Preparation of $(Me_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SPh)$ by reaction of Pd(0) complex with allyl phenyl sulfide

Kohtaro Osakada *, Youichi Ozawa and Akio Yamamoto *,*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

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Abstract

$Pd(CH_2=CHPh)(PMe_3)_2$, prepared in situ by reaction of $PdEt_2(PMe_3)_2$ with styrene, reacts with allyl phenyl sulfide to give $(Me_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SPh)$ (1). Complex 1 has been characterized by means of NMR (^1H, ^{13}C, and ^{31}P) spectroscopy as well as X-ray crystallography. Space group $P2_1/n$, $a = 11.662(1)$, $b = 17.898(2)$, $c = 9.849(2)$ Å, $\beta = 91.22(1)°$, $Z = 4$, $R = 0.049$, and $Rw = 0.050$. The molecule has a bridging allyl ligand which coordinates symmetrically to two palladium centers. The distance between the palladium atoms (2.613(1) Å) indicates the presence of Pd–Pd bonding in the molecule. Reaction of 1 with CO gives allyl phenyl sulfide.

Introduction

Dinuclear palladium(I) complexes having μ-allyl ligand have been prepared by reactions of π-allyl palladium(II) halide or acetate complexes with tertiary phosphine ligands or with palladium(0) complexes having phosphine ligands [1–5]. We previously reported that reactions of $PdL_2(L = PCy_3$ (tricyclohexylphosphine) or $P(t\text{-Bu})_3$) with allyl acetate and with allyl phenyl sulfide, respectively, gave dinuclear μ-allyl palladium(I) complexes formulated as $L_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-E})$ (E = OAc, SPh) [6,7]. This oxidative addition of the allylic compounds to Pd^0 complexes provides a good preparative method of the dinuclear palladium(I) complexes having both bridging allyl ligand and bridging acetate or thiolate ligand. Although these complexes were unequivocally characterized by means of NMR spectroscopy, there have been no reports of their crystallographic study. Recently we found that $Pd(CH_2=CHPh)(PMe_3)_2$, prepared in situ by reaction of $PdEt_2(PMe_3)_2$ with styrene [8], underwent oxidative addition of allylic phenyl carbonate to give π-allyl palladium(II) complexes having PMe_3 ligands [9]. The Pd^0-styrene complex also reacted with allyl phenyl sulfide to give the μ-allyl dinuclear palladium(I) complex

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* Present Address: Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo Shinjuku-ku, Tokyo 169, Japan.

which was characterized by X-ray crystallography. In this paper we report preparation and structure of the dinuclear palladium(I) complex as well as its reaction with CO.

Results and discussion

Preparation of (Me₃P)₂Pd₂(μ-η³-C₃H₅)(μ-SPh) (1)

Preparation of (Me$_3$P)$_2$Pd$_2$(μ-η^3-C$_3$H$_5$)(μ-SPh) (1)

