Synthesis and Solution Behavior of Some π-Allyl Monothiodibenzoylmethanatopalladium(II) Complexes[1a]

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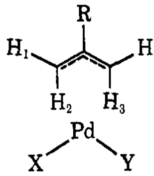
Abstract: The synthesis of several monothiodibenzoylmethanato(π-allyl)palladium(II) complexes is reported. The structural and dynamic properties of these complexes in chlorobenzene solution have been studied over a range of temperatures and concentrations using proton nuclear magnetic resonance spectroscopy. The absolute assignments of the limiting low-temperature spectra were made on the basis of chemical shifts, coupling constants, and the observation of substantial nuclear Overhauser effects for the geminal proton pairs. The influence of the sulfur donor atom to promote low-field shifts of the trans allylic protons was substantiated through analysis of the spectrum of the asymmetric π-*syn*-1-*tert*-butyl-2-methallyl derivative, the crystal structure of which has been determined in a separate study. With increasing temperature, the proton resonances broaden, collapse, and eventually coalesce to a single broad peak. Preferential syn/anti exchange of the protons cis to sulfur is observed and interpreted in terms of a short-lived σ-bonded intermediate. At higher concentrations, cis/trans as well as syn/anti exchange is accelerated and various mechanisms involving bimolecular processes are considered. Ligand exchange which is slow on the pmr time scale has also been demonstrated, and the effect of added triphenylarsine is discussed.

Numerous π-allyl complexes of palladium have been synthesized and their structural[2] and dynamic[4] properties investigated. Two general classes of compounds exist, those containing an identical pair of donor atoms in the coordination sphere with the π-allyl ligand (**1**, X = Y = halide,[5] acetate,[6] β-diketonate,[7] or a diphosphine[8]) and asymmetric complexes with different donor atoms (**1**, X = halide or acetate, Y = tertiary phosphine,[9,10] arsine, or stibine,[10] amine,[7,9] or dimethyl sulfoxide;[11] X = trichlorotin, Y = tertiary phosphine;[12] and X = N, Y = S in the thiocyanate bridged dimer).[13]



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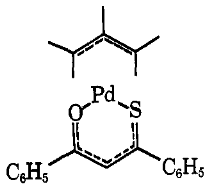
The dynamic properties of π-allyl complexes have been extensively investigated.[4,8,13–17] Two commonly occurring processes studied by pmr spectroscopy are syn/anti exchange (equilibration of H_1/H_2 and H_3/H_4 proton pairs in **1**) involving a short lived σ-allyl intermediate and cis/trans exchange (equilibration of H_1/H_4 and H_2/H_3 proton pairs in **1**) in which pentacoordinate intermediates, possibly involving intermolecular ligand-transfer reactions, have been implicated. In an effort to eliminate the latter kind of process in asymmetric complexes of type **1** (X ≠ Y) for eventual study in stereospecific syntheses, and in order to provide further clarification of the mechanisms for site exchange, a number of monothio-β-diketonato(π-allyl)palladium(II) compounds, **2**, have been prepared. The solid-state structures of two members of this class of compounds have been determined,[3,18] and the insertion of dienes into the palladium–carbon bond has been established.[19] The present paper reports the synthesis, properties, and solution behavior of several complexes of type **2**.



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Experimental Procedure

All chemicals used as starting materials were obtained commercially at the highest purity available. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. A Mechrolab vapor pressure osmometer was used for molecular weight determinations at 37° and was calibrated

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(1) (a) Abstracted in part from the Ph.D. Thesis of S. M. Morehouse, Columbia University, 1971. (b) National Institutes of Health Predoctoral Fellow, 1967–1970.

(2) See ref 3 for a tabular summary of structural data.

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(16) C. W. Alexander, W. R. Jackson, and R. Spratt, *J. Amer. Chem. Soc.*, **92**, 4990 (1970).

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with benzil. The estimated accuracy of the molecular weight results is ±5%.

Di-μ-chloro-di(π-allyl)dipalladium Complexes. Di-μ-chloro-di-π-2-methallyldipalladium was prepared as described by Dent, Long, and Wilkinson[20] and identified by its melting point and infrared spectrum. The π-allyl and π-1-methallyl analogs were obtained by the same procedure using the appropriate allyl chloride.[20] Di-μ-chlorodi-π-*syn*-1-*tert*-butyl-2-methallyldipalladium was prepared according to a published method.[21]

Monothio-β-diketone and β-Diketone Ligands. The ligand 3-mercapto-1,3-diphenylprop-2-en-1-one (monothiodibenzoylmethane, HSDBM)[22] was prepared by Livingstone's method[23] and recrystallized from petroleum ether as red needles.

Anal. Calcd for $C_{15}H_{12}OS$: C, 75.0; H, 5.03; S, 13.3. Found: C, 75.5; H, 5.30; S, 12.9.

3-Thio-1,3-diphenylprop-2-en-1-onethallium(I), $C_{15}H_{11}OSTl$. A methanolic solution of 3.4 g (14 mmol) of monothiodibenzoylmethane was neutralized with aqueous NaOH (0.6 g). When combined with a saturated aqueous solution of 3.6 g of thallous sulfate (7.1 mmol), an orange precipitate formed which was filtered off and washed with water and cold ether. The crude product (5.8 g. ~93% yield) was recrystallized from tetrahydrofuran to give red crystals (mp 154°).

Anal. Calcd for $C_{15}H_{11}OSTl$: C, 40.6; H, 2.50; S, 7.23. Found: C, 40.5; H, 2.58; S, 7.19.

1,3-Diphenylpropane-1,3-dionatothallium(I), $C_{15}H_{11}O_2Tl$. This compound was prepared as described above for Tl(SDBM) using 2.24 g of dibenzoylmethane with 0.56 g of KOH and a saturated aqueous solution containing 2.52 g of thallous sulfate. Yellow crystals [mp 163° (lit.[24] 158–160°)] were obtained by recrystallization of the crude product from chloroform and petroleum ether.

Anal. Calcd for $C_{15}H_{11}O_2Tl$: C, 42.13; H, 2.59. Found: C, 42.10; H, 2.60.

