The Solid-State Structure of Monothiodibenzoylmethanato-π-methallylpalladium(II)

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Abstract: The crystal and molecular structure of monothiodibenzoylmethanato-π-methallylpalladium(II) [(π-C_4H_7)Pd(S–DBM)] has been determined by a three-dimensional X-ray crystallographic analysis. The orange compound crystallizes in space group P2$_1$/c with unit cell dimensions $a = 11.257 (5), b = 8.432 (3), c = 19.997 (8)$ Å, $\beta = 119.31 (5)°, Z = 4$. From 1402 independent observable reflections collected on a full-circle automated diffractometer, the structure was solved by use of conventional Patterson, Fourier, and least-squares refinement techniques. All atoms including hydrogen were located, and refinement converged at final values for the discrepancy indices R_1 and R_2 of 0.048 and 0.057, respectively. The coordination geometry of the palladium atom is defined by Pd–O and Pd–S bonds of 2.067 (6) and 2.291 (2) Å and by Pd–C distances of 2.08 (1), 2.15 (1), and 2.21 (1) Å to the three carbon atoms of the methallyl backbone. The long Pd–C bond length of 2.21 (1) Å is opposite the sulfur atom and may be ascribed to a *trans* effect. Despite this asymmetry in the palladium–methallyl attachment, the two olefinic C–C bond distances in the methallyl group, 1.40 (2) and 1.42 (2) Å, are essentially equivalent. The structure of the S–DBM chelate ring is shown to differ in several notable ways from its β-diketonate analogs.

There has been considerable interest in transition metal π-allyl complexes since the discovery[3] of [(π-C_3H_5)PdCl]$_2$. The structures of this[4] and related molecules[5-15] have been determined with considerable accuracy, and shown to contain the following basic unit. In I the organic ligand is depicted as having a delocalized π-electron system. Certain nmr[16] and X-ray[7,9] structural results for complexes in which the ligands L are not identical have been interpreted in terms of the more localized bonding scheme shown in II. The need for this kind of interpretation has been questioned, however.[17]

In addition to solid-state structural studies of π-allyl complexes, their dynamic properties in solution have been extensively investigated.[18] In particular, under appropriate conditions of temperature, concentration, and

I

II
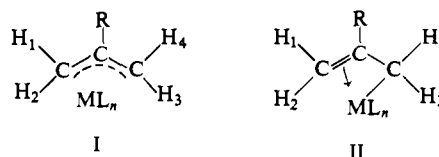
often in the presence of additional basic ligands, complexes of type I display proton nmr spectra in which H_1, H_2, H_3, and H_4, or some combination thereof, appear to be equivalent on the time scale of the measurement.[19] A variety of interpretations, in the form of detailed mechanisms describing the intramolecular reactivity and motion of the molecules, have been set forth to account for this behavior. The systems investigated to date have been reasonably complex, however, and even though a consistent and rational picture seems to have evolved for some systems, uncertainties still exist.

In order to provide further information concerning the structural and dynamic possibilities for metal π-allyl complexes, we have set out to prepare and characterize molecules containing a transition metal bound to one or more allyl groups and, at the same time, to one or more anionic ligands of general formula RCOCHCSR'. A number of such compounds have been synthesized and shown by nmr spectroscopy to be fluxional in solution.[20,21] The solid-state structural determination of one or more of these molecules seemed especially worthwhile, in order to assess the effect of an asymmetric, sulfur-containing ligand on the geometry of the metal–allyl attachment, and in view of the general lack of geometric data for the monothioacetylacetonate ligand system. The present paper reports the crystal and molecular structure of monothiodibenzoylmethanato-π-methallylpalladium(II), (π-C_4H_7)Pd(S–DBM), chosen for X-ray study because of its inherent stability in the solid state.

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(2) National Institutes of Health Predoctoral Fellow.

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Experimental Procedure

Collection and Reduction of X-Ray Data Crystals of (π-C_4H_7)Pd(S–DBM), prepared as described elsewhere,[20] were mounted with clear fingernail polish on the ends of glass fibers. Preliminary Weissenberg and precession photographs taken at 20° with Zr-filtered Mo Kα radiation (λ 0.7107 Å) showed the complex to have Laue symmetry 2/m. From the observed extinctions, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, the probable space group was ascertained to be P2$_1$/c (no 14).[22] The unit cell parameters obtained from the film data were refined by a least-squares technique to give the best fit between calculated and observed settings for 18 independent reflections, carefully centered in the counter window of a Picker full-circle automated X-ray diffractometer.[23] The results are $a = 11.257 \pm 0.005$ Å, $b = 8.432 \pm 0.003$ Å, $c = 19.997 \pm 0.008$ Å, and $\beta = 119.31 \pm 0.05°$. The calculated cell volume, 1655 Å^3, requires a density of 1.61 g/cc assuming four molecules per unit cell. This value was checked by observing that a crystal of the complex remains suspended in a 50% aqueous ZnCl$_2$ solution (ρ = 1.57 g/cc). The error on measurements of this kind is generally estimated[24] to be $\sim\pm 1\%$, or ± 0.02 g/cc.

