July, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1961—1967 (1990) 1961

Synthesis of Binuclear Palladium(I) and (II) Complexes Containing (Benzylthiomethyl)diphenylphosphine as Bridging Ligand. The X-Ray Crystal Structure and Reactions of $[Pd_2Cl_2(\mu\text{-}PhCH_2SCH_2PPh_2)_2]$

Yoshio Fuchita,*,† Kenneth I Hardcastle,*,†† Katsuma Hiraki, and Masanori Kawatani
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University,
Bunkyo-machi, Nagasaki 852
††Department of Chemistry, California State University, Northridge, 18111
Nordohoff Street, Northridge, California 91324, U. S. A.

(Received December 8, 1989)

The side-by-side type palladium(I) complex $[Pd_2Cl_2(\mu\text{-btmp})_2]$ (**2**) was synthesized either by the reaction among $[PdCl_2(NCMe)_2]$, $[Pd(dba)_2]$ (dba=dibenzylideneacetone), and (benzylthiomethyl)diphenylphosphine (btmp) or by the reaction of $[PdCl_2(\text{btmp-}P)_2]$ (**1**) and $[Pd(dba)_2]$. The structure of **2** was established by a single-crystal X-ray diffraction study; the crystals were monoclinic, space group $P2_1/c$, with $a=13.537(3)$, $b=19.550(3)$, $c=17.240(4)$ Å, $\beta=114.59(2)°$, and $Z=4$; final R factor 0.049 for 5490 observed reflections. The structure showed that there is a metal–metal bond [Pd–Pd 2.590(2) Å]. Treatment of **2** with sodium iodide afforded the diiodo complex $[Pd_2I_2(\mu\text{-btmp})_2]$, whereas that with 4-methylpyridine (4-MePy) in the presence of $AgClO_4$ gave $[Pd_2(\mu\text{-btmp})_2(4\text{-MePy})_2][ClO_4]_2$. Moreover, **2** reacted with substituted acetylenes ($RC{\equiv}CR'$: R=Ph, R′=H; $R=CO_2Me$, R′=H; $R=R'=CO_2Me$) to yield A-frame type complexes $[Pd_2Cl_2(\mu\text{-}RC{=}CR')(\mu\text{-btmp})_2]$. All the complexes obtained in this study were characterized by means of elemental analysis, and IR and NMR spectroscopy.

Considerable current interest has been shown in recent years in mono- and bi-metallic complexes of "short bite" ligands such as bis(diphenylphosphino)methane (dpm),[1–4] bis(diphenylarsino)methane (dpam),[5] (diphenylarsino)(diphenylphosphino)methane (dapm),[6,7] and 2-(diphenylphosphino)pyridine (Ph_2PPy).[8] These "short bite" ligands can act as unidentate, bidentate chelating, or bidentate bridging mode in complexes, depending on the nature of ligands and each metal center, and on the oxidation state of the metal ion.

As for the bidentate ligands with different donor sites P and S, only a few reports have been published. Sanger reported the synthesis of some complexes using (phenylthiomethyl)diphenylphosphine as bridging ligands; a heterobimetallic complex of $[RhCl_2(HgCl)(CO)(\mu\text{-}PhSCH_2PPh_2)_2]$[9] having a metal–metal bond, and complexes of $[PdCl_2(HgCl_2)(\mu\text{-}PhSCH_2PPh_2)_2]$[9] $[\{PdCl_2(\mu\text{-}PhSCH_2PPh_2)\}_4]$[10] both lacking metal–metal bond. The coordination ability of the phenylthiomethyl group seems weak, while it favorably coordinates to mercury in the former two complexes. As for palladium complex of the neutral ligand involving different donor sites of P and S, there seemed possibility to form a palladium(I) complex containing a metal–metal bond. In order to investigate this possibility, we newly prepared (benzylthiomethyl)diphenylphosphine (btmp) in which benzyl group was introduced to enhance the donor ability in sulfide moiety.

In this paper, we wish to report the synthesis, single-crystal X-ray structural analysis, and some reactivities of the side-by-side type palladium(I) complex, $[Pd_2Cl_2(\mu\text{-btmp})_2]$ (**2**). During our study, Anderson and Kumar[11] recently reported the syntheses of platinum and rhodium complexes containing (methylthiomethyl)diphenylphosphine, including the complexes of $[Pt_2Cl_2(\mu\text{-}MeSCH_2PPh_2)_2]$ and $[Rh_2Cl_2(CO)_2(\mu\text{-}MeSCH_2PPh_2)_2]$. However, X-ray crystal-structure analyses on these two complexes have not been reported.

