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Structure and reactivity of the cyclic tetranuclear palladium(II) complexes having *o*-phenylene, dialkyl sulfide and acetato as bridging ligands

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Abstract

A mixture containing palladium(II) acetate and dialkyl sulfide in a molar ratio of 1:2/3 is refluxed in benzene to afford yellow crystals $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ ($SR_2=SPr_2^i$ (**1**), SPr_2 (**2**)). The X-ray diffraction analysis of **1** shows that **1** has a cyclic tetranuclear structure containing *o*-phenylene, diisopropyl sulfide and acetato as bridging ligands. Thermolysis of **1** gives triphenylene and the reaction of **1** with styrene yields 1,2-di[(*E*)-styryl]benzene. The formation process to **1** from palladium(II) acetate has been discussed.

Introduction

There has been much interest in the activation of C–H bonds by transition metals [1]. One of the methods to prepare σ-aryl complexes directly from arenes is electrophilic substitution of arenes by metal complexes. To date, $AuCl_3$ [2], H_2PtCl_6 [3] and the [Rh(octaethylporphyrinato)Cl]-Ag salt [4] have been successfully used to prepare various type of σ-aryl complexes.

Previously, we reported that the palladium(II) acetate–dialkyl sulfide system reacted with benzene at 70 °C or *p*-xylene at 90 °C to give trinuclear complexes of a zigzag type, $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$ (Ar = Ph and 2,5-dimethylphenyl) [5, 6]. In connection with these studies, we have also found that another σ-aryl species was obtained when the reaction between the palladium(II) acetate–diisopropyl sulfide system and benzene was performed under severe conditions. We have preliminarily assigned this new species as a cyclic trinuclear complex containing an *o*-phenylene group, $[Pd_3(\mu\text{-}C_6H_4)(\mu\text{-}O_2CMe)_4(SR_2)_2]$ [7]. However, X-ray crystallographic study has shown that it does not have a trinuclear but a tetranuclear cyclic structure, and moreover it contains novel bridging dialkyl sulfide.

In this paper, we would like to report the correct structure and detailed reactivity of the novel cyclic tetranuclear complex $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$.

Experimental

The general procedures and apparatus were the same as those reported in a previous publication from our laboratory [6]. Zigzag type trinuclear complexes $[Pd_3Ph_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$ (**6**–**9**) were prepared as previously described [5].

X-ray structural determination

Suitable crystals were grown in a mixed solvent of dichloromethane and hexane in a refrigerator.

Reflection data were measured on a Rigaku AFC-5 automated four-cycle diffractometer with graphite monochromated Mo Kα radiation at 20±1 °C. The cell dimensions were determined by 25 high-angle reflections in the range $20<2\theta<30°$. Three standard reflections were monitored every 100 reflections and their intensities showed no decay. The diffraction data were corrected for Lorentz and polarization effects but not for absorption. Crystal data and details of the data collection and reduction are as follows: $C_{32}H_{48}O_8Pd_4S_2$, $M=1050.54$, crystal size 0.2×0.1×0.16 mm, monoclinic, space group $P2_1/n$, $a=13.166(5)$, $b=12.669(3)$, $c=11.512(4)$ Å, $\beta=105.01(3)°$, $U=1854.6$ Å^3, $Z=2$, $D_c=1.881$ g cm^{-3}, μ(Mo Kα) = 5.61 cm^{-1}, scan mode

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θ–2θ, scan range 2.5–45°, scan width $(1.2+0.35 \tan \theta)°$, octant measured $+h$, $+k$, $+l$, number of observed reflections ($|F_o|>3\sigma|F_o|$) 3388, $R=0.0562$, $R'=0.0624$.

The structure was solved by the direct method and refined by the block-diagonal least-squares method, where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ and $w=1$ was adopted. Hydrogen atoms were inserted in their calculated positions and included in the structure-factor calculation but not refined. Atomic scattering factors were taken from ref. 8. All the calculations were carried out on a FACOM M 780 computer at the Computer Center of Kyushu University using a local version of the UNICS III and ORTEP programs [9]. The final positional parameters of non-hydrogen atoms, and selected bond lengths and angles are listed in Tables 1 and 2, respectively. See also 'Supplementary material'.

