process, slow on the pmr time scale, has also been established for mixtures of ($\pi$-methallyl)Pd(SDBM) and ($\pi$-allyl)Pd(DBM). These conclusions are sustained by comparison with studies of other asymmetric $\pi$-allyl–Pd systems.[4,8,13]

**Acknowledgments.** This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Miss Janet Sadownick for experimental assistance, Dr. K. Wüthrich of the Bell Telephone Laboratories for obtaining the 220-MHz pmr spectra, Drs. M. C. Woods, R. Grubbs, and Mr. Howard Heitner for valuable discussions, and Dr. B. G. Segal, Miss V. Parmakovich, and Mr. I. Miura for technical assistance. S. J. L. expresses his appreciation to the Alfred P. Sloan Foundation for a Research Fellowship (1968–1970).

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# Crystal and Molecular Structure of Monothiodibenzoylmethanato-$\pi$-*syn*-1-*tert*-butyl-2-methallylpalladium(II)

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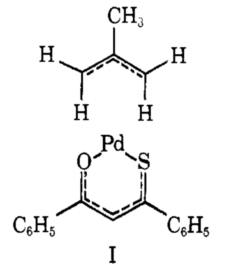
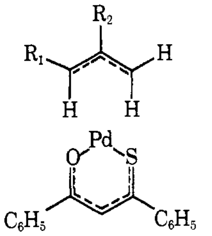
*Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received December 17, 1971*

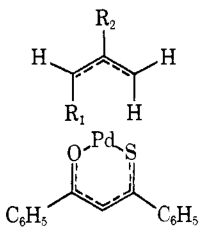
**Abstract:** The structure of the title compound, $1,2,3\text{-}h^3\text{-}[(tert\text{-}C_4H_9)CHC(CH_3)CH_2]Pd(C_6H_5COCHCSC_6H_5)$, has been determined in a single-crystal X-ray diffraction study. The *tert*-butyl substituent syn to the methyl group in the $\pi$-allyl ligand is trans to the sulfur atom of the chelating monothiodibenzoylmethane anion (SDBM). The Pd–S and Pd–O distances are 2.297 (3) and 2.047 (7) Å, respectively, and the S–Pd–O angle is 94.4 (2)°. The trans influence of the sulfur atom may be judged by the nonequivalence of the bond lengths Pd–C(1) (trans to sulfur), 2.18 (1) Å, Pd–C(2), 2.141 (9) Å, and Pd–C(3) (cis to sulfur), 2.05 (1) Å. Both the C(1)–C(2) and C(2)–C(3) bond lengths are 1.39 (1) Å. The geometry of the SDBM ligand is comparable to that found in the $\pi$-methallyl analog. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell dimensions of $a = 12.251$ (6) Å, $b = 11.524$ (9) Å, $c = 8.514$ (5) Å, $\alpha = 112.89$ (5)°, $\beta = 107.61$ (2)°, $\gamma = 90.31$ (5)°, $Z = 2$. From 2363 independent observed reflections collected by diffractometer, the structure was solved and refined to a final value for the discrepancy index $R_1 = 0.073$.

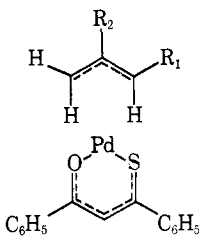
The solid-state structure of monothiodibenzoylmethanato-$\pi$-methallylpalladium(II), I, has been

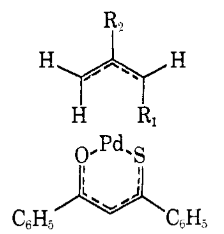

I

described previously,[2] and several other structural studies of ($\pi$-allyl)PdXY complexes containing a symmetric $\pi$-allylic group bonded to a palladium atom in a nonsymmetric ligand environment have been carried out.[3–5] The geometries of various asymmetrically substituted $\pi$-allyl palladium complexes have also been determined,[6,7] but there has not yet been a structural investigation of an asymmetrically substituted $\pi$-allyl group coordinated to palladium in a compound of the type ($\pi$-allyl)PdXY. In conjunction with our study of the solution behavior of ($\pi$-allyl)Pd(SDBM) complexes,[8] a number of compounds of this kind were synthesized, for which structures IIa–d are possible. As discussed previously,[8] structure IIa predominates at


IIa, syn/trans


IIb, anti/trans


IIc, syn/cis


IId, anti/cis

low temperatures in solution, a conclusion facilitated by the present solid-state structural determination. It

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[1] National Institutes of Health Predoctoral Fellow, 1967–1970.

[2] S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 91, 2504 (1969).

[3] R. Mason and D. R. Russell, *Chem. Commun.*, 26 (1966).

[4] A. E. Smith, *Acta Crystallogr., Sect. A*, 25, S161 (1969).