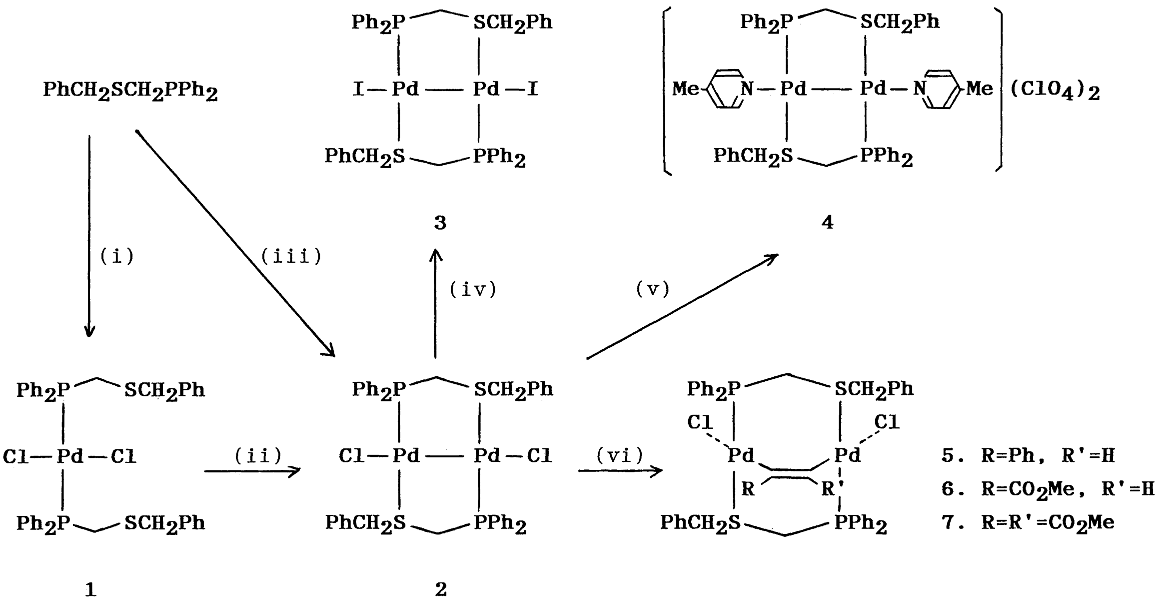
Results and Discussion

Syntheses and Characterization of the Complexes. The methods of preparation of the complexes are summarized in Scheme 1. Yields, melting points, and analytical data are collected in Table 1. NMR data are listed in Tables 2 and 3. The unidentate (benzylthiomethyl)diphenylphosphine (btmp) complex, $[PdCl_2(\text{btmp-}P)_2]$ (**1**), was obtained by reacting $Na_2[PdCl_4]$ with two equivalents of btmp. Complex **1** exhibited a single band at 331 cm^{-1} in its Far-IR spectrum, indicating a trans configuration of chlorides. Moreover, a conductance measurement in acetone solution ($\Lambda_M=2.0$ S cm^2 mol^{-1}) showed that **1** is a nonelectrolyte. These results are consistent with the unidentate btmp coordination mode in **1**. This behavior of btmp ligands in **1** is different from that of bis(diphenylphosphino)methane (dpm) in similar system; two equivalents of dpm react with $[PdCl_2(NCPh)_2]$ to yield the salt $[Pd(\text{dpm-}P,P')_2]Cl_2$.[2] However, bis(diphenylarsino)methane (dpam) and (diphenylarsino)(diphenylphosphino)methane (dapm) formed *trans*-$[PtCl_2(\text{dpam-}As)_2]$[5] and *cis*-$[PtCl_2(\text{dapm-}P)_2]$,[12] in which dpam and dapm act as a unidentate ligand.

On treating **1** with one equivalent of $[Pd(dba)_2]$, a side-by-side type palladium(I) complex, $[Pd_2Cl_2(\mu\text{-btmp})_2]$ (**2**), was produced. This complex can also be

---

† Present address: Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-Ku, Fukuoka 810.



Scheme. 1. (i) $Na_2[PdCl_4]$. (ii) $[Pd(dba)_2]$. (iii) $[PdCl_2(NCMe)_2]$ and $[Pd(dba)_2]$. (iv) NaI. (v) 4-MePy and $AgClO_4$. (vi) $RC{\equiv}CR'$.

Table 1. Yields, Melting Points, and Analytical Data of the Complexes

Complex	Yield	Mp$^{a)}$	Found (Calcd)		
	%	°C	C/%	H/%	N/%
1·$2CH_2Cl_2$$^{b)}$	68	151	50.67(50.85)	4.35(4.27)	—
2·$CH_2Cl_2$$^{b)}$	55$^{c)}$ 85$^{d)}$	143	48.29(48.59)	3.97(3.98)	—
3	72	135	41.34(42.23)	3.22(3.45)	—
4·$CH_2Cl_2$$^{b)}$	26	174	48.10(47.44)	3.93(4.10)	2.12(2.11)
5	63	153	55.92(55.94)	4.36(4.30)	—
6	81	175	52.06(52.19)	4.22(4.18)	—
7·$CH_2Cl_2$$^{b)}$	78	183	48.87(48.85)	4.11(4.10)	

a) With decomposition. b) Presence of CH_2Cl_2 solvent is confirmed by ^1H NMR spectroscopy. c) Yield in the reaction of **1** with $[Pd(dba)_2]$. d) Yield in the reaction among $[PdCl_2(NCMe)_2]$, $[Pd(dba)_2]$, and btmp.

