

Synthesis of a tripalladium cluster containing an $\eta^1:\eta^2:\eta^2$ -bridging butadienyl ligand stabilized by a zwitterionic structure

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Abstract

An η^1 -butadienyl complex $[(trans-\eta^1-CH_2=C(Me)C=CH_2)Pd(PPh_3)_2Cl]$ (**1**) reacted with $[(\mu-\eta^2:\eta^2-1,3-butadiene)Pd_2(PPh_3)(\mu-Cl)Cl]$ (**2**) to result in displacement of the diene ligand of **2** accompanied by exchange of PPh_3 of **1** with Cl anion of **2** producing a butadienyl tripalladium cluster $[(\mu-CH_2=C(Me)C=CH_2)Pd(PPh_3)Cl_2] \cdot \{Pd_2(PPh_3)_2(\mu-Cl)\}$ (**3**) stabilized by the zwitterionic structure in moderate yield. The X-ray structure analysis of **3** revealed rigid binding of $[Pd_2(PPh_3)_2(\mu-Cl)]^+$ and $[(CH_2=C(Me)C=CH_2)Pd(PPh_3)Cl_2]^-$ through the π -bond coordination of the butadienyl group to the dipalladium cation.

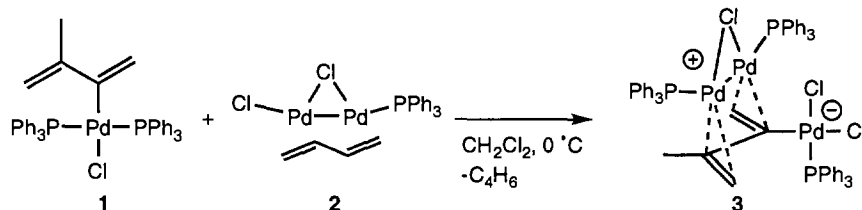
Keywords: Palladium; Butadienyl; Cluster; Zwitterionic; Bridging ligand

1. Introduction

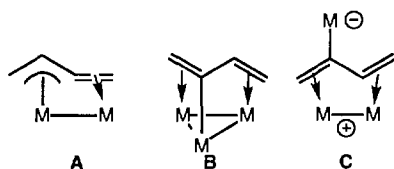
Recently, much attention has been paid to the structures and bonding of complexes containing unsaturated hydrocarbon ligands bridging on dipalladium units [1] as chemical adsorption models on a Pd metal surface. As the bridging ligand on Pd–Pd, a butadienyl group appeared of particular interest because of the presence of several functional units, e.g. vinyl, allyl and 1,3-diene, capable of coordinating to metals, exemplified by di- or trimetallic complexes of Fe and Ru (Scheme 1, type A–B) [2]. In this paper, we wish to report the synthesis and structure of another μ -butadienyl trimetallic cluster of type C in which an ate-type organopalladium(II) unit and the cationic Pd(I)–Pd(I) fragment are held together through π -diene coordination.

2. Results and discussion

Previously, we reported [3] that treatment of 1,3-diene bridged dipalladium complexes with additional 1,3-diene results in facile exchange of the coordinated and free butadiene. Therefore, $[(trans-\eta^1-CH_2=C(Me)C=CH_2)Pd(PPh_3)_2Cl]$ (**1**) [4] was added to $[(\mu-\eta^2:\eta^2-butadiene)Pd_2(PPh_3)Cl(\mu-Cl)]$ (**2**) in CH_2Cl_2 or $CDCl_3$ at $0^\circ C$, and then the solution stirred for 15 min, leading indeed to liberation of butadiene as confirmed by 1H NMR spectra. After workup, brownish-red microcrystals of **3** were obtained in 61% yield.



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Scheme 1.

The elemental analysis for $3 \cdot \text{CH}_2\text{Cl}_2$ (found: C, 52.38; H, 4.13; calc.: C, 52.81; H, 3.99%) indicated that **3** was composed of equimolar amounts of **1** and the fragment obtained from **2** by loss of butadiene. The ^1H NMR spectra of **3** (see below) showed a new set of butadienyl resonances at higher fields compared with those of **1** [4], suggesting coordination of a butadienyl–palladium unit through C=C bonds to a low valent palladium species such as Pd(0) or Pd(I)–Pd(I). ^{31}P NMR spectra exhibited a broad singlet and two doublet peaks ($J_{\text{PP}} = 86\text{ Hz}$), one of which was further split slightly ($J_{\text{PP}} = 4\text{ Hz}$).

