

Synthesis and Stereochemistry of π -Allylmonothio- β -diketonatopalladium(II)-Olefin Insertion Products

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The synthesis of several π -allylmonothio- β -diketonatopalladium(II) complexes and their diene insertion products is reported. 1,3-Butadiene inserts into the allyl-palladium bond to give a new fluxional allylic product in which the terminal 2-methyl-1-butenyl group is situated trans to the sulfur atom at low temperatures in solution. Norbornadiene inserts into the palladium-allyl bond to give a complex containing both a coordinated olefin and a metal-carbon σ bond. In solution, the palladium-carbon σ bond is situated cis to the sulfur atom, as evidenced by its pmr spectrum, and the complex undergoes an intermolecular exchange with π -allylpalladium complexes that is slow on the pmr time scale. The molecular structure of the insertion product monothiodibenzoylmethanato-1-norbornenyl-2-methylallylpalladium(II) was determined by single-crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell and cell constants $a = 6.480$ (2) Å, $b = 15.814$ (5) Å, $c = 22.426$ (8) Å, and $\beta = 108.21$ (3)°. Refinement converged at final values for the discrepancy indices $R = 0.064$ and $R_w = 0.081$. There is essentially square geometry about the palladium atom with the coordinated olefin trans to sulfur. The long palladium-olefin bond length of 2.13 (1) Å, as well as the long palladium-oxygen bond of 2.10 (1) Å, is attributed to the trans influence of the sulfur and σ -bonded carbon atoms, respectively. The palladium-carbon σ -bond distance of 2.05 (2) Å is comparable to the values found in several asymmetric palladium-allyl complexes.

Introduction

Allylic palladium complexes have been known for some time and have been extensively characterized. Only recently, however, have reactions on allyls that lead to coordinated products been investigated.¹⁻⁵ So far, reactions with dienes that produce insertion products have been carried out only on complexes containing identical donor atoms where the allyl attachment is symmetric. When any asymmetry occurred, it resulted from an inherent asymmetry of the allyl group itself because of the nature or placement of substituent groups. The presence of these groups could direct the attack of inserting dienes to give stereoselective product formation. It was of interest to see whether asymmetry in the allylic attachment generated by the presence of different donor atoms could also alter its reaction with dienes, causing different rates of reaction or stereospecific reaction products.

In previous work from this laboratory, asymmetric π -allylic complexes containing sulfur and oxygen donor atoms were synthesized and characterized.^{6,7} The insertion of dienes into these and related π -allylic monothio- β -diketonatopalladium(II) complexes was studied in order to assess the effect of the asymmetry on the products formed. The solid-state structure of the norbornadiene insertion product of monothiodibenzoylmethanato- π -methylallylpalladium(II) has also been determined.

Experimental Procedure

Methods and Materials. All complexes were prepared using commercially available starting materials. Di- μ -chloro-di(π -allyl)dipalladium(II) and the 2-methylallyl and crotyl derivatives were prepared by the method of Dent, Long, and Wilkinson.⁸ 1,1,1-Trifluoro-4-mer-

captopent-3-en-2-one, 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)but-3-en-2-one and their lead salts were prepared by a modification of the procedures described by Ho, Livingston, and Lockyer and by Berg and Reed.^{9,10} 3-Thio-1,3-diphenylprop-2-en-1-one- π -methylallylpalladium(II) was prepared in a manner similar to that described by Lippard and Morehouse for the π -allyl analog.¹¹

2-Thenoyltrifluoroacetylacetonato- π -allylpalladium(II) and the corresponding 2-methylallyl derivative were prepared by stirring 1.0 mmol of the chloride-bridged allylic dimer with 2.0 mmol of the thallium(I) salt of the appropriate ligand in 30-40 ml of benzene. The TiCl₄ was filtered off and the benzene evaporated under reduced pressure at room temperature. The complexes were crystallized from petroleum ether (bp 37-47°) and identified by their pmr spectra. (π -C₃H₅)Pd(TTA) pmr spectrum (CDCl₃, 39°): H-1 and H-4, δ 4.06; H-2 and H-3, δ 3.05; H-5, δ 5.62; H-7, δ 6.29; thienyl, δ 7.0-7.7; $J_{1,5} = 6.5$; $J_{2,4} = 12.5$. (π -C₄H₇)Pd(TTA) pmr spectrum (CDCl₃, 39°): H-1 and H-4, δ 3.85; H-2 and H-3, δ 2.91; CH₃, δ 2.25; H-7, δ 6.28; thienyl, δ 7.0-7.7. Norbornadiene was allowed to react with these complexes and the insertion products were identified by their pmr spectra; pertinent chemical shifts are cited in the text.

Molecular weights were determined on a Mechrolab 301A vapor pressure osmometer calibrated with benzil; all measurements were performed in chloroform solution at 37° with an estimated accuracy of $\pm 2\%$. Ir spectra were recorded on a Perkin-Elmer 621 grating spectrometer and calibrated with polystyrene; KBr disks and Nujol mulls between KBr plates were employed. Pmr spectra were recorded on Varian A-60A and HA100 spectrometers equipped with a variable-temperature probe calibrated with methanol and ethylene glycol for low and high temperature ranges, respectively. Chemical shifts are given as δ (ppm) from the internal standard, tetramethylsilane; coupling constants, J , are in Hz. Protons are labeled as described in ref 11 or Figure 1. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, New York, New York. Results of the microchemical analyses are summarized in Table I.¹²

π -Allylic Monothio- β -diketonatopalladium(II) Complexes. 1,1,1-Trifluoro-4-thiolopent-3-en-2-one- π -allylpalladium(II), (π -C₃H₅)Pd(TFAS). A 1.0-mmol sample of Pb(TFAS)₂ was added to a solution of 1.0 mmol of di- μ -chloro-di(π -allyl)dipalladium(II) in approximately 30 ml of methylene chloride or benzene and stirred for 5-10 min.

(9) R. K. Y. Ho, S. E. Livingston, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1179 (1966).

(10) E. W. Berg and K. P. Reed, *Anal. Chim. Acta*, **36**, 372 (1966).

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

(12) Abbreviations: TFAS, anion of 1,1,1-trifluoro-4-mercapto-pent-3-en-2-one; STA, anion of 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)but-3-en-2-one; DMBS, anion of monothiodibenzoylmethane; TFA, anion of 1,1,1-trifluoroacetylacetonate; TTA, anion of 2-thenoyltrifluoroacetylacetonate; DBM, anion of dibenzoylmethane; π -methylallyl and π -crotyl, allyls with a methyl substituent at the 2 and 1 positions, respectively.