Table 2. Selected ^1H and $^{31}P\{^1H\}$ NMR Data of the Complexes

Complex	^1H NMR$^{a)}$					$^{31}P\{^1H\}$ NMR$^{b)}$
	PCH_2S		$PhCH_2S$		Others	
1	3.14s		3.56s		—	16.5s
2	3.95d$^{c)}$		4.29s		—	6.1s
3	3.97d$^{d)}$		4.44s		—	—$^{e)}$
4	3.99s,br		4.65s,br		2.19s(Me) 6.82d(H^β),$^{f)}$ 7.76(H^α)$^{f)}$	—$^{e)}$
5	2.54ddd,$^{g,h)}$	2.73ddd$^{g,i)}$	3.10d,$^{j)}$	3.48d$^{j)}$	6.41dd(=CH)$^{k)}$	27.7s
	3.03d,$^{g)}$	3.04d$^{g)}$	4.25d,$^{j)}$	4.27d$^{j)}$		30.7s
6	2.7m		3.34d,$^{j)}$	3.61d$^{j)}$	—$^{l)}$	25.3s
	3.00dd,$^{m)}$	3.15dd$^{m)}$	4.22d,$^{j)}$	4.24d$^{j)}$	3.07s(OMe)	26.2s
7	2.70ddd$^{g,n)}$	3.39ddd$^{g,o)}$	3.47dd,$^{j,p)}$	4.26d$^{j)}$	3.15s(OMe)	26.1s

a) Recorded in $CDCl_3$ solution at 400 MHz and 50 °C. Chemical shifts (δ) in ppm relative to $SiMe_4$. Phenyl signals are omitted. br=broad, s=singlet, d=doublet, dd=doublet of doublets, ddd=doublet of doublets of doublets, m=multiplet. b) Recorded in $CDCl_3$ solution at 162 MHz and 50 °C. Chemical shifts (δ) in ppm relative to external 85% H_3PO_4 in $CDCl_3$. c) $^2J_{PH}$=5.5 Hz. d) $^2J_{PH}$=4.4 Hz. e) Not measured. f) $^3J_{HH}$=5.9 Hz. g) $^2J_{HH}$=13.1 Hz. h) J_{PH}=10.3, 5.9 Hz. i) J_{PH}=8.3, 5.0 Hz. j) $^2J_{HH}$=14.4 Hz. k) $^3J_{PH}$=20.9 Hz, $^4J_{PH}$=18.7 Hz. l) A signal due to =CH was overlapped with phenyl-proton resonances. m) $^2J_{HH}$=12.5 Hz, J_{PH}=3.7 Hz. n) J_{PH}=10.5, 6.6 Hz. o) J_{PH}=3.1 Hz. p) J_{PH}=2.2 Hz.

Table 3. Selected $^{13}C\{^1H\}$ NMR[a] Data of Some Complexes

Complex	$P\underline{C}H_2S$	$Ph\underline{C}H_2S$	$\underline{C}=\underline{C}$	$O\underline{C}H_3$	$\underline{C}=O$
2	40.77d[b]	41.55s	—	—	—
5	25.60d,[c] 26.50d[d]	38.61s, 39.08s	139.38,[e,f] 147.33[e,g]	—	—
6	26.55d,[d] 26.70d[h]	39.49s, 39.72s	138.3s,br 156.1s,br	50.99s	162.6s,br
7	26.74d[h]	39.08s	145.39dd[i]	51.14s	164.42[e,j]

a) Recorded in $CDCl_3$ solution at 101 MHz and 30 °C. Chemical shift (δ) in ppm relative to $SiMe_4$. br=broad, s=singlet, d=doublet, dd=doublet of doublets. Phenyl signals are omitted. b) $^1J_{PC}=27.4$ Hz. c) $^1J_{PC}=25.5$ Hz. d) $^1J_{PC}=29.3$ Hz. e) See text. f) $J_{PC}=7.8$ Hz. g) $J_{PC}=9.8$ Hz. h) $^1J_{PC}=27.4$ Hz. i) $^2J_{PC}=13.7$ Hz, $^3J_{PC}=6.0$ Hz. j) $J_{PC}=8.8$ Hz.

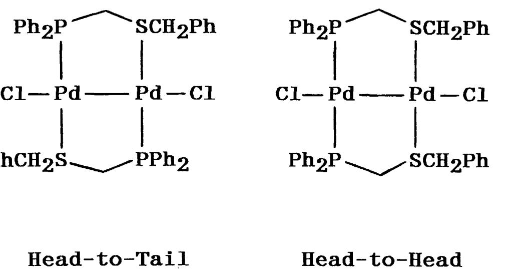


Fig. 1. Possible structures for **2**.

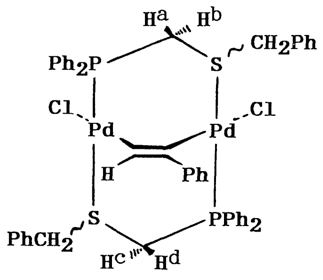


Fig. 2. Structure of **5**.

obtained by the reaction of [$PdCl_2(NCMe)_2$], [$Pd(dba)_2$], and btmp. In the ^1H NMR spectrum of **2** at 50 °C, two kinds of methylene proton resonances were observed at δ=4.29 ($PhC\underline{H_2}S$) and a doublet at δ=3.95 ($PC\underline{H_2}S$) due to coupling with ^{31}P nucleus. Upon cooling, these resonances broadened gradually, indicating that the inversion of the benzyl groups on the sulfur atoms was slow down. However, further discussion about the inversion of the benzyl groups was not described, as **2** gave no low-temperature limiting spectrum even at −50 °C. As for the complexes **3**—**7** (see below), low-temperature limiting spectra were not obtained either. Moreover, $^{31}P\{^1H\}$ NMR showed only one singlet at δ=6.1. Two structures are possible for **2**; one is the head-to-tail isomer and the other is the head-to-head isomer as illustrated in Fig. 1. By X-ray crystallography, **2** was revealed to have the head-to-tail arrangement (see below). It is noted that the P–Pd–P coordination in **1** was converted into the P–Pd–S coordination during the reaction from **1** to **2**.