[5] (a) R. Mason, G. B. Robertson, P. O. Whimp, and D. A. White, *Chem. Commun.*, 1655 (1968); (b) R. Mason and P. O. Whimp, *J. Chem. Soc. A*, 2709 (1969).

[6] For references see Table VI, ref 2.

[7] K. Oda, N. Yasuoka, T. Ueki, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jap.*, 43, 362 (1970).

[8] S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 94, 6949 (1972).

was also felt that the results of such an investigation would provide an indirect calibration of solution structural assignments for other asymmetric ($\pi$-allyl)PdXY complexes, *e.g.*, chlorotriphenylphosphine-$\pi$-1-methallylpalladium(II).[9]

Apart from the question of structural isomerism, knowledge of the geometry of a compound of type II was desired for several other reasons. By comparing the results with those for I, the effect of the $R_1$ group on the allyl–palladium geometry could be assessed. It was also of interest to obtain a second measure of the $\mathrm{C\overset{\cdots}{-}C}$ bond distances within the allylic backbone, especially since the low-temperature X-ray study of chlorotriphenylphosphine-$\pi$-allylpalladium(II) revealed carbon–carbon bond lengths differing by 0.19 Å.[4] In compound I at room temperature the $\mathrm{C\overset{\cdots}{-}C}$ distances are equal within experimental error.[2] The continuing interest in the chemical and physical properties of monothio-$\beta$-diketonate ligands provided additional incentive for the structural determination, and comparison with the results for two $\mathrm{Ni(RCSCHCOR')_2}$ complexes has very recently become possible.[10,11]

Although several compounds of type II were prepared and obtained as single crystals,[8] the complex with $R_1$ = *tert*-$C_4H_9$ and $R_2$ = $CH_3$ provided the best diffraction patterns. The crystallographic structural determination of this derivative is now reported.

## Experimental Procedure and Results

**Collection and Reduction of the Data.** The compound was prepared as described in the preceding paper[8] and recrystallized from benzene and petroleum ether. Crystals were mounted on glass fibers and examined by precession photography. Since only $\bar{1}$ Laue symmetry and no systematic extinctions were apparent, a triclinic cell was chosen, the dimensions of which were later refined by a least-squares technique to give the best fit between calculated and observed values for the $\chi$, $\phi$, and $2\theta$ angular settings of 14 independent reflections which were centered in the counter window of a Picker four-circle diffractometer.[12] The cell constants are $a$ = 12.251 (6) Å, $b$ = 11.524 (9) Å, $c$ = 8.514 (5) Å, $\alpha$ = 112.89 (5)°, $\beta$ = 107.61 (2)°, $\gamma$ = 90.31 (5)°, $V$ = 1045 Å.[3] Reduction of these parameters by standard methods[12,13] produced the equivalent unit cell defined by $a$ = 11.356 Å, $b$ = 12.251 Å, $c$ = 8.514 Å, $\alpha$ = 107.61°, $\beta$ = 110.79°, $\gamma$ = 76.57°, which satisfies the conditions for a positive type I reduced cell with no hidden symmetry.[13] The original cell constants were used in all subsequent calculations. The space group was assumed to be the centrosymmetric $P\bar{1}$, a choice ultimately justified by the successful refinement. The calculated density of 1.453 g/cm$^2$ based on two formula units of $\mathrm{C_{23}H_{26}SOPd}$ per unit cell was checked by suspension of a single crystal in an aqueous solution of KI, $\rho$ = 1.44 g/cm$^3$.

A polyhedral crystal approximately 0.2 × 0.3 × 0.5 mm was mounted along the $b^*$ axis on a eucentric head and the dimensions of the habit measured optically. The mosaic spread was found to be satisfactory for several $\omega$ scans on the diffractometer. The intensities of 2439 independent reflections were measured by the $\theta$–$2\theta$ scan technique to $\sin \theta_{\max}$ = 0.75 in the automated mode using Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å) at 23°. The take-off angle was 3.3° and a symmetric scan range of 1.5° in $2\theta$ plus the K$\alpha_1$–K$\alpha_2$ allowance was used. The scan rate was 1°/min, with stationary-counter, stationary-crystal background counts of 10 sec being measured at both ends of the scan range. Four standard reflections were used to monitor the crystal alignment and instrument stability. During the five-day period required to collect the data, their maximum variation was ±5% and showed no systematic trends.

