# Stoichiometric Complexation of Palladium(II) with 1,4-Dihydro-1,4-diarsinine as a Rigid Symmetrical Bidentate Ligand

Kensuke Naka,*,† Akiko Nakahashi, Manabu Arita, and Yoshiki Chujo*

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

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*Summary: Bimetallic and monometallic palladium(II) complexes with 1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(methoxycarbonyl)-1,4-diarsinine (**1**) were selectively obtained by stoichiometric addition of $PdCl_2(PhCN)_2$ to **1** as $[Pd_2Cl_4(\mathbf{1})_2]$ (**2**) (yield 83%) and $[PdCl_2(\mathbf{1})_2]$ (**3**) (yield 99%), respectively. The structures of $[Pd_2Cl_4(\mathbf{1})_2]$ (**2**) and $[PdCl_2(\mathbf{1})_2]$ (**3**) were confirmed by $^1H$ NMR spectra, X-ray crystallography, and elemental analysis.*

The self-assembly of finite structures through coordination chemistry has become a very topical field.[1] Many of the finite structures have been prepared using Pt(II)/Pd(II) ions as acceptor units with bidentate donor bridging linkers.[1f] Nitrogen and phosphorus donor linkers are often used as bridging ligands in direct self-assembly.[1e,f] The structure, conformation, and topology of these supramolecules should depend on the nature of the organic backbone as well as the nature of the metal–ligand interaction. Trivalent arsenic compounds have lone pairs, which can coordinate with various kinds of transition metals. Recently, several studies of organoarsine−transition-metal complexes have been reported to show attractive properties.[2,3] On comparison of the trivalent arsenic compounds with phosphorus analogues, there are several different aspects which can significantly affect the properties of their transition-metal complexes. The s character of the lone pair on an arsenic atom is stronger than that of a phosphorus atom, which results in a weaker coordination strength. The $\pi$-acceptor property of an arsenic atom is stronger than that of a phosphorus atom.[4] Palladium complexes of organoarsenic compounds have higher catalytic activity, due to an easier dissociation of the organoarsenic ligand.[3,5] The trivalent organoarsenic compounds are more stable toward oxygen and moisture than are the organophosphorous analogues.

Recently, we have reported a facile synthesis of 1,4-dihydro-1,4-diarsinines (1,4-diarsa-2,5-cyclohexadienes) without using volatile arsenic intermediates.[6] The 1,4-dihydro-1,4-diarsinine has a unique structure: two arsenic atoms are connected with two rigid ethylene bridges and have divergent syn conformations of the two lone pairs on the arsenic atoms. Their stability toward air and moisture was great enough to allow their handling in air. Although similar structures, for example 5,10-dihydro 5,10-disubstituted arsanthrenes, have been reported,[7] no complexation of diarsenic ring compound to metal ions has been studied. Herein, we report that bimetallic and monometallic palladium(II) complexes with 1,4-dihydro-1,4-diarsinine (**1**) were selectively obtained by stoichiometric addition of $PdCl_2(PhCN)_2$ to **1** in high yields (Scheme 1). To our knowledge, this is the first example of the stoichiometric complexation of metal ions with symmetrical bidentate ligands.

1,4-Dihydro-1,4-dimethyl-2,3,5,6-tetrakis(methoxycarbonyl)-1,4-diarsinine (**1**) was prepared by the radical reaction of pentamethylcyclopentaarsine (*cyclo*-$(MeAs)_5$) and dimethyl acetylenedicarboxylate according to our previous report.[6] Complexation of **1** with an equimolecular amount of $PdCl_2(PhCN)_2$ was carried out referring to a literature procedure.[3a] When a toluene solution of $PdCl_2(PhCN)_2$ was added to **1** under dry argon, the solution became heterogeneous immediately. To complete a complexation, the reaction was performed at 85 °C for 17 h. After the reaction, the precipitate was filtered, washed with toluene several times, and dried in vacuo to give a complex (**2**) as an orange powder (yield 83%). The elemental analysis of **2** supported a 1:1 complex of **1** and $PdCl_2$ (see the Supporting Information). The obtained complex **2** was insoluble in toluene

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* To whom correspondence should be addressed. Fax: (+81)75-383-2605. Tel: (+81)75-383-2604. E-mail: chujo@chujo.synchem.kyoto-u.ac.jp.