The chloro ligands in **2** were readily replaced by iodo ions and by 4-methylpyridine (4-MePy) ligands in the presence of $AgClO_4$ to give the diiodo derivative [$Pd_2I_2(\mu\text{-btmp})_2$] (**3**) and the dicationic complex [$Pd_2(\mu\text{-btmp})_2(4\text{-MePy})_2$][$ClO_4$]$_2$ (**4**), respectively. The ^1H NMR spectrum of **3** was similar to that found for **2**, indicating that **3** has the same structure to **2**. As for the ^1H NMR spectrum of **4**, α- and β-protons of the two 4-MePy ligands appeared at δ=7.76 and 6.82 as only one pair of doublets, respectively, suggesting that the head-to-tail mode of the btmp ligands remains unchanged.

Furthermore, **2** reacted with unsymmetrical acetylenes, phenylacetylene and methyl propiolate, to afford A-frame type palladium(II) complexes [$Pd_2Cl_2(\mu\text{-}RC{=}CH)(\mu\text{-btmp})_2$] (**5**, R=Ph; **6**, R=CO_2Me). In the ^1H NMR spectrum of **5**, the methylene protons between P and S atoms of the btmp ligand showed their unusual sensitivity to structure. Because of the unsymmetrical A-frame structure (Fig. 2), the four protons in both methylene groups are inequivalent. Consequently, the methylene resonances of **5** resonated as two AB quartets with a 13.1 Hz coupling between the geminal protons. Each higher field resonance at δ=2.54 and 2.73 in the AB quartet was further split into doublet of doublets, whereas each lower field resonance at δ=3.03 and 3.04 in the AB quartet was split into doublet. Lack of couplings between methylene protons of PCH_2S and $PhCH_2S$ was confirmed by measuring ^1H-^1H COSY spectrum of **5**. So, the further splittings of the AB quartets are ascribed to P–H couplings. As for the benzyl–methylene groups in **5**, they are also inequivalent and two methylene protons of each methylene group are diastereotopic. Therefore, the methylene resonances of **5** appeared as two AB quartets at δ=3.10 (d), 3.48 (d), 4.25 (d), and 4.27 (d) ($^2J_{HH}=14.4$ Hz). The CH signal of the inserted phenylacetylene moiety resonated as doublet of doublets at δ=6.41 owing to couplings with two inequivalent ^{31}P nuclei, which appeared as two singlets at δ=27.7 and 30.7 in the $^{31}P\{^1H\}$ NMR spectrum.

Moreover, in the $^{13}C\{^1H\}$ NMR spectrum, reflecting the unsymmetrical structure of **5**, the two methylene carbons between P and S atoms and the two benzyl–methylene carbons resonated inequivalently as two doublets (δ=25.60 and 26.50) and as two singlets (δ= 38.61 and 39.08), respectively. As for the olefinic carbons derived from the acetylene, they were also observed inequivalently at δ=139.38 and 147.33 as apparent triplets. As for **6**, the observed NMR spectra were quite similar to those of **5** (Tables 2 and 3).

Dimethyl acetylenedicarboxylate, a symmetrical substituted acetylene, also reacted with **2** to give a A-frame type complex $[Pd_2Cl_2\{\mu\text{-}(MeO_2C)_2C_2\}(\mu\text{-btmp})_2]$ (**7**). In this case, two methylene groups between P and S atoms are equivalent although the two protons of each methylene group are inequivalent. Consequently, the methylene resonances appeared at δ=2.70 and 3.39 as a basic AB pattern with a 13.1 Hz geminal coupling. Each doublet was further split into doublet of doublets due to P–H couplings. The diastereotopic metylene protons of equivalent benzyl–methylene groups also resonated as an AB pattern at δ=3.47 and 4.26; the former doublet was coupled with ^{31}P nucleus and split into doublet. The methoxy protons of the inserted acetylene moiety appeared as only one singlet at δ=3.15, supporting that the head-to-tail structure remains unchanged after the conversion of **2** to **7**. In the $^{13}C\{^1H\}$ NMR spectrum, two metylene carbon signals due to PCH_2S and $PhCH_2S$ were observed at δ=26.74 and 39.08, respectively. As for the olefinic carbons of the inserted acetylene moiety, they appeared at δ=145.39 as a doublet of doublets, whereas the carboxylate carbons resonated apparently as a triplet.