π-Allylpalladium SDBM and DBM Complexes. 3-Thio-1,3-diphenylprop-2-en-1-one-π-methallylpalladium(II), [(π-C_4H_7)Pd(SDBM)]. A solution of 5.4 g of Tl(SDBM) in ethyl ether was added to 2.4 g of the methallylpalladium chloride dimer dissolved in tetrahydrofuran. The thallous chloride precipitate was filtered off and washed with tetrahydrofuran. The orange filtrate was then reduced to about 10 ml on the steam bath and refrigerated overnight. The orange precipitate was collected and air-dried. Recrystallization from acetone gave orange crystals (mp 129°). Electronic spectrum: λ_{max} (log ϵ) 292 (4.43), 430 nm (4.23).

Anal. Calcd for $C_{19}H_{18}OSPd$: C, 56.9; H, 4.53; S, 8.00; mol wt, 401. Found: C, 57.1; H, 4.42; S, 7.92; mol wt, 401.

3-Thio-1,3-diphenylprop-2-en-1-one-π-allylpalladium(II), [(π-C_3H_5)Pd(SDBM)]. A solution of 0.825 mmol of the allylpalladium chloride dimer in 15 ml of benzene was added to 1.65 mmol of Tl-(SDBM) in *ca.* 20 ml of benzene. The thallous chloride precipitate was filtered off and washed with benzene. The orange filtrate was concentrated under reduced pressure to about 3 ml and when cooled in an ice bath yielded 0.593 g of crude product (93% yield). The solid was recrystallized from benzene to give orange crystals (mp 116°). Electronic spectrum: λ_{max} (log ϵ) 292 (4.45), 430 nm (4.25).

Anal. Calcd for $C_{18}H_{16}OSPd$: C, 55.9; H, 4.17; S, 8.29. Found: C, 55.8; H, 4.14; S, 8.43.

3-Thio-1,3-diphenylprop-2-en-1-one-π-crotylpalladium(II), [(π-C_4H_7)Pd(SDBM)]. This complex was obtained as orange crystals (mp 136–137°) by treatment of the π-crotylpalladium chloride dimer with Tl(SDBM) as described for the π-allyl derivative.

Anal. Calcd for $C_{19}H_{18}OSPd$: C, 56.9; H, 4.53; S, 8.00. Found: C, 56.9; H, 4.56; S, 8.15.

3-Thio-1,3-diphenylprop-2-en-1-one-π-*syn*-1-*tert*-butyl-2-methallylpalladium(II), [(π-C_8H_{15})Pd(SDBM)]. This complex was obtained as orange crystals (mp 169°) by treating the appropriate π-allylic palladium chloride dimer with Tl(SDBM) as described for the π-allyl derivative.

Anal. Calcd for $C_{23}H_{26}OSPd$: C, 60.5; H, 5.74; S, 7.02. Found: C, 60.4; H, 5.63; S, 7.05.

1,3-Diphenylpropane-1,3-dionato-π-methallylpalladium(II), (π-C_4H_7)Pd(DBM). Tl(DBM) (1.44 g) was dissolved in a minimum amount of chloroform. Addition of a chloroform solution containing 0.66 g of [(π-C_4H_7)PdCl]$_2$ caused precipitation of thallous chloride. The yellow solution was filtered off and reduced to about 2 ml on a rotary evaporator. Upon cooling to 0°, the pale yellow product solidified and was collected and recrystallized from acetone (mp 148–150°).

Anal. Calcd for $C_{19}H_{18}O_2Pd$: C, 59.3; H, 4.72. Found: C, 59.0; H, 4.63.

1,3-Diphenylpropane-1,3-dionato-π-allylpalladium(II), (π-C_3H_5)-Pd(DBM). This complex was prepared in a similar fashion to the π-methallyl analog from 0.428 g of Tl(DBM) and 0.183 g of [(π-allyl)PdCl]$_2$ in benzene. The pale, cream-yellow compound was recrystallized from petroleum ether (mp 102° dec) and identified by its pmr spectrum.

Decomposition to Bis(monothiodibenzoylmethanato)palladium(II). The π-allylic monothiodibenzoylmethanato complexes of palladium slowly decompose in solution to the known compound, Pd-(SDBM)$_2$.[25] The decomposition product was recovered from solution as dark red crystals with mp >200° (lit.[25] 133°).

Anal. Calcd for $C_{30}H_{22}O_2S_2Pd$: C, 61.6; H, 3.79; S, 11.0; mol wt, 585. Found: C, 62.7; H, 4.60; S, 10.9; mol wt, 586.

Physical Measurements. Proton nuclear magnetic resonance (pmr) spectra were recorded on Varian A-60A and HA-100 spectrometers, both equipped with a variable temperature probe. Temperature calibration was achieved using standard Varian samples of methanol and ethylene glycol. Variable temperature pmr spectra of (π-allyl)Pd(SDBM) were also obtained at 220 MHz. Chemical shift values were standardized internally with tetramethylsilane. Nuclear Overhauser effects (NOE) were studied at −45° on the HA-100 using the frequency sweep mode. Samples were recrystallized twice and dissolved in Diaprep 98% chlorobenzene-d_5 which had been previously saturated with nitrogen. Each allylic proton was irradiated while simultaneously observing changes in the integrated intensities of neighboring protons. Intensities were integrated three times before and after irradiation with changes estimated to be accurate to ±2%. This integration procedure was followed for both increasing and decreasing frequency sweeps. Ultraviolet and visible spectra were recorded on a Cary-15 spectrophotometer in the region 260–500 nm. Carbon tetrachloride solutions 3×10^{-5} *M* in complex were studied using 1-cm matched quartz cells. A Perkin-Elmer 137 grating spectrophotometer was used to record infrared spectra. Solid samples were mulled in Nujol and examined between NaCl plates. The spectra were calibrated using polystyrene at 6.238 μ.

Results and Discussion

General Characterization. The synthesis of the (π-allyl)Pd(SDBM) complexes was achieved in a straightforward manner by metathesis of the chloride-bridged dimer with Tl(SDBM), a reaction used in the preparation of acetylacetonato(π-allyl)palladium compounds.[7] The complexes are monomeric in the crystalline state with the well-known 1,2,3-*trihapto*allylpalladium attachment[3,18] and mononuclear in chloroform solution as determined for the π-methallyl derivative by vapor-pressure osmometry. On standing for prolonged periods in solution or upon heating, decomposition to the known Pd(SDBM)$_2$ compound[25] occurs. The organic product(s) of this decomposition reaction was not identified.