- (1) S. O'Brien, *J. Chem. Soc. A*, **9** (1970).
- (2) Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **16**, 177 (1969).
- (3) R. P. Hughes and J. Powell, *J. Amer. Chem. Soc.*, **94**, 7723 (1972).
- (4) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **30**, C45 (1971).
- (5) M. C. Gallazzi, T. L. Hanlon, G. Vitulli, and L. Porri, *J. Organometal. Chem.*, **33**, C45 (1971).
- (6) S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, **91**, 2504 (1969).
- (7) S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, **94**, 6956 (1972), and references cited therein.
- (8) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

Table I. Analytical Results

Complex ^a	Elemental formula	% calcd			% found		
		C	H	S	C	H	S
(π -allyl)Pd(TFAS)	C ₈ H ₉ OSF ₃ Pd	30.35	2.87	10.13	30.24	2.85	10.11
(π -methallyl)Pd(TFAS)	C ₉ H ₁₁ OSF ₃ Pd	32.69	3.35	9.70	32.08	3.39	9.74
(π -crotyl)Pd(TFAS)	C ₉ H ₁₁ OSF ₃ Pd	32.69	3.35	9.70	32.98	3.40	9.30
(π -allyl)Pd(STTA)	C ₁₁ H ₉ OS ₂ F ₃ Pd	34.25	2.61	16.63	34.38	2.42	17.05
(π -methallyl)Pd(STTA)	C ₁₂ H ₁₁ OS ₂ F ₃ Pd	36.15	2.78	16.08	36.04	3.02	15.30
(π -crotyl)Pd(STTA)	C ₁₂ H ₁₁ OS ₂ F ₃ Pd	36.15	2.78	16.08	36.72	3.02	15.97
(1-norbornenyl-2-methylallyl)Pd(DBMS)	C ₁₆ H ₂₆ OSPd	63.35	5.32	6.50	63.79	5.22	6.26
(1-norbornenyl-2-methylallyl)Pd(STTA)	C ₁₉ H ₁₉ OS ₂ F ₃ Pd	46.49	3.90	13.06	47.09	4.18	12.96
(π -syn-1-(2-methyl-1-butenyl)allyl)Pd(DBMS)	C ₂₃ H ₂₄ OSPd	60.73	5.32	7.05	61.01	5.27	7.29

^a See ref 12 for abbreviations.

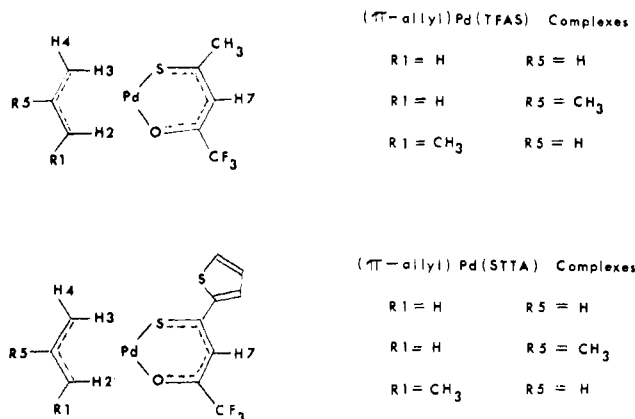


Figure 1.

A 120-ml amount of petroleum ether (bp 37–47°) was added, the PbCl₂ filtered off, and the filtrate evaporated to dryness under reduced pressure at room temperature. The complex was extracted with petroleum ether and filtered. The filtrate was concentrated and chromatographed on silica gel, eluting with petroleum ether. The first fraction was collected, concentrated, and kept at 0° to give orange needles. The same procedure was followed for the π -methallyl and π -crotyl derivatives. Pmr spectrum (CDCl₃, -58°): H-1, 4.66; H-2, 3.73; H-3, 2.82; H-4, 3.67; H-5, 5.73; H-7, 6.82; R-8, 2.65; J_{3,5} = 12.0; J_{4,5} = 6.0; J_{1,4} = 1.5; J_{2,5} = 12.5; J_{1,5} = 7.0.

1,1,1-Trifluoro-4-thiolopent-3-en-2-one- π -methallylpalladium(II), (π -C₈H₇)Pd(TFAS). Orange needles were produced, prepared as above. Pmr spectrum (CDCl₃, -58°): H-1, 4.47; H-2, 3.58; H-3, 2.75; H-4, 3.50; R-5, 2.20; H-7, 6.83; H-8, 2.65.

1,1,1-Trifluoro-4-thiolopent-3-en-2-one- π -crotylpalladium(II), (π -C₈H₇)Pd(TFAS). Yellow needles were produced, prepared as above. Pmr spectrum¹³ (CDCl₃, -60°): R-1, 1.66 (1.44); H-2, 4.42; H-3, 2.63; H-4, 3.49; H-5, 5.42; H-7, 6.73; R-8, 2.60; J_{4,5} = 6.0; J_{1,2} = 6.0.

1,1,1-Trifluoro-4-thiolo-4-(2-thienyl)but-3-en-2-one- π -allylpalladium(II), (π -C₈H₇)Pd(STTA). A 1.0-mmol sample of Pb(STTA)₂ was added to a solution of 1.0 mmol of di- μ -chloro-di(π -allyl)dipalladium(II) in approximately 40 ml of benzene or methylene chloride and stirred for 10 min. The PbCl₂ was filtered off and the filtrate evaporated to dryness at room temperature under reduced pressure. The complex was extracted with petroleum ether (bp 37–47°) and filtered. The filtrate was evaporated, the complex was redissolved in a small quantity of benzene and chromatographed on silica gel, and the first fraction was collected. Recrystallization from petroleum ether gave orange needles. The same procedure was followed for the π -methallyl and π -crotyl derivatives. Mol wt: calcd for C₁₁H₉OS₂F₃Pd, 386; found, 381. Pmr spectrum (C₆H₆Cl₂, -20°): H-1, 4.02; H-2, 3.08; H-3, 2.31; H-4, 3.15; H-5, 5.03; J_{1,5} = 6.0; J_{3,5} = 12.0; J_{4,5} = 6.0; J_{2,5} = 12.0.

1,1,1-Trifluoro-4-thiolo-4-(2-thienyl)but-3-en-2-one- π -methallylpalladium(II), (π -C₈H₇)Pd(STTA). Orange needles were produced, prepared as above. Mol wt: calcd for C₁₂H₁₁OS₂F₃Pd, 399; found, 403. Pmr spectrum (C₆H₆Cl₂, -23°): H-1, 3.91; H-2, 3.03; H-3, 2.28; H-4, 3.02; R-5, 1.57.

(13) The value in parentheses is that of the lesser isomer. Extensive overlap of the other resonances prevented the complete assignment of this isomer.

1,1,1-Trifluoro-4-thiolo-4-(2-thienyl)but-3-en-2-one- π -crotylpalladium(II), (π -C₈H₇)Pd(STTA). Yellow needles were produced, prepared as above. Mol wt: calcd for C₁₁H₉OS₂F₃Pd, 399; found, 402. Pmr spectrum¹³ (CDCl₃, -60°): R-1, 1.63 (1.45); H-2, 4.43; H-3, 2.70; H-4, 3.56; H-5, 5.43; H-7-R-8, 7.0–7.8; J_{3,5} = 11.5; J_{1,2} = 6.0.

