	-65.	-63.
10	0	-49.	-54.
10	1	-43.	-41.
10	-1	-61.	-58.
10	-2	-76.	-72.
11	1	28.	23.
11	-1	14.	0.
12	1	29.	30.
12	-1	54.	46.
13	-1	31.	29.
H = 1			
0	0	93.	100.
0	1	-65.	-59.
0	-1	201.	194.
0	2	103.	91.
0	-2	89.	102.
0	3	-56.	-24.
0	-3	259.	262.
0	4	-148.	-155.
0	-4	253.	222.
0	5	-140.	-135.
0	-5	294.	281.
0	6	-104.	-100.
0	-6	299.	281.
0	7	-116.	-125.
0	-7	190.	186.
0	8	-86.	-85.
0	-8	138.	131.
0	9	-86.	-80.
0	-9	77.	64.
0	10	-109.	-104.
0	-10	71.	71.
0	11	-65.	-68.
0	-11	86.	73.
0	12	-48.	-45.
0	-12	49.	41.
0	13	-30.	-28.
0	-13	28.	27.
1	0	-422.	-364.
1	1	-729.	-627.
-1	1	76.	55.
-1	-1	290.	291.
1	2	-265.	-289.
1	-2	-230.	-189.
-1	2	283.	279.
-1	-2	190.	167.
1	3	-241.	-249.
1	-3	109.	48.
-1	3	208.	224.
-1	-3	272.	285.
1	4	-229.	-238.
1	-4	116.	85.
-1	4	258.	263.
-1	-4	212.	217.
1	5	-216.	-227.
1	-5	-97.	-84.
-1	5	125.	115.
-1	-5	275.	260.
1	6	-188.	-198.
1	-6	-36.	-28.
-1	6	94.	84.
-1	-6	256.	236.
1	7	-157.	-157.
1	-7	57.	43.
-1	-7	138.	143.
1	8	-110.	-110.
1	-8	98.	91.
-1	-8	59.	67.
1	9	-87.	-83.
1	-9	89.	85.
-1	9	-15.	-20.
-1	-9	15.	15.
1	10	-58.	-58.
1	-10	74.	71.
-1	10	-43.	-42.
-1	-10	16.	17.
1	11	-34.	-32.
1	-11	62.	57.
-1	-11	-17.	-2.
-1	12	-25.	-21.
-1	-12	-17.	-9.
2	0	-861.	-742.
-2	0	465.	345.
2	1	-221.	-247.
2	-1	-341.	-351.
-2	1	215.	232.
-2	-1	338.	320.
2	2	-104.	-111.
2	-2	-133.	-124.
-2	2	351.	381.
-2	-2	87.	100.
2	3	-229.	-260.
2	-3	-235.	-231.
-2	3	411.	371.
-2	-3	67.	50.
2	4	-104.	-115.
2	-4	-280.	-262.
-2	4	326.	345.
-2	-4	-12.	-17.
2	5	-130.	-129.
2	-5	-285.	-270.
-2	5	231.	275.
-2	-5	20.	21.
2	6	-117.	-116.
2	-6	-215.	-203.
-2	6	186.	205.
-2	-6	-22.	-7.
2	7	-39.	-39.
2	-7	-117.	-111.
-2	7	83.	77.
-2	-7	-62.	-63.
2	8	13.	8.
2	-8	-26.	-33.
-2	8	67.	49.
-2	-8	-84.	-84.
2	9	14.	10.
2	-9	-14.	-20.
-2	9	124.	132.
-2	-9	-63.	-61.
2	-10	-15.	-15.
-2	10	93.	97.
-2	-10	-37.	-28.
-2	11	46.	49.
-2	-11	-52.	-48.
-2	-12	-44.	-47.
-2	-13	-34.	-33.
3	0	-259.	-224.
-3	0	65.	55.
3	1	-35.	-40.
3	-1	-172.	-163.
-3	1	-50.	-54.
-3	-1	-18.	-20.
3	2	-37.	-22.
3	-2	-113.	-113.
-3	2	-121.	-110.
-3	-2	-135.	-120.
3	3	79.	80.
3	-3	-232.	-221.
-3	3	-19.	-18.
-3	-3	-258.	-231.
3	4	112.	118.
3	-4	-237.	-220.
-3	4	146.	159.
-3	-4	-267.	-272.
3	5	58.	45.
3	-5	-185.	-183.
-3	5	114.	119.
-3	-5	-175.	-174.
3	6	83.	79.
3	-6	-200.	-189.
-3	6	118.	111.
-3	-6	-176.	-175.
3	7	92.	89.
3	-7	-156.	-154.
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-2	1	74.	74.
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2	2	17.	10.
2	-2	-17.	-16.
-2	2	59.	61.
-2	-2	90.	94.
2	3	17.	25.
2	-3	-17.	-17.
-2	-3	103.	100.
2	4	34.	30.
2	-4	-17.	-39.
-2	-4	98.	101.
2	5	-41.	-41.
-2	-5	79.	76.
2	6	-41.	-34.
-2	-6	47.	48.
2	-7	-34.	-43.