The following major infrared bands were observed in the 1700–800-cm^{-1} region for the (π-allyl)Pd(SDBM) complexes: 1540 (m), 1500 (m), 1435 (s), 1340 (w), 1260 (s), and 955 cm^{-1} (w). The band at 1260 cm^{-1} is shifted to about 1225 cm^{-1} in the spectrum of Tl(SDBM) and is absent in the infrared spectra of all the dibenzoylmethanato complexes. Bands in the 1220–1270-cm^{-1} range are characteristic of M(SDBM)$_n$ complexes and have been assigned to the C═S stretching frequency.[25] Recent normal coordinate analyses of related divalent

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(20) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(21) H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, 88, 225 (1969).

(22) Abbreviations used in this paper are: SDBM = monothiodibenzoylmethane anion; DBM = dibenzoylmethane anion; π-methallyl = π-2-methallyl; π-crotyl = π-1-methallyl.

(23) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, 18 666 (1965).

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(25) S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, 20, 1065 (1967).

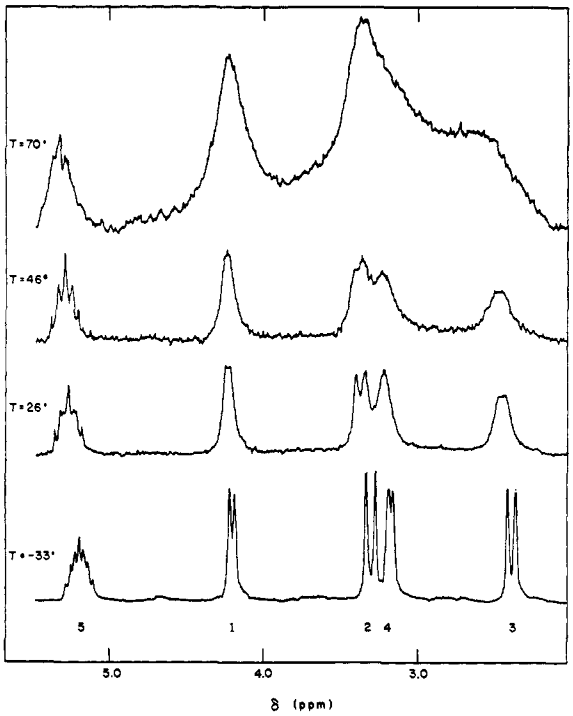

Figure 1. 220-MHz pmr spectra of a 5.5% solution of (π-allyl)-Pd(SDBM) in chlorobenzene-d_5 showing the exchange of syn/anti protons cis to sulfur as the temperature is raised. At 70° a precipitate was present in the solution indicating that some decomposition had occurred.

metal monothio-β-diketonate complexes indicate, however, that the C=S stretching bands in these molecules appear close to 710 cm^{-1}.[26] Since the calculations were not performed on SDBM derivatives, the origin of the 1260-cm^{-1} frequency remains obscure.

Assignment of Pmr Spectra and Stereochemistry. The pmr spectrum of (π-allyl)Pd(SDBM) in chlorobenzene-d_5 at $-33°$ is shown in Figure 1. Since resonances 2 and 4 are not resolved at 100 MHz, a 220-MHz spectrum was obtained. From the observed coupling constants $J_{15} = 7$ Hz, $J_{25} = 13$ Hz, $J_{35} = 11$ Hz, and $J_{45} = 5$ Hz, resonances 1 and 4 are assigned to protons syn, and resonances 2 and 3 to protons anti to the central proton by analogy to results for numerous π-allyl complexes in which $J_{\text{syn}} \simeq 6$ Hz and $J_{\text{anti}} \simeq 12$ Hz.[27] The identification of resonances 1 and 2 with the protons trans to the sulfur atom was made by analogy to the spectral assignment (discussed in detail below) for the 1-*tert*-butyl-2-methallyl derivative, for which it has been established that the protons trans to the sulfur atom resonate at lower fields than the cis protons in these compounds. This result, together with the observed asymmetry of the allylic coupling constants (*vide infra*), appears to support the theory[10b] that partial localization of the double bonds has occurred within the allyl group, structure 3, conveying more vinylic character to the carbon atom trans to sulfur. The conclusion that δ(trans) > δ(cis) has also been reached on the basis of an assumed preferential coupling of the ^{31}P nucleus to the trans allylic protons in asymmetric complexes of type **1**.[10,28] Although this assignment was recognized as somewhat arbitrary[29] (it is *possible*, if unlikely,[30] that $J(^{31}\text{P-cis}) > J(^{31}\text{P-trans})$), it receives substantial support from the present work, which may be taken as a general validation of many indirect arguments which have been presented previously.

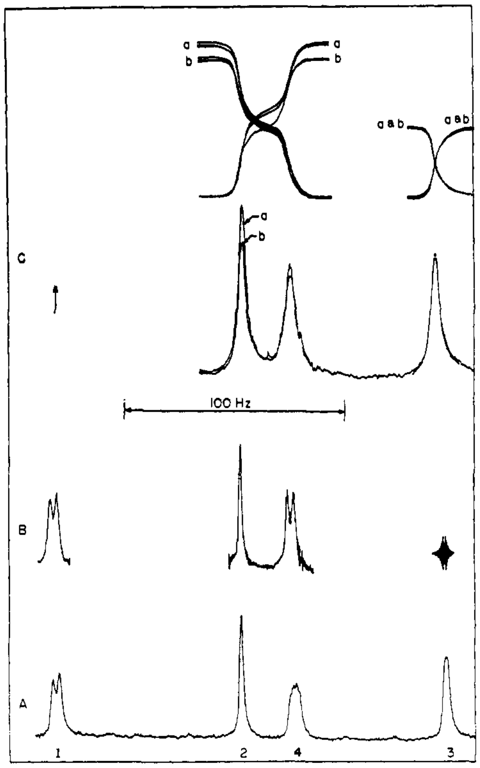

Figure 2. (A) 100-MHz pmr spectrum of (π-methallyl)Pd(SDBM) in chlorobenzene at $-4°$ showing the four allylic resonances. (B) Decoupling of geminal protons cis to sulfur at $-4°$. (C) Nuclear Overhauser effect in chlorobenzene-d_5 at $-45°$. Resonance 1 is irradiated (arrow) and the integration of resonances 2, 3, and 4 is shown before (b) and after (a) irradiation. Viscosity broadening obscures spin–spin coupling at the lower temperature.

