Reactivity of the cyclic tetranuclear complex $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr^i_2)_2]$

Yoshio Fuchita* and Shigeru Nakashita

Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810 (Japan)

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Abstract

Bridge splitting reactions of the cyclic tetranuclear complex, $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr^i_2)_2]$, with neutral and anionic ligands afforded a variety of dinuclear palladium(II) complexes. In addition to the common one bridging *o*-phenylene ligand, the products contained different bridging ligands depending upon the ligand used. Dpm ($Ph_2PCH_2PPh_2$) or btmp ($PhCH_2SCH_2PPh_2$) acted as bidentate bridging ligands to give $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(O_2CMe)_2(\mu\text{-}L_2)_2]$ (L_2 = dpm, btmp). In contrast, Me_2bpy (4,4′-dimethyl-2,2′-bipyridyl) behaved as a bidentate chelating ligand to afford a cationic complex bearing the μ-acetato ligand, $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](MeCO_2)$. In the case of Tl(acac), the acac ligand coordinated in a bidentate chelating fashion to yield a μ-sulfide complex, $[Pd_2(\mu\text{-}o\text{-}C_6H_4))(acac\text{-}O, O')_2(\mu\text{-}SPr^i_2)]$. This complex further reacted with 3,5-lutidine to give $[Pd_2(\mu\text{-}o\text{-}C_6H_4))(acac\text{-}O, O')_2(3,5\text{-lut})_2]$. Complexes obtained here were characterized by means of elemental analyses, NMR and IR spectroscopies.

Introduction

Previously, we have reported the synthesis and the structure of the cyclic tetranuclear palladium(II) complexes having the dimetallated benzene molecule, $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$. These complexes are of value in view of the fact that they were formed directly from benzene via C–H bond activation by the $Pd(O_2CMe)_2$–SR_2 system [1] and that they have bridging dialkyl ligands, rare for palladium complexes. These complexes consist of *o*-phenylene, acetato and dialkyl sulfide ligands, the coordination modes of which are all bidentate bridging. It is interesting to investigate how these three different bridging ligands behave in bridge splitting reactions by incoming ligands. Here, we wish to report the reactions of the cyclic tetranuclear complex $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr^i_2)_2]$ with several neutral and anionic ligands.

Results and discussion

The reactions of $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SPr^i_2)_2]$ (**1**) are summarized in Scheme 1. Analytical and physical data are listed in Table 1, while ^1H NMR data are summarized in Table 2.

Reactions of 1 with bis(diphenylphosphino)methane (dpm) and (benzylthiomethyl)diphenylphosphine (btmp)

Complex **2** was precipitated when **1** was stirred with dpm in benzene, and was converted by NaI into the diiodo complex **3**. Complex **3** was assigned as an A-frame type complex, $[Pd_2(\mu\text{-}o\text{-}C_6H_4)I_2(\mu\text{-dpm})_2]$, on the basis of the similarity of the ^1H NMR spectrum to the previously reported data by Balch *et al.* who obtained **3** by oxidative addition of *o*-diiodobenzene to $[Pd_2(dpm)_3]$ [2]. Accordingly, the precursor **2** was also assigned as a similar A-frame type complex $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(O_2CMe)_2(\mu\text{-dpm})_2]$.

In a similar way, reaction of **1** with btmp gave an A-frame type complex $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(O_2CMe)_2(\mu\text{-btmp})_2]$ (**4**). In **4** there is the possibility of head-to-tail/head-to-head isomerism. The ^1H NMR spectrum exhibited the *o*-phenylene protons as a typical $A'_2X'_2$ pattern at δ 6.08 ppm and showed the methyl protons of the two acetato ligands equivalently at δ 1.74 ppm as one singlet. These data strongly confirmed that **4** has the head-to-tail structure as illustrated in Fig. 1. If **4** had the head-to-head structure, the *o*-phenylene protons would appear as an ABCD pattern and the two acetato-methyl signals would resonate as two singlets. As this complex is an A-frame type complex, the two protons of the PCH_2S moieties are originally inequivalent and were observed as an AB quartet. The diastereotopic protons of the CH_2Ph moieties also resonated as an AB quartet. These coupling