Intensity measurements were taken on the Picker diffractometer using a well-formed crystal of approximate dimensions 0.10 × 0.07 × 0.30 mm mounted along a^*. The mosaic spread of the crystal was checked by doing ω scans for several reflections with a narrow source and an open counter window. Data were obtained with Ni-filtered Cu Kα radiation (λ 1.5418 Å) at 20°. Experimental details are as reported previously[25] with the following differences: the scan range was 1.25° in 2θ plus the Kα_1–Kα_2 allowance, the symmetrically varying receiving aperture was set at a 3.0 × 3.0 mm opening to minimize extraneous background, and the take-off angle was 2.4°. Approximately 1400 crystallographically independent reflections within the sphere $\theta < 45°$ were collected in a period of 3 days.

The raw data, I, were corrected for background, use of attenuators, Lorentz–polarization, and absorption effects as indicated previously.[25] Absorption corrections were judged to be quite important, since $\mu = 104.5$ cm^{-1}, and were calculated by the program ACAC.[23] The resultant transmission factors, which ranged from 0.2 to 0.5, were checked against an experimental measure of the change in peak intensity with ϕ for several reflections at $\chi = 90°$ and found to agree quite well. The data were then placed on an approximately absolute scale through a modification of Wilson's method.[23] From the resultant values for $|F_o|$ and $|F_o|^2$, the structure was solved by the usual Patterson, Fourier, and least-squares refinement processes (see below). The scattering factors for Pd, S, O, and C were taken from the "International Tables,"[26] with the Pd values corrected for the effects of anomalous dispersion.[27] The hydrogen scattering factors were those of Stewart, et al.[28] Form factors used were for the neutral atoms. Weights, $w = \sigma(F)^{-2}$, were assigned to each reflection according to the following scheme:[29] $\sigma(F) = (LpT)^{-1/2}[(I + \sigma(I))^{1/2} - (I)^{1/2}]$, where L, p, and T are the Lorentz, polarization, and transmission factors, respectively, I is the integrated intensity corrected for background, and $\sigma(I)$ is the standard deviation of I, estimated[30] to be

$$\sigma(I) = [E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$$

In the above expression, E is the total counts in the peak plus background observed for a time T_E, B_1 and B_2 are the background counts observed for time T_B at each extreme of the scan, and ϵ is the "ignorance factor",[30c] set equal to 0.03, to prevent excessively high weight being given to the strong reflections. All reflections for which $I > 0$ were included in the refinement. Although in the final list of observed and calculated structure factors the strongest reflections showed signs of extinction effects, no corrections were made.

X-Ray Structure Determination The corrected data were used to compute a Patterson map which was solved for the palladium and sulfur coordinates (x, y, z in the general position of the space group P2$_1$/c). After a cycle of least-squares refinement[31] of these positional parameters and the scale factor, the resulting structure factors were used in a difference Fourier synthesis.

The electron density map revealed the positions of the oxygen and 19 carbon atoms. Several cycles of isotropic refinement of the scale factor, atomic positional parameters, and isotropic thermal parameters reduced the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ from 0.302 and 0.387 to 0.081 and 0.099, respectively. At this stage, examination of a difference Fourier map indicated some residual, nonisotropic electron density at the positions of all atoms, as well as several possible hydrogen atoms. A few cycles of anisotropic refinement of all non-hydrogen atoms converged at $R_1 = 0.057$ and $R_2 = 0.070$.[32] Inspection of a difference Fourier yielded the location of four of the methallyl hydrogen atoms and four other hydrogen atoms. Subsequent structure factor calculations (in which all nonhydrogen atoms were refined) and Fourier syntheses led to the location of all the hydrogen atoms. The peak heights of these "observed" hydrogen atoms were ~ 0.5 e/Å^3, compared to the estimated[34] error in the difference electron density of 0.2 e/Å^3.