Diene Insertion Products. 3-Thio-1,3-diphenylprop-2-en-1-one-1-norbornenyl-2-methylallylpalladium(II), (C₁₁H₁₅)Pd(DBMS). An excess of norbornadiene was added to a solution of 0.25 g of (π -methallyl)Pd(DBMS) in 50 ml of benzene and maintained at 39–40° in an oil bath for 4 days. After concentration under reduced pressure, the solution was absorbed on a small quantity of silica gel and allowed to dry in air. The mixture was packed into a silica gel column and eluted with carbon tetrachloride; the first fraction was collected. The solution was evaporated under reduced pressure at room temperature and the complex recrystallized as yellow needles from benzene at 6°.

1,1,1-Trifluoro-4-thiolo-4-(2-thienyl)but-3-en-2-one-1-norbornenyl-2-methylallylpalladium(II), (C₁₁H₁₅)Pd(STTA). An excess of norbornadiene was added to a solution of 0.25 g of (π -methallyl)Pd(STTA) in 50 ml of benzene and maintained at 37° in an oil bath for 3 days. The solution was concentrated and chromatographed on silica gel eluting with benzene, and the first fraction was collected. Orange pyramids were obtained after recrystallization at 0° from petroleum ether (bp 37–47°). Pmr spectrum (CDCl₃, 39°): H-1, 4.55 (s); H-2, 4.67 (s); CH₃, 2.09 (s); H-7-H-8, 6.02 (t); thienyl, 7.00–7.80 (m).

3-Thio-1,3-diphenylprop-2-en-1-one- π -syn-1-(2-methyl-1-butenyl)allylpalladium(II), (π -C₈H₁₃)Pd(DBMS). A solution of 0.45 g of (π -methallyl)Pd(DBMS) in 50 ml of benzene was saturated with 1,3-butadiene and maintained at 35° in an oil bath for 3 days. After concentration under reduced pressure, the solution was added to a small quantity of silica gel, sufficient for absorption, and allowed to dry at room temperature. The mixture was placed on a silica gel column and eluted with a 4:1 mixture of carbon tetrachloride-petroleum ether (bp 37–47°). The second fraction (orange-yellow) was collected, concentrated under reduced pressure at room temperature, and kept at 0°. At this temperature, a semicrystalline orange powder precipitated. The complex turns to a gum at room temperature. Pmr spectrum (CDCl₃, -20°): H-2, 4.39 (m); H-3, 2.65 (d); H-4, 3.43 (d); H-5, 5.46 (m); H-6-H-7, 2.41 (m); CH₃, 1.78 (s); H-9, 4.78 (s); J_{3,5} = 11.0; J_{4,5} = 6.0.

Collection and Reduction of X-Ray Data

All work was done at 24° using Ni-filtered Cu K α radiation (λ 1.5418 Å). Crystals of 3-thio-1,3-diphenylprop-2-en-1-one-1-norbornenyl-2-methylallylpalladium(II), prepared as described above, were mounted on a glass fiber with clear nail polish. Precession photographs showed 2/m Laue symmetry and revealed the extinctions $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, indicative of the space group P2₁/c.¹⁴ The angular settings χ , ϕ , and 2θ of 30 reflections, centered on a Picker full-circle automated diffractometer, were refined by a least-squares technique. The refinement converged giving cell constants $a = 6.480$ (2) Å, $b = 15.814$ (5) Å, $c = 22.426$ (8) Å, and $\beta = 108.21$ (3)°. Assuming four molecules per unit cell, the calculated cell volume of 2183 Å³ requires a density of 1.50 g cm⁻³ which compares to the observed density of 1.49 (1) g cm⁻³ determined by suspension of a single crystal in aqueous KI. The linear absorption coefficient μ was calculated to be 80.3 cm⁻¹.

A crystal of approximate dimensions 0.065 \times 0.071 \times 0.245 mm, with the longest dimension along the a axis, was chosen and mounted along the a^* axis. The mosaic spread was checked for several reflections by an ω scan and found to be satisfactory. Integrated intensities

(14) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 99.

were measured by the θ - 2θ scan method to $(\sin \theta_{\max})/\lambda = 0.486$ in the automated mode with the pulse height analyzer set to accept 95% of the peak. Copper foil was used to attenuate reflections above 10,000 counts sec^{-1} ; the detector was a scintillation counter employing a thallium-activated sodium iodide crystal. The symmetrically variable receiving aperture, located 23 cm from the crystal, was set at an opening of 4.5×4.5 mm to reduce extraneous background. Data were taken¹⁵ with a takeoff angle of 2.0° , a scan rate of 1°min^{-1} , and a symmetric scan range of 1.25° in 2θ for $2\theta \leq 40^\circ$ and 1.50° in 2θ for $2\theta > 40^\circ$, plus an allowance for the $K\alpha_1$ - $K\alpha_2$ separation. In order to monitor the crystal alignment and instrument stability, four moderately strong reflections were chosen as standards and measured after every 100 reflections. Their intensities, showing no systematic variation during data collection, had a mean random variation on the order of $\pm 2.3\%$.

The observed intensities were corrected for background, use of attenuators, and Lorentz, polarization, and absorption effects. Background was estimated by recording the counts for 10 sec at each end of the 2θ scan range and multiplying the mean counts per second by the time required to scan that peak. The transmission factors, ranging from 0.408 to 0.632, were checked by comparing the observed intensity variation of two axial reflections at $\chi = 90^\circ$ for different ϕ values. No corrections were made for secondary extinction effects. Each reflection was assigned a standard deviation, $\sigma(I)$,¹⁶ based on I , the integrated intensity corrected for background and attenuators. $\sigma(I)$ was obtained from the expression $\sigma(I) = (E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2)^{1/2}$ where E equals the peak and background counts observed for a time T_E , B_1 and B_2 are the background counts observed for a time T_B at each end of the scan, and ϵ is the ignorance factor set at 0.04 to prevent excessive weight being given to the strong reflections. Equivalent $0kl$ reflections were averaged; the R value for averaging was found to be 0.045. The data were then put on an approximately absolute scale by means of a Wilson plot which produced values for $|F_o|$ and $|F_c|^2$ used in subsequent calculations; the estimated mean value for B , the isotropic temperature factor, was 4.2 \AA^2 . Scattering factors for neutral¹⁷ Pd, S, O, C, and H¹⁸ atoms were used along with corrections for anomalous dispersion¹⁹ for the Pd and S atoms. Of the 2108 independent reflections collected, only those for which $I \geq 3\sigma(I)$ were included in the refinement, a total of 1411 data points. Each accepted reflection was given a weight, $w = 1/\sigma^2(F_o)$, equivalent to $w = 4F_o^2/\sigma^2(F_o^2)$. The standard deviation of F_o^2 , $\sigma(F_o^2)$, was obtained from $\sigma(I)$ after corrections for absorption and Lorentz and polarization effects, $\sigma(F_o^2) = (LpT)^{-1}\sigma(I)$.