Pd(CH$_2$=CHPh)(PMe$_3$)$_2$, which was prepared in situ by reaction of *trans*-PdEt$_2$(PMe$_3$)$_2$ with styrene, reacts with 0.5 equiv. of allyl phenyl sulfide to give complex formulated as (Me$_3$P)$_2$Pd$_2$(μ-η^3-C$_3$H$_5$)(μ-SPh) (1). Complex 1 is obtained as yellow crystals by recrystallization from acetone and characterized by NMR spectroscopy as well as X-ray crystallography.
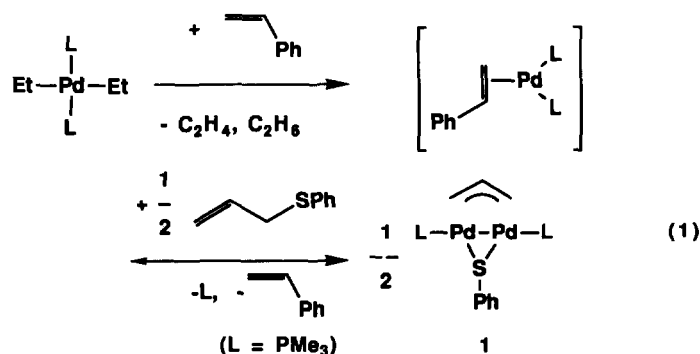
NMR (^{1}H and ^{31}P) spectra of the reaction mixture before recrystallization indicate formation of *trans*-Pd(SPh)$_2$(PMe$_3$)$_2$ (2) in a small amount (ca. 10%). Reaction of Pd(CH$_2$=CHPh)(PMe$_3$)$_2$ with equimolar allyl phenyl sulfide gives a mixture of 1 and 2 in a ratio of 60:40. Since reaction of isolated 1 with allyl phenyl sulfide gives complex 2 quite slowly, 2 is not considered to be formed by reaction of 1 and allyl phenyl sulfide. The reaction mixtures of eqs. 1 and 2 seem to contain a
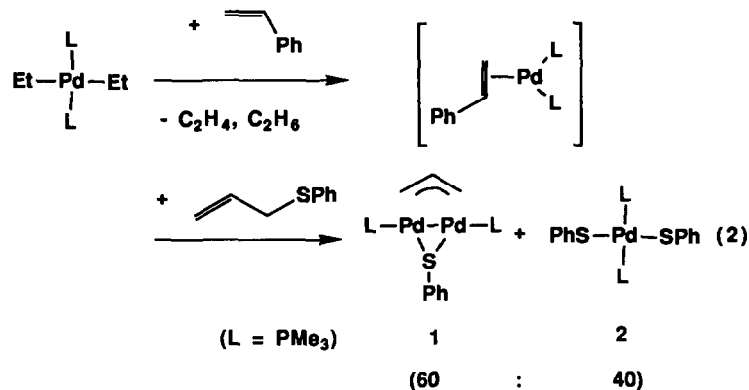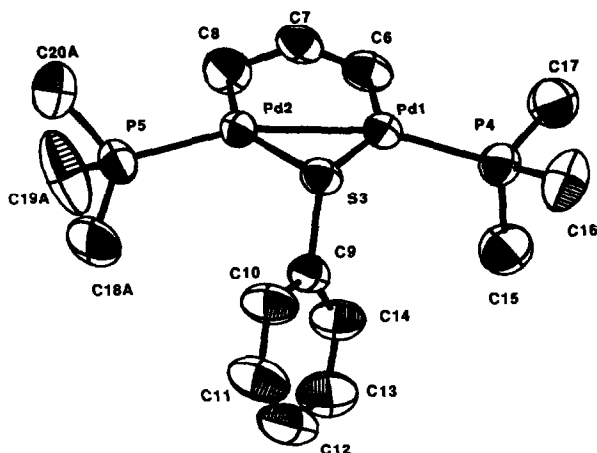
Fig. 1. ORTEP drawing of $(Me_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SPh)$ (1) showing 50% probability thermal ellipsoids. One of the positions were shown for the disordered carbon atoms (C18, C19, and C20). Occupancies of the shown positions are 70%.

small amount of mononuclear Pd^{II} π-allyl complex such as $[Pd(\eta^3\text{-}C_3H_5)(SPh)(PMe_3)_n]$ (A) which readily reacts with the Pd^0 complex to give 1 [10 *]. In reaction 2 intermolecular disproportionation of (A) or reaction of (A) with allyl phenyl sulfide may be responsible for the formation of 2.

NMR spectra of complex 1

The $^{13}C\{^1H\}$ NMR spectrum of 1 shows signals at 34.4 and 71.5 ppm. Under gated ^1H decoupled conditions these signals appear as a triplet and a doublet, respectively. These observations as well as the $^1J(CH)$ values (152 Hz) indicate that these signals are due to the terminal and the central carbons of the bridging allyl ligand, respectively. ^1H NMR spectrum of complex 1 shows signals due to the hydrogens of the allyl ligand at 1.32, 2.28 and 2.99 ppm respectively. These signals are assigned to the *anti*, central, and *syn* hydrogens of the bridging allyl ligand, respectively, based on comparison of their coupling patterns with those of already reported complexes such as $L_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(SPh)$ (L = PCy_3 and $P(t\text{-}Bu)_3$) [6b]. Chemical shifts of the *anti* and central hydrogens agree well with those of the above complexes although the peak of the *syn* hydrogens of 1 appear at a somewhat higher field than the similar complexes· with bulky phosphine ligands. ^1H and $^{13}C\{^1H\}$ NMR spectra of complex 1 show signals due to the PMe_3 ligands as apparent triplets probably due to virtual coupling arising from large coupling constant between the two phosphorus nuclei [11].