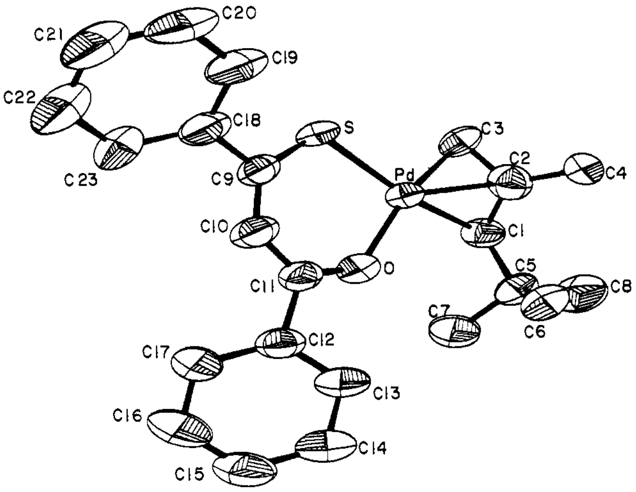

Figure 1. The molecular structure showing the numbering scheme of the atoms and the 50% probability thermal ellipsoids.

After correcting the intensities for background, attenuator use, Lorentz, and polarization effects, an appropriate absorption correction was applied using ACAC-3[12] since $\mu$ = 83.3 cm$^{-1}$. The calculated transmission factors ranged from 0.095 to 0.246 and the agreement with the observed variation in the intensities at four values of $\phi$ was checked for axial reflections measured at $\chi$ = 90°. The data were then scaled by XDATA[12] to produce values of $|F_o|$ and $|F_o|^2$ for subsequent use in Fourier summations and structure factor calculations. The scattering factors for neutral Pd, S, O, and C atoms were obtained from the International Tables,[14a] and a correction for anomalous dispersion was included in the contribution of Pd to the calculated structure factors.[14b] A weight, $w = 4F^2/\sigma^2(F^2)$, was assigned to each reflection, where $\sigma(F^2)$ is the standard deviation of $F^2$ obtained from $\sigma(I)$ after absorption and Lorentz-polarization corrections were made, and $I$ is the integrated intensity corrected for background and attenuators. These terms have been defined previously, and the value of $\epsilon$ used in determining $\sigma(I)$ was set at 0.03.[15,16] The 76 reflections for which $I \leq 3\sigma(I)$ were excluded from the refinement. The observed data were not corrected for secondary extinction.

**Solution and Refinement of the Structure.** The palladium coordinates were obtained from a sharpened Patterson map, computed using the corrected data. The sulfur and oxygen atoms were found from a difference Fourier phased on the metal atom. Repetitive cycles of structure factor calculations and Fourier summations disclosed the positions of all nonhydrogen atoms. Minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, the least-squares refinement of the scale factor, positional parameters, and anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ converged at final values for $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.073 and 0.105, respectively. Since the number of parameters varied in this refinement produced a matrix larger than the core storage available in the computer, the thermal parameters of the SDBM and $\pi$-allyl groups were refined on alternate cycles. A final difference Fourier map showed several peaks of electron density ranging from 0.05 to 0.20 times that for a carbon atom, but since the largest of these was in the vicinity of the palladium atom, and, in view of a noticeable

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[9] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

[10] J. Sieler, Ph. Thomas, E. Uhlemann, and E. Höhne, *Z. Anorg. Allg. Chem.*, **380**, 160 (1971).

[11] L. Kutschabsky and L. Beyer, *Z. Chem.*, **11**, 30 (1971).

[12] Programs for an IBM 360 computer used in this work include local versions of MODE-1, the Brookhaven diffractometer setting program and cell constant and orientation refinement program, TRACER II, the Lawton lattice transformation and cell reduction 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, CULS, a modified version of ORFLS, the Busing–Martin–Levy structure factor calculation and least-squares refinement program, ORFFE, the Busing–Martin–Levy molecular geometry and error function program, ORTEP, the Johnson thermal ellipsoid plotting program, and MEAN PLANE, the Pippy–Ahmed best planes program.

[13] "International Tables for X-ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 530 ff.

[14] (a) Reference 13, Vol. III, 2nd ed, 1962, pp 202, 210; (b) p 213 ff.

[15] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).

[16] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *ibid.*, **6**, 197 (1967).