It has been reported that the well-known side-by-side type complex of dpm, $[Pd_2Cl_2(\mu\text{-dpm})_2]$, reacts with substituted acetylenes having one or two electron-withdrawing groups (i.e., $CF_3C\equiv CCF_3$, $MeO_2CC\equiv CCO_2Me$, and $MeO_2CC\equiv CH$) to give A-frame type complexes like **6** and **7**, whereas other acetylenes without activating groups such as $PhC\equiv CH$ and $PhC\equiv CPh$ failed to react.[13] In our study, though diphenylacetylene did not react with **2**, it is noteworthy that phenylacetylene did react with **2** to give **5**. However, very recently Shaw et al.[14] reported the acid-catalyzed addition of non-activating acetylenes to $[Pd_2Cl_2(\mu\text{-dpm})_2]$.

Crystal Structure of $[Pd_2Cl_2(\mu\text{-btmp})_2]$ (2). This material crystallized with one molecule of the complex and a partial, disordered solvent molecule of dichloromethane lying in channels in the lattice between $[Pd_2Cl_2(\mu\text{-btmp})_2]$ molecules, with no unusual intermolecular contacts. The structure is shown in Fig. 3 and selected bond lengths and bond angles are given in Table 4.

Each palladium atom is in the center of an approximately square-planar arrangement formed by coordinated chlorine, phosphorous, palladium, and sulfur atoms. The bridging btmp ligands are trans to one another and are arranged in a head-to-tail fashion. The Pd(2)–Pd(1)–Cl(1) and Pd(1)–Pd(2)–Cl(2) angles are 177.4 (1)° and 178.8 (1)°, respectively, indicating that Cl–Pd–Pd–Cl chain is approximately linear. The Pd–Cl distances of 2.408 (5) Å for Pd(1)–Cl(1) and 2.412 (5) Å for Pd(2)–Cl(2) are at the long end of the range of known Pd–Cl distances (2.24—2.45 Å),[15] and probably reflect the high trans influence of the metal–metal bond. The Pd–Pd single bond distance in this

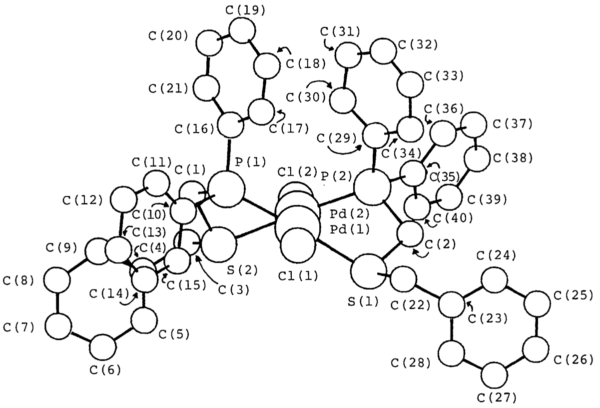


Fig. 3. Molecular structure of **2** showing the principal atomic numbering.

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) for $[Pd_2Cl_2(\mu\text{-btmp})_2]$ (**2**) with Estimated Standard Deviations (esds) in Parentheses

Pd(1)–Pd(2)	2.590(2)		
Pd(1)–Cl(1)	2.408(5)	Pd(2)–Cl(2)	2.412(5)
Pd(1)–S(1)	2.333(3)	Pd(2)–S(2)	2.352(3)
Pd(1)–P(1)	2.249(3)	Pd(2)–P(2)	2.226(3)
S(1)–C(2)	1.77(2)	S(2)–C(1)	1.79(2)
P(1)–C(1)	1.87(2)	P(2)–C(2)	1.84(2)
Pd(2)–Pd(1)–Cl(1)	177.4(1)	Pd(1)–Pd(2)–Cl(2)	178.8(1)
Pd(2)–Pd(1)–S(1)	85.8(1)	Pd(1)–Pd(2)–S(2)	83.6(1)
Pd(2)–Pd(1)–P(1)	85.5(1)	Pd(1)–Pd(2)–P(2)	82.1(1)
Cl(1)–Pd(1)–S(1)	92.7(1)	Cl(2)–Pd(2)–S(2)	95.6(1)
Cl(1)–Pd(1)–P(1)	95.9(1)	Cl(2)–Pd(2)–P(2)	98.7(2)
S(1)–Pd(1)–P(1)	170.5(2)	S(2)–Pd(2)–P(2)	165.7(1)
Pd(1)–S(1)–C(2)	107.9(7)	Pd(2)–S(2)–C(1)	97.1(5)
Pd(1)–P(1)–C(1)	114.3(5)	Pd(2)–P(2)–C(2)	109.2(6)
S(2)–C(1)–P(1)	104.1(8)	S(1)–C(2)–P(2)	109.1(8)

molecule [2.590(2) Å] is a little longer than the Pd–Pd bond in $[Pd_2(CNMe)_6][PF_6]_2$ [2.5310(9) Å],16) but shorter than those found in $[Pd_2Br_2(\mu\text{-dpm})_2]$ [2.699(5) Å]17) and $[Pd_2Mn_2(CO)_9(\mu\text{-dpm})_2]$ [2.681(1) Å].18)

The dihedral angle between the two palladium coordination planes (S, Pd, Cl, P) is 51.6°, which is larger than that found in $[Pd_2Br_2(\mu\text{-dpm})_2]$ (39°).17) In contrast, the dihedral angle in $[Pd_2(CNMe)_6][PF_6]_2$ where two palladium atoms are directly bonded without bridging ligands, has a considerably larger value, 86.2°.16)

Experimental

General. All the reactions were carried out under dry nitrogen. Solvents were dried by usual methods and distilled. The IR spectra were measured on a JASCO A-100 and a Shimadzu IR 450 spectrometers. The NMR spectra were recorded on a JEOL JMN GX-400 instrument. Conductivity measurements were carried out for 1.0×10^{-3} mol dm^{-3} acetone solution at 25 °C on a Toa Electronics CM-6A conduct meter. Melting points were determined with a Yanaco micro melting point apparatus.