X-Ray diffraction study of complex 1

Figure 1 shows a molecular structure of 1 determined by X-ray crystallography. In tables 1 and 2 are listed the atomic coordinates, and the bond distances and angles, respectively. Two palladium and two phosphorus atoms are arranged in

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* A reference number with an asterisk indicates a note in the list of references.

Table 1

Fractional coordinates and equivalent isotropic temperature factors for $(Me_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SPh)$ [a]

Atom	x	y	z	B_{eq}
Pd1	0.86169(2)	0.00558(2)	−0.07824(3)	3.87
Pd2	0.81413(3)	0.11077(2)	0.09576(5)	4.03
S3	0.82421(11)	−0.01711(7)	0.15464(15)	4.10
P4	0.84848(14)	−0.08687(10)	−0.23319(15)	4.97
P5	0.72546(16)	0.18599(10)	0.2439(2)	6.30
C6	0.8907(5)	0.0899(4)	−0.2221(6)	5.0
C7	0.9172(5)	0.1381(4)	−0.1114(6)	4.7
C8	0.8428(6)	0.1918(4)	−0.0540(7)	5.8
C9	0.6806(5)	−0.0470(3)	0.1854(6)	4.2
C10	0.6496(6)	−0.0561(4)	0.3184(7)	6.2
C11	0.5415(7)	−0.0804(5)	0.3500(8)	7.7
C12	0.4642(6)	−0.0954(5)	0.2504(11)	7.5
C13	0.4937(6)	−0.0863(5)	0.1175(9)	7.3
C14	0.6016(5)	−0.0620(4)	0.0863(7)	5.7
C15	0.8881(8)	−0.1810(5)	−0.1857(9)	8.1
C16	0.7040(7)	−0.0996(5)	−0.3027(9)	8.0
C17	0.9288(7)	−0.0754(5)	−0.3874(8)	8.1
C18A	0.6253(15)	0.1478(9)	0.3594(20)	10.3
C19A	0.6438(16)	0.2658(10)	0.1649(16)	12.0
C20A	0.8213(12)	0.2436(9)	0.3571(18)	10.1
C18B	0.568(3)	0.158(4)	0.240(7)	12.8
C19B	0.749(8)	0.156(5)	0.428(4)	20.5
C20B	0.744(5)	0.277(2)	0.247(5)	10.2

[a] C18A and C18B, C19A and C19B, and C20A and C20B show the two disordered positions of C18, C19, and C20, respectively. See Experimental.

almost a straight line; the P–Pd–Pd bond are slightly bent (163.83(5) and 164.16(5)°, respectively). The distance between the two palladium atoms is 2.613(1) Å, indicating the presence of a Pd–Pd bond. This value is similar to those of the already reported dinuclear palladium(I) complexes having bridging allyl ligands (2.61–2.72 Å) [2,3,4a,4c,5]. The bridging allyl ligand shows a symmetrical coordination to the two palladium centers.

Reaction of CO with complex 1

Complex 1 reacts with CO under mild conditions (1 atm at room temperature) causing reductive elimination of the allyl and phenyl thiolate ligands to give allyl phenyl sulfide and palladium(0) carbonyl complexes. Formation of S-phenyl-thio-3-butenoate expected as a product of CO insertion into the Pd–C bond of 1 and reductive elimination of the butenoyl and phenylthiolate groups is not observed in the reaction, while mononuclear π-allyl palladium complex $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PMe_3)_2]OCOOR$ was reported to undergo facile insertion of CO into the Pd–C bond [9].