Solution and Refinement of the Structure

A sharpened Patterson map revealed the coordinates of the palladium atom and subsequent cycles of isotropic refinement on F followed by difference Fourier maps revealed all the nonhydrogen atoms. Residual electron density suggested a shift to anisotropic refinement was necessary. The anisotropic thermal parameters took the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Owing to the small number of accepted reflections, the carbon atoms in the phenyl rings were subsequently refined isotropically as members of rigid groups;²⁰ this decreased the number of independently variable parameters to 178 for the overall scale factor and positional and thermal parameters. An empirical weighting scheme was determined in the later stages of refinement in order to improve the constancy of

(15) Programs for the IBM 360-91 computer include the following: MODE-1, the Brookhaven diffractometer setting, crystal orientation, and cell constant refinement program; GSET, the Prewitt diffractometer setting program; ACAC-3, a revised version of the Prewitt absorption correction and data reduction program; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; BUGLS, the Brown University version of ORFLS (the Busing-Martin-Levy structure factor calculation and least-squares refinement program) equipped to handle refinement of rigid groups; ORFFE, the Busing-Martin-Levy molecular geometry and error function program; ORTEP, the Johnson thermal ellipsoid plotting program.

(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

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

(19) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(20) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965); S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965). We thank Professor R. Eisenberg and Dr. C. G. Pierpont, Jr., for kindly providing the group refinement program.

$w\Delta^2$ over the various classes²¹ of reflections. The weights were set equal to $w = 1/\sigma^2$ where $\sigma^2 = 29.0 - 0.959|F_o| + 0.0117|F_o|^2$. The refinement converged to give values of $R = 0.064$ and $R_w = 0.081$ for the discrepancy indices $R = \sum \|F_o| - |F_c|\|/\sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The value $R = [\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO is the number of accepted reflections and NV is the number of independently variable parameters, was 1.002. A final difference Fourier map revealed no peaks above 0.8 e \AA^{-3} on a scale where a carbon atom is approximately 4 e \AA^{-3} . Additional peaks of about 0.6 - 0.5 e \AA^{-3} at positions expected for hydrogen atoms could be seen; however, they were neither refined nor included in the structure. In the last cycle of refinement, the parameters varied by no more than 0.05% of their estimated standard deviations.

Results and Discussion

Synthesis and Solution Properties. Allylic palladium complexes containing the sulfur-oxygen ligand 1,1,1-trifluoro-4-thiolopent-3-en-2-one or 1,1,1-trifluoro-4-thiolo-4-(2-thienyl)but-3-en-2-one were synthesized and are shown in Figure 1. The complexes are orange crystalline solids, monomeric in solution, and undergo a temperature-dependent proton site exchange as evidenced by pmr studies. The complexes exhibit a concentration-dependent cis-trans exchange (resonance pairs H-1-H-4 and H-2-H-3 average) as well as an underlying syn-anti exchange (causing enhanced collapse of resonances H-3 and H-4) with increasing temperature. This behavior parallels that observed for monothiodibenzoyl-methanato- π -allylpalladium(II) complexes.¹¹

The low-temperature limiting spectra of the π -crotyl complexes indicates the presence of two isomers, with the syn methyl group being either trans or cis to sulfur. The latter isomer constitutes approximately 30% of the mixture. These complexes all undergo intermolecular exchange with their dioxygen analogs that is slow on the pmr time scale.

The reactions of these sulfur-oxygen complexes with dienes were found to be similar to those of symmetric allylic palladium complexes containing a dioxygen ligand or bridging chloride ligands.²⁻⁵ Here the possibility of additional isomers exists, however. 1,3-Butadiene inserts into the palladium-allyl bond to give a new allylic complex containing a 1-butenyl-2-methyl substituent at the 1 position of the allyl. The insertion product with monothiodibenzoyl-methanato- π -methallylpalladium(II), shown in Figure 2, is fluxional at ambient temperatures. The predominant isomer was assigned to have the butenyl group in the syn position trans to the sulfur on the basis of its coupling constants and chemical shifts.^{11,22} For hexafluoroacetylacetonato- π -syn-1-(2-methyl-1-butenyl)allylpalladium(II),³ the H-2 resonance occurs at δ 4.06 (m) and the H-3 and H-4 resonances are at δ 3.12 (d) and 4.15 (d), respectively. The low-temperature limiting spectrum (Figure 2) of 3-thio-1,3-diphenylprop-2-en-1-one- π -syn-1-(2-methyl-1-butenyl)allylpalladium(II) shows the H-2 resonance is shifted downfield to δ 4.39 (m) and resonances H-3 and H-4 are shifted upfield to δ 2.65 (d) and 3.43 (d), respectively. These results indicate that in solution the butenyl group occupies a position mainly trans to sulfur.²³

Norbornadiene reacts with these complexes to give an insertion product containing a palladium-carbon σ bond and a palladium-carbon π bond. The pmr spectrum of the addition product of (π -methallyl)Pd(SITA), given in Figure 3, indicates that one olefinic bond of norbornadiene inserts while the other bond remains uncoordinated in solution.

(21) D. W. J. Cruickshank, "Computing Methods of Crystallography," J. S. Rollet, Ed., Pergamon Press, New York, N. Y., 1965, pp 112-115.

(22) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 71 (1965).

(23) P. W. N. M. van Leeuwen, A. P. Pratt, and M. van Diepen, *J. Organometal. Chem.*, **29**, 433 (1971). See also ref 11.

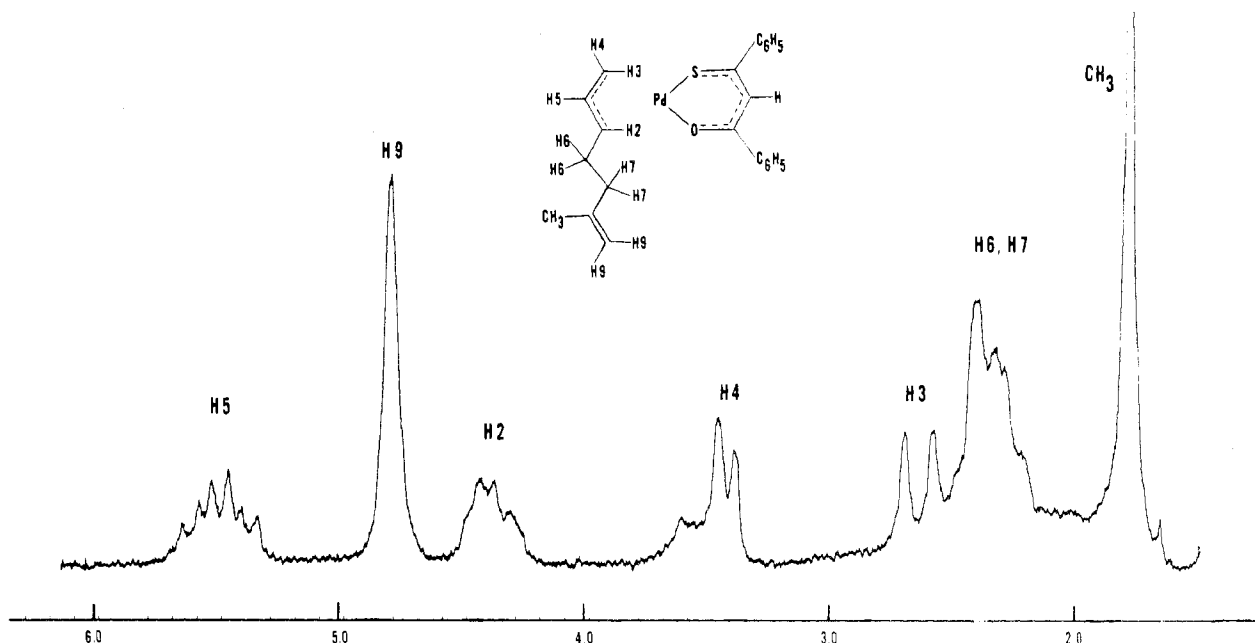


Figure 2. The 100-MHz proton nmr spectrum of 3-thio-1,3-diphenylprop-2-en-1-one- π -syn-1-(2-methyl-1-butenyl)allylpalladium(II) in CDCl_3 at -20° .