The complexes $[PdCl_2(NCMe)_2]$19) and $[Pd(dba)_2]$20) were prepared by the literature methods.

(Benzylthiomethyl)diphenylphosphine (btmp). Potassium diphenylphosphide was prepared by the reaction of Ph_2PCl (22.3 g, 0.10 mol) with metallic potassium (7.90 g, 0.20 g-atom) in 1,4-dioxane (270 cm^3). To this solution benzyl chloromethyl sulfide21) (15.7 g, 0.091 mol) in THF (50 cm^3) was added dropwise during the course of 20 min. The mixture was successively stirred overnight at room temperature. A THF (90 cm^3)–water (5 cm^3) mixture was added to destroy remaining $KPPh_2$, after which all the volatile materials were evaporated in vacuo. To the resulting residue, acetone (110 cm^3) and water (175 cm^3) were added successively to afford white precipitates. The precipitates were collected, washed with water, and then dried in vacuo to give btmp (29.3 g, 92%): mp 58 °C; ^1H NMR ($CDCl_3$) δ=3.91 (2H, d, $^2J_{PH}$=3.7 Hz, PCH_2S), 4.52 (2H, s, $PhCH_2S$), and 7.2—7.4 (15H, m, Ph). Found: C, 74.84; H, 6.10%. Calcd for $C_{20}H_{19}PS$: C, 74.51; H, 5.94%.

$[PdCl_2(btmp\text{-}P)_2]\cdot 2CH_2Cl_2$. Solid btmp (0.230 g, 0.74 mmol) was added to a solution of $Na_2[PdCl_4]$ (0.100 g, 0.34 mmol) in MeOH (39 cm^3). A thick suspension immediately formed, was stirred for 3 h. The resulting yellow precipitates were collected, and recrystallized from CH_2Cl_2–Et_2O to give **1**$\cdot 2CH_2Cl_2$ as yellow crystals.

$[Pd_2Cl_2(\mu\text{-btmp})_2]\cdot CH_2Cl_2$. a) Solid $[Pd(dba)_2]$ (0.070 g, 0.12 mmol) was added to a solution of **1**$\cdot 2CH_2Cl_2$ (0.10 g, 0.10 mmol) in CH_2Cl_2 (30 cm^3). The resulting red solution was stirred for 3 h at room temperature, and then filtered. The filtrate was diluted with MeOH to give **2**$\cdot CH_2Cl_2$ as reddish orange crystals. b) $[PdCl_2(NCMe)_2]$ (0.256 g, 0.99 mmol), $[Pd(dba)_2]$ (0.568 g, 0.99 mmol), and btmp (0.637 g, 1.97 mmol) were refluxed together in CH_2Cl_2 (20 cm^3) for 1 h. The resulting red solution was diluted with MeOH to afford **2**$\cdot CH_2Cl_2$ as reddish orange crystals.

$[Pd_2I_2(\mu\text{-btmp})_2]$ (3). A methanol (20 cm^3) suspension containing **2**$\cdot CH_2Cl_2$ (0.150 g, 0.15 mmol) and sodium iodide (0.121 g, 0.81 mmol) was stirred for 3 days at room temperature. The solvent was removed under reduced pressure and the residue was extracted into CH_2Cl_2 (20 cm^3). The extract was concentrated and diluted with hexane to give the required product as orange-purple powders.

$[Pd_2(\mu\text{-btmp})_2(4\text{-MePy})_2][ClO_4]_2\cdot CH_2Cl_2$. A mixture of **2**$\cdot CH_2Cl_2$ (0.150 g, 0.15 mmol) and 4-methylpyridine (0.032 g, 0.34 mmol) in CH_2Cl_2 (15 cm^3) was treated with $AgClO_4$ (0.072 g, 0.35 mmol) in CH_2Cl_2 (5 cm^3), and resulting mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and then the residue was extracted into CH_2Cl_2 (20 cm^3). The extract was concentrated and diluted with hexane to produce **4**$\cdot CH_2Cl_2$ as yellow microcrystals.