^1H NMR (CDCl_3), δ 7.8–7.2 (m, Ph), 4.20 (br s, 1H), 3.46 (br dd, 1H), 3.25 (br dd, 1H), 2.20 (br m, 1H), 0.19 (br dd, Me); ^{31}P NMR (CDCl_3 , ext. $\text{P}(\text{OMe})_3$), δ –111.45 (d, $J = 86\text{ Hz}$), –112.52 (br s), –114.11 (dd, $J = 86\text{ Hz}$, 4 Hz).

The exact structure of **3** was determined by X-ray structure analysis. Crystal data for $3 \cdot (\text{CH}_2\text{Cl}_2)_{1.5}$, $\text{Pd}_3\text{C}_{60.5}\text{H}_{55}\text{Cl}_6\text{P}_3$, $M = 1406.94$, triclinic, space group $P1(\text{No. } 2)$, $a = 14.337(4)$, $b = 20.189(4)$, $c = 10.937(5)\text{ \AA}$, $\alpha = 99.93(2)$, $\beta = 92.96(3)$, $\gamma = 81.01(2)^\circ$, $U = 3078(1)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.517\text{ g cm}^{-3}$, $F(000) = 1406$, $\mu(\text{Mo K}\alpha) = 12.41\text{ cm}^{-1}$, 652 variables refined with 6762 reflections collected up to $2\theta = 50^\circ$ with $I > 3\sigma(I)$ to $R = 0.082$, $R_w = 0.095$. Non-hydrogen atoms of one of two solvate molecules (CH_2Cl_2) in the crystal were refined isotropically with the occupancy set as 0.5.

The tripalladium cluster was revealed (Fig. 1) to contain the cationic dipalladium fragment $[\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-Cl})]^+$ and the anionic η^1 -butadienyl monopalladium moiety which are rigidly bound to each other through 1,3-diene coordination, accomplishing the novel bridging mode of the butadienyl group. Exchange of PPh_3 in **1** with terminal Cl in **2** has produced the anionic and the cationic fragments. No direct metal–metal interaction was observed between these two components; Pd1–Pd3 (3.795(2) Å) and Pd2–Pd3 (3.605(2) Å) are out of the range of Pd–Pd single bond (2.50–2.84 Å). The dihedral angle between the coordination plane for the mononuclear unit [Pd3–Cl2–Cl3–P3–C3] and the C1–C2–C3–C4 plane is 84.77° with Cl3 brought closer to Pd1. By such tilting, the lengths Cl3–Pd1 (3.130(4) Å) and Cl3–Pd2 (3.101(4) Å) became similar to each other. These are shorter than the

sum of the van der Waals radii of Cl and Pd (3.38 Å), but cannot indicate any strong bonding interaction between Cl3 and the Pd–Pd unit; a possible implication for electrostatic interactions will be discussed later.

The Pd1–Pd2 bond distance of 2.711(2) Å is longer than those of anionic and neutral μ -1,3-diene dipalladium complexes ($[(\mu\text{-}\eta^2\text{:}\eta^2\text{-isoprene})\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})]^-$, 2.578(1) Å; **2**, 2.662(1) Å) [3], reflecting the change of the trans influences of the terminal ligands L and L' in the L–Pd–Pd–L' unit. More significantly, the present Pd–Pd distance is considerably longer than that of the μ -allyldipalladium complex $[(\mu\text{-CH}_2\text{CHCH}_2)\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-Cl})]$ (2.623(1) Å) [5] containing the same cationic dipalladium fragment. The 1,3-diene unit is in an s-trans form and C1–C2 and C3–C4 distances (1.41(2), 1.44(2) Å) are longer than the C2–C3 distance (1.35(2) Å). This trend is unusual when compared with several structurally characterized μ -1,3-diene dimetal complexes with a metal–metal bond in which the C2–C3 distance is almost equal to or longer than the C1–C2 distance [6]. In contrast, a considerable number of mononuclear complexes with the s-cis form have been reported to show the same trend as that in **3** [7].