A final cycle of refinement was performed varying the heavy atoms anisotropically and the positional and isotropic thermal parameters of the hydrogen atoms on the methallyl group. Because of computer core storage limitations, the coordinates of the remaining 11 hydrogen atoms were not refined, and their isotropic thermal parameters were fixed at 6.0. The final values for R_1 and R_2 thus attained were 0.048 and 0.057, respectively. The standard deviation of an observation of unit weight[35] was 1.32.

Results

The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the last least-squares refinement cycle,[36] are given in Table I. The root-mean-square amplitudes of vibration derived from the thermal parameters of all nonhydrogen atoms are presented in Table II. The magnitudes (0.1–0.3 Å) and distribution of these values among the atoms are reasonable, indicating that the thermal parameters have physical significance. A perspective drawing of the molecule showing the atom-labeling scheme appears in Figure 1. Intramolecular bond distances and interbond angles are summarized in Tables III and IV. A selected number of best weighted least-squares planes,

(22) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962, p 99.

(23) Programs for the IBM 7094 computer used in this work include local versions of MODE 1, the Brookhaven diffractometer setting program and cell constant and orientation refinement program, GSET, the Prewitt diffractometer setting program, ACAC, the Prewitt absorption correction and data reduction program, XDATA, the Brookhaven Wilson plot and scaling program, FORDAP, the Zalkin Fourier program, OR-FLS, the Busing–Martin–Levy structure factor calculation and least-squares refinement program, OR-FFE, the Busing–Martin–Levy molecular geometry and error function program, and MGEOM, the Wood molecular geometry program.

(24) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 80.

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(26) See ref 22, Vol. III, pp 202, 210.

(27) See ref 22, Vol. III, p 213ff.

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

(29) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1660 (1964).

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(31) The function minimized in all refinement cycles was $w(|F_o| - |F_c|)^2$.

(32) Using Hamilton's test,[33] the reduction in R_2 upon anisotropic refinement indicates the anisotropic model to be significantly better than the isotropic model at the 0.5% confidence level.

(33) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

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(36) A compilation of observed and calculated structure factor amplitudes has been deposited as Document No. NAPS-00202 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Copies may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money order payable to: ASIS–NAPS.