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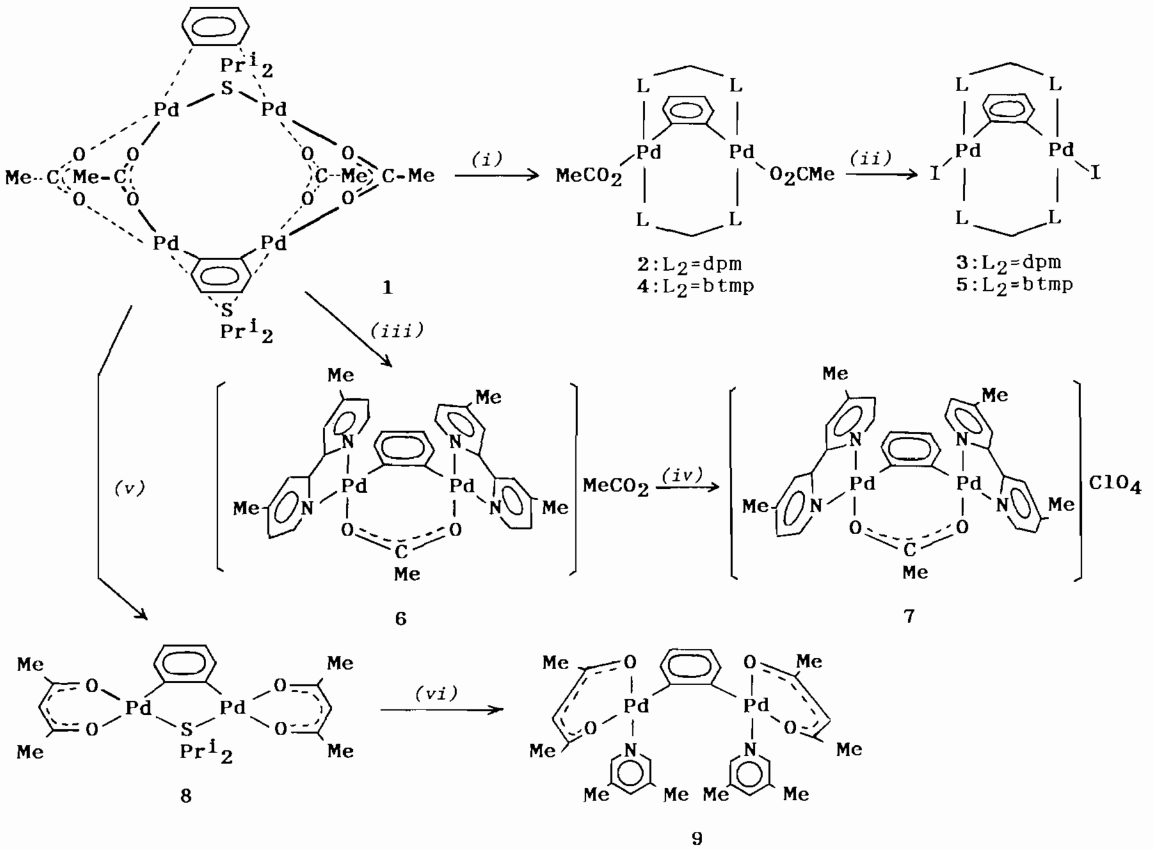
*Author to whom correspondence should be addressed.



Scheme 1. (i) dpm or btmp in benzene; (ii) NaI in acetone–water; (iii) Me_2bpy in benzene; (iv) $NaClO_4$ in MeOH; (v) Tl(acac) in CH_2Cl_2; (vi) lut in benzene.

TABLE 1. Analytical[a] and physical data for the complexes

Complex	M.p.[b] (θ (°C))	Yield (%)	Analysis (%)			Λ_M (S cm^2 mol^{-1})
			C	H	N	
2	194	54	63.35 (63.2)	5.0 (4.8)		0.19[c]
3		76				
4	173	60	56.95 (57.1)	4.7 (4.6)		
5	174	87	48.25 (47.9)	3.9 (3.7)		
6	224	47	49.6 (49.2)	4.6 (4.85)	6.8 (6.75)	72[d]
7	282	95	46.65 (47.1)	3.85 (3.85)	6.8 (6.85)	80[d]
8	185	48	43.5 (43.65)	5.2 (5.3)		
9	126	76	51.15 (51.35)	5.35 (5.15)	3.9 (4.0)	

[a] Calculated values in parentheses. [b] With decomposition. [c] In acetone. [d] In MeOH.

patterns were quite similar to those of the previously reported A-frame type complex $[Pd_2Cl_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(\mu\text{-}btmp)_2]$ [3].