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

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[c] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pd | 0.22096 (5) | −0.01592 (5) | 0.18991 (9) | 7.82 (8) | 6.99 (9) | 24.8 (2) | 0.23 (5) | 4.60 (9) | 4.4 (1) |
| S | 0.3239 (2) | 0.1338 (2) | 0.1541 (2) | 8.6 (2) | 6.3 (2) | 28.3 (6) | −0.4 (2) | 5.1 (3) | 3.9 (3) |
| O | 0.2346 (5) | −0.1645 (6) | −0.0313 (8) | 8.3 (5) | 8.6 (7) | 24 (1) | 0.2 (5) | 5.1 (7) | 5.2 (8) |
| C(1) | 0.1375 (9) | −0.1208 (9) | 0.297 (1) | 11.8 (9) | 9 (1) | 23 (2) | 1.6 (8) | 6 (1) | 7 (1) |
| C(2) | 0.1018 (9) | −0.002 (1) | 0.334 (1) | 11.3 (9) | 13 (1) | 27 (2) | 2.7 (9) | 10 (1) | 8 (1) |
| C(3) | 0.1927 (8) | 0.097 (1) | 0.424 (1) | 8.7 (8) | 12 (1) | 19 (2) | −2.0 (8) | 0 (1) | 5 (1) |
| C(4) | −0.0220 (9) | 0.024 (1) | 0.257 (2) | 9.3 (9) | 12 (1) | 36 (3) | 2.6 (8) | 7 (1) | 7 (2) |
| C(5) | 0.0649 (8) | −0.253 (1) | 0.180 (1) | 10.4 (9) | 10 (1) | 32 (3) | −0.5 (8) | 7 (1) | 9 (1) |
| C(6) | −0.0156 (9) | −0.267 (1) | −0.006 (1) | 10.5 (9) | 12 (1) | 25 (2) | −1.6 (8) | 2 (1) | 5 (1) |
| C(7) | 0.154 (1) | −0.348 (1) | 0.157 (2) | 14 (1) | 10 (1) | 45 (4) | 3.2 (9) | 9 (2) | 11 (2) |
| C(8) | −0.008 (1) | −0.284 (1) | 0.284 (2) | 18 (1) | 15 (1) | 36 (3) | −2 (1) | 12 (2) | 11 (2) |
| C(9) | 0.3480 (7) | 0.0652 (8) | −0.048 (1) | 6.4 (7) | 8 (1) | 30 (2) | 0.3 (6) | 3 (1) | 7 (1) |
| C(10) | 0.3275 (7) | −0.0618 (9) | −0.166 (1) | 8.1 (7) | 9 (1) | 27 (2) | 0.2 (7) | 4 (1) | 7 (1) |
| C(11) | 0.2805 (7) | −0.1668 (8) | −0.146 (1) | 6.6 (7) | 7.7 (9) | 27 (2) | 0.9 (6) | 2 (1) | 5 (1) |
| C(12) | 0.2752 (7) | −0.2987 (8) | −0.291 (1) | 8.4 (8) | 8 (1) | 24 (2) | 1.0 (7) | 3 (1) | 5 (1) |
| C(13) | 0.188 (1) | −0.3903 (9) | −0.329 (2) | 13 (1) | 7 (1) | 34 (3) | 1.4 (8) | 7 (1) | 6 (1) |
| C(14) | 0.181 (1) | −0.514 (1) | −0.459 (2) | 16 (1) | 8 (1) | 31 (3) | 0.6 (9) | 6 (1) | 4 (1) |
| C(15) | 0.264 (1) | −0.541 (1) | −0.540 (2) | 16 (1) | 9 (1) | 34 (3) | 3 (1) | 9 (2) | 5 (1) |
| C(16) | 0.351 (1) | −0.451 (1) | −0.504 (2) | 15 (1) | 12 (1) | 31 (3) | 6 (1) | 9 (1) | 8 (2) |
| C(17) | 0.3601 (9) | −0.327 (1) | −0.374 (1) | 10.0 (9) | 10 (1) | 32 (3) | 2.9 (8) | 7 (1) | 6 (1) |
| C(18) | 0.3932 (7) | 0.1562 (9) | −0.107 (1) | 7.4 (7) | 9 (1) | 31 (2) | −0.6 (7) | 2 (1) | 8 (1) |
| C(19) | 0.3523 (9) | 0.276 (1) | −0.073 (2) | 11 (1) | 11 (1) | 36 (3) | −1.2 (9) | 1 (1) | 10 (2) |
| C(20) | 0.391 (1) | 0.354 (1) | −0.140 (2) | 16 (1) | 10 (1) | 41 (4) | −3 (1) | 3 (2) | 11 (2) |
| C(21) | 0.471 (1) | 0.322 (1) | −0.225 (2) | 14 (1) | 17 (2) | 47 (4) | −3 (1) | 5 (2) | 17 (2) |
| C(22) | 0.516 (1) | 0.206 (1) | −0.251 (2) | 11 (1) | 20 (2) | 43 (4) | −3 (1) | 3 (1) | 18 (2) |
| C(23) | 0.4753 (8) | 0.125 (1) | −0.194 (1) | 7.9 (8) | 15 (1) | 29 (3) | −1.0 (9) | 2 (1) | 12 (1) |

[a] Atoms are numbered as shown in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. See also discussion in the text. [c] The form of the anisotropic thermal ellipsoid is given in the text. Values are reported $\times 10^3$.