Table I. Final Positional and Thermal Parameters of the Atoms[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.01617 (6)	0.31445 (7)	0.06977 (3)	8.1 (1)	11.1 (1)	1.96 (3)	0.38 (8)	2.28 (4)	−0.27 (4)
S	−0.1796 (2)	0.2374 (3)	−0.0374 (1)	6.3 (3)	15.3 (5)	1.9 (1)	0.9 (3)	2.0 (1)	0.0 (1)
O	0.1463 (6)	0.2544 (7)	0.0284 (4)	6.7 (8)	14 (1)	1.9 (3)	−1.9 (8)	1.7 (4)	−2.1 (5)
C1A	−0.068 (1)	0.410 (1)	0.1332 (6)	16 (2)	11 (2)	3.8 (5)	2 (2)	5.8 (9)	−0.2 (8)
C2A	0.062 (1)	0.358 (1)	0.1860 (5)	12 (2)	11 (2)	2.0 (4)	1 (1)	3.1 (7)	−1.9 (7)
C3A	0.172 (1)	0.422 (1)	0.1781 (6)	13 (2)	16 (2)	3.4 (4)	−4 (2)	4.5 (7)	−2.8 (9)
C4A	0.084 (2)	0.220 (2)	0.2384 (7)	18 (2)	16 (2)	2.5 (5)	1 (2)	4.5 (9)	0.0 (9)
C1	−0.137 (1)	0.154 (1)	−0.1009 (5)	9 (1)	7 (1)	2.2 (4)	0 (1)	3.0 (7)	1.4 (6)
C2	−0.007 (1)	0.134 (1)	−0.0929 (6)	7 (1)	9 (2)	2.3 (4)	1 (1)	2.4 (7)	−0.8 (7)
C3	0.119 (1)	0.187 (1)	−0.0334 (6)	7 (2)	6 (2)	2.3 (4)	1 (1)	1.5 (7)	0.7 (7)
C4	0.342 (1)	0.282 (1)	−0.0177 (5)	6 (1)	14 (2)	2.8 (4)	−2 (1)	1.3 (7)	0.6 (7)
C5	0.2406 (9)	0.168 (1)	−0.0465 (5)	5 (1)	12 (2)	2.3 (4)	3 (1)	2.3 (6)	1.7 (7)
C6	0.456 (1)	0.151 (1)	−0.0776 (6)	8 (1)	19 (2)	3.4 (5)	1 (2)	3.2 (7)	0.3 (9)
C7	−0.268 (1)	0.145 (1)	−0.2430 (5)	8 (1)	11 (2)	1.9 (4)	−1 (1)	1.9 (7)	0.2 (7)
C8	−0.350 (1)	−0.009 (1)	−0.1721 (5)	8 (1)	12 (2)	3.1 (5)	−1 (1)	2.4 (7)	0.3 (7)
C9	−0.2539 (9)	0.096 (1)	−0.1723 (5)	7 (1)	9 (2)	1.9 (4)	1 (1)	1.3 (7)	0.6 (7)
C10	0.2497 (9)	0.042 (1)	−0.0894 (5)	6 (1)	14 (2)	3.0 (4)	1 (1)	2.3 (6)	0.7 (8)
C11	−0.380 (1)	0.095 (1)	−0.3103 (6)	13 (2)	14 (2)	2.1 (5)	2 (2)	1.6 (8)	0.1 (8)
C12	0.448 (1)	0.273 (1)	−0.0335 (6)	6 (1)	17 (2)	4.0 (5)	−3 (1)	1.9 (7)	0.8 (9)
C13	−0.476 (1)	−0.010 (1)	−0.3110 (6)	8 (1)	11 (2)	3.7 (5)	0 (1)	1.67 (7)	−1.4 (8)
C14	0.358 (1)	0.034 (1)	−0.1032 (5)	8 (1)	14 (2)	2.9 (4)	2 (2)	2.0 (7)	−0.5 (7)
C15	0.460 (1)	−0.061 (1)	−0.2401 (6)	7 (1)	13 (2)	3.7 (5)	−4 (1)	1.4 (8)	−0.8 (8)
H1A1	−0.095 (9)	−0.48 (1)	0.114 (5)	5 (2)[d]					
H1A2	−0.15 (1)	0.36 (1)	0.130 (5)	4 (3)					
H3A1	0.164 (9)	−0.47 (1)	0.155 (5)	2 (3)					
H3A2	0.26 (1)	0.35 (1)	0.193 (5)	7 (3)					
H4A1	0.066 (9)	0.27 (1)	0.280 (6)	6 (3)					
H4A2	0.01 (1)	0.15 (1)	0.223 (5)	8 (3)					
H4A3	0.15 (1)	0.17 (1)	0.243 (6)	8 (4)					
H2[e]	−0.007	0.091	−0.143	6					
H4	0.343	0.394	0.021	6					
H6	−0.465	0.141	−0.086	6					
H7	−0.202	0.245	−0.247	6					
H8	−0.339	−0.042	−0.122	6					
H10	0.159	−0.047	−0.103	6					
H11	−0.394	0.115	−0.357	6					
H12	0.524	0.355	−0.012	6					
H13	0.426	−0.054	−0.367	6					
H14	0.358	−0.061	−0.139	6					
H15	0.434	−0.150	−0.260	6					

[a] Atoms are labeled as indicated in Figure 1. Hydrogen atoms are labeled to correspond to the carbon atoms to which they are attached. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are $\times 10^3$. [d] $\beta_{11} = B$, Å^2, since hydrogen atoms were assigned isotropic thermal parameters. [e] This and subsequent hydrogen atoms were not refined.

deviations of individual atoms from the planes, and interplanar angles are collected in Table V.

Discussion

The crystal structure of monothiodibenzoylmethanato-π-methallylpalladium(II) consists of the monomolecular units shown in Figure 1. The molecule has no symmetry and therefore can have two enantiomorphic forms. These are present in an equimolar mixture in the crystal structure, as required by the centrosymmetric space group.

The coordination of the π-methallyl ligand to the palladium atom is similar to that found for many other metal π-allyl complexes.[3–15] For reference, the pertinent geometric features of a number of palladium π-allyl compounds have been summarized in Table VI.[37] Most of the tabulated results are for [(π-allyl)PdX]₂ or (π-allyl)-

(37) Excluded from the summary are the structures of two metal cyclobutenyl isomers of [(C₆H₅)₄C₄OC₂H₅]₂Pd₂Cl₂,[38] since non-bonded interactions have an appreciable influence on the geometry of these compounds.