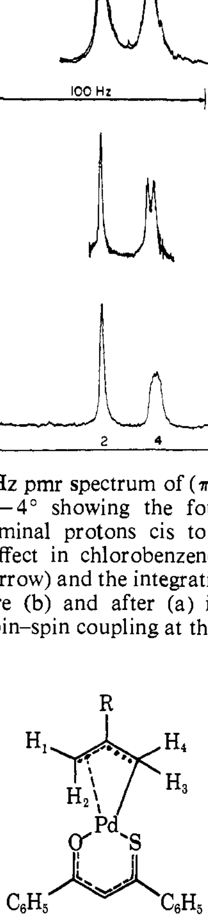

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Figure 2A shows the pmr spectrum of (π-methallyl)-Pd(SDBM) at $-4°$. Resonances 1 and 3 were assigned to the syn,trans (**3**, H$_1$) and cis,anti (**3**, H$_3$) protons, respectively. This assignment was based on arguments similar to those described above for the π-allyl analog and the knowledge that, within a geminal pair, the proton syn to the methyl group will occur at lower fields than the anti proton.[31] Resonances 2 and 4 cannot be identified with confidence by analogy to the π-allyl derivative because of the small chemical shift difference (0.12 ppm) between resonances 2 and 4 in the spectrum of the latter compound (Figure 1). Assignment of

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(26) O. Siiman and J. Fresco, *J. Chem. Phys.*, **54**, 734, 740 (1971).

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

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

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(30) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

(31) C. W. Fong and W. Kitching, *Aust. J. Chem.*, **22**, 477 (1969), and references cited therein.

resonance 2 to H_2 and resonance 4 to H_4 was tentatively made on the basis of the long-range coupling observed between the syn protons, $J_{14} = 2.5$ Hz. This coupling was clarified in a double resonance experiment in which resonance 3 was irradiated (Figure 2B) to remove the coupling between the geminal protons cis to sulfur (discussed below). Long-range syn–syn coupling has been previously reported and is thought to be larger than anti–anti or syn–anti coupling.[31-33]

In support of arguments based on the analysis of chemical shifts and coupling constants, it is often possible to make assignments on the basis of nuclear Overhauser effects (NOE).[34-36] The relaxation time T_1 of a given proton depends to a large extent upon dipole–dipole interactions with its nearest neighbors. If a proton H_a contributes efficiently to the relaxation of H_b, saturation of resonance H_b should cause an enhancement of the *integrated intensity* of the H_a resonance and *vice versa*.[34] The degree of enhancement is proportional to the inverse sixth power[35,36] of the internuclear distance, but its effect may be diluted by other contributions to the relaxation mechanism. A number of experimental precautions must be taken in this regard. Intermolecular contributions are reduced by using magnetically inert solvents, and care is taken to eliminate dissolved oxygen and other paramagnetic species. Instrumental considerations are important.[35] In addition, it is necessary to measure the effects at temperatures low enough to ensure the absence of site exchange.[36a]

The crystal structure determination of (π-methallyl)Pd(SDBM)[3] shows that the average distance between geminal protons is ~1.7 Å, nearly 1 Å smaller than any other intramolecular proton–proton distance. A definitive assignment for resonances 2 and 4 can therefore be made on the basis of the increase in integrated intensities observed when irradiating the resonances assigned to H_1 and H_3 (Figure 2). A summary of the NOE results obtained from a 15% solution of (π-methallyl)Pd(SDBM) in chlorobenzene-d_5 appears in Table I, and a representative spectrum is included in Figure 2. The integrated intensity of each proton absorption increased by ~20% when its geminal partner was irradiated. The proximate pairs are clearly H_1 and H_2, H_3 and H_4. These results confirm the assignments formerly based on the long-range coupling between the syn protons observed here and in related complexes.[31-33]

Irradiation of the methyl resonance at δ 1.68 in the spectrum of (π-methallyl)Pd(SDBM) produced no nuclear Overhauser effect on resonances 2, 3, and 4, but resonance 1 increased by about 9–10%. This is the first piece of pmr evidence which indicates an asymmetry in the bonding within the methallyl group. The second is the observation that $J_{34} = 1$ Hz whereas $J_{12} \sim 0$ Hz (Figure 2).[37] This result could mean a small difference in the hybridization of the terminal carbon atoms since the coupling constants are a function of the H–C–H angle.[38] Although such an interpretation is consistent with structure **3**, geminal J values are sensitive not only to the geometrical orientation of the interacting protons but also to changes in the electronegativity of the environment. There is a correlation between the magnitude of coupling constants and long-range inductive effects. The observed coupling might simply result from the asymmetric attachment of the allyl group. It should be noted, however, that in (π-allyl)Pd(SDBM) $J_{15} \neq J_{45}$ and $J_{25} \neq J_{35}$ (Figure 1). The coupling constants between the central proton and both the syn and anti protons trans to the sulfur atom are 2 Hz larger than the corresponding values for protons trans to the oxygen atom. When one considers that vicinal coupling constants are much less sensitive to electronegativity effects than geminal coupling constants,[38] this seems to imply some asymmetry within the allyl group itself (structure **3**). The nonequivalence of coupling constants between the central and syn or anti protons in asymmetric π-allyl complexes has been observed previously (see, for example, ref 29), but no interpretation was offered.