Preparation of the cyclic tetranuclear complexes $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ *(1–3)*

Complexes **1**–**3** were prepared similarly. A typical example is as follows. A benzene solution (20 cm^3) containing palladium(II) acetate (0.500 g, 2.23 mmol) and diisopropyl sulfide (0.176 g, 1.49 mmol) was heated in an oil bath at 90–95 °C for 1 h. After reprecipitation with hexane, the precipitates were purified by silica gel column chromatography (200 mesh, 1.5×20 cm). A yellow fraction eluted by ether was collected and was recrystallized from CH_2Cl_2–hexane to give **1** as yellow crystals (0.082 g; 14%).

TABLE 1. Atomic coordinates for $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr^i_2)_2]$ (**1**)

Atom	*x*	*y*	*z*
Pd(1)	0.0654(1)	0.0579(1)	−0.1582(1)
Pd(2)	0.0989(1)	0.1477(1)	0.0914(1)
S	0.1037(2)	0.0017(2)	0.2065(3)
O(1)	0.2555(6)	0.1364(6)	0.0701(6)
O(2)	0.2219(6)	0.0961(6)	−0.1248(6)
O(3)	0.0404(6)	0.2247(6)	−0.1916(6)
O(4)	0.0903(6)	0.2882(6)	−0.0032(6)
C(1)	0.2816(8)	0.1222(8)	−0.0247(10)
C(2)	0.3964(9)	0.1366(11)	−0.0217(10)
C(3)	0.0684(8)	0.2994(9)	−0.1180(10)
C(4)	0.0680(10)	0.4099(9)	−0.1609(11)
C(5)	−0.0397(8)	0.1738(8)	0.1214(8)
C(6)	−0.1013(8)	0.0962(8)	0.1461(9)
C(7)	−0.1967(9)	0.1223(9)	0.1695(9)
C(8)	−0.2275(9)	0.2262(10)	0.1731(10)
C(9)	−0.1615(9)	0.3052(9)	0.1475(10)
C(10)	−0.0698(9)	0.2790(8)	0.1228(9)
C(11)	0.2078(8)	−0.0841(9)	0.1726(10)
C(12)	0.3149(8)	−0.0476(10)	0.2460(10)
C(13)	0.1930(9)	−0.1986(10)	0.1858(11)
C(14)	0.1506(9)	0.0290(10)	0.3696(9)
C(15)	0.0823(9)	0.1182(11)	0.4013(9)
C(16)	0.1436(11)	−0.0719(11)	0.4378(11)

TABLE 2. Selected bond lengths (Å) and angles (°) of **1** with e.s.d.s. in parentheses

Pd(1)–Pd(2)	3.015(2)	Pd(1)–Pd(2′)	3.595(2)
Pd(1)–Pd(1′)	4.652(2)	Pd(2)–Pd(2′)	4.731(2)
Pd(1)–O(2)	2.054(7)	Pd(2)–O(1)	2.143(8)
Pd(1)–O(3)	2.158(8)	Pd(2)–O(4)	2.074(8)
Pd(1)–S′	2.279(3)	Pd(2)–S	2.267(3)
Pd(1)–C(6′)	2.005(10)	Pd(2)–C(5)	1.971(10)
C(5)–C(6)	1.351(14)	C(6)–C(7)	1.392(15)
C(7)–C(8)	1.373(17)	C(8)–C(9)	1.391(17)
C(9)–C(10)	1.351(16)	C(5)–C(10)	1.392(15)
O(2)–Pd(1)–O(3)	84.4(3)	O(4)–Pd(2)–O(1)	85.5(3)
O(3)–Pd(1)–S′	100.8(2)	O(1)–Pd(2)–S	97.5(2)
S′–Pd(1)–C(6′)	83.8(3)	S–Pd(2)–C(5)	85.4(3)
C(6′)–Pd(1)–O(2)	90.5(4)	C(5)–Pd(2)–O(4)	91.2(4)
O(2)–Pd(1)–S′	173.3(2)	O(4)–Pd(2)–S	175.2(3)
O(3)–Pd(1)–C(6′)	171.2(4)	O(1)–Pd(2)–C(5)	173.2(4)
Pd(2)–S–C(11)	105.3(4)	Pd(2)–S–C(14)	113.1(4)
Pd(2)–S–Pd(1′)	104.5(1)	Pd(1′)–S–C(11)	118.6(4)
Pd(1′)–S–C(14)	111.0(4)	C(11)–S–C(14)	104.5(5)
Pd(2)–C(5)–C(6)	123.3(8)	Pd(2)–C(5)–C(10)	116.2(8)
C(6)–C(5)–C(10)	120.4(10)	C(5)–C(6)–C(7)	119.3(10)
C(5)–C(6)–Pd(1′)	125.4(8)	C(7)–C(6)–Pd(1′)	115.3(8)
Pd(2)–O(1)–C(1)	127.2(6)	Pd(1)–O(2)–C(1)	126.3(8)
Pd(2)–O(4)–C(3)	127.0(7)	Pd(1)–O(3)–C(3)	127.7(6)
O(1)–C(1)–O(2)	126.4(10)	O(3)–C(3)–O(4)	123.9(10)
O(1)–C(1)–C(2)	117.7(9)	O(4)–C(3)–C(4)	115.3(9)
O(2)–C(1)–C(2)	115.8(10)	O(3)–C(3)–C(4)	120.6(10)