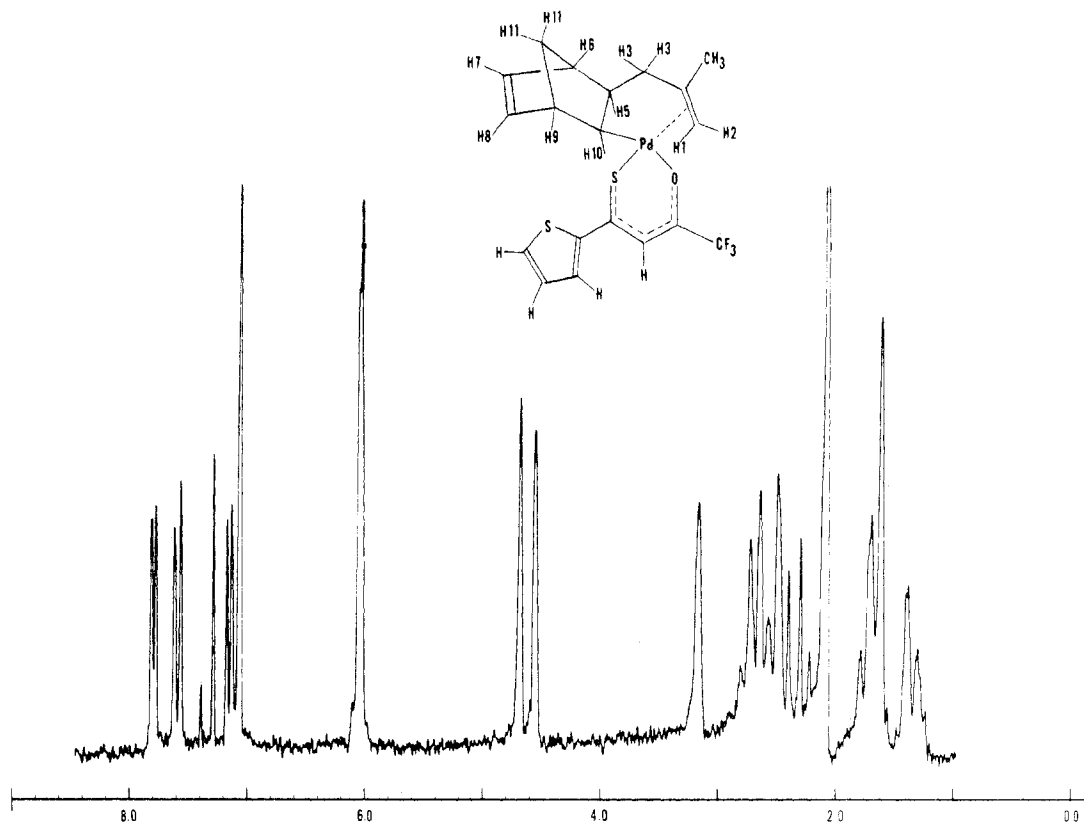


Figure 3. The 100-MHz proton nmr spectrum of 1,1,1-trifluoro-4-thio-4-(2-thienyl)but-3-en-2-one-1-norbornenyl-2-methylallylpalladium(II) in CDCl_3 at ambient probe temperature. See text for partial assignment.

The coordinated olefinic resonances, occurring at δ 4.55 and 4.67, exhibit a significant downfield shift from the values of δ 3.95 and 4.11 found for the coordinated olefinic resonances of the addition product of norbornadiene with $(\pi$ -methylallyl)-Pd(TTA) (see Experimental Section). In addition, resonance H-10 of (1-norbornenyl-2-methylallyl)Pd(STTA) is shifted sufficiently upfield so that it occurs in the region of the other saturated proton resonances. Both of these results

indicate that in solution the sulfur and σ -bonded carbon atoms are cis to one another.²³ The assignment of resonances H-1 and H-2 was by analogy to the norbornadiene insertion product of $(\pi$ -allyl)Pd(TTA) (see Experimental Section). In this complex, substitution of a hydrogen atom for the methyl group at the 2 position makes assignment possible on the basis of syn and anti olefinic coupling constants; resonances H-1 (δ 4.17) and H-2 (δ 4.42) are coupled to the other