Table I. Summary of Observed Nuclear Overhauser Effects and Proton Assignments in Chlorobenzene-d_5

Proton irradiated		Proton	Intensity
δ, ppm	Assignment	observed (δ)	increase, %
	(π-methallyl)Pd(SDBM)[a]		
4.09	H_1	H_2 (3.27)	21
3.27	H_2	H_1 (4.09)	18
3.04	H_4	H_3 (2.37)	17
2.37	H_3	H_4 (3.04)	23
1.68	CH_3[b]	H_1 (4.09)	10
	(π-*syn*-*tert*-butyl-2-methallyl)Pd(SDBM)[c]		
3.77	H_2	No change	
2.93	H_4	H_3 (2.24)	39
2.24	H_3	H_4 (2.93)	36
1.87	CH_3	No change	
1.31	$(CH)_3$	No change	

[a] At −45°, 0.2 *M*; see structure **3** for atom labeling. [b] At −5°. [c] At −40°, 0.05 *M*; see structure **4** for atom labeling.

The spectrum of (π-*syn*-1-*tert*-butyl-2-methallyl)Pd(SDBM) consists of three vinylic proton resonances, the methyl resonance at δ 1.87, and the *tert*-butyl resonance at δ 1.31 with relative intensities of 1:1:1:3:9.[39] The crystal structure of this compound establishes the syn/trans isomer **4** in the solid state.[18] Assuming that the compound has the same structure in solution, the assignment was made with the aid of NOE experiments (Table I) as follows. Irradiation of the resonance at δ 2.93 assigned to H_4 caused a 39% enhancement of the integrated intensity of the resonance at δ 2.24 attributed to H_3. Similarly, the H_4 resonance intensity increased by 36% when H_3 was irradiated. The remaining resonance at δ 3.77 is, therefore, H_2. Since the high-field proton pair, H_3 and H_4, is cis to the sulfur

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

(33) K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organometal. Chem.*, 11, 353 (1968).

(34) (a) R. Kaiser, *J. Chem. Phys.*, 42, 1838 (1965); (b) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 87, 5250 (1965).

(35) R. E. Schirmer, J. H. Noggle, J. P. Davis, and P. A. Hart, *ibid.*, 92, 3266 (1970), and references cited therein.

(36) (a) J. K. Saunders and R. A. Bell, *Can. J. Chem.*, 48, 512 (1970); (b) R. A. Bell and J. K. Saunders, *ibid.*, 48, 1114 (1970).

(37) A syn–anti coupling constant of 0.45 Hz has been reported[15b] for $[(\pi\text{-allyl})PdCl]_2$ (see also ref 28 and literature cited therein).

(38) See, for example, J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 116.

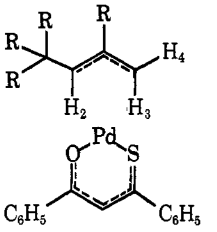
(39) Minor peaks in the methyl and vinylic regions of the spectrum suggest the additional presence of the cis or anti isomer, but no attempt was made to assign these extra resonances. Under certain conditions the anti isomer can be formed preferentially for $[(\pi\text{-1-}tert\text{-butyl-2-methallyl})PdCl]_2$.[40]

(40) J. Lukas, S. Coren, and J. E. Blom, *Chem. Commun.*, 1303 (1969).

Table II. Proton Chemical Shifts and Assignments for (π-allyl)Pd(SDBM) and (π-allyl)Pd(DBM) Complexes[a]

Complex	T, °C	Chemical shifts, δ, ppm H_1	H_2	H_3	H_4	H_5	Other	Coupling constants, Hz
(π-allyl)Pd(SDBM) (**3**, R = H_5)	−33	4.21	3.31	2.40	3.19	5.20		$J_{15} = 7, J_{25} = 13,$ $J_{35} = 11, J_{45} = 5$
(π-methallyl)Pd(SDBM) (**3**, R = CH_3)	−38	4.12	3.29	2.39	3.07		1.67[b]	$J_{14} = 2.5, J_{34} = 1$
trans-(π-*syn*-1-*tert*-butyl-2-methallyl)Pd(SDBM) (**4**)	−40		3.77	2.24	2.93		1.87[b] 1.34[c]	
trans-(π-*syn*-crotyl)-Pd(SDBM) (**5**)	−42		3.96	2.30	3.09	4.95	1.46[b]	$J_{25} = 12, J_{35} = 11,$ $J_{45} = 6, J_{2(\mathrm{CH_3})} = 6$
(π-allyl)Pd(DBM)[d]	amb[e]			2.63	3.63	5.27		$J_{35} = 13, J_{45} = 6.5$
(π-methallyl)Pd(DBM)[d]	amb[e]			2.26	3.20		1.48[b]	

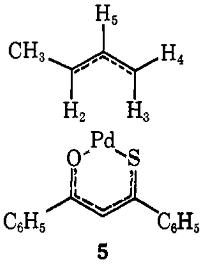
[a] From the limiting low-temperature spectra in chlorobenzene or chlorobenzene-d_5 solution. The chemical shifts quoted are for the temperature cited and showed slight variations at different temperatures. [b] Methyl group. [c] *tert*-Butyl group. [d] $H_1 = H_4 = H_s$ (syn); $H_2 = H_3 = H_a$ (anti). [e] Ambient probe temperature, *ca.* 40°.



4, R = CH_3

atom,[18] the influence of sulfur (*vs.* oxygen) to promote low-field shifts of the trans allylic protons is substantiated, and all previous assignments are verified.

The spectrum of the π-crotyl analog indicated structure **5** to be the major species in solution. The as-



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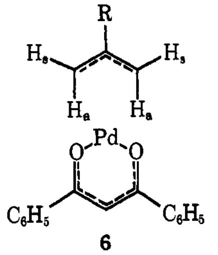
signment of resonances, $\delta(H_2) = 3.96$, $\delta(H_3) = 2.30$, $\delta(H_4) = 3.09$, $\delta(H_5) = 4.95$, and $\delta(CH_3) = 1.46$ ppm, was made directly on the basis of the coupling constants $J_{2(\mathrm{CH_3})} = 6$ Hz, $J_{25} = 12$ Hz, $J_{35} = 11$ Hz, and $J_{45} = 6$ Hz. Again there was evidence for additional species in solution, for example, a methyl doublet ($J = 6$ Hz) at δ 1.23 which probably signifies the presence of <20% of the cis isomer. The tendency for the carbon atom with the alkyl substituent to be aligned trans to the better labilizer in asymmetrically substituted (π-allyl)-Pd(SDBM) complexes parallels the behavior in numerous related complexes and has been thoroughly discussed elsewhere.[10b,15a,18] The above results and assignments are summarized for convenience in Table II, along with data for the π-allyl and π-methallyl DBM complexes.