Experimental

All manipulations of the complexes were carried out under nitrogen or argon. NMR spectra were recorded on FX-100 and GX-500 spectrometers by Dr. Yoshiyuki

Table 2

Bond distances (Å) and angles (°) in complex 1

Pd1–Pd2	2.613(1)	Pd1–P4	2.254(3)
Pd1–S3	2.379(2)	Pd1–C6	2.102(7)
Pd1–C7	2.483(6)	Pd2–P5	2.253(2)
Pd2–S3	2.363(1)	Pd2–C8	2.099(7)
Pd2–C7	2.440(6)	S3–C9	1.791(6)
C6–C7	1.420(9)	C7–C8	1.419(9)
C9–C10	1.376(9)	C10–C11	1.375(11)
C11–C12	1.345(12)	C12–C13	1.370(14)
C13–C14	1.373(10)	C14–C9	1.354(8)
P4–C15	1.805(9)	P4–C16	1.820(8)
P4–C17	1.814(8)		
P5–C18A	1.78(2)	P5–C19A	1.88(2)
P5–C20A	1.87(2)	P5–C18B	1.90(4)
P5–C19B	1.91(5)	P5–C20B	1.64(4)
C6–Pd1–P4	94.6(2)	C6–Pd1–S3	143.9(2)
C6–Pd1–Pd2	88.0(2)	C8–Pd2–P5	97.2(2)
C8–Pd2–S3	146.4(2)	C8–Pd2–Pd1	89.9(2)
Pd1–C6–C7	87.4(4)	Pd2–C8–C7	85.5(4)
C6–C7–C8	126.3(6)		
Pd1–S3–C9	113.9(2)	Pd2–S3–C9	106.8(2)
S3–C9–C10	117.5(5)	C9–C10–C11	120.9(6)
C10–C11–C12	120.2(8)	C11–C12–C13	119.6(7)
C12–C13–C14	120.1(7)	C13–C14–C9	120.9(6)
Pd1–P4–C15	119.8(3)	Pd1–P4–C16	113.3(3)
Pd1–P4–C17	117.1(3)	C15–P4–C16	113.3(3)
C16–P4–C17	101.0(4)	C15–P4–C17	100.9(4)
Pd2–P5–C18A	120.0(5)	Pd2–P5–C19A	115.0(5)
Pd2–P5–C20A	116.0(5)	Pd2–P5–C18B	106.7(1.9)
Pd2–P5–C19B	113(3)	Pd2–P5–C20B	123(2)
C18A–P5–C19A	102.9(8)	C19A–P5–C20A	96.8(7)
C18A–P5–C20A	102.8(8)	C18B–P5–C19B	94(4)
C19B–P5–C20B	105(3)	C18B–P5–C20B	113(3)
C18A–P5–C18B	43(2)	C19A–P5–C20B	47(2)
C20A–P5–C19B	61(3)		

Preparation of (Me$_3$P)$_2$Pd$_2$(μ-η^3-C$_3$H$_5$)(μ-SPh) (1)

A mixture of *trans*-PdEt$_2$(PMe$_3$)$_2$ (830 mg, 2.6 mmol) and styrene (900 mg, 8.7 mmol) was dissolved in acetone (20 ml) at $-40°$C. Temperature of the reaction mixture was raised gradually to $45°$C with stirring it and was kept at that temperature for 10 h. A small amount of black solid formed was removed by filtration. Allyl phenyl sulfide (200 mg, 1.3 mmol) was added to the resulting slightly yellow solution at room temperature to cause formation of intense yellow solution which was stirred at that temperature for 1 h. The solvent and styrene were removed by evaporation under high vacuum. Recrystallization of the resulting yellow oily product from acetone at $5°$C gave 1 as yellow crystals (440 mg, 0.86 mmol, 65%). Found: C, 35.4; H, 5.6; S, 6.2. C$_{15}$H$_{28}$P$_2$SPd$_2$ calcd: C, 35.0; H, 5.5; S, 6.2%.