† Present address: Department of Chemistry and Materials Technology, Graduate School of Science and Technology, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

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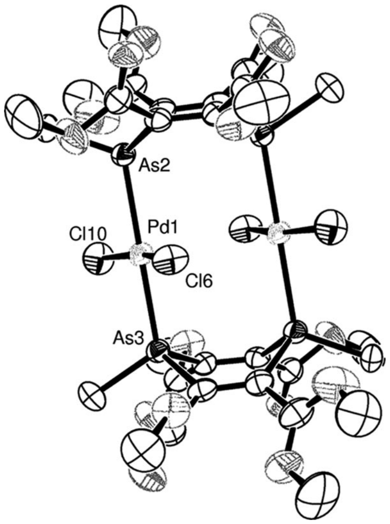


**Figure 1.** ORTEP drawing of **2** (50% probability thermal ellipsoids) isolated by recrystallization from $CH_3CN$. The hydrogen atoms and a minor carbon atom in the disordered structure (C14) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2) = 3.349, As(2)−Pd(1) = 2.397, Pd(1)−Cl(6) = 2.296, As(2)−C(methyl) = 1.943, As(2)−C(ring) = 1.953; As(2)−Pd(1)−As(3) = 177.91(3), As(2)−Pd(1)−Cl(6) = 90.1, Cl(6)−Pd(1)−Cl(10) = 168.41(9).

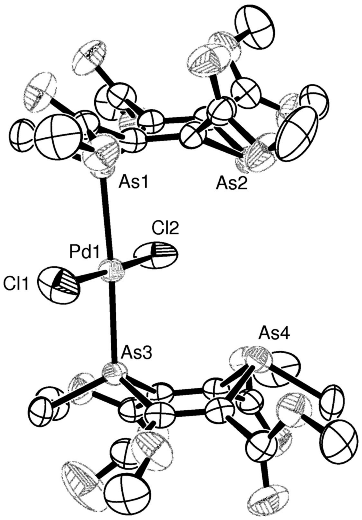
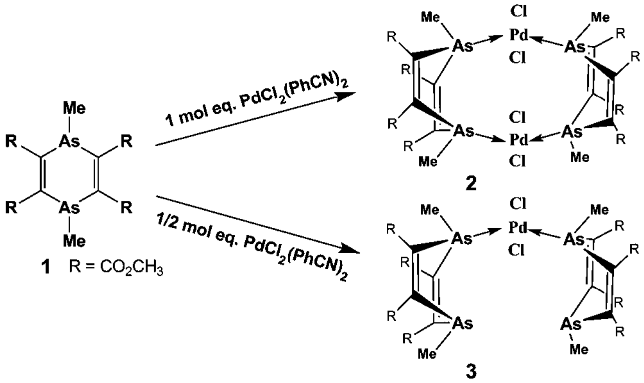


**Figure 2.** ORTEP drawing of **3** (50% probability thermal ellipsoids) isolated by recrystallization from $CH_3CN$. Selected bond lengths (Å) and angles (deg): As(1)−Pd(1) = 2.396, Pd(1)−Cl(1) = 2.291, As(1)−C(methyl) = 1.936, As(1)−C(ring) = 1.333; As(2)−Pd(1)−As(3) = 176.06(2), As(2)−Pd(1)−Cl(6) = 89.56, Cl(6)−Pd(1)−Cl(10) = 177.40(6).