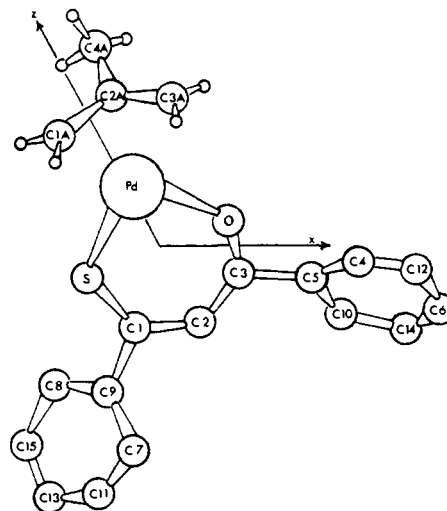(38) L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, 4, 629 (1965).

Figure 1. The molecular structure in the (010) projection. Hydrogen atoms of the S–DBM ligand are omitted for clarity.

Table II. Root-Mean-Square Amplitudes of Vibration (in Å)[a]

Atom	Minimum	Intermediate	Maximum
Pd	0.161	0.197	0.205
S	0.157	0.177	0.236
O	0.15	0.18	0.24
C1A	0.16	0.22	0.29
C2A	0.11	0.22	0.24
C3A	0.18	0.22	0.29
C4A	0.17	0.24	0.30
C1	0.11	0.19	0.21
C2	0.14	0.19	0.21
C3	0.14	0.19	0.21
C4	0.16	0.20	0.25
C5	0.12	0.16	0.23
C6	0.17	0.23	0.26
C7	0.17	0.19	0.21
C8	0.18	0.21	0.23
C9	0.16	0.19	0.20
C10	0.16	0.21	0.23
C11	0.18	0.21	0.28
C12	0.16	0.23	0.28
C13	0.19	0.20	0.27
C14	0.18	0.21	0.25
C15	0.16	0.24	0.27

[a] Taken along the principal axes of the thermal ellipsoids. The orientations of these axes may be worked out from the data of Table I and the unit cell parameters.

Table III. Intramolecular Bond Distances[a,b]

Atoms	Distance, Å	Atoms	Distance, Å
(i) From Palladium Atom		**(iii) In Monothiodibenzoyl-methanato Ligand**	
Pd–S	2.291 (2)	S–C1	1.712 (9)
Pd–O	2.067 (6)	C1–C2	1.40 (1)
Pd–C1A	2.08 (1)	C2–C3	1.41 (1)
Pd–C2A	2.151 (9)	O–C3	1.26 (1)
Pd–C3A	2.21 (1)	C1–C9	1.47 (1)
		C3–C5	1.52 (1)
(ii) In Methallyl Ligand		C9–C8	1.40 (1)
		C8–C15	1.38 (1)
C1A–C2A	1.40 (2)	C15–C13	1.40 (1)
C2A–C3A	1.42 (2)	C13–C11	1.40 (1)
C2A–C4A	1.50 (2)	C11–C7	1.38 (1)
C1A–H1A1	1.01 (9)	C7–C9	1.40 (1)
C1A–H1A2	1.0 (1)	C5–C4	1.38 (1)
C3A–H3A1	1.00 (9)	C4–C12	1.38 (1)
C3A–H3A2	1.10 (9)	C12–C6	1.38 (2)
C4A–H4A1	1.02 (9)	C6–C14	1.37 (2)
C4A–H4A2	1.0 (1)	C14–C10	1.38 (1)
C4A–H4A3	0.9 (1)	C10–C5	1.40 (1)
		C–H (av)	1.09

[a] See footnotes *a* and *b*, Table I. [b] Reported values have not been corrected for thermal motion.

Table IV. Intramolecular Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
(i) From Palladium Atom		**(iii) In monothiodibenzoyl-methanato Ligand**	
S–Pd–O	95.8 (2)	Pd–S–C1	108.7 (3)
C1A–Pd–C3A	67.8 (4)	S–C1–C2	128.2 (7)
C1A–Pd–S	99.4 (4)	C1–C2–C3	128.9 (8)
C3A–Pd–O	96.7 (4)	C2–C3–O	129.2 (8)
		Pd–O–C3	128.8 (6)
(ii) In Methallyl Ligand		S–C1–C9	114.5 (6)
		C1–C9–C8	122.1 (8)
C1A–C2A–C3A	116.7 (9)	C9–C8–C15	120.9 (9)
C1A–C2A–C4A	121.4 (9)	C8–C15–C13	120.8 (9)
C3A–C2A–C4A	120.9 (9)	C15–C13–C11	117.7 (9)
H1A1–C1A–H1A2	108 (7)	C13–C11–C7	122.0 (9)
H3A1–C3A–H3A2	120 (7)	C11–C7–C9	119.9 (9)
H1A1–C1A–C2A	126 (5)	C7–C9–C8	118.6 (8)
H3A1–C3A–C2A	121 (5)	C7–C9–C1	119.3 (8)
H1A2–C1A–C2A	120 (6)	C9–C1–C2	117.3 (8)
H3A2–C3A–C2A	119 (5)	O–C3–C5	114.2 (8)
H4A1–C4A–H4A2	88 (8)	C3–C5–C4	119.3 (8)
H4A1–C4A–H4A3	110 (9)	C5–C4–C12	120.0 (9)
H4A1–C4A–C2A	105 (6)	C4–C12–C6	121 (1)
H4A2–C4A–C2A	115 (6)	C12–C6–C14	119 (1)
H4A3–C4A–C2A	108 (7)	C6–C14–C10	120.9 (9)
		C14–C10–C5	119.6 (9)
		C10–C5–C4	119.2 (9)
		C10–C5–C3	121.5 (8)
		C5–C3–C2	116.5 (8)
		C–C–H (av)	119.7[b]