3	0	47.	55.
-3	0	73.	67.
3	1	57.	53.
3	-1	39.	39.
-3	1	49.	45.
-3	-1	87.	87.
3	2	50.	42.
3	-2	30.	21.
-3	2	96.	97.
-3	-2	62.	62.
3	3	34.	36.
-3	3	94.	92.
-3	-3	68.	69.
3	4	24.	36.
-3	4	78.	74.
-3	-4	64.	56.
3	5	34.	27.
-3	5	75.	74.
-3	6	54.	49.
-4	0	19.	12.
4	1	40.	31.
4	-1	42.	41.
-4	1	39.	29.
-4	-1	-34.	-36.
-4	2	65.	61.
-4	-2	-49.	-41.
-5	0	-34.	-43.
5	1	-14.	-12.
-5	1	-39.	-38.
-5	-1	-91.	-94.
-5	2	-48.	-48.
-5	-2	-109.	-106.
-6	0	-88.	-89.
6	1	-32.	-25.
-6	1	-91.	-93.
-6	-1	-83.	-81.
-6	2	-81.	-81.
-6	-2	-53.	-52.
-7	0	-19.	-20.
-7	1	-39.	-32.
-7	-1	14.	2.
-8	0	55.	66.
-8	1	44.	44.
-8	-1	82.	79.
-8	-2	73.	74.
-9	0	57.	65.
-9	1	60.	55.
-9	-1	66.	59.
-9	-2	54.	45.
-10	1	25.	17.
-10	-1	-20.	-9.
-11	1	-38.	-35.
-11	-1	-38.	-36.
-12	1	-32.	-30.
-12	-1	-28.	-26.
H = 8			
0	0	-34.	-35.
0	1	-37.	-32.
0	-1	-47.	-44.
0	2	-32.	-23.
0	-2	-46.	-44.
0	3	-15.	-0.
0	-3	-43.	-45.
0	-4	-47.	-53.
0	-5	-41.	-45.
0	-6	-35.	-36.
1	0	17.	14.
-1	0	-49.	-47.
1	1	16.	3.
1	-1	19.	10.
-1	1	-33.	-36.
-1	-1	-65.	-65.
1	2	17.	15.
1	-2	-17.	-5.
-1	2	-69.	-65.
-1	-2	-58.	-53.
1	3	34.	35.
1	-3	-17.	-5.
-1	3	-60.	-55.
-1	-3	-46.	-46.
1	4	29.	30.
1	-4	-17.	-16.
-1	4	-39.	-35.
-1	-4	-38.	-36.
1	5	17.	27.
1	-5	-37.	-31.
-1	5	-34.	-35.
-1	-5	-17.	-15.
1	6	28.	22.
1	-6	-32.	-27.
-1	6	-29.	-20.
1	[illegible]	[illegible]	[illegible]
[illegible]	0	[illegible]	[illegible]
-2	0	-19.	-20.
2	1	40.	37.
2	-1	31.	31.
-2	1	-27.	-24.
-2	-1	-14.	-0.
2	2	17.	39.
2	-2	29.	27.
2	3	-38.	-35.
-2	-2	34.	36.
-3	0	35.	39.
3	1	27.	18.
3	-1	31.	28.
-3	1	40.	34.
-3	-1	67.	68.
3	2	17.	27.
3	-2	63.	65.
-3	2	39.	34.
-3	3	52.	55.
3	-3	39.	42.
-3	-4	45.	46.
-3	-5	45.	42.
-3	6	39.	41.
-3	7	30.	35.
-3	8	46.	42.
-4	0	65.	72.
-4	1	63.	60.
-4	-1	79.	78.
-5	0	19.	24.
-5	1	40.	34.
-5	-1	14.	4.
-5	2	41.	38.
-6	0	-41.	-47.
-6	1	-32.	-28.
-6	-1	-60.	-61.
-6	2	-59.	-58.
-7	0	-57.	-63.
-7	1	-60.	-56.
-7	-1	-66.	-61.
-7	2	-51.	-50.
-7	-2	-51.	-48.
-8	1	-32.	-31.
-8	-1	14.	1.
-9	1	28.	25.
-9	-1	28.	25.
-9	-2	42.	31.
-10	1	42.	43.
-10	-1	31.	30.
-11	-1	28.	16.
H = 9			
0	0	20.	18.
0	-1	27.	6.
1	0	20.	26.
-1	0	-16.	-15.
1	1	35.	37.
-1	1	-14.	-9.
-1	-1	-36.	-33.
-1	-2	-37.	-34.
-1	-3	-28.	-32.
-1	-4	-28.	-32.
-1	-5	-27.	-30.
-1	-6	-25.	-26.
-2	0	-45.	-42.
-2	1	-37.	-33.
-2	-1	-41.	-44.
-2	2	-42.	-35.
-2	-2	-24.	-32.
-2	-3	-29.	-32.
-3	0	-24.	-27.
-3	1	-36.	-31.
-3	-1	-14.	-13.
-3	2	-35.	-34.
-4	0	17.	21.
-4	1	20.	7.
-4	-1	34.	35.
-5	0	43.	43.
-5	1	51.	47.
-5	-1	40.	41.
-6	0	30.	29.
-6	1	47.	40.
-6	-1	20.	12.
-7	0	-17.	-24.
-7	1	-20.	-19.
-7	-1	-14.	-12.
-8	0	-39.	-39.
-8	1	-42.	-36.
-8	-1	-39.	-35.
-9	1	-19.	-18.
H = 10			
-4	-1	-13.	-12.
-5	-1	22.	10.
-6	1	26.	22.
-6	-1	28.	21.
-7	1	29.	22.