Nmr Averaging Processes. The (π-allyl)Pd(SDBM) complexes synthesized for this investigation all show fluxional behavior at increasing temperatures involving proton site exchange. The symmetrical (π-allyl)- and (π-methallyl)Pd(DBM) complexes, **6**, do not appear to undergo syn (H_s)/anti (H_a) exchange in inert solvents and in the absence of basic ligands. Averaging cannot be detected below ~100°, at which temperature serious



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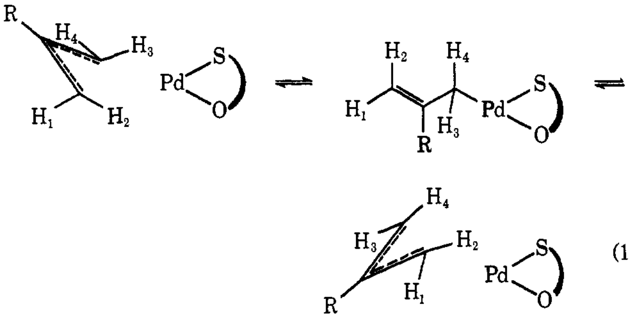
decomposition impairs the spectra. One must conclude in these instances that rearrangement does not occur at a rate fast enough to be observed using line-broadening techniques although the exchange might be rapid enough to be detected by double resonance studies, as was the case for $[(\pi\text{-allyl})PdCl]_2$.[15b]

Figure 1 depicts the behavior of a fairly dilute (*ca.* 5%) solution of (π-allyl)Pd(SDBM) with increasing temperature. The resonances assigned to protons H_3 and H_4 cis to sulfur broaden and collapse with increasing temperature until, at 70°, appreciable decomposition occurs. The preferential exchange of syn and anti protons on the carbon atom cis to sulfur is consistent with a π–σ–π equilibration process (eq 1). Such a



(1)

process has been extensively discussed and proved for a number of related (π-allyl)palladium complexes of type **1**,[4,8,10,14] and there is no reason to consider possible alternative modes for the rearrangement here. The preferential syn/anti exchange of protons cis to sulfur reflects the greater stability of the σ-isobutenyl intermediate shown in eq 1 compared to the alternative intermediate having a Pd–C σ bond trans to the sulfur atom.[41] It is significant, moreover, that at the concen-

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(41) The fact that the chemical shift difference between the cis protons (H_3 and H_4, structure **3**) is smaller than between the trans protons for both (π-allyl)Pd(SDBM) and (π-methallyl)Pd(SDBM) (Table II) cannot account for the observed preferential collapse cis to sulfur, as shown by comparison of the observed spectra with computer-simulated spectra assuming equal exchange rates.

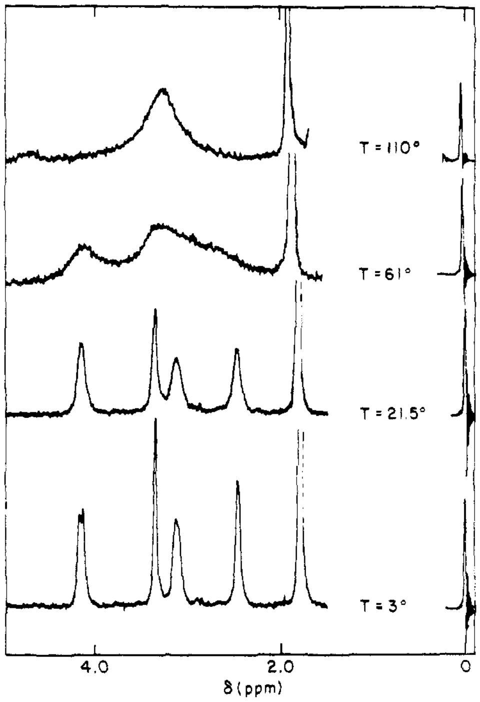


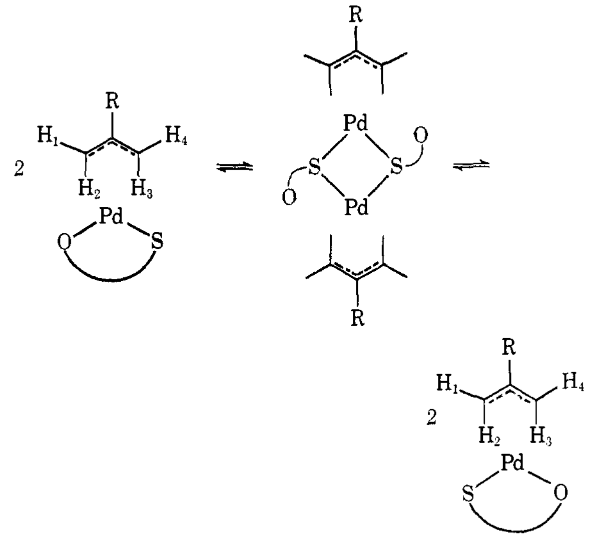
Figure 3. Temperature dependence of the 60-MHz pmr spectrum of a 0.404 *M* solution of (π-methallyl)Pd(SDBM) in chlorobenzene.

tration used (the concentration dependence is discussed below) to obtain the high-temperature spectra for Figure 1, cis/trans equilibration is occurring at a slower rate. This result may be contrasted with the behavior of (π-allyl)PdXY complexes containing monodentate X and Y groups[4,10,14] and is attributed to the chelating effect of the monothio-β-diketonate ligand (*cf.* also the study of the [(π-methallyl)Pd(diphos)]$^+$ cation).[8]

Solutions of the compound (π-methallyl)Pd(SDBM) exhibit similar temperature-dependent pmr spectra (Figure 3) but are more stable and spectral observations at higher temperatures were possible. As indicated in Figure 3, the resonances eventually coalesce into a single broad line at the average of all four proton-chemical shifts. This result indicates that cis/trans as well as syn/anti exchange in structure **3** is occurring. The spectral changes were found to be reversible with temperature, although decomposition does occur if the samples are heated for any length of time. Again there is preferential syn/anti exchange cis to sulfur at the intermediate temperatures.[41]