Thermolysis of 1

Complex **1** (0.187 g, 0.178 mmol) was refluxed in benzene (15 cm^3) for 21 h. The reaction mixture was filtered and then evaporated to dryness. The residue was chromatographed on a silica gel column (200 mesh, 1.5×20 cm). A fraction eluted by hexane was collected and was recrystallized by hexane to give triphenylene (**4**, 0.006 g; 22%), m.p. 197 °C [10]. The ^{1}H NMR spectrum was the same as the authentic sample.

Reaction of 1 with styrene

Styrene (0.092 g, 0.885 mmol) in THF (10 cm^3) was added to a CH_2Cl_2 solution (5 cm^3) of **1** (0.155 g, 0.148 mmol). The resulting mixture was refluxed for 3 h, and then evaporated to dryness. The residue was chromatographed on a silica gel column (200 mesh, 1.5×22 cm). A pale yellow fraction eluted by hexane was collected and was recrystallized by hexane to give 1,2-di[(*E*)-styryl]benzene (**5**, 0.064 g; 77%), m.p. 118 °C. *Anal.* Found: C, 93.6; H, 6.4%; M^+ 282. Calc. for $C_{22}H_{18}$: C, 93.6; H, 6.4%; M^+ 282. δ_H ($CDCl_3$): 7.01 (2H, d, ^4J(HH)=16.1 Hz, =CH), 7.47 (2H, d, ^4J(HH)=16.1 Hz, =CH), 7.25–7.4 and 7.5–7.65 (14H, m, C_6H_4 and C_6H_5).

Results and discussion

Synthesis of the cyclic tetranuclear palladium(II) complexes $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ ($SR_2 = SPr^i_2$ (1), SPr_2 (2)) and molecular structure of 1

A benzene solution containing palladium(II) acetate and dialkyl sulfide in a molar ratio of 1:2/3 was refluxed in benzene to give yellow crystals $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ ($SR_2 = SPr_2^i$ (**1**), SPr_2 (**2**)) (Scheme 1). In the presence of triethyl sulfide, a similar cyclic tetranuclear complex (**3**) was obtained, but it could not be isolated in a pure state. On the contrary, when diisobutyl sulfide was used, no such tetranuclear species was obtained. Yields, melting points, analytical data and NMR data are collected in Table 3.

The molecular structure of **1** was established by an X-ray structure determination. An ORTEP drawing with the numbering scheme used is shown in Fig. 1.