only three atoms of the 2,4-dienyl system. The complex is therefore an α–β unsaturated π-allylpalladium derivative. With the acetylacetonate anion and the π-allyl anion each contributing four electrons to the metal, the molecule may *formally* be regarded as a square-planar complex of a d^8 Pd(II) ion, with 16 electrons in its outermost bonding and nonbonding orbitals; the value of 90.4° found for the angle O_1–Pd–O_2 is close to the ideal value expected for a square-planar stereochemistry. The acetylacetonate ligand is bonded to the metal *via* its two oxygen atoms, the mean palladium–oxygen distance being 2.085 (±0.008) A; within the limits of experimental error, the acetylacetonate group has the expected C_{2v} symmetry and is planar (excluding hydrogen atoms). The packing diagrams, Figures 2 and 3, illustrate this clearly. The complex is seen to be monomeric; there are no short intermolecular contacts involving the unsaturated carbon atoms C_9 and C_{10}, and the shortest Pd–Pd distance (3.558 A from Pd(x, y, z) to Pd($-x$, $-y$, $-z$) is considerably longer than that in dimeric π-allylpalladium acetate,[12] where the Pd–Pd distance of 2.94 A represents, at most, an extremely weak bonding situation. The cyclooctadienyl ligand is in a puckered conformation, somewhat reminiscent of octasulfur,[13] but rather irregular, due to the constraints imposed by the variation in the car-