Over a range of concentrations, the contribution of cis/trans exchange to the broadening of the spectral lines is apparent even at ambient temperature. The exchange rate is clearly concentration dependent. Line-width measurements in the slow-exchange region[42] of 0.310 and 0.625 *M* solutions of (π-methallyl)Pd(SDBM) were reasonably consistent with a first-order dependence on concentration of the inverse exchange lifetimes of all four allylic protons at the lower temperatures ($-10 < T < 10°$). These results imply a bimolecular mechanism for cis/trans averaging, a process which has been observed previously[4,13,43] for π-allyl compounds. At slightly higher temperatures ($10 < T < 25°$) preferential syn/anti exchange cis to sulfur becomes apparent. Again line broadening was greater in the more concentrated samples, revealing the contribution of a higher (probably second) order term in the rate law for syn/anti proton site exchange. From these and similar results obtained at other concentrations and with different batches of compound it appeared that the rates of cis/trans and syn/anti exchange were of the same order of magnitude and that their relative contributions to the line broadening could vary with both concentration and temperature.[44] A quantitative analysis of the kinetics of cis/trans and syn/anti exchange by comparison of observed to calculated (such a calculation would involve fitting a large number of variable parameters) spectra was therefore not attempted.

The bimolecular cis/trans exchange seen in concentrated (π-methallyl)Pd(SDBM) solutions might be accompanied by ligand transfer. A simple mechanism that would account for such behavior is written as eq 2.



(2)

The dimeric intermediate shown in eq 2 bears some resemblance to the tetranuclear intermediate proposed for the bimolecular ligand exchange process postulated to explain cis/trans averaging in the [(π-methallyl)Pd(SCN)]$_2$ system[13] and was suggested by the fact that monothio-β-diketonate ligands are known to exist primarily in the ene-thiol form.[18] Moreover, recent studies of closely related monothio-β-diketonate complexes have shown that these ligands can coordinate in a monodentate fashion using the sulfur atom only.[46] The possibility of a bimolecular intermediate in which the allyl group is coordinated to both metal atoms is an alternative[47] to the intermediate shown in eq 2, since bridging allyl groups were found to occur in the X-ray structural study of the dimeric compound [(π-allyl)-

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[42] T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968), and references cited therein.

[43] K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometal. Chem.*, **12**, 533 (1968).

[44] In one instance, pmr spectral studies showed H_1/H_4 and H_2/H_3 site exchange to occur at lower temperatures than syn/anti exchange. This result could not be repeated, however, and may have been caused by the presence of a small amount of impurity in the solvent or complex. Related studies of (diolefin)Rh(SDBM) complexes have demonstrated that cis/trans exchange can occur at appreciable rates in the presence of trace amounts of impurity.[45]

[45] H. I. Heitner and S. J. Lippard, *Inorg. Chem.*, **11**, 1447 (1972).

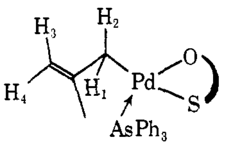
[46] (a) E. Uhlemann and U. Eckelmann, *Z. Anorg. Allg. Chem.*, **383**, 321 (1971); (b) G. H. Barnett and M. K. Cooper, *Chem. Commun.*, 1082 (1971).

[47] For discussion of this and another possible mechanism involving bridging SDBM ligands, see ref 1a.

Pt(acac)]$_2$.[48] In either case, the kinetic precursor has one end of a chelating ligand uncoordinated which could then also participate in the intermediate required for the bimolecular syn/anti exchange process by filling the empty coordination site shown in the central structure of eq 1. The need for a donor ligand to occupy this empty site has recently been emphasized by Powell[49] and is presumably responsible for the observed concentration dependence of the syn/anti exchange.

Further insight into the possible mechanism for the bimolecular cis/trans averaging process is provided by the pmr spectrum of a chlorobenzene solution containing 0.16 M (π-methallyl)Pd(SDBM) and 0.10 M triphenylarsine, recorded at ambient probe temperature. Two broad resonances appeared at the average chemical shift of protons H_1 and H_4, H_2 and H_3, indicative of cis/trans exchange. The ability of added donor ligands to promote such a left–right interchange in asymmetric π-allyl complexes of type **1** ($X \neq Y$) is a well-documented phenomenon,[4] which probably occurs through formation of a five-coordinate intermediate followed by pseudorotation and eventual loss of the donor ligand.[4,50] Similar behavior is exhibited by (diene)-RhXY compounds in the presence of donor ligands[4,45,51] and by analogous pentacoordinate rhodium(I) and iridium(I) diene complexes.[52] For solutions containing only (π-methallyl)Pd(SDBM) in moderate to high concentrations, cis/trans averaging might occur through a similar process involving a bimolecular intermediate in which the dissociated end of a unidentate SDBM or π-methallyl ligand on one palladium atom serves as the fifth ligand for the second palladium atom. In order to distinguish between this possibility and mechanisms involving intermolecular ligand exchange (such as eq 2 or various other possible reactions mentioned previously), it would be of interest to examine the corresponding platinum derivative, (π-methallyl)Pt(SDBM), in the hope of using the coupling to the ^{195}Pt nucleus ($I = {}^1/_2$) to determine whether or not ligand transfer is occurring. Some preliminary attempts to synthesize this compound gave mainly Pt(SDBM)$_2$, and further studies of this system are in progress.[19]

An interesting result was obtained when smaller concentrations of triphenylarsine were added to (π-methallyl)Pd(SDBM) in chlorobenzene. In particular, a solution containing 0.009 M triphenylarsine and 0.154 M complex exhibited complete collapse of resonances 1 and 2, whereas resonances 3 and 4 had broadened but remained discernible. One possible explanation is that the triphenylarsine attacks the allylic side of the molecular to form the σ intermediate **7**, but this seems unlikely in view of the trans-directing effect of the sulfur atom. An alternative explanation is that the triphenylarsine displaces one end of the SDBM ligand to give the intermediate **8** (*cf.* the intermediate in eq 2), in which solvent might occupy the vacant position in the coordination sphere. Intermediate **8** would be preferred if the arsine atom is a better trans labilizer than the sulfur atom, promoting collapse of resonances 1 and 2 *via* the Pd–C σ bond trans to sulfur.