Table II. Intramolecular Bond Distances[a,b]

| Atoms | Distance, Å | Atoms | Distance, Å |
|---|---|---|---|
| (i) From Palladium Atom | | (iii) In Monothiodibenzoylmethanato Ligand | |
| Pd–S | 2.297 (3) | S–C(9) | 1.71 (1) |
| Pd–O | 2.047 (7) | C(9)–C(10) | 1.38 (1) |
| Pd–C(1) | 2.18 (1) | C(10)–C(11) | 1.43 (1) |
| Pd–C(2) | 2.141 (9) | C(11)–O | 1.26 (1) |
| Pd–C(3) | 2.05 (1) | C(9)–C(18) | 1.49 (1) |
| | | C(18)–C(19) | 1.42 (1) |
| | | C(19)–C(20) | 1.39 (2) |
| | | C(20)–C(21) | 1.36 (2) |
| | | C(21)–C(22) | 1.42 (2) |
| (ii) In Allylic Moiety | | C(22)-C(23) | 1.36 (2) |
| | | C(23)–C(18) | 1.39 (1) |
| C(1)–C(2) | 1.39 (1) | C(11)–C(12) | 1.52 (1) |
| C(2)–C(3) | 1.39 (1) | C(12)–C(13) | 1.36 (1) |
| C(2)–C(4) | 1.54 (1) | C(13)–C(14) | 1.41 (2) |
| C(1)–C(5) | 1.54 (1) | C(14)–C(15) | 1.37 (2) |
| C(5)–C(6) | 1.53 (1) | C(15)–C(16) | 1.37 (2) |
| C(5)–C(7) | 1.55 (1) | C(16)–C(17) | 1.40 (2) |
| C(5)–C(8) | 1.57 (1) | C(17)–C(12) | 1.40 (1) |

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

Table III. Intramolecular Bond Angles[a]

| Atoms | Angle, deg | Atoms | Angle, deg |
|---|---|---|---|
| (i) Around Palladium Atom | | S–C(9)–C(10) | 128.7 (7) |
| | | C(9)–C(10)–C(11) | 127.5 (9) |
| S–Pd–O | 94.4 (2) | C(10)–C(11)–O | 128.2 (9) |
| C(1)–Pd–C(3) | 66.2 (4) | C(11)–O–Pd | 130.8 (6) |
| C(1)–Pd–O | 99.5 (3) | S–C(9)–C(18) | 114.9 (7) |
| C(3)–Pd–S | 99.6 (3) | C(9)–C(18)–C(19) | 119.8 (9) |
| | | C(18)–C(19)–C(20) | 118 (1) |
| (ii) In Allylic Moiety | | C(19)–C(20)–C(21) | 122 (1) |
| | | C(20)–C(21)–C(22) | 121 (1) |
| C(1)–C(2)–C(3) | 113.2 (9) | C(21)–C(22)–C(23) | 119 (1) |
| C(1)–C(2)–C(4) | 126 (1) | C(22)–C(23)–C(18) | 121 (1) |
| C(3)–C(2)–C(4) | 120 (1) | C(23)–C(18)–C(9) | 120.5 (9) |
| C(2)–C(1)–C(5) | 128.7 (9) | C(23)–C(18)–C(19) | 119.7 (9) |
| C(1)–C(5)–C(6) | 114.4 (8) | C(18)–C(9)–C(10) | 116.4 (9) |
| C(1)–C(5)–C(7) | 105.3 (8) | C(10)–C(11)–C(12) | 116.6 (9) |
| C(1)–C(5)–C(8) | 109.4 (9) | C(11)–C(12)–C(13) | 117.7 (9) |
| C(6)–C(5)–C(7) | 110 (1) | C(12)–C(13)–C(14) | 120 (1) |
| C(6)–C(5)–C(8) | 109.2 (9) | C(13)–C(14)–C(15) | 119 (1) |
| C(7)–C(5)–C(8) | 108.1 (9) | C(14)–C(15)–C(16) | 122 (1) |
| | | C(15)–C(16)–C(17) | 120 (1) |
| (iii) In Monothiodibenzoylmethanato Ligand | | C(16)–C(17)–C(12) | 118 (1) |
| | | C(17)–C(12)–C(13) | 121.0 (9) |
| | | C(17)–C(12)–C(11) | 121.2 (8) |
| Pd–S–C(9) | 109.1 (3) | C(12)–C(11)–O | 114.9 (8) |

[a] See footnotes *a* and *b*, Table II.

splitting in the chart recorder profiles observed for a small number of reflections (not given any special treatment in the refinement) during the data collection, no attempt was made to identify the hydrogen atoms. In the final refinement cycles, all parameters varied by less than 10% of their estimated standard deviations.[17]

The final positional and thermal parameters, with standard deviations derived from the inverse matrix of the last least-squares refinement cycle, are presented in Table I. The size and relative orientations of the individual atomic thermal ellipsoids are shown in Figure 1, along with the atom numbering scheme. The molecular geometry is summarized in Tables II–IV. From the figure it is apparent that the thermal ellipsoids are oriented with their major axes more or less in one direction. This result may have its origin in an inadequate absorption correction. For this reason, and because of the blocking of parameters in the refinement mentioned above, the errors quoted in Tables II–IV must be regarded as lower limits.