Reactions of 2$\cdot CH_2Cl_2$ with Substituted Acetylenes. a) With Phenylacetylene: A solution of phenylacetylene (0.080 g, 0.78 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of **2**$\cdot CH_2Cl_2$ (0.200 g, 0.20 mmol) in CH_2Cl_2 (10 cm^3). The color of the resulting solution gradually changed from orange to pale yellow. After stirring for 1 day at room temperature, the volatile materials were removed under reduced pressure. The residue was extracted into benzene, and the extract was diluted with Et_2O and hexane to give **5** as yellow crystals.

b) With Methyl Propiolate: A solution of methyl propiolate (0.050 g, 0.59 mmol) in CH_2Cl_2 (10 cm^3) was added to a suspesion of **2**$\cdot CH_2Cl_2$ (0.300 g, 0.30 mmol) in Et_2O (10 cm^3). The initial orange suspension changed to a pale yellow solution within 5 min, and was slowly diluted with hexane (50 cm^3) to afford yellow precipitates (0.290 g). The yellow precipitates were purified by passing through a silica-gel column with CH_2Cl_2/Et_2O (10/1) mixed solvent. A yellow fraction was evaporated to dryness, and the residue was recrystallized from benzene–Et_2O to give **6** as yellow microcrystals.

c) With Dimethyl Acetylenedicarboxylate: A solution of dimethyl acetylenedicarboxylate (0.122 g, 0.86 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of **2**$\cdot CH_2Cl_2$ (0.200 g, 0.20 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 1 day at room temperature. Hexane (20 cm^3) was added to the resulting pale yellow solution to yield **7**$\cdot CH_2Cl_2$ as yellow crystals.

Crystallography. Suitable crystals of $[Pd_2Cl_2(\mu\text{-btmp})_2]\cdot CH_2Cl_2$ were grown from dichloromethane–hexane.

a) Crystal Data: $C_{40}H_{38}Cl_2Pd_2P_2S_2$, M=928.53, monoclinic, a=13.537 (3), b=19.550 (3), c=17.240 (4) Å, β=114.59 (2)°, U=4148.8 Å^3, Z=4, space group $P2_1/c$. D_c=1.49 g cm^{-3}, μ(Mo-K_α)=11.8 cm^{-1}, F(000)=1864, λ=0.7107 Å, T=25± 1 °C.

b) Data Collection: A reddish-orange rectangular crystal of approximate dimensions $0.37\times0.12\times0.03$ mm was mounted on a glass fiber, placed on an Enraf-Nonius CAD4 diffractometer and exposed to graphite-monochromated Mo-K_α radiation. Cell constants and an orientation matrix for data collection were obtained from least-square refinement, using the setting angles of 25 reflections in the range $2<\theta<9$. The data were collected using the ω scan technique, where the scan rate varied from 1 to 10 min^{-1} (in ω) and data were collected to a maximum 2θ angle of 44.0°. The scan range in degrees was determined as a function of θ to correct for the separation of the K_α doublet as follows: θ scan width=$0.8+0.350\tan\theta$. Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range.

Table 5. Atom Coordinates for [Pd$_2$Cl$_2$(μ-btmp)$_2$] (**2**) with Estimated Standard Deviations (esds) in Parentheses

Atom	x	y	z	Atom	x	y	z
Pd(1)	0.31955(8)	0.20212(6)	0.85002(6)	C(17)	0.233(1)	0.382(1)	0.803(1)
Pd(2)	0.43678(8)	0.18074(6)	0.76597(7)	C(18)	0.243(2)	0.453(1)	0.807(1)
Cl(1)	0.2102(3)	0.2164(2)	0.9290(2)	C(19)	0.246(2)	0.490(1)	0.742(1)
Cl(2)	0.5430(3)	0.1619(3)	0.6851(3)	C(20)	0.230(2)	0.454(1)	0.663(1)
S(1)	0.4503(3)	0.1383(2)	0.9587(2)	C(21)	0.218(2)	0.386(1)	0.659(1)
S(2)	0.2726(3)	0.1401(2)	0.6600(2)	C(22)	0.444(1)	0.151(1)	1.061(1)
P(1)	0.2032(3)	0.2544(2)	0.7307(2)	C(23)	0.539(1)	0.113(1)	1.131(1)
P(2)	0.5666(3)	0.2238(2)	0.8839(2)	C(24)	0.625(1)	0.149(1)	1.190(1)
C(1)	0.206(1)	0.221(1)	0.6300(9)	C(25)	0.708(2)	0.113(1)	1.252(1)
C(2)	0.579(1)	0.171(1)	0.976(1)	C(26)	0.704(2)	0.042(1)	1.252(1)
C(3)	0.286(1)	0.1171(9)	0.5614(9)	C(27)	0.619(2)	0.007(1)	1.196(1)
C(4)	0.191(1)	0.0786(8)	0.5026(8)	C(28)	0.531(2)	0.040(1)	1.133(1)
C(5)	0.190(2)	0.007(1)	0.516(1)	C(29)	0.548(1)	0.3109(9)	0.9040(9)
C(6)	0.102(1)	−0.032(1)	0.455(1)	C(30)	0.513(1)	0.3526(9)	0.835(1)
C(7)	0.019(2)	0.001(1)	0.391(1)	C(31)	0.509(1)	0.425(1)	0.846(2)
C(8)	0.017(1)	0.071(1)	0.383(1)	C(32)	0.541(2)	0.446(1)	0.935(1)
C(9)	0.107(1)	0.1085(9)	0.440(1)	C(33)	0.562(3)	0.401(2)	0.999(2)
C(10)	0.061(1)	0.2439(8)	0.7105(9)	C(34)	0.569(2)	0.336(1)	0.982(2)
C(11)	−0.013(1)	0.297(1)	0.686(1)	C(35)	0.708(1)	0.2201(9)	0.8983(9)
C(12)	−0.119(2)	0.286(2)	0.672(2)	C(36)	0.777(1)	0.2742(9)	0.933(1)
C(13)	−0.154(1)	0.222(2)	0.676(1)	C(37)	0.886(1)	0.267(1)	0.942(1)
C(14)	−0.084(2)	0.165(2)	0.700(2)	C(38)	0.924(1)	0.206(1)	0.929(1)
C(15)	0.026(1)	0.179(1)	0.719(1)	C(39)	0.853(2)	0.154(2)	0.895(2)
C(16)	0.221(1)	0.3471(9)	0.7305(9)	C(40)	0.750(1)	0.160(1)	0.884(1)