Table II. Final Positional and Thermal Parameters for the Atoms^{a,b}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.2192 (2)	0.22416 (7)	0.30972 (6)	29.9 (4)	3.15 (6)	2.92 (4)	1.0 (1)	2.89 (8)	-0.40 (4)
S	0.2538 (6)	0.3350 (3)	0.3777 (2)	30 (1)	4.0 (2)	3.1 (1)	1.9 (4)	1.5 (3)	-0.7 (1)
O	-0.0914 (2)	0.2616 (7)	0.2526 (5)	39 (4)	4.8 (6)	3.3 (3)	0 (1)	3 (1)	-1.9 (4)
C1	0.229 (3)	0.1330 (9)	0.2343 (8)	38 (6)	3.2 (7)	2.9 (5)	-3 (1)	4 (1)	0.0 (5)
C2	0.147 (3)	0.0923 (9)	0.2753 (9)	33 (6)	2.7 (7)	4.0 (6)	2 (2)	5 (2)	-0.9 (6)
C3	0.281 (3)	0.0453 (9)	0.3347 (8)	43 (7)	2.6 (7)	3.0 (5)	2.9 (2)	4 (1)	-0.5 (5)
C4	-0.096 (3)	0.073 (1)	0.2560 (9)	31 (6)	5.0 (9)	4.2 (6)	-1 (2)	5 (2)	-0.9 (6)
C5	0.516 (3)	0.079 (1)	0.3588 (7)	31 (6)	3.8 (8)	2.6 (5)	2 (3)	3 (1)	-0.3 (5)
C6	0.624 (3)	0.058 (1)	0.4294 (9)	38 (7)	6 (1)	3.3 (6)	3 (2)	3 (2)	0.5 (6)
C7	0.857 (3)	0.084 (1)	0.4410 (8)	42 (7)	6 (1)	3.1 (6)	0 (2)	3 (2)	0.1 (6)
C8	0.869 (3)	0.168 (1)	0.4386 (8)	35 (6)	7 (1)	3.1 (6)	0 (2)	3 (1)	-0.5 (7)
C9	0.635 (3)	0.201 (1)	0.4255 (9)	33 (6)	6 (1)	3.4 (5)	2 (2)	3 (1)	-0.9 (6)
C10	0.523 (3)	0.179 (1)	0.3563 (8)	46 (7)	4.9 (9)	3.1 (5)	-1 (2)	5 (2)	-1.1 (6)
C11	0.538 (3)	0.134 (1)	0.4600 (9)	49 (7)	7 (1)	3.5 (6)	4 (2)	4 (2)	-0.7 (7)
C12	0.023 (2)	0.3979 (8)	0.3517 (7)	30 (5)	2.4 (7)	2.6 (4)	-1 (2)	4 (1)	0.0 (4)
C13	-0.163 (2)	0.3874 (9)	0.3025 (7)	25 (5)	3.1 (7)	2.3 (4)	-1 (2)	2 (1)	0.5 (5)
C14	-0.213 (2)	0.322 (1)	0.2572 (7)	28 (5)	3.8 (8)	2.2 (4)	-2 (2)	2 (1)	-1.2 (5)
CA1	-0.820 (1)	0.332 (1)	0.1097 (5)	6.3 (4)					
CA2	-0.802 (2)	0.367 (1)	0.1681 (6)	6.4 (4)					
CA3	-0.605 (2)	0.3631 (7)	0.2162 (4)	4.8 (3)					
CA4	-0.426 (1)	0.325 (1)	0.2060 (4)	4.6 (3)					
CA5	-0.444 (2)	0.2897 (9)	0.1476 (5)	5.0 (3)					
CA6	-0.641 (2)	0.2933 (8)	0.0995 (4)	6.2 (4)					
CB1	0.046 (2)	0.6219 (6)	0.4617 (5)	6.0 (4)					
CB2	-0.145 (1)	0.5753 (7)	0.4397 (5)	5.6 (4)					
CB3	-0.150 (1)	0.5019 (6)	0.4052 (5)	4.4 (3)					
CB4	0.037 (2)	0.4750 (5)	0.3926 (5)	4.2 (3)					
CB5	0.228 (1)	0.5215 (7)	0.4146 (5)	5.0 (4)					
CB6	0.232 (1)	0.5950 (7)	0.4491 (5)	6.0 (4)					

^a Atoms are labeled as indicated in Figure 4. ^b Standard deviations, in parentheses, occur in the last significant figure for each parameter. ^c Atoms Pd through C14 were refined anisotropically and values reported for β_{ij} are $\times 10^3$. The form of the anisotropic ellipsoid is given in the text. Atoms CA1 through CB6 were refined isotropically as members of rigid rings in the group refinement program; here, β_{11} represents *B*, the isotropic temperature factor.

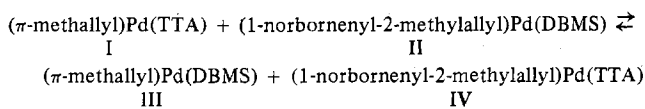
Table III. Root-Mean-Square Amplitudes of Thermal Vibration, \AA^a

Atom	Min	Intermed	Max
Pd	0.190 (2)	0.243 (1)	0.265 (2)
S	0.203 (6)	0.236 (5)	0.300 (6)
O	0.18 (2)	0.27 (1)	0.33 (1)
C1	0.18 (2)	0.25 (2)	0.28 (2)
C2	0.16 (3)	0.25 (2)	0.31 (2)
C3	0.16 (3)	0.27 (2)	0.30 (2)
C4	0.23 (2)	0.24 (2)	0.32 (2)
C5	0.20 (2)	0.25 (2)	0.26 (2)
C6	0.24 (2)	0.28 (2)	0.29 (2)
C7	0.26 (2)	0.28 (3)	0.29 (3)
C8	0.26 (2)	0.26 (2)	0.30 (3)
C9	0.23 (2)	0.26 (2)	0.32 (3)
C10	0.21 (2)	0.27 (2)	0.31 (2)
C11	0.24 (3)	0.29 (2)	0.34 (3)
C12	0.17 (2)	0.21 (2)	0.26 (2)
C13	0.18 (2)	0.21 (2)	0.25 (2)
C14	0.17 (3)	0.24 (2)	0.27 (2)

^a Taken along the principal axes of the thermal ellipsoids. The relative orientation of these axes may be seen from Figure 4. ^b See footnotes *a* and *b*, Table II.

olefinic proton with *J* values of 15 and 9.5 Hz, respectively.

The insertion products undergo an intermolecular exchange that is slow on the pmr time scale. For instance, when 0.142 mmol of (1-norbornenyl-2-methylallyl)Pd(DBMS) is added to 0.172 mmol of (2-methylallyl)Pd(TTA) in chloroform at 39°, there is intermolecular exchange and all four possible products are seen in the pmr spectrum.



Two protons, clearly distinguishable at δ 6.18 and 6.28 in

Table IV. Intramolecular Geometry^a

Bond Lengths \AA			
Pd-S	2.287 (4)	C9-C10	1.54 (2)
Pd-O	2.10 (1)	C10-C5	1.59 (2)
Pd-C1	2.24 (2)	C11-C6	1.56 (2)
Pd-C2	2.22 (1)	C11-C9	1.56 (3)
Pd-C10	2.05 (2)	S-C12	1.74 (2)
C1-C2	1.36 (2)	C12-C13	1.37 (2)
C2-C3	1.54 (2)	C13-C14	1.42 (2)
C2-C4	1.53 (2)	C14-O	1.27 (2)
C3-C5	1.54 (2)	C12-CB4	1.51 (2)
C5-C6	1.55 (2)	C14-CA4	1.50 (2)
C6-C7	1.51 (3)	C-C av over	1.55
C7-C8	1.34 (2)	norbornenyl	
C8-C9	1.54 (2)	moiety	
Bond Angles, Deg			
S-Pd-O	93.9 (3)	C6-C7-C8	109 (2)
S-Pd-C10	92.9 (5)	C7-C8-C9	106 (2)
O-Pd-C1	88.0 (5)	C8-C9-C10	104 (1)
O-Pd-C2	89.5 (5)	C8-C9-C11	102 (1)
C1-Pd-C2	35.5 (5)	C10-C9-C11	102 (1)
C1-Pd-C10	84.8 (6)	C5-C10-C9	102 (1)
C2-Pd-C10	85.0 (6)	C6-C11-C9	93 (1)
Pd-C1-C2	71.6 (9)	Pd-C10-C5	110 (1)
Pd-C2-C1	72.9 (9)	Pd-C10-C9	121 (1)
C1-C2-C3	125 (1)	Pd-S-C12	108.7 (5)
C1-C2-C4	119 (2)	Pd-O-C14	131.5 (9)
C3-C2-C4	114 (1)	S-C12-C13	131 (1)
C2-C3-C5	112 (1)	C12-C13-C14	128 (1)
C3-C5-C6	112 (1)	O-C14-C13	127 (1)
C3-C5-C10	111 (1)	S-C12-CB4	112.2 (6)
C6-C5-C10	103 (1)	C13-C12-CB4	117 (1)
C5-C6-C7	103 (1)	O-C14-CA4	114 (1)
C5-C6-C11	101 (1)	C13-C14-CA4	118.6 (9)
C7-C6-C11	101 (2)		