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(12) M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964).

(13) S. C. Abrahams, *Acta Cryst.*, **8**, 661 (1955).

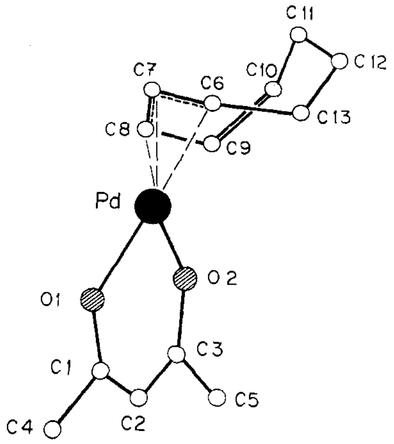

Figure 1.—$C_8H_{11}Pd(CH_3COCHCOCH_3)$: stereochemistry and numbering of atoms. The molecule is projected along *a*.

TABLE IV

$C_8H_{11}Pd(CH_3COCHCOCH_3)$: INTERATOMIC DISTANCES AND ANGLES[a,b]

Atoms	Distance, A	Atoms	Angle, deg
	(i) From Palladium Atom		
$Pd–O_1$	2.080	$O_1–Pd–O_2$	90.4
$Pd–O_2$	2.089	$C_6–Pd–C_7$	39.4
$Pd–C_6$	2.115	$C_7–Pd–C_8$	38.6
$Pd–C_7$	2.103	$C_6–Pd–C_8$	69.8
$Pd–C_8$	2.120	$O_1–Pd–C_8$	98.6
$Pd–C_1$	2.983	$O_2–Pd–C_6$	100.3
$Pd–C_3$	2.973	$O_1–Pd–C_6$	167.7
$Pd–C_2$	3.335	$O_2–Pd–C_8$	165.8
$Pd–C_4$	4.323		
$Pd–C_5$	4.368		
$Pd–C_9$	2.917		
$Pd–C_{13}$	2.914		
$Pd–C_{10}$	3.940		
$Pd–C_{11}$	4.284		
$Pd–C_{12}$	4.070		
	(ii) In Acetylacetonato Ligand		
$O_1–C_1$	1.275	$Pd–O_1–C_1$	123.7
$O_2–C_3$	1.291	$Pd–O_2–C_3$	121.3
$C_1–C_2$	1.372	$O_1–C_1–C_2$	127.8
$C_2–C_3$	1.348	$O_2–C_3–C_2$	130.2
$C_1–C_3$	2.423	$C_1–C_2–C_3$	126.1
$C_1–C_4$	1.492	$O_1–C_1–C_4$	112.7
$C_3–C_5$	1.554	$O_2–C_3–C_5$	111.3
$O_1–C_2$	2.378	$C_2–C_1–C_4$	119.4
$O_2–C_2$	2.393	$C_2–C_3–C_5$	118.5
$O_1–O_2$	2.959		
$C_2–C_4$	2.473		
$C_2–C_5$	2.496		
$O_1–C_4$	2.308		
$O_2–C_5$	2.354		
	(iii) In Cycloocta-2,4-dienyl Ligand		
$C_6–C_7$	1.417	$C_{13}–C_6–C_7$	129.8
$C_7–C_8$	1.394	$C_6–C_7–C_8$	119.0
$C_8–C_9$	1.475	$C_7–C_8–C_9$	129.1
$C_9–C_{10}$	1.380	$C_8–C_9–C_{10}$	121.1
$C_{10}–C_{11}$	1.451	$C_9–C_{10}–C_{11}$	125.0
$C_{11}–C_{12}$	1.496	$C_{10}–C_{11}–C_{12}$	114.9
$C_{12}–C_{13}$	1.464	$C_{11}–C_{12}–C_{13}$	118.6
$C_{13}–C_6$	1.495	$C_{12}–C_{13}–C_6$	116.8

[a] Average estimated standard deviations are as follows: $\sigma(Pd–O) = 0.008$ A; $\sigma(Pd–C) = 0.012$ A; $\sigma(O–C) = 0.015$ A; $\sigma(C–C) = 0.018$ A; these values do not include any contribution from errors in the unit-cell dimensions. [b] Chemically equivalent distances and angles are enclosed in braces.