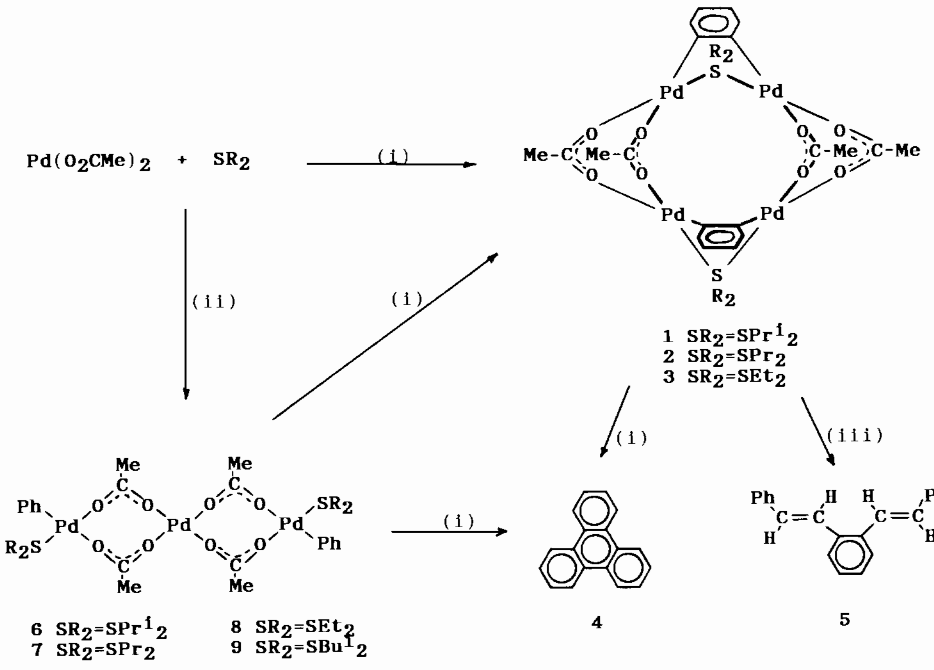
This tetranuclear complex has an imposed crystallographic C_i symmetry, and consists of two $Pd(\mu\text{-}C_6H_4)(\mu\text{-}SPr_2^i)Pd$ units with each Pd atom joined by two acetato ligands to form a cyclic structure.

It is noteworthy that this complex contains bridged dialkyl sulfide ligands. Among Group 10 elements, such dialkyl sulfide bridges have been reported in several dinuclear platinum complexes (e.g. $[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$ [11], $[Br_2Pt(\mu\text{-}SEt_2)_2PtBr_2]$ [12], etc. [13]). However, in the case of palladium complexes this is the first example to our knowledge. The Pd–S distances of 2.279(3) and 2.267(3) Å are slightly shorter than the Pd–S distance found in the terminal dialkyl sulfide complex of $[(Me_2S)BrPd(\mu\text{-}Br)_2PdBr(SMe_2)]$ (2.30(2) Å) [11] and in the chelating dialkyl sulfide complex of $[PdCl_2(SCH_2CH_2OCH_2CH_2OCH_2CH_2)_2]$ (2.302(2) and 2.305(2) Å) [14]. This shortening of the distance might come from the absence of repulsion between the non-bonding lone pair of electrons and the metal non-bonding d electrons when the sulfur is bridging. However, in the amino–sulfide complexes of $[PdCl_2\{NH_2CH(CO_2H)(CH_2)_nSMe\}]$ ($n = 1, 2$) [15], the Pd–S distances were reported to be 2.261(4) and 2.265(4) Å, respectively, slightly shorter than the distance in **1**. As for the Pd–O distances, the distances *trans* to the carbon atom are longer than those *trans* to the sulfur atom due to the high *trans* influence of the palladium–carbon bond. Similar results were obtained in the cyclopalladated complex of 2-*p*-tolylbenz-thiazole and -oxazole [16]. The Pd–Pd distances are over 3 Å, indicating the absence of bonding interaction.

The dihedral angles of the adjacent palladium square planar planes are 35.94° and each benzene ring is bent from the palladium square planar planes (26.95 and 27.81°).