[a] See footnotes *a* and *b*, Table III. [b] A value of 120.0° would be required by geometry if the phenyl rings were rigorously planar.

PdX$_2$ complexes. Prior to the present study, only one (π-allyl)PdXY structure had been reported,[39] chlorotriphenylphosphine-π-methallylpalladium(II).[7] In both this complex and in (π-C$_4$H$_7$)Pd(S–DBM) the metal–allyl attachment is significantly asymmetric, as judged by the Pd–C bond lengths. It is of interest and importance that in both molecules the Pd–C distance *trans* to the more polarizable ligand atom, phosphorus or sulfur, is unusually long. In terms of the discussion by Kettle and Mason[40] of the nature of the bonding in metal π-allyl

complexes, the observed *trans* effects[41] may be visualized as being transmitted primarily through the metal d$_{xz}$ orbital. This orbital is involved in σ bonding with the ligand atoms X and Y and with the a$_2$ π-orbital combination of the allyl ligand (structure I of Kettle and Mason[40]). From the observed geometry (Figure 1), mesomeric effects[42] would appear to be minimal based on orbital overlap considerations, and would be rigorously excluded if the π-methallyl group were at right angles to the palladium coordination plane. We, therefore, attribute the observed Pd–C bond lengthenings in [(π-C$_4$H$_7$)Pd(S–DBM)] and the related triphenylphosphine complex[7] to an inductive *trans* effect.[41,42] The role of the sulfur atom in S–DBM (and presumably in related ligands) as a *trans* labilizer should, if static properties of molecules are any indication, have some usefulness in designing reactions of its metal complexes.

Despite the asymmetry in the palladium–methallyl linkage in (π-C$_4$H$_7$)Pd(S–DBM), the two olefinic C–C bond lengths are essentially equivalent (Δ/σ = 1.0). This result is less consistent with localized bond models such as II than with the delocalized model I. Indeed, the bulk of bond-length data in Table VI are compatible with structure I, to within the limits of error quoted. This observation does not rule out the possibility of structures such as II for other systems (*e.g.*, bis-π-allylrhodium chloride[9]), however. As is the case for other 2-methallyl-metal complexes,[7,12−14] the methyl carbon atom in [(π-C$_4$H$_7$)Pd(S–DBM)] is displaced from the plane of the

(39) At least one other complex, chlorotriphenylphosphine-π-1,1,3,3-tetramethallylpalladium(II), has been studied,[14] but the details are not yet available.

(40) S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, **5**, 573 (1966).
(41) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).
(42) For a recent discussion of and further references to this kind of behavior, *cf.* J. Chatt and A. D. Westland, *J. Chem. Soc., A*, 88 (1968).

Table V. Best Weighted Least-Squares Planes[a]

Plane 1 through Atoms C7, C8, C9, C11, C13, C15
$$-0.6251X + 0.7804Y + 0.0139Z = 1.311$$

Distances (in Å) of carbon atoms from plane
C7, −0.02; C8, 0.00; C9, 0.01; C11, 0.01; C13, 0.00; C15, 0.00

Plane 2 through Atoms C4, C5, C6, C10, C12, C14
$$0.1343X − 0.5332Y + 0.8352Z = −0.9967$$

Distances (in Å) of carbon atoms from plane
C4, 0.01; C5, −0.01; C6, −0.02; C10, 0.00; C12, 0.00; C14, 0.02

Plane 3 through Atoms S, O, C1, C2, C3, C5, C9
$$-0.1140X − 0.8934Y + 0.4345Z = −1.877$$