c) **Data Reduction:** A total of 5490 reflections were collected, of which 5278 were unique and not systematically absent. As a check on crystal and electronic stability three representative reflections were measured every 120 min, and a linear decay correction applied to the data. Lorenz and polarization correction based on a series of Ψ-scans was applied to the data. Relative transmission coefficients ranged from 0.890 to 0.999 with an average value of 0.964. A secondary extinction correction also was applied.[22]

d) **Structure Solution and Refinement:** The structure was solved by direct methods. Using 300 reflections (minimum E of 0.07) and 64 relationships, a total of 32 phase sets were produced. A total of 6 atoms were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit= 1.08 and residual=2.84. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-square where the function minimized was $w(|F_o|-|F_c|)^2$ and the weight w is defined as $4F_o{}^2/[\sigma(F_o)^2]^2$.

Scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion effects were included in F_c;[24] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[25] Only the 1980 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 434 variable parameters and converged with a maximum parameter shift of 0.01 times its estimated standard deviation and unweighted and weighted agreement factors of 0.049 and 0.062, respectively. The standard deviation of an observation of unit weight was 1.47. There were no correction coefficients greater than 0.50. The largest peak in the final difference Fourier had a height of 0.44 e Å^{-3} with an estinated error based on ΔF[26] of 0.08. No attempt was made to incorporate the disordered solvent molecule in the final refinements. Plots of $\Sigma w(|F_o|-|F_c|)^2$ versus F_o, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a MicroVAX II computer using SDP/VAX.[27] The final atomic coordinates and their standard deviations are listed in Table 5.[28]

References

1) R. J. Puddephatt, *Chem. Soc. Rev.*, **12**, 99 (1983).

2) F. S. M. Hassan, D. P. Markham, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, **1985**, 279.

3) R. Uson, J. Fornies, P. Espinet, R. Navarro, and C. Fortuno, *J. Chem. Soc., Dalton Trans.*, **1987**, 2077.

4) C. R. Langrick, D. M. McEvan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, **1983**, 2487.

5) G. B. Jacobson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, **1987**, 151.

6) P. D. Enlow and C. Woods, *Organometallics,* **2**, 64 (1983).

7) A. L. Balch, R. R. Guimererans, J. Linehan, M. M. Olmstead, and D. E. Oram, *Organometallics,* **4**, 1445 (1985).

8) J. P. Farr, F. E. Wood, and A. L. Balch, *Inorg. Chem.*, **22**, 3387 (1983), and references therein.

9) A. L. Sanger, *Can. J. Chem.*, **62**, 822 (1984).

10) A. L. Sanger, *Can. J. Chem.*, **61**, 2214 (1983).

11) G. K. Anderson and R. Kumar, *J. Organomet. Chem.*, **342**, 263 (1988).

12) R. R. Guimererans, F. E. Wood, and A. L. Balch, *Inorg. Chem.*, **23**, 1308 (1984).

13) C-L. Lee, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, **20**, 2498 (1981).

14) S. J. Higgins and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, **1988**, 457.

15) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **15**, 2432 (1976).

16) D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Am. Chem. Soc.*, **97**, 1961 (1975).

17) R. G. Holloway, B. R. Penfold, R. Colton, and M. J. McCormic, *J. Chem. Soc., Chem. Commun.*, **1976**, 485.

18) P. Braunstein, Jean-Maric Jud, and J. Fischer, *J. Chem. Soc., Chem. Commun.*, **1983**, 5.

19) B. Crociani, T. Boshi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

20) T. Ukai, H. Kawazura, and Y. Ishii, *J. Organomet. Chem.*, **65**, 253 (1974).

21) H. Bohme, H. Fischer, and R. Frank, *Liebigs Ann. Chem.*, **563**, 54 (1949).

22) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

23) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham(1947), Vol. 4, Table 2. 2B.

24) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

25) D. T. Cromer, "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. 4, Table 2.3.1.

26) D. W. J. Cruickshank, *Acta Crystallogr.*, **2**, 154 (1949).

27) B. A. Frenz, "The Enraf-Nonius CAD4 SDP-A Real-time System for Concurrent X-Ray Data Collection and Crystal Structure Determination," in Computing in Crystallography, ed by H. Scenk, R. Olthof-Hazelkamp, H. van Konigsveld, and G. C. Bassi, Delft University Press, Delft (1976), pp. 64—71.

28) Tables of selected least-square planes, anisotropic thermal parameters, and complete bond distances and angles, and a list of observed and calculated structure factors are deposited as Document No.8926 at the Office of the Editor of Bull. Chem. Soc. Jpn.