Characterization and reactivity of cyclic tetranuclear complexes

The ^1H NMR spectra of both **1** and **2** showed an A_2B_2 pattern centred near δ 6.6 due to the protons of the two equivalent *o*-phenylene groups, together with the four equivalent acetato-methyl signals near δ 2.0. As for the protons of the non-equivalent propyl groups in each sulfide moiety, two sets of signals were observed



Scheme 1. (i) Reflux in benzene; (ii) in benzene at 70 °C; (iii) with styrene, reflux in CH_2Cl_2–THF.

TABLE 3. Analytical[a], physical and ^{1}H NMR data for the cyclic tetranuclear complexes $[\mathrm{Pd_4(\mu\text{-}C_6H_4)_2(\mu O_2CMe)_4(\mu\text{-}SR_2)_2}]$ (**1–3**)

Complex	Yield[b] (%)	Melting point[c]	^{1}H NMR[d]	Analysis (%)	
				C	H
1 $\mathrm{SR_2=SPr^i{}_2}$[e]	14	177	1.05 [d, 12H, $\mathrm{SCH_2C}H_3$, J(HH) 6.8], 1.62 [d, 12H, $\mathrm{SCH_2C}H_3$, J(HH) 6.8], 2.00 (s, 12H, $\mathrm{O_2CC}H_3$), 3.10 [hept, 2H, $\mathrm{SC}H_2$, J(HH) 6.8], 3.46 [hept, 2H, $\mathrm{SC}H_2$, J(HH) 6.8], 6.56 and 6.68 ($\mathrm{A_2B_2}$, m, 8H, $\mathrm{C_6H_4}$)	36.1(36.6)	4.5(4.6)
2, $\mathrm{SR_2=SPr_2}$	5	185	0.36 [t, 6H, $\mathrm{SCH_2CH_2C}H_3$, J(HH) 7.3], 1.08 [t, 6H, $\mathrm{SCH_2CH_2C}H_3$, J(HH) 7.3], 2.00 (s, 12H, $\mathrm{O_2CC}H_3$], *c.* 1.55[f] ($\mathrm{SCH_2C}H_2$), 2.08 (c, 4H, $\mathrm{SCH_2C}H_2$), 2.34 (c, 4H, $\mathrm{SC}H_2$), 3.07 (c, 4H, $\mathrm{SC}H_2$), 6.58 and 6.73 ($\mathrm{A_2B_2}$, m, 8H, $\mathrm{C_6H_4}$)	36.9(36.6)	4.7(4.6)
3 $\mathrm{SR_2=SEt_2}$	–[g]	–	1.01 [t, 6H, $\mathrm{SCH_2C}H_3$, J(HH) 7.3], 1.59 [t, 6H, $\mathrm{SCH_2C}H_3$, J(HH) 7.3], 2.01 (s, 14H, $\mathrm{O_2CC}H_3$), 2.46 [q, 4H, $\mathrm{SC}H_2$, $J(HH)$ 7.3], 3.19 [*q*, 4*H*, *S*CH_2, J(HH) 7.3], 6.59 and 6.73 ($\mathrm{A_2B_2}$, m, 8H, $\mathrm{C_6H_4}$)	–	

[a] Calculated values in parentheses. [b] Based on $\mathrm{Pd(O_2CMe)_2}$. [c] With decomposition. [d] Recorded in $\mathrm{CDCl_3}$ solution at 270 MHz and 30 °C. Chemical shifts (δ) in ppm, coupling constants in Hz. s = singlet, d = doublet, t = triplet, q = quartet, hep = heptet, m = multiplet, c = complex. [e] ^{13}C NMR spectrum, recorded in $\mathrm{CDCl_3}$ at 67.5 MHz and 30 °C. Chemical shifts (δ) in ppm: 20.88 ($\mathrm{SCHC}H_3$), 24.87 ($\mathrm{O_2C}C\mathrm{H_3}$), 25.15 ($\mathrm{SCHC}H_3$), 44.92 ($\mathrm{S}C\mathrm{H}$), 49.24 ($\mathrm{S}C\mathrm{H}$), 124.19 (3,6-C of μ-$\mathrm{C_6H_4}$), 132.16 (4,5-C of μ-$\mathrm{C_6H_4}$), 153.75 (1,2-C of μ-$\mathrm{C_6H_4}$) and 180.54 ($\mathrm{O_2}C\mathrm{CH_3}$). [f] Overlapped with $\mathrm{H_2O}$ signal in the $\mathrm{CDCl_3}$. [g] Complex **3** could not be isolated in pure state.