^{1}H NMR (500 MHz, $-40\,^\circ$C in CD_2Cl_2, ppm referred to the center of the solvent signal (5.32 ppm); for numbering of the protons, see below): δ 1.32 (d, 2H, H^{1b}, $J(H^{1b}H^2) = 13$ Hz), 1.39 (apparent triplet due to virtual coupling (4 Hz), 18H, $P(CH_3)_3$), 2.28 (m, 1H, H^2), 2.99 (dt, 2H, H^{1a}, $J(H^{1a}H^2) = 7$ Hz, $J(H^{1a}P) = 7$ Hz), 6.87 (m, 1H, H^6), 6.95 (m, 2H, H^5), 7.31 (m, 2H, H^4). ^{13}C NMR (125 MHz, $-40\,^\circ$C in CD_2Cl_2, ppm referred to the center of the signal of the solvent (53.8 ppm)) 18.2 (apparent triplet due to virtual coupling (11 Hz), $P(CH_3)_3$), 34.4 (C^1, $^1J(CH) = 152$ Hz), 71.5 (C^2, $^1J(CH) = 152$ Hz), 123.0 (C^6, $^1J(CH) = 161$ Hz, $^2J(CH) = 8$ Hz), 127.5 (C^4, $^1J(CH) = 158$ Hz, $^2J(CH) = 8$ Hz), 133.7 (C^5, $^1J(CH) = 159$ Hz), 145.2 (C^3, $^2J(CH) = 8$ Hz). ^{31}P{^{1}H} NMR (40 MHz, $-40\,^\circ$C in CD_2Cl_2, ppm from ext. 85% H_3PO_4): -24.1(s).
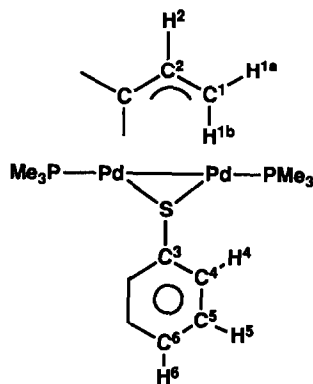
X-Ray crystallography

Crystals of **1** suitable for X-ray crystallography were grown in acetone at $0\,^\circ$C. A yellow prism ($0.12 \times 0.15 \times 0.54$ mm) was sealed in a glass capillary under argon and subjected to X-ray crystallography. Lattice constants were determined by a least-squares calculation of 2θ values of 25 reflections with $19^\circ < 2\theta < 22^\circ$. Intensities of graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71068$ Å) were collected on a Rigaku AFC-5 four-cycle automated diffractometer.

Calculations were carried out with the program system CRYSTAN on a FACOM A-70. The structure was solved by combination of direct method (SAPI85) and Fourier technique. Parameters were refined by full-matrix least-squares calculations by applying anisotropic temperature factors for all the non-hydrogen atoms. Peaks in the difference map as well as temperature factors of the carbon atoms clearly indicated the possible disorder in the carbon atoms of one PMe$_3$ ligand. Occupancies of the two positions for each disordered atom were fixed to 70% and 30%, respectively, and not refined. Hydrogen atoms except for those bonded to the disordered carbon atoms were located at idealized positions with isotropic temperature factors, and their parameters were not refined. Empirical absorption correction [12] was applied after parameters of all the non-hydrogen atoms were refined using anisotropic temperature factors.

Crystal data. $C_{15}H_{28}P_2S_1Pd_2$, Mw = 514.97, monoclinic, space group $P2_1/n$, $a = 11.662(1)$, $b = 17.898(2)$, $c = 9.849(2)$ Å, $\beta = 91.22(1)^\circ$, $V = 2055.1$ Å^3, $Z = 4$,

$D_c = 1.665$ g cm^{-3}, $\mu(\text{Mo-}K\alpha) = 19.7$ cm^{-1}. Intensities were measured by the $\omega - 2\theta$ method with a scan speed of $6°$ min^{-1} in the range of $3° < 2\theta < 45°$. Of the 2689 independent reflections collected 2414 reflections with $F_o \geqslant 3\sigma(F_o)$ were used in the structure calculations. Four standard reflections measured after data collection of each 200 reflections showed decrease in the intensities in the range of 96–92% during the data collection. Refinement using the weight, $w = [\{\sigma(F_o)\}^2 + \{0.024\,(F_o)\}^2]^{-1}$, converged to give final agreement indexes R of 0.049 and Rw of 0.050.

Lists of anisotropic thermal parameters and structure factors are available from the author (K.O.).

Reaction of CO with complex 1

To a THF (2 ml) solution of **1** (55 mg, 0.11 mmol) was introduced carbon monoxide at 1 atm at room temperature. The orange solution immediately turned into deep red. GC analysis of the reaction mixture revealed the formation of allyl phenyl sulfide in 83% yield. IR measurement of the reaction mixture after removal of the solvent showed a broad peak at 1800–1700 cm^{-1}, indicating the presence of a mixture of Pd(CO)$_m$(PMe$_3$)$_n$ [13].

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Pd⁰ complex, although the mononuclear intermediate could not be obtained from the reaction mixtures due to its high reactivity toward the Pd^0 complexes.

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