## Discussion

The crystal structure consists of the monomolecular units shown in Figure 1, the two possible enantiomorphic forms occurring in equal numbers in the centrosymmetric lattice. Examination of an extensive table

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(17) A list of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6956. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

**Table IV.** Best Weighted Least-Squares Planes, $Ax + By + Cz - D = 0^{a,b}$

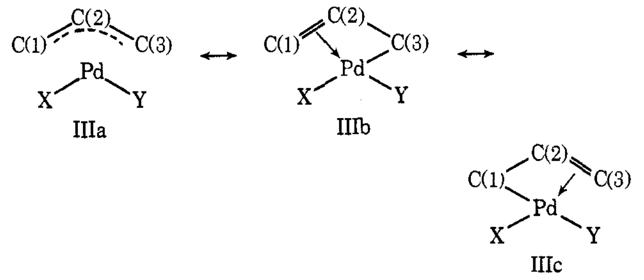
| Plane no. | $A$ | $B$ | $C$ | $D$ | Distances (in Å) of atoms from plane |
|---|---|---|---|---|---|
| 1 | 4.254 | −6.889 | 6.445 | 1.361 | C(12), −0.008 (9); C(13), 0.010 (11); C(14), −0.008 (12); C(15), 0.009 (12); C(16), −0.012 (11); C(17), 0.013 (11) |
| 2 | 5.804 | 0.879 | 5.011 | 1.897 | C(18), −0.012 (9); C(19), 0.024 (11); C(20), −0.018 (13); C(21), −0.010 (14); C(22), 0.020 (12); C(23), −0.003 (10) |
| 3 | 9.868 | −3.732 | 2.683 | 3.027 | C(18), −0.016 (9); C(9), 0.034 (8); C(10), −0.012 (9); C(11), −0.029 (8); C(12), 0.023 (9) |
| 4 | 9.539 | −4.549 | 2.929 | 2.928 | S, 0.004 (3); C(9), −0.047 (8); C(10), −0.011 (9); C(11), 0.078 (8); O, −0.034 (6) |

[a] See footnotes *a* and *b*, Table I. [b] Weights were based on the variance–covariance matrix obtained from the final cycle of least-squares refinement; $x$, $y$, and $z$ are fractional coordinates of the atoms in the triclinic cell.

of interatomic distances revealed the packing to be influenced only by the normal van der Waals forces, with the closest Pd···Pd, Pd···S, and S···S nonbonded contacts all being greater than 5 Å.

The molecule has adopted the syn/trans configuration, structure IIa, which is the major geometric isomer found for the complex at low temperatures in solution.[8] The assignments of cis and trans isomers for ($\pi$-allyl)PdXY complexes containing an asymmetrically substituted $\pi$-allyl group have been previously made on the basis of pmr spectroscopy using, for example, the preferential coupling of the $^{31}P$ nucleus to the trans allylic protons in a phosphine complex.[9,18–20] The structure of the asymmetrically substituted monothiodibenzoylmethanato-$\pi$-*syn*-1-*tert*-butyl-2-methallylpalladium(II) complex, together with its low-temperature pmr spectrum,[8] provides substantial evidence confirming the validity of the previous assignments.

The attachment of the $\pi$-*syn*-1-*tert*-butyl-2-methallyl ligand to the palladium closely resembles that of its $\pi$-methallyl analog (structure I). In both complexes the Pd–C(1) bond is 0.13 Å longer than Pd–C(3), reflecting the greater trans influence of the sulfur atom.[2] This structural feature may explain the preponderance of the trans geometrical isomers for asymmetrically substituted ($\pi$-allyl)PdXY compounds. In the complexes chlorotriphenylphosphine-$\pi$-crotylpalladium(II),[9] ($\pi$-crotyl)Pd(SDBM),[8] and ($\pi$-crotyl)PdCl(DMSO),[19,21] the 1-methyl group is situated trans to the better labilizer. Since alkyl groups display positive inductive effects with respect to hydrogen atoms, the preferential trans substitution might be expected to provide some compensation for the weakened metal–carbon bond. In certain compounds steric factors may also influence the choice of cis or trans isomer.[22]