(Table 3). Correspondingly, in the ^{13}C NMR spectrum of **1** (see footnote of Table 3), only one set of signals was observed for acetato-methyl and acetato-carboxylato carbons, and one set of three signals was detected for *o*-phenylene carbons. On the contrary, non-equivalent methyl and methine carbons of each sulfide ligand appeared as two set of signals. In the IR spectra of **1** and **2**, two characteristic bands due to bridging acetato ligands [17] were observed at 1560 and 1405 cm^{-1}, and 1580 and 1420 cm^{-1}, respectively.

Thermolysis of **1** in refluxing benzene gave triphenylene (**4**) in 22% yield, which is the trimerization product of the *o*-phenylene moieties. Furthermore, **1** reacted with styrene to give 1,2-di[(*E*)-styryl]benzene (**5**) in 77% yield, which is the arylated compound of styrene by the *o*-phenylene group.

Speculation about the formation of cyclic tetranuclear complexes 1–3

We have reported that at 70 °C palladium(II) acetate reacted with benzene in the presence of dialkyl sulfides to give zigzag type trinuclear complexes $[\mathrm{(R_2S)PhPd(\mu\text{-}O_2CMe)_2Pd(\mu\text{-}O_2CMe)_2PdPh(SR_2)}]$ ($\mathrm{SR_2=SPr_2{}^i}$ (**6**), $\mathrm{SPr_2}$ (**7**), $\mathrm{SEt_2}$ (**8**), $\mathrm{SBu_2{}^i}$ (**9**)) [5]. Thermal reactions of the zigzag type trinuclear complexes were carried out in refluxing benzene, and ^{1}H NMR spectra of the evaporated residues were measured. In the case of **6–8**, the major products were the cyclic tetranuclear complex (**1–3**), biphenyl and triphenylene (**4**). Furthermore, when the above reaction was performed in mesitylene, benzene was detected by GLC analysis of the reaction mixture. On the contrary, **9** gave only biphenyl and did not yield any detectable amount of a cyclic tetranuclear complex or triphenylene.

Taking these facts into consideration, it is probable that at first a zigzag type trinuclear complex is formed by the reaction of palladium(II) acetate with benzene in the presence of dialkyl sulfide. It is well established that acetato bridges show inversion motion [18]. At high temperatures such inversion motion takes place to form the conformational isomer **A** (Scheme 2). Then, one of the terminal phenyl groups in **A** is further palladated intramolecularly at its *ortho* position to afford the cyclic trinuclear complex **B**, liberating the benzene molecule. However, a molecular model of **B** indicated that two sulfide groups are located very close to each other, indicating that species **B** is not so stable. In the case of **9**, further palladation on one of the phenyl groups is supposed to be limited by the bulky sulfide.

Thermal reaction of equimolar amounts of **6** and **8** was also carried out in refluxing benzene for 1 h, and the reaction mixture was purified by column chromatography. A yellow fraction eluted with ether was collected and the ^{1}H NMR spectrum (together with