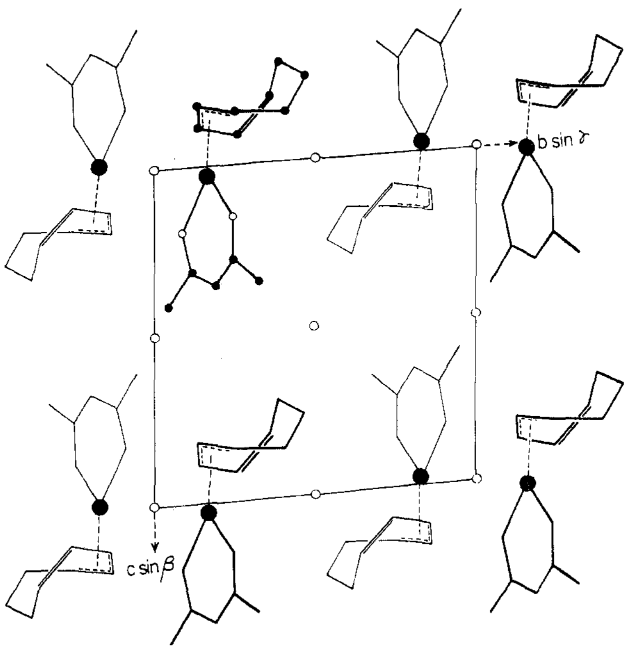

Figure 2.—$C_8H_{11}Pd(CH_3COCHCOCH_3)$: the packing of molecules in the crystal, viewed along *a*.

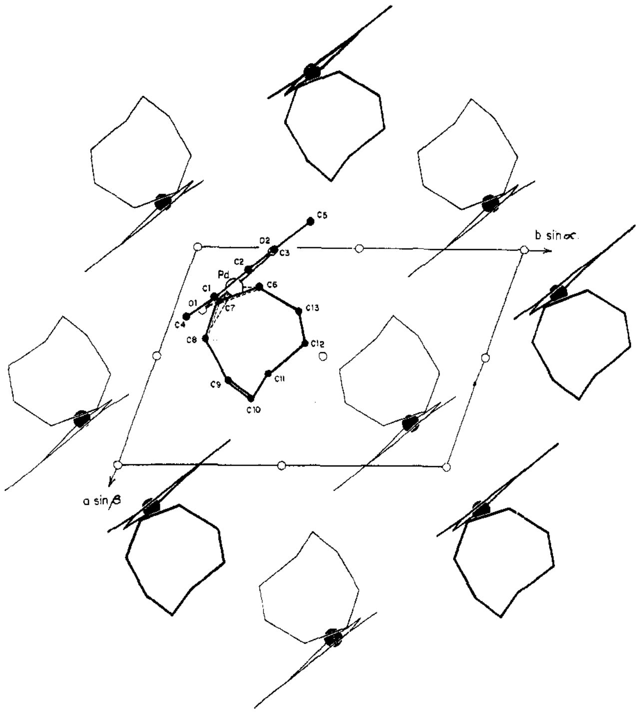

Figure 3.—$C_8H_{11}Pd(CH_3COCHCOCH_3)$: the packing of molecules in the crystal, viewed along *c*.

bon–carbon bond order around the ring and by the metal–ligand bonding. The dihedral angles between the four "quadrants" of the cyclooctadienyl ligand are: $C_6–C_7–C_8$, $C_8–C_9–C_{10}$, 71.3°; $C_8–C_9–C_{10}$, $C_{10}–C_{11}–C_{12}$, 82.3°; $C_{10}–C_{11}–C_{12}$, $C_{12}–C_{13}–C_6$, 79.6°; $C_{12}–C_{13}–C_6$, $C_6–C_7–C_8$, 85.8°. The carbon atoms C_9 and C_{10} are distant 2.917 and 3.940 A from the palladium ion and are obviously not involved in the metal–ligand bonding; the $C_9–C_{10}$ bond distance of 1.38 A indicates that this is the remaining part of the unsaturated system. The carbon atoms of the π-allyl grouping, C_6, C_7, and C_8, are, respectively, 2.115, 2.103, and 2.120 A distant from the palladium ion. These values are in excellent agreement with those obtained by Smith[14] in his accurate low-temperature analysis of dimeric π-allylpalladium chloride (2.123, 2.108, 2.121 A; $\sigma = 0.008$ A). It is interesting to note that, in each case, the central carbon atom is slightly closer to the metal than are the terminal carbon atoms. The differences are, however, too small to be considered statistically significant. The apical angle of 119.0° for the allyl group and a mean carbon–carbon bond length of 1.405 A for the allyl system in the present complex may be compared to Smith's values of 119.8° and 1.376 A.