IIIa IIIb IIIc

As in structure I, the C(1)–C(2) and C(2)–C(3) bond lengths within the allylic backbone are equivalent (Table II), supporting the delocalized bonding scheme IIIa. In the low-temperature (−150°) X-ray study of chlorotriphenylphosphine($\pi$-allyl)palladium(II),[4] however, the allylic carbon–carbon bond trans to the phosphorus atom was found to be 1.28 Å compared with a value of 1.47 Å for the neighboring bond (IIIb, Y = P). This difference in C–C bond lengths is much more pronounced than observed for the same compound[23] or the $\pi$-2-methallyl analog[3] at room temperature, and it is therefore a possibility that the carbon–carbon distances in compounds I and II might be distinctly nonequivalent at −150°. Such an asymmetry within the allyl group itself would be consistent with the observed geminal coupling between the two protons on the carbon atom cis to sulfur in the low-temperature limiting pmr spectrum of ($\pi$-methallyl)Pd(SDBM).[8]

The three Pd–C bond distances in the present structure are only slightly shorter (1–3$\sigma$) than the distances observed in the $\pi$-methallyl structure. Although this result is probably not statistically meaningful, it is consistent with the greater inductive effect of the *tert*-butyl group. In addition, the angle C(1)–C(2)–C(3) (113.2 (9)°) is significantly smaller ($\Delta/\sigma = 3.9$) in this substituted methallyl complex. A parallel observation has been made in the case of the $\pi$-allyl and $\pi$-methallyl palladium chloride dimers,[25] the latter having a C(1)–C(2)–C(3) angle which is 7.4° smaller ($\Delta/\sigma = 4.0$) than the former. The effect observed for the SDBM compounds originates in the steric interference between the methyl and *tert*-butyl groups in IIa, which is also evident from the nonequivalence of the angles C(3)–C(2)–C(4) < C(1)–C(2)–C(4) (Table III). The angle C(2)–C(1)–C(5) has also increased from its idealized value of 120–128.7 (9)° for similar reasons.

The plane of the allyl carbon atoms, C(1), C(2), and C(3), makes a dihedral angle of 113.7° with the coordination plane formed by the palladium, sulfur, and oxygen atoms. Atoms C(1), C(2), and C(3) are respectively −0.22 (1), 0.53 (1), and −0.10 (1) Å from the coordination plane. The allyl group is thus seen to be tipped slightly, bringing the midpoint of the C(1)–C(2) bond axis and the C(3) atom closer to the coordination plane, and suggesting a slight distortion toward

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(18) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1839 (1967).

(19) G. L. Statton and K. C. Ramey, *J. Amer. Chem. Soc.*, **88**, 1327 (1966).

(20) For further references, see K. Vrieze and P. W. N. M. van Leeuwen, *Progr. Inorg. Chem.*, **14**, 1 (1971).

(21) Abbreviations: $\pi$-crotyl = 1,2,3-*trihapto*-1-methallyl; DMSO = dimethyl sulfoxide; Sacac = any monothio-$\beta$-diketone.

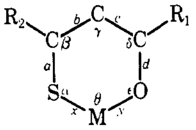
(22) J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, **93**, 2642 (1971).

(23) The structure of ($\pi$-$C_3H_5$)Pd[P($C_6H_5$)$_3$]Cl has been reinvestigated at 18° and the allylic C–C bond lengths were found to be nearly equal: 1.385 ± 0.013 and 1.360 ± 0.013 Å for bonds cis and trans to phosphorus, respectively.[24]

(24) A. E. Smith, private communication.

(25) R. Mason and A. G. Wheeler, *J. Chem. Soc. A*, 2549 (1968).

**Table V.** Comparison of Chelate Ring Geometry[a] for Several Monothio-$\beta$-diketonate Complexes



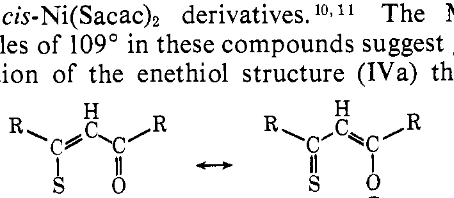
| Parameters | Compd I[b] | Compd IIa[c] | Ni($p$-Br-$C_6H_4$COCH-CSH)$_2$,[d] cis isomer | Ni[$CH_3$COCH-CS($i$-$C_3H_7$)]$_2$,[e] cis isomer |
|---|---|---|---|---|
| $R_1$ | $C_6H_5$ | $C_6H_5$ | $p$-Br-$C_6H_4$ | $CH_3$ |
| $R_2$ | $C_6H_5$ | $C_6H_5$ | H | $i$-$C_3H_7$ |
| $x$ | 2.291 (2) | 2.297 (3) | 2.13 | 2.15 |
| $y$ | 2.067 (6) | 2.047 (7) | 1.89 | 1.87 |
| $a$ | 1.712 (9) | 1.71 (1) | 1.69 | 1.69 |
| $b$ | 1.40 (1) | 1.38 (1) | 1.36 | 1.29 |
| $c$ | 1.41 (1) | 1.43 (1) | 1.42 | 1.45 |
| $d$ | 1.26 (1) | 1.26 (1) | 1.29 | 1.31 |
| $\alpha$ | 108.7 (3) | 109.1 (3) | 109 | 109 |
| $\beta$ | 128.2 (7) | 128.7 (7) | 130 | 130 |
| $\gamma$ | 128.9 (8) | 127.5 (9) | 125 | 125 |
| $\delta$ | 129.2 (8) | 128.2 (9) | 123 | 123 |
| $\epsilon$ | 128.8 (6) | 130.8 (6) | 135 | 135 |
| $\theta$ | 95.8 (2) | 94.4 (2) | 96 | 95 |