Distances (in Å) of atoms from plane
S, −0.01; O, 0.02; C1, 0.02; C2, 0.07; C3, 0.03; C5, −0.11; C9, −0.02; Pd, 0.09

Plane 4 through Atoms C1, C2, C3, C5, C9
$$-0.0670X − 0.9228Y + 0.3793Z = −1.793$$

Distances (in Å) of atoms from plane
C1, −0.03; C2, 0.08; C3, 0.01; C5, −0.04; C9, −0.01; Pd, −0.16; S, −0.19; O, −0.09
Angle between planes 1 and 4 = 132°
Angle between planes 2 and 4 = 143°

[a] The equations used to describe the planes are expressed in orthogonal coordinates, where Y is coincident with the cell b axis, Z is in the direction $a \times b$, and X is chosen according to the right-hand rule.

Table VI. Structural Features of Palladium π-Allyl Complexes[a]

| Complex | Bond distances, Å | | | | | Dihedral angle, deg | Ref |
	$Pd-C_1$	$Pd-C_2$	$Pd-C_3$	C_1-C_2	C_2-C_3		
[(π-CH$_2$CHCH$_2$)PdCl]$_2$[b]	2.123 (7)	2.108 (9)	2.121 (8)	1.40·(2)	1.36 (2)	111.5 (9)	4a
[(π-CH$_3$CHCHCHCH$_3$)PdCl]$_2$[c]	2.14 (4)	2.08 (3)	2.05 (3)	...	...	125	11
{[π-(CH$_3$)$_2$CCHC(CH$_3$)$_2$]PdCl}$_2$[c]	2.12 (3)	2.14 (3)	2.14 (3)	1.41 (4)	1.42 (4)	121	14
[(π-CH$_2$C(CH$_3$)CH$_2$)PdCl]$_2$	2.08 (2)	2.10 (2)	2.06 (2)	1.37 (3)	1.35 (3)	112	14
[(π-CH$_2$C(t-C$_4$H$_9$)CH$_2$)PdCl]$_2$	2.14	2.15	2.14	1.39	1.39	119.5	10
[(π-C$_2$H$_5$O$_2$CCHC(OH)CH$_2$)PdCl]$_2$	2.10	2.19	2.13	1.33	1.43	108	15
[(π-CH$_2$CHCH$_2$)Pd(O$_2$CCH$_3$)]$_2$[d]	2.08	2.05	2.08	1.38 (4)	1.35 (2)	116 (5)	5
[(π-C$_8$H$_{11}$)Pd(acac)][e]	2.12 (1)	2.10 (1)	2.12 (1)	1.42 (2)	1.39 (2)	121.5	f
[(π-C$_{12}$H$_{17}$)Pd(acac)][g]	2.14 (2)	2.11 (2)	2.13 (2)	1.44 (3)	1.43 (3)	121	h
[(π-CH$_2$C(CH$_3$)CH$_2$)PdCl(PPh$_3$)][i]	2.14 (3)	2.22 (3)	2.28 (3)	1.47 (4)	1.40 (4)	119	7
[(π-CH$_2$C(CH$_3$)CH$_2$)Pd(S–DBM)]	2.08 (1)	2.15 (1)	2.21 (1)	1.40 (2)	1.42 (2)	115.8	This work
Average values	2.11	2.13	2.13	1.40	1.39	117	...

[a] Estimated standard deviations occur in parentheses beside the entry if reported; unless stated otherwise the numbering of carbon atoms in the π-allyl backbone, C_1, C_2, C_3, corresponds to the left, center, and right carbon atoms as written in the table; dihedral angle is computed between the plane of $C_1-C_2-C_3$ and the coordination plane of the palladium atom; ... means value not reported. [b] Data taken at −140°; hydrogen atoms found in the plane of the allyl group. [c] Methyl carbon atoms not in plane of allyl group. [d] Values reported are averaged over the two halves of the molecule. [e] C_8H_{11} = cycloocta-2,4-dienyl; acac = acetylacetonato. [f] M. R. Churchill, *Inorg. Chem.*, **5**, 1608 (1966). [g] $C_{12}H_{17}$ = hexamethyl Dewar benzene; acac = acetylacetonato. [h] J. F. Malone, W. S. McDonald, B. L. Shaw, and G. Shaw, *Chem. Commun.*, 869 (1968). [i] Ph = C_6H_5; C_1 *trans* to Cl.