^a See footnotes *a* and *b*, Table II.

the ratio of 1.375:1, correspond to the γ protons of TTA for complexes IV and I, respectively. The same two resonances

Table V. Group Refinement Parameters, Best Planes, and Dihedral Angles

Group	Orientation of the Phenyl Rings ^a					
	Basis <i>x</i>	Basis <i>y</i>	Basis <i>z</i>	ϕ	θ	ρ
CR1	-0.623 (1)	0.3282 (4)	0.1579 (3)	-2.43 (1)	2.256 (6)	-0.88 (1)
CR2	0.041 (1)	0.5484 (5)	0.4272 (2)	-1.438 (6)	2.909 (6)	2.541 (7)

Plane through atoms Pd, S, O, C12, C13, C14: $4.0 (3)X + 8.7 (6)Y - 16 (1)Z + 2.2 (1) = 0$

Distance of atoms from plane, Å: Pd, 0.000 (1); S, -0.006 (5); O, 0.00 (1); C12, 0.04 (1); C13, 0.00 (1); C14, -0.03 (2)

Plane through atoms C1, C2, C3, C4: $-1.6 (3)X + 13 (2)Y + 12 (2)Z - 4.3 (7) = 0$

Distance of atoms from plane, Å: C1, -0.03 (2); C2, 0.07 (1); C3, -0.02 (1), C4, -0.03 (2)

Dihedral angle between planes defined by atoms Pd, S, O and C12, C13, C14: $1.8 (8)^\circ$

Dihedral angle between planes defined by atoms Pd, S, O and Pd, C1, C2: $88 (1)^\circ$

Dihedral angle between planes defined by atoms Pd, S, O and Pd, S, C10: $178.0 (6)^\circ$

Angle between C1-C2 bond axis and coordination plane defined by Pd, S, and O along the Pd-olefin bond: 85°

Distance of Pd to midpoint of C1-C2 bond: 2.13 Å

Distance of C1 to coordination plane defined by Pd, S, and O: 0.50 Å

Distance of C2 to coordination plane defined by Pd, S, and O: 0.86 Å

^a *x*, *y*, and *z* are the fractional coordinates of the center of gravity of the rigid-body constrained phenyl rings, and ϕ , θ , and ρ are the orientational angles given in radians. These parameters are defined in ref 20.

are also seen when the reaction of (2-methylallyl)Pd(TTA) with norbornadiene is followed by pmr; here, the spectra indicated the presence of both reacted and unreacted complex. The equilibrium constant for the above exchange reaction was estimated at $K_{eq} = 3.3$. This value indicates preferential formation of the (1-norbornenyl-2-methylallyl)Pd(TTA) complex, where there is no competition between two strong trans labilizers, sulfur and σ -bonded carbon, in the same molecule. The exchange may involve partial dissociation of the sulfur-oxygen ligand, formation of a sulfur-bridged intermediate, and subsequent interchange of the sulfur-oxygen and dioxygen ligands.¹¹

When chloroform solutions of norbornadiene and (π -allyl)-Pd(STTA) or (π -allyl)Pd(TTA) are mixed, broadening of the allylic resonances occurs followed by decrease in the intensity of the free diene resonances and the emergence of new resonances attributable to the diene insertion product. The immediate broadening of the resonances, before insertion is observed, supports the theory that the rate-determining step is actually insertion of the diene rather than initial coordination.²⁴ Although initial coordination may occur more readily with the sulfur-oxygen complex, resulting in total collapse of allylic resonances, the rate of insertion into the two complexes is of the same order of magnitude. When equal concentrations, 0.325 *M*, of norbornadiene and (π -allyl)Pd(STTA) or (π -allyl)Pd(TTA) are mixed at 39° in chloroform, the decrease of the free diene resonances may be observed by pmr. Assuming the absence of other reactions in competition for the free diene, the data initially fit the second-order rate equation $-dA/dt = k(A^2)$ for equal concentrations, *A*, of reactants. Second-order rate constants for product formation were estimated at $k = 0.044$ and 0.021 l. mol⁻¹ min⁻¹ for (π -allyl)Pd(STTA) and (π -allyl)Pd(TTA), respectively.

X-Ray Structural Results. The structure of 3-thio-1,3-diphenylprop-2-en-1-one-1-norbornenyl-2-methylallylpalladium(II), the norbornadiene insertion product of (π -methylallyl)Pd(DBMS), was determined by single-crystal X-ray diffraction in order to assess the trans effects of sulfur and σ -bonded carbon atoms in the same molecule and to establish the overall geometry. The results are summarized in Tables II-V and Figures 4 and 5.²⁵

(24) R. P. Hughes and J. Powell, *Chem. Commun.*, 275 (1971).

(25) See paragraph at end of paper regarding supplementary material.

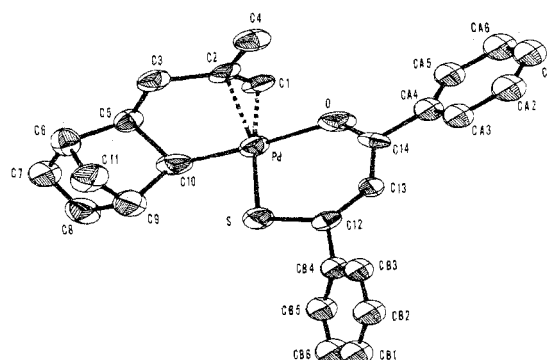


Figure 4. Molecular geometry of 3-thio-1,3-diphenylprop-2-en-1-one-1-norbornenyl-2-methylallylpalladium(II) showing the 40% probability thermal ellipsoids and the atom-labeling scheme.

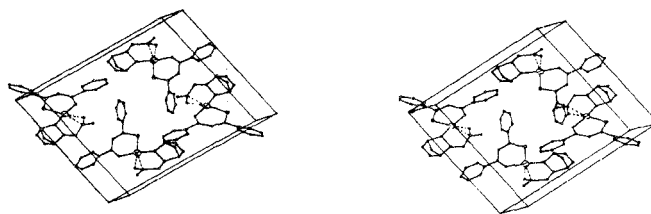


Figure 5. A stereoscopic view of the packing in the unit cell.