The coordination plane of the palladium ion, as defined by the atoms Pd, O_1, and O_2, fits the equation $1.924X + 3.616Y + 0.590Z = 1$. Atoms C_6 and C_8 are 0.22 and 0.40 A above, and C_7 is 0.30 A below, this plane. The π-allyl group (C_6–C_7–C_8) makes a dihedral angle of 121.5° with the coordination plane of the palladium ion. This is not an isolated example of this phenomenon. Other π-allyl complexes show the same effect to varying degrees (see Table V). This rather surprising result has been explained by Kettle and Mason,[15] who are able to predict a value of approximately 110°, by considering the various π-allylpalladium overlap integrals.

TABLE V

THE DIHEDRAL ANGLE BETWEEN THE METAL COORIDNATION PLANE AND THE π-ALLYL SYSTEM IN A NUMBER OF π-ALLYLPALLADIUM COMPLEXES

Complex	Dihedral angle, deg	Ref
[*exo*-$C_2H_5O[C_4(C_6H_5)_4]PdCl]_2$	95[a]	*b*
[*endo*-$C_2H_5O[C_4(C_6H_5)_4]PdCl]_2$	95[a]	*b*
$[C_3H_5PdCl]_2$	111.5	13
$CH_3C_3H_4Pd[P(C_6H_5)_3]Cl$	116	*c*
$[C_3H_4PdCH_3CO_2]_2$	117 (av)	11
$C_8H_{11}Pd(CH_3COCHCOCH_3)$	121	

[a] This angle would probably be greater but for the effect of the nonbonding interaction between the fourth carbon of the cyclobutenyl system and the palladium atom. [b] L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965). [c] R. Mason and D. R. Russell, *Chem. Commun.*, 26 (1966).

Acknowledgments.—The author is indebted to Dr. S. D. Robinson, who provided the sample. This research has been generously supported by grants from the William F. Milton Fund of Harvard University, the National Science Foundation (grant No. GP-4225), and the Advanced Research Projects Agency.

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[14] A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).

[15] S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, in press.

Notes

CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
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Behavior of Bis(hexamethylphosphoramide)cobalt(II) Complexes in Solutions Containing Excess Hexamethylphosphoramide

BY MICHAEL R. ROSENTHAL[1] AND RUSSELL S. DRAGO

Received November 22, 1965

The complexes $Co(HMPA)_2X_2$, in which HMPA is hexamethylphosphoramide, $O{=}P[N(CH_3)_2]_3$, and X is chloride, bromide, iodide, or thiocyanate, have been characterized[2] as pseudo-tetrahedral complexes. Some of these complexes have been found to undergo interesting reactions with excess HMPA. Since no changes in the absorption spectrum of the thiocyanato or chloro complexes, $Co(HMPA)_2X_2$, were observed when the complex was dissolved in a solution containing an excess of HMPA, it was concluded that no reaction occurred. Extensive displacement of iodide occurred for the iodo complex. The spectrophotometric data in chloroform solution fit an equilibrium constant expression for dissociation of one iodide per molecule, but in nitromethane, containing excess ligand, dissociation of both iodides occurs, producing the species $Co(HMPA)_4^{2+}$.

In contrast to this behavior, the $CHCl_3$ solutions of a similar series of complexes of general formula CoL_2X_2—in which L is pyridine or isoquinoline and which contain excess ligand L—exhibit an equilibrium[3,4] between the four-coordinate species and a six-coordinate species, CoL_4X_2.

These reactions can be rationalized by employing steric considerations and the principles outlined in the coordination model for nonaqueous solvent behavior.[5,6]

Experimental Section

The compounds were prepared by a method previously reported.[2] Reagent grade nitromethane was used after 2-weeks storage over Linde 4A Molecular Sieves. Chloroform was shaken over calcium chloride, stored overnight, and distilled. Hexamethylphosphoramide was distilled under reduced pressure from barium oxide. The portion boiling at 127° (20 mm) was used. Electronic spectra were obtained with a Cary Model 14 M recording spectrometer, using matched quartz cells. When excess ligand was added to a solution, the same amount of ligand was added to the reference solution. Equilibrium constant measurements were performed with a Beckman DU spectrometer using matched quartz cells and a sample compartment

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[1] Abstracted in part from the Ph.D. thesis of Michael R. Rosenthal, University of Illinois, Urbana, Ill., 1965.

[2] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).

[3] H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

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[5] R. S. Drago, D. M. Hart, and R. L. Carlson, *J. Am. Chem. Soc.*, **87** 1900 (1965).

[6] R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1965).