Table VII. Comparison of S–DBM Ring Geometry with Its β-Diketonate Analogs[a]

| | Interatomic distances, Å | | | | | | | |
	M–O	M–S	O–C	S–C	C–C$_l$	C–C$_x$	O–O	O–S
Present structure	2.07	2.29	1.26	1.71	1.40	1.50	...	3.24
Lit av	1.96	...	1.27	...	1.39	1.52	2.78	...

| | Interatomic angles, deg | | | | | | | | |
	OMO	OMS	MOC	MSC	OCC	SCC$_l$	CC$_l$C	OCC$_x$	SCC$_x$
Present structure	...	95.8	128.8	108.7	129.2	128.2	128.9	114.2	114.5
Lit av	90.7	...	126.5	...	125.3	...	124.0	114.9	...

[a] Literature average (lit av) values are taken from ref 44; C_l and C_x are as defined in that reference.

allyl group toward the palladium atom by 0.26 Å. A discussion of the origin of displacements of this kind has been given by Kettle.[43]

Although the H–C–C and H–C–H angles in the allyl ligand range from 108–126°, the average value is 119°, in accord with the expected sp^2 hybridization at the carbon atoms. In view of the large (5–9°) esd's for the individual bond angles, no significance can be attached to their deviations from the idealized value of 120°. The same may be said for the bond angles within the methyl group. Further details about the geometry of the π-methallyl group may be obtained from Tables III, IV, and VI. The pertinence of the tabulated dihedral angles (Table VI) is discussed in ref 40.

Apart from the present work, the only other X-ray diffraction study of the S–DBM ligand is a brief report[44] of Pd–S distances, 2.26 and 2.22 Å, and a S–Pd–S angle of 90° in cis-[Pd(S–DBM)₂]. No other monothioacetylacetonate complex has yet been structurally characterized, although many have been synthesized.[45] The analogous β-diketonate complexes have been subjected to extensive structural investigations, however. For comparison, the results of a recent literature survey[46] are summarized with the present findings in Table VII.

In general, the geometric features of the S–DBM chelate ring resemble those of its β-diketonate analogs, but there are some notable exceptions. The Pd–S bond length, 2.291 Å, is shorter than the value of 2.49 Å which can be calculated from the observed Pd–O distance and the difference between sulfur and oxygen covalent radii.[47] The shortening is even more pronounced in cis-[Pd(S–DBM)]₂,[44] and may be suggestive of Pd–S π bonding.[48] Other differences between the geometry of the S–DBM chelate ring and its β-diketonate analogs (Table VII)

(43) S. F. A. Kettle, *Inorg. Chim. Acta*, 1, 303 (1967).

(44) E. A. Shugam, L. M. Shkol'nikova, and S. E. Livingstone, *Zh. Strukt. Khim.*, 8, 550 (1967).

(45) *Cf.* R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Austr. J. Chem.*, 21, 103 (1968), and references contained therein.

(46) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, 88, 2951 (1966).

(47) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224, 228.

(48) D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Commun.*, 1080 (1967), and references cited therein.

reflect the asymmetry induced in the former by the presence of the large sulfur atom. Moreover, since structure III, rather than IV, its valence bond resonance isomer, has been shown[49,50] to predominate in the free monothio-β-diketonate anions, it is tempting to suggest the preponderance of forms such as III in the metal chelate structure. Such an argument, while not unequivocal, would explain the nearly tetrahedral value found

III   IV
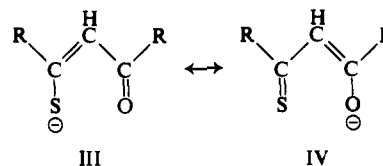
for the Pd–S–C angle and the puckering of the ring (Tables IV and V) at the sulfur atom. The equivalence of C–C bond lengths and other features of the ring geometry, however, indicate that π-delocalization may still be important.

Other features of the S–DBM ligand, summarized in the tables, appear to be normal. One possible exception is the C_1–C_9 bond length of 1.47 ± 0.01 Å, nearly 4σ shorter than the expected value, which could suggest a small amount of π delocalization between C_1 and C_9. The dihedral angles included in Table V indicate considerable rotation of both phenyl rings out of the plane of the chelate ring, however. Similar rotations are found in several structural studies of metal β-diketonate complexes where one, or both, of the R groups is phenyl, and have been ascribed to crystal packing forces.[51]

(49) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austr. J. Chem.*, 18, 673 (1965).

(50) S. H. H. Chaston and S. E. Livingstone, *ibid.*, 20, 1079 (1967).

(51) P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, 6, 731 (1967).