By reaction with NaI, **4** was converted into the diiodo derivative $[Pd_2(\mu\text{-}o\text{-}C_6H_4)I_2(\mu\text{-}btmp)_2]$ (**5**). This complex could be prepared separately by the reaction of $[Pd(dba)_2]$ (dba = dibenzylideneacetone) with btmp and *o*-diiodobenzene. This reaction was supposed to proceed via the formation of a Pd(0) species such as $[Pd_2(btmp)_3]$ (this complex could not be isolated) by the reaction

TABLE 2. ^{1}H NMR data for the complexes[a]

Complex	C_6H_4[b]	CH_3CO_2	Others
2	5.41	1.80(s)	1.25(dt, ^2J(HH) = 12.2 Hz, ^2J(PH) = 5.9 Hz, CH_2), 2.53(dt, ^2J(HH) = 12.2 Hz, ^2J(PH) = 3.9 Hz, CH_2), 6.95–7.15(m, *m*- and *p*-H of Ph), 7.35–7.45 (m, *m*- and *p*-H of Ph), 7.55(m, *o*-H of Ph), 8.15(m, *o*-H of Ph), 7.36 (s, C_6H_6)
3	5.90		1.79(dt, ^2J(HH) = 11.7 Hz, ^2J(PH) = 5.9 Hz, CH_2), 2.51(dt, ^2J(HH) = 11.7 Hz, ^2J(PH) = 3.9 Hz, CH_2), 6.9–7.1(m, Ph), 7.25–7.7(m, Ph)
4	6.08	1.74(s)	1.60(dd, ^2J(HH) = 11.0 Hz, ^2J(PH) = 5.6 Hz, SCH_2P), 2.44(ddd, ^2J(HH) = 11.0 Hz, J(PH) = 11.0, 6.1 Hz, SCH_2P), 3.87(d, ^2J(HH) = 13.7 Hz, CH_2Ph), 4.27(d, ^2J(HH) = 13.7 Hz, CH_2Ph), 7.05–7.9(m, Ph)
5	6.47		1.67(dd, ^2J(HH) = 12.0 Hz, ^2J(PH) = 3.7 Hz, SCH_2P), 2.37(ddd, ^2J(HH) = 12.0 Hz, J(PH) = 10.0, 6.1 Hz, SCH_2P), 3.52(d, ^2J(HH) = 13.9 Hz, CH_2Ph), 4.09(d, ^2J(HH) = 13.9 Hz, CH_2Ph), 7.1–8.05(m, Ph), 7.36(s, C_6H_6)
6	6.96	2.01(s) 2.21(s)	2.44(s, Me_2bpy), 2.52(s, Me_2bpy), 6.85(br d, ^3J(HH) = 5.4 Hz, 5- or 5′-H of Me_2bpy), 7.18(br d, ^3J(HH) = 5.4 Hz, 5- or 5′-H of Me_2bpy), 7.84(d, ^3J(HH) = 5.4 Hz, 6- or 6′-H of Me_2bpy), 8.12(d, ^3J(HH) = 5.4 Hz, 6- or 6′-H of Me_2bpy), 8.35(br s, 3- or 3′-H of Me_2bpy), 8.39 (br s, 3- or 3′-H of Me_2bpy), 1.99(br s, H_2O)
7	6.96	2.20(s)	2.42(s, Me_2bpy), 2.50(s, Me_2bpy), 6.82(dd, ^3J(HH) = 5.9 Hz, ^4J(HH) = 1.0 Hz, 5- or 5′-H of Me_2bpy), 7.15(dd, ^3J(HH) = 5.9 Hz, ^4J(HH) = 1.0 Hz, 5- or 5′-H of Me_2bpy), 7.82(d, ^3J(HH) = 5.9 Hz, 6- or 6′-H of Me_2bpy), 8.06(br s, 3- or 3′-H of Me_2bpy), 8.08(d, ^3J(HH) = 5.9 Hz, 6- or 6′-H of Me_2bpy), 8.12(br s, 3- or 3′-H of Me_2bpy)
8	6.85		1.65(d, ^3J(HH) = 6.8 Hz, Me of Pr^i), 1.89(s, Me of acac), 2.04(s, Me of acac), 3.92(h, ^3J(HH) = 6.8 Hz, CH of Pr^i), 5.32(s, CH of acac)
9	6.77		1.46(s, Me of acac), 1.94(s, Me of acac), 2.17(s, Me of lut), 5.09(s, CH of acac), 7.18(s, γ-H of lut), 8.47(s, α-H of lut)

[a] Recorded in $CDCl_3$ solution at 270 MHz and at 25 °C. Chemical shifts (δ) in ppm relative to $SiMe_4$, s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = double of triplets, h = heptet, m = multiplets and br = broad. [b] Observed as an $A'_2X'_2$ pattern except for **7** and **8** (A_4 pattern). Chemical shifts are read from the central value of two separated multiplets.