[a] Bond distances are in Å and angles in deg; numbers in parentheses are estimated standard deviations in the least significant figures. [b] Monothiodibenzoylmethanato($\pi$-methallyl)palladium(II), ref 2. [c] Monothiodibenzoylmethanato($\pi$-*syn*-1-*tert*-butyl-2-methallyl)palladium(II), this work. [d] Reference 11; standard deviations in bond lengths and angles are ±0.02 Å, and ±2°, respectively. [e] Reference 10; no standard deviations reported.

the completely localized structure IIIb (X = O, Y = S). Both the methyl and *tert*-butyl substituents are displaced by 0.22 (1) and 0.18 (1) Å, respectively, out of the plane of the allyl group toward the metal atom. The value for the dihedral angle and the displacement of R groups from the plane of atoms C(1), C(2), and C(3) are in good agreement with the results for analogous $\pi$-allyl palladium(II) complexes,[2–7,25,26] for which a theoretical interpretation has been given.[27,28]

The Pd–S and Pd–O bond distances of 2.297 (3) and 2.047 (7) Å and S–Pd–O angle of 94.4 (2)° are very similar to the values of 2.291 (2) Å, 2.067 (6) Å, and 95.8 (2)°, respectively, found for ($\pi$-methallyl)Pd(SDBM).[2] The mean value of 2.294 ± 0.003 Å for the Pd–S distance in the two structures corresponds closely to the value of 2.295 ± 0.002 Å found in isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II) and to the values found in several related complexes.[29] The constancy of the metal–sulfur distances in these seemingly very different palladium(II) compounds is interesting.

As indicated in Table V, the chelate ring geometry of the SDBM ligand is nearly the same as that observed for ($\pi$-methallyl)Pd(SDBM), and may be compared with the results of recent X-ray structural studies of two *cis*-Ni(Sacac)$_2$ derivatives.[10,11] The M–S–C bond angles of 109° in these compounds suggest greater participation of the enethiol structure (IVa) than the



IVa IVb

enol valence bond isomer (IVb) in the resonance hybrid that represents the bonding within the monothio-$\beta$-diketonate ring, as discussed previously,[2] but the data of Table V do not fully corroborate this conclusion. Thus while the C–O distance ($d$) in the ligand is short, so is the C–S distance ($a$), and it is difficult to assess the importance of the apparent difference in the $b$ and $c$ bond lengths, since $\Delta/\sigma \simeq 3$ or $\sigma$ is not reported. More accurate structural work, preferably at low temperatures, is needed to provide a definitive assessment of the reality of the enethiol structure (IVa), which has frequently been proposed in the literature for monothio-$\beta$-diketonate complexes.[10,11,30]

As indicated in Table IV, the backbone of the SDBM chelate ring, defined by the carbon atoms C(18), C(9), C(10), C(11), and C(12), is nearly planar (plane no. 3). The chelate ring itself (plane no. 4) is slightly puckered, however, as found for ($\pi$-methallyl)Pd(SDBM).[2] The phenyl rings are planar to within ±0.02 Å (Table IV) and are rotated out of the plane of the chelate ring by +35° (plane no. 1) and −38° (plane no. 2). A discussion of the factors that determine the angles of the phenyl rings with respect to the enol ring plane has been given in the paper describing the crystal structure of dibenzoylmethane[31] and is applicable here. The geometry of the phenyl rings, given in terms of bond distances and angles (Tables II, III), is normal.

**Acknowledgments.** We are grateful to the donors of the Petroleum Research Fund for support of this work, under PRF Grant 3799-A3, and to Dr. A. E. Smith for permission to quote his results on the room-temperature structure determination of ($\pi$-allyl)chlorotriphenylphosphinepalladium(II). S. J. L. also thanks the Alfred P. Sloan Foundation for a Research Fellowship (1968–1970).

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