There is approximately square coordination about the palladium atom with the palladium-carbon σ bond situated in a position cis to sulfur (Figure 4). The alternation of the bond lengths C12-C13 and C13-C14 suggest greater participation of the ene-thiol form in the DBMS ligand.⁷ The palladium-olefin bond length is significantly longer than that found for the complex di- μ -acetato-bis(2-methylallyl-3-norbornyl)di-palladium(II)²⁶ and shows the increased ability of sulfur *vs.* oxygen to lengthen the bond trans to it. The palladium-carbon σ bonds, in both cases trans to oxygen atoms, are comparable. The value of the Pd-C σ bond in the present case, 2.05 (2) Å, is similar to values found in several related palladium compounds having an asymmetric π -allyl attachment.^{6,7}

The plane defined by Pd-C1-C2 makes an angle of $88 (1)^\circ$ with the coordination plane defined by Pd, S, and O. The olefinic bond axis makes an angle of 85° with this plane, and the coordination plane passes closer to C1 than to C2. In

the acetate complex,²⁶ the olefinic bond axis was found to make an angle of 72° with the coordination plane. Perhaps the lengthened palladium-olefin bond length found for the DBMS complex relieves some of the strain in the carbon chain allowing the olefin to adopt a more natural configuration. The palladium-oxygen bond is longer than that found for the allylic complexes^{6,7} (π -methallyl)Pd(DBMS), 2.067 (6) Å, and (π -*syn*-1-*tert*-butyl-2-methylallyl)Pd(DBMS), 2.047 (7) Å, reflecting the increased trans effect of σ -bonded carbon over allylic-bonded carbon. The palladium-sulfur bond lengths are all very similar for the three complexes.

The olefin bond of the norbornenyl group remains uncoordinated in the solid state, the packing of the molecule being influenced chiefly by van der Waals forces (Figure 5). There are no unusually short nonbonded interatomic distances.

Summary and Conclusions

Allylic palladium complexes containing sulfur-oxygen ligands undergo reactions with dienes similar to those of their dioxygen analogs. This behavior suggests the possibility of many other reactions²⁷ in which such a substitution is feasible.²⁸ Intra- and intermolecular exchange in solution prevents determination of the presence of any stereoselective

(26) M. Zocchi, G. Tieghi, and A. Albinati, *J. Organometal. Chem.*, **33**, C47 (1971). Corresponding bond distances: Pd-C1, 2.16 (1) Å; Pd-C2, 2.17 (1) Å; Pd-C10, 2.04 (1) Å.

(27) D. A. White, *J. Chem. Soc. A*, 145 (1971).

(28) In like manner, a sulfur-oxygen ligand may be substituted for the dioxygen ligand in the formation of cationic complexes of the type (1,5-cyclooctadiene)PdCl₂ + AgBF₄ + HDBMS → [(1,5-cyclooctadiene)Pd(DBMS)]⁺BF₄⁻: J. A. Sadownik, unpublished results.

insertion, however, since it cannot be ascertained whether the final product obtained undergoes rearrangement to reach the thermodynamically more stable form. The conformation expected, considering the relative trans-directing abilities of sulfur and oxygen atoms, was realized as evidenced by the low-temperature limiting spectrum of the 1,3-butadiene insertion product as well as the pmr spectrum and solid-state structure of the norbornadiene adduct.

Acknowledgments. Support of this work by the National Science Foundation under Grant GP 27239X2 is gratefully acknowledged.

Registry No. (π -allyl)Pd(TFAS), 41517-11-7; (π -methallyl)Pd(TFAS), 41517-12-8; (π -crotyl)Pd(TFAS), 41517-13-9; (π -allyl)Pd(STTA), 41517-14-0; (π -methallyl)Pd(STTA), 41517-15-1; (π -crotyl)Pd(STTA), 41560-88-7; (1-norbornenyl-2-methylallyl)Pd(DBMS), 41517-16-2; (1-norbornenyl-2-methylallyl)Pd(STTA), 41517-17-3; (π -*syn*-1-(2-methyl-1-butenyl)allyl)Pd(DBMS), 41517-18-4; Pb(TFAS)₂, 15744-71-5; Pb(STTA)₂, 15282-47-0; (π -methallyl)Pd(DBMS), 32875-75-5; (π -allyl)Pd(TTA), 41517-20-8; (π -methallyl)Pd(TTA), 41517-21-9; di- μ -chloro-di(π -allyl)dipalladium(II), 12012-95-2; di- μ -chloro-di(π -methallyl)dipalladium(II), 12081-18-4; di- μ -chloro-di(π -crotyl)dipalladium(II), 12081-22-0; norbornadiene, 121-46-0; 1,3-butadiene, 106-99-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2659.

Contribution from the Departments of Chemistry of the University of California, Davis, California 95616, and Los Angeles, California 90024¹

Crystal and Molecular Structure of 1-Oxa-4-telluracyclohexane 4,4-Diiodide, C₄H₈OTeI₂

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Received March 9, 1973

The structure of 1-oxa-4-telluracyclohexane 4,4-diiodide, C₄H₈OTeI₂, has been determined by use of three-dimensional data collected on an automated X-ray diffractometer with Mo K α radiation. The space group symmetry is *P*2₁/*c* with four molecules in the unit cell for which *a* = 8.738 (2) Å, *b* = 7.973 (2) Å, *c* = 14.353 (3) Å, and β = 110.35 (1)°. The measured density is 3.20 g cm⁻³ while that calculated from the X-ray data is 3.213 (1) g cm⁻³. Full-matrix least-squares refinement based on 1661 observed reflections converged to a conventional *R* index of 3.1%. The molecule closely approximates mirror symmetry through the I, Te, and O atoms with the six-membered ring in the chair form. The bonding about tellurium is octahedral. There are two Te-C bonds at 2.15 (1) and 2.17 (1) Å which make a C-Te-C angle of 94.1 (4)°. Approximately perpendicular to the C-Te-C plane, tellurium forms axial bonds with I(1) at 2.886 (1) Å and I(2) at 2.938 (1) Å, with an I-Te-I angle of 177.08 (4)°. The octahedron about Te is completed through formation of weak intermolecular bonds with an I(1) atom in a second molecule at 3.814 (1) Å and an I(2) atom in a third molecule at 3.692 (1) Å. Other observed distances and angles of interest are as follows: O-C, 1.41 (1) and 1.41 (1) Å; C-C, 1.52 (2) and 1.52 (2) Å; C-H (average), 0.96 (12) Å; C-O-C, 114.2 (8)°; O-C-C, 113.5 (9) and 114.0 (9)°; Te-C-C, 112.8 (6) and 113.5 (7)°.

Introduction

Although the syntheses of 1-oxa-4-telluracyclohexane (1,4-oxatellurane) and several of its derivatives were reported almost 30 years ago,³ no structural study involving this interesting ring system has been published. Such a study has

been the main objective of the present research, but an important second objective has been an investigation of the intermolecular bonding between the heavy atoms which usually occurs in organochalcogen halides.⁴⁻⁸

(1) Contribution No. 3123 from the UCLA Department of Chemistry.

(2) (a) University of California, Davis. (b) University of California, Los Angeles.

(3) W. V. Farrar and J. M. Gulland, *J. Chem. Soc.*, 11 (1945).

(4) C. Knobler and J. D. McCullough, *Inorg. Chem.*, **11**, 3026 (1972).

(5) J. D. McCullough, Abstracts, Winter Meeting, American Crystallographic Association, Albuquerque, N. M., April 3-7, 1972, Paper K-9.

(6) C. Knobler, J. D. McCullough, and H. Hope, *Inorg. Chem.*, **9**, 797 (1970).