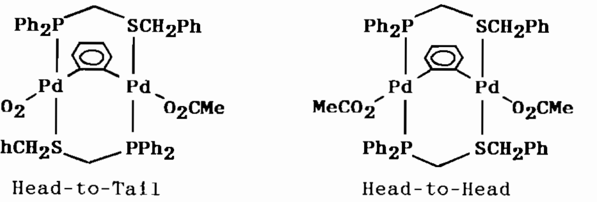


Fig. 1. Possible isomers for **4**.

of $[Pd(dba)_2]$ with btmp, followed by an oxidative addition of *o*-diidobenzene to the Pd(0) species.

Reaction of 1 with 4,4′-dimethyl-2,2′-bipyridyl (Me_2bpy)

When the reaction between **1** and Me_2bpy was performed in benzene, reddish orange crystals (**6**) were precipitated. The ^{1}H NMR spectrum exhibited *o*-phenylene protons as an $A'_2X'_2$ pattern at δ 6.96 ppm. Acetatomethyl protons were observed inequivalently at δ 2.01 and 2.21 ppm. Signals due to 3-, 5-, 6- and methyl protons of the two pyridyl moieties in Me_2bpy appeared as two sets, indicating that the two 2-(4-methyl)pyridyl moieties are in different environments in **6**. These results were in sharp contrast to those of **1**–**4**, excluding the possibility that **6** is a similar A-frame type complex.

Moreover, one acetato ligand in **6** was easily removed by reaction with $NaClO_4$ and $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](ClO_4)$ (**7**) was obtained. Furthermore, both **6** and **7** showed characteristic IR bands due the μ-acetato ligand [4] (1405 and 1565 cm^{-1} for **6**, and 1403 and 1535 cm^{-1} for **7**), together with the Cl–O frequency of perchlorate ion (1075 cm^{-1}) in the case of **7**. On the basis of these results and conductivity measurements (Table 1), **6** and **7** were assigned as cationic dinuclear complexes, $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](MeCO_2)\cdot 3H_2O$ and $[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](ClO_4)$, respectively.

Reaction of 1 with Tl(acac)

Complex **1** reacted with Tl(acac) to afford the yellow complex **8** whose IR spectrum exhibited characteristic bands due to the O,O′-chelating acetylacetonato group at 1515 and 1585 cm^{-1}. The ^{1}H NMR spectrum lacked the signals due to the acetato ligand and instead showed resonances owing to SPr^i_2. Methyl protons as well as methine protons of the two isopropyl groups were observed as only one set of signals, indicating that the two isopropyl groups of SPr^i_2 in **8** are located in equivalent positions. As for the acac ligands, two methyl and two methine protons resonated as one set of signals. These results and the elemental analysis supported the proposed structure of **8** shown in Scheme 1, where two palladium square planar planes are nearly on the same level and two isopropyl groups of the SPr^i_2 ligand are situated up and down from that level.

Bridging diisopropyl sulfide in **8** was easily removed by 3,5-lutidine (lut) to give **9**. Elemental analysis indicated that **9** contained two mole of lut and two mole of acac ligands. The IR spectrum showed characteristic bands due to the O,O′-chelating acac ligand at 1510 and 1575 cm^{-1}, and the ^1H NMR spectrum exhibited one set of signals for acac ligands, indicating that two acac ligands locate at an equal environment. On the basis of these results, **9** was assigned the structure shown in Scheme 1 where two acac planes are perpendicular to the plane of the benzene ring. As for the two lut ligands, they resonated in the ^1H NMR spectrum as one set of signals which showed that the lut ligands are rotating freely around the Pd–N bond. This rotation could not be quenched even at −60 °C.

In summary, incoming neutral bidentate ligands, dpm, btmp and Me_2bpy, removed the bridged diisopropyl sulfide from **1**. While dpm and btmp coordinated in a bidentate bridging manner in **2** and **4**, Me_2bpy ligated in a bidentate chelating manner in **6**. The different coordination modes between dpm and btmp in **2** and **4** and Me_2bpy in **6** can be explained by the structural nature of the bidentate ligands. The dpm and btmp ligands are so-called short bite ligands which usually bind two metals in a bidentate bridging fashion [3, 5, 6] whereas Me_2bpy is a typical chelating ligand producing a stable five-membered chelate ring. In contrast, the incoming anionic ligand, acac, removed the bridging acetato ligand from **1** and coordinated in a bidentate chelating manner in **8**.