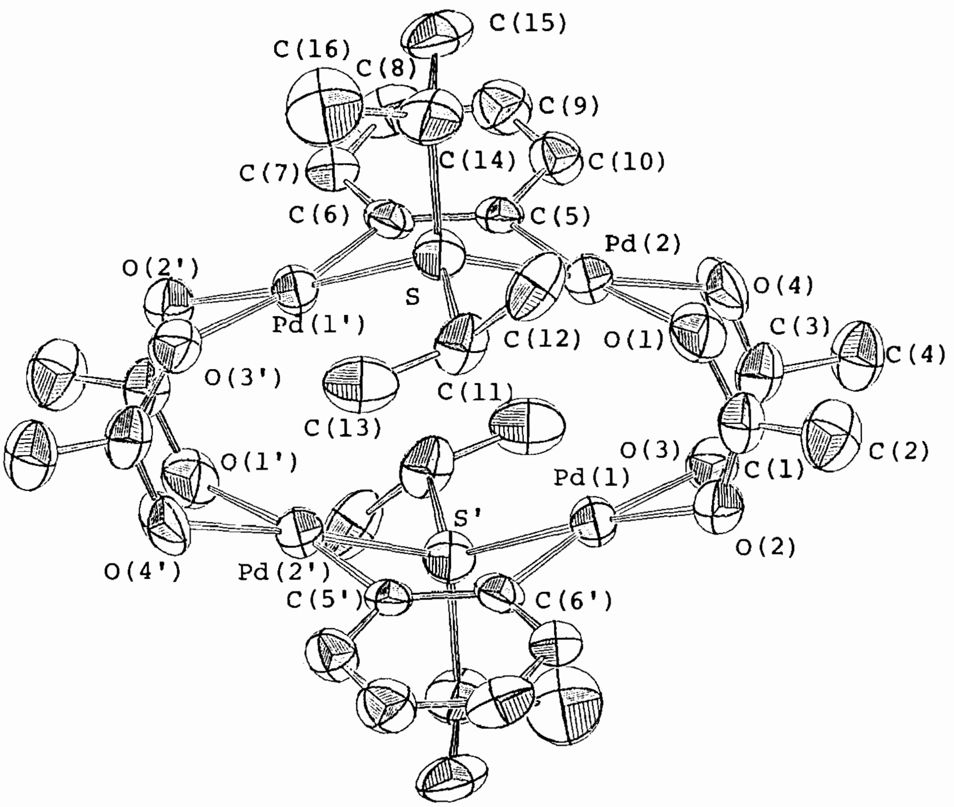
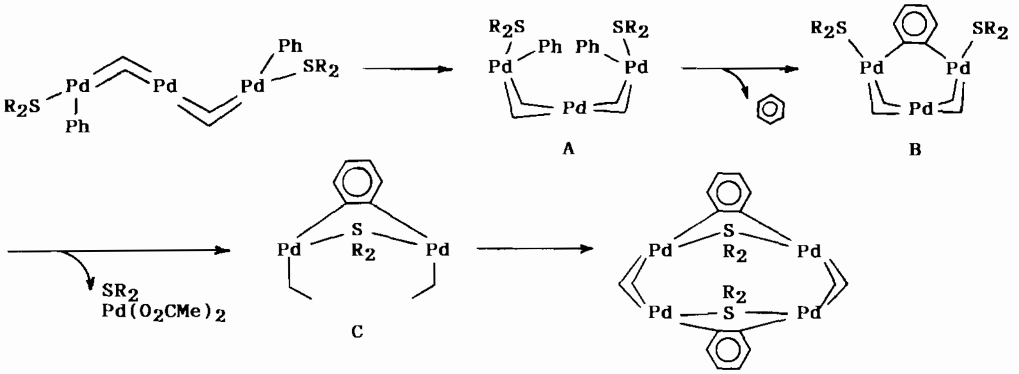


Fig. 1. Molecular structure of $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr_2^i)_2]$ (**1**), showing the atom labeling scheme.



Scheme 2. Speculative mechanism for the formation of cyclic tetranuclear complexes **1**–**3**.

COSY spectrum) was measured. In addition to the major signals due to **1** and **3**, it showed new signals at δ 1.57 (d, $J=6.8$, CH_3), 1.67 (d, $J=6.8$, CH_3), 3.43 (hep, $J=6.8$, CH) and 3.58 (hep, $J=6.8$, CH) for SPr_2^i, and 0.94 (t, $J=7.3$, CH_3), 1.49 (t, $J=7.3$, CH_3), 2.19 (q, $J=7.3$, CH_2) and 2.85 (q, $J=7.3$, CH_2) for SEt_2. These new signals might be associated with a mixed μ-sulfide complex of $[Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr_2^i)(\mu\text{-}SEt_2)]$. Taking these data into consideration, it is most plausible that the cyclic tetranuclear complex is formed by coupling of a reactive intermediate **C** which might be generated from **B** by losing one dialkyl sulfide and the palladium acetate moiety owing to its instability.

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and the remaining bond lengths and angles.

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