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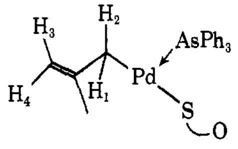

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The following experiment established that a slow, underlying ligand-transfer reaction was occurring at room temperature. Solutions of (π-methallyl)Pd-(SDBM) and (π-allyl)Pd(DBM) were mixed and the resulting pmr spectrum was recorded immediately. The resonances of the four species indicated by the exchange eq 3 appeared in the spectrum. The appearance of each of the individual resonances, however, the methyl singlets of the two π-methallyl complexes being the most easily distinguished, proves that the rate of ligand exchange (eq 3), while fast enough to produce the observed spectrum, is slow on the pmr time scale. The allylic absorptions of the two asymmetric SDBM complexes collapsed with increasing temperature as cis/trans and syn/anti averaging commenced. Even at 70° the two methyl resonances, which differ in their chemical shift values by substantially less than the chemical shift difference between the allylic proton resonances in the two SDBM complexes (Table II), had not yet coalesced.

$$(\pi\text{-methallyl})\text{Pd(SDBM)} + (\pi\text{-allyl})\text{Pd(DBM)} \rightleftharpoons (\pi\text{-methallyl})\text{Pd(DBM)} + (\pi\text{-allyl})\text{Pd(SDBM)} \quad (3)$$

The π-*syn-tert*-butyl-2-methallyl and π-crotyl complexes, **4** and **5**, respectively, also exhibit reversible fluxional behavior as a function of temperature, but the interpretation of the spectra is complicated by the existence of isomerism. In both cases the low-temperature spectrum shows a preponderance of the syn isomer in which the R group is trans to the sulfur atom. At higher temperatures, preferential syn/anti exchange of protons cis to the sulfur atom was observed for the π-crotyl derivative, and the chemical shift of the proton gem to the R group did not change. Similar results were obtained for (π-crotyl)PdCl[P(C$_6$H$_5$)$_3$][28] and imply that syn/anti exchange at the substituted carbon atom is inhibited to some extent. This seems reasonable considering steric effects alone, but it is also consistent with the greater stability expected for the σ-isobutenyl transition state with the more highly substituted olefin.

In summary, the data are consistent with syn/anti exchange through a short-lived σ intermediate involving preferential Pd–C σ bonding cis to sulfur. The observed cis/trans exchange probably occurs in a bimolecular process involving either pseudoroatation within a pentacoordinate transition state and/or intermolecular ligand exchange. The cis/trans exchange is promoted by high concentrations and the addition of triphenylarsine. An underlying intermolecular ligand exchange

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(48) W. S. McDonald, B. E. Mann, G. Raper, B. L. Shaw, and G. Shaw, *Chem. Commun.*, 1254 (1969).

(49) J. Powell, *J. Chem. Soc. A*, 2233 (1971).

(50) J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, **19**, P13 (1969), and references cited therein.

(51) H. I. Heitner and S. J. Lippard, *J. Amer. Chem. Soc.*, **92**, 3486 (1970).

(52) D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, **30** C84 (1971), and references cited therein.

process, slow on the pmr time scale, has also been established for mixtures of (π-methallyl)Pd(SDBM) and (π-allyl)Pd(DBM). These conclusions are sustained by comparison with studies of other asymmetric π-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).

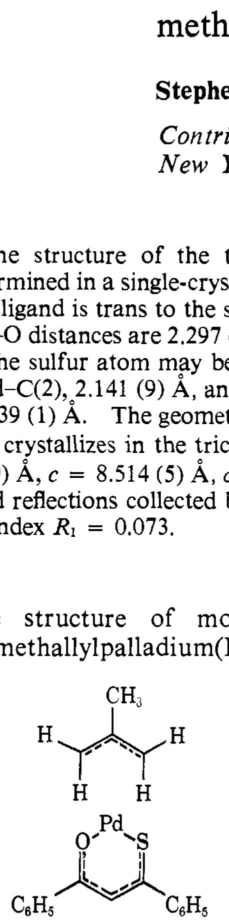
Crystal and Molecular Structure of Monothiodibenzoylmethanato-π-*syn*-1-*tert*-butyl-2-methallylpalladium(II)

Stephen J. Lippard* and Sheila M. Morehouse[1]

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-h^3-[(*tert*-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 π-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 π-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, α = 112.89 (5)°, β = 107.61 (2)°, γ = 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-π-methallylpalladium(II), I, has been described previously,[2] and several other structural studies of (π-allyl)PdXY complexes containing a symmetric π-allylic group bonded to a palladium atom in a nonsymmetric ligand environment have been carried out.[3–5] The geometries of various asymmetrically substituted π-allyl palladium complexes have also been determined,[6,7] but there has not yet been a structural investigation of an asymmetrically substituted π-allyl group coordinated to palladium in a compound of the type (π-allyl)PdXY. In conjunction with our study of the solution behavior of (π-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 low temperatures in solution, a conclusion facilitated by the present solid-state structural determination. It



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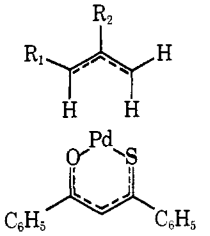
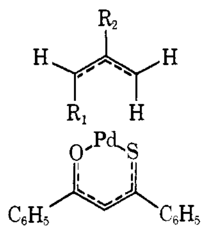
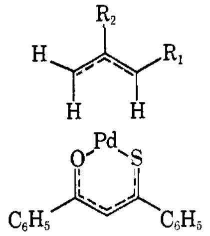


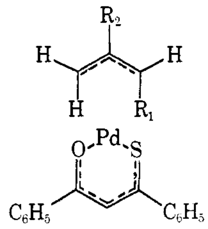
IIa, syn/trans



IIb, anti/trans



IIc, syn/cis



IId, anti/cis

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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).