Experimental

The cyclic tetranuclear complex **1** [1], (benzylthiomethyl)diphenylphosphine (btmp) [5], and $[Pd(dba)_2]$ (dba = dibenzylideneacetone) [7] were synthesized as previously described. The other procedures and apparatus were the same as those reported in a previous publication from our laboratory [8]. Conductivity measurements were carried out for 1.0×10^{-3} mol dm^{-3} acetone solutions at 25 °C on a Toa Electronics CM-20E conductometer.

$[Pd_2(\mu\text{-}o\text{-}C_6H_4)(O_2CMe)_2(\mu\text{-}L_2)_2]$ (2: L_2 = dpm, 4: L_2 = btmp)

Solid dpm (0.242 g, 0.628 mmol) was added to a solution of **1** (0.100 g, 0.0952 mmol) in benzene (20 cm^3), and the mixture was stirred at room temperature for 15 h. The precipitated yellow solids were collected and washed with hexane to give $\mathbf{2}\cdot C_6H_6$ (0.128 g). Complex **4** was similarly prepared.

$[Pd_2(\mu\text{-}o\text{-}C_6H_4)I_2(\mu\text{-}L_2)_2]$ (3: L_2 = dpm, 5: L_2 = btmp)

A solution of NaI (0.046 g, 0.306 mmol) in water (2 cm^3) was added to a solution of **2** (0.096 g, 0.0766 mmol) in acetone (10 cm^3), and the resulting mixture was stirred at ambient temperature for 12 h. After evaporating the volatile materials, the residue was extracted with CH_2Cl_2. The extract was concentrated and dilution with hexane gave yellow microcrystals of **3** (0.076 g). Complex $\mathbf{5}\cdot 1/2C_6H_6$ was similarly prepared after recrystallization from benzene and hexane.

Complex **5** was prepared by another route. Solid btmp (0.112 g, 0.348 mmol) was added to a solution of $[Pd(dba)_2]$ (0.200 g, 0.348 mmol)in benzene (15 cm^3) and the mixture was stirred at room temperature for 5 min. Then, to the resulting solution a solution of *o*-diiodobenzene (0.057 g, 0.174 mmol) in benzene (2 cm^3) was added. After refluxing the mixture for 1 h, the resulting mixture was chromatographed on a silica gel column (200 mesh, 1.5×35 cm) with the mixed solvent CH_2Cl_2/hexane (4/1). The yellow fraction was collected and was recrystallized from benzene–hexane to give $\mathbf{5}\cdot 1/2C_6H_6$ (0.033 g, 15%).

$[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](MeCO_2)\cdot 3H_2O$ (6)

Solid Me_2bpy (0.074 g, 0.400 mmol) was added to a solution of **1** (0.100 g, 0.0952 mmol) in benzene solution (20 cm^3), and the mixture was stirred at room temperature for 6 h. Reddish orange precipitates appeared which were collected and washed with hexane to give **6** (0.095 g).

$[Pd_2(\mu\text{-}o\text{-}C_6H_4)(\mu\text{-}O_2CMe)(Me_2bpy)_2](ClO_4)$ (7)

A solution of $NaClO_4\cdot H_2O$ (0.009 g, 0.064 mmol) in methanol (2 cm^3) was added to a solution of **6** (0.048 g, 0.058 mmol) in methanol (10 cm^3), and the mixture was stirred at ambient temperature for 12 h. After evaporating the volatile materials, the residue was extracted with CH_2Cl_2. The extract was concentrated and diluted with hexane to give reddish brown microcrystals of **7** (0.045 g).

$[Pd_2(\mu\text{-}o\text{-}C_6H_4)(acac\text{-}O,O')_2(\mu\text{-}SPr^i_2)]$ (8)

Solid Tl(acac) (0.061 g, 0.200 mmol) was added to a solution of **1** (0.050 g, 0.0476 mmol) in CH_2Cl_2 solution (20 cm^3), and the mixture was stirred at room temperature for 12 h. After evaporating off the volatile materials of the resulting suspension, the residue was extracted with benzene. The extract was concentrated and diluted with hexane to give yellow microcrystals of **8** (0.028 g).

[$Pd_2(\mu$-o-$C_6H_4)$(acac-O,O'$)_2$(3,5-lut$)_2$] (9)
A solution of 3,5-lutidine (0.012 g, 0.111 mmol) in benzene (5 cm^3) was added to a solution of **8** (0.032 g, 0.053 mmol) in benzene (5 cm^3), and the mixture was stirred for 12 h at room temperature. Concentration of the resulting solution and dilution with hexane gave yellow microcrystals of **9** (0.028 g).

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