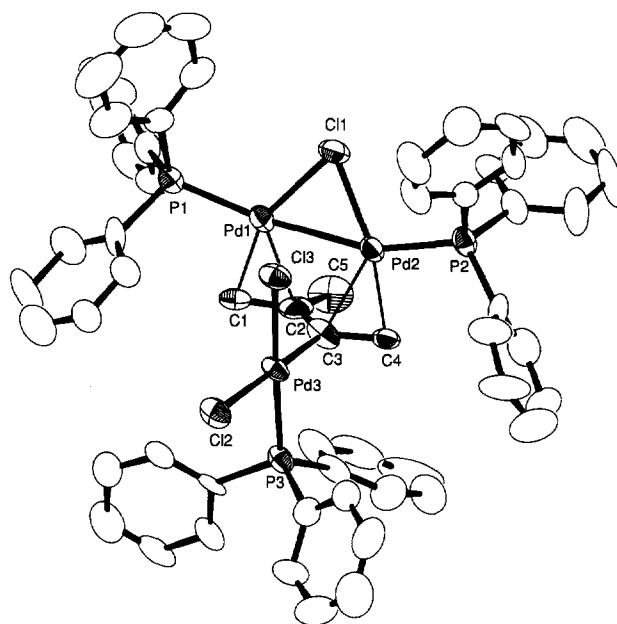


Fig. 1. ORTEP drawing of **3** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Pd1–Pd2 2.711(2), Pd1–P1 2.252(4), Pd1–Cl1 2.387(4), Pd2–Cl1 2.367(4), Pd2–P2 2.261(4), Pd1–C1 2.08(2), Pd1–C2 2.34(2), Pd2–C3 2.28(2), Pd2–C4 2.11(1), C1–C2 1.41(2), C2–C3 1.35(2), C3–C4 1.44(2), C2–C5 1.57(3), Pd3–C3 2.03(2), Pd3–P3 2.245(4), Pd3–Cl2 2.395(4), Pd3–Cl3 2.378(4); P1–Pd1–Pd2 164.7(1), P2–Pd2–Pd1 160.4(1), P1–Pd1–Cl1 114.2(2), P2–Pd2–Cl1 104.9(2), Pd1–Cl1–Pd2 69.5(1), C1–C2–C3 119(2), C2–C3–C4 122(2), C1–C2–C5 121(2), C2–C3–Pd3 119(1), C3–Pd3–P3 90.2(5), C3–Pd3–Cl3 91.3(5), C3–Pd3–Cl2 176.6(5).

The most remarkable feature in the reaction of **1** with **2** is the great ease with which the very bulky diene unit displaced 1,3-butadiene almost quantitatively, as detected by ^1H NMR monitoring experiments. Competitive coordination equilibrium measurements indicated unfavorable coordination of bulkier dienes to Pd–Pd [3]. Use of a cationic dipalladium complex [$(\mu\text{-}\eta^2\text{:}\eta^2\text{-butadiene})\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-Cl})[\text{PF}_6]$] instead of **2** in the reaction with **1** resulted in only gradual decomposition of **1** under the same reaction conditions. We postulate that the zwitterionic structure plays an important role for this unusual behavior of **1** in 1,3-diene exchange on Pd–Pd. Aggregation of cationic and anionic organometallic fragments through the π -bond coordination has rarely been observed, except in some Pt_2 or PtPd systems recently reported by Fornies and co-workers [8,9]. In the former case, one of the alkynyl group of $[\text{Pt}(\text{RC}\equiv\text{C})_2(\text{PPh}_3)_2]$ migrated to the other platinum center of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})(\text{THF})]$ to yield a stable zwitterionic diplatinum complex, $[\{(\mu\text{-RC}\equiv\text{C})\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})\}^- \cdot \{\text{Pt}(\text{PPh}_3)_2(\text{RC}\equiv\text{C})\}^+]$ in which the $\text{C}\equiv\text{C}$ bond of the anionic part coordinates to Pt of the cationic part, instead of directly forming a neutral-donor–neutral-acceptor complex, $[\{(\mu\text{-RC}\equiv\text{C})\text{Pt}(\text{PPh}_3)_2(\text{RC}\equiv\text{C})\} \cdot \{\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})\}]$ [8]. The other case involved π -acetylene chelate coordination of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{RC}\equiv\text{C})_2]^{2-}$ to the cation, $[\text{M}(\eta^3\text{-allyl})]^+$ ($\text{M} = \text{Pd}, \text{Pt}$) [9].

Further studies are in progress to develop the potential of the ionic Pd–Pd unit for stabilizing localized charge on bridging ligands.

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