**Scheme 1. Stoichiometric Complexation of Palladium(II) with 1**



and *n*-hexane, almost soluble in $CH_2Cl_2$, and soluble in DMSO and acetonitrile. The structure of **2** was confirmed by X-ray crystallography. The ORTEP drawing of **2** shows that two molecules of **1** have inside-directed lone pairs of **1** on the arsenic atoms and are connected with two palladium atoms (Figure 1). Averages of As−C (methyl) and As−C distances in the ring structure are shorter than those in **1**.[6] Furthermore, the C−As−C angles in the 1,4-dihydro-1,4-diarsinine ring structure and the other C−As−C angles for the coordinated arsenic atoms of **2** are wider than those of **1**.[6] Averages of the Pd−As bond length and the distance of the two palladium atoms are 2.397 and 3.349 Å, respectively.

A half-equimolar amount of $PdCl_2(PhCN)_2$ was used for complexation with **1** to evaluate the coordination behavior in a way similar to that for the synthesis of **2**. The reaction mixture became heterogeneous in several minutes after addition of a toluene solution of $PdCl_2(PhCN)_2$ to **1**. After reaction at 85 °C for 17 h, complex **3** was obtained as a yellow powder (yield 99%). The elemental analysis of **3** supported a 2:1 complex of **1** and $PdCl_2$ (see the Supporting Information). The obtained complex was insoluble in toluene and *n*-hexane, slightly soluble in acetone, and soluble in $CH_2Cl_2$, DMSO, and acetonitrile. The ORTEP drawing of **3** shows that two molecules of **1** were bridged with a palladium ion (Figure 2). The average Pd−As bond length is 2.396 Å, which is almost the same length as in **2**.

The $^1H$ NMR spectrum of **2** in $CD_3CN$ (see the Supporting Information) showed two peaks: the peak at $\delta$ 1.37 ppm corresponds to the proton of the methyl group on the arsenic atom, and the other peak at $\delta$ 3.79 ppm corresponds to the methyl group of the methoxycarbonyl group. Both of the peaks are shifted downfield on complexation compared with those of **1**. In the $^1H$ NMR spectrum of **3** in $CD_3CN$, a broad peak corresponding to the proton of the methyl group on the arsenic atom was observed (see the Supporting Information). The broadened peaks in the $^1H$ NMR spectrum of **3** are probably due to palladium exchange at the coordination site being faster than the NMR time scale.[8] $^1H$ NMR analyses with decreasing temperature were carried out in $CD_2Cl_2$. At room temperature, the peak corresponding to the proton of the methyl group on the arsenic atom appeared as a broad peak, due to exchange equilibrium, which is reasonably fast in relation to the NMR time scale. At −40 °C, two sharp peaks ($\delta$ 2.03 and 1.34 ppm) are observed corresponding to the protons of the methyl groups on the arsenic atoms; the peaks can be attributed to the coordinated methyl arsine group and the uncoordinated group, respectively. These results suggest that **2** is more stable than **3**.

The UV–vis absorption spectra of **2** and **3** in $CH_2Cl_2$ showed long-wavelength absorption maxima at 371 nm (16 400 $M^{-1}$ $cm^{-1}$) and 365 nm (14 300 $M^{-1}$ $cm^{-1}$), respectively, which are derived from mixed metal ($d_M$)-to-ligand ($s/p^*_{As}$)/(ligand ($p_{Cl}$)-to-ligand ($s/p^*_{As}$) (MLCT/LLCT) charge transfer transitions (Figure 3).[4] It was reported that the acceptor orbitals are composed of metal d orbitals and the antibonding component of the lone pair ($s/p^*_{As}$). An increase in accepting properties of the antibonding component of the lone pair on the arsine ligands would decrease the energies of the charge transfer transition.

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[8] Although a fluxional ring process of **3** may be another possible explanation of the broad signal at room temperature, this process may be ruled out by a $^1H$ NMR analysis of a platinum analogue of **3**. These results will be discussed in an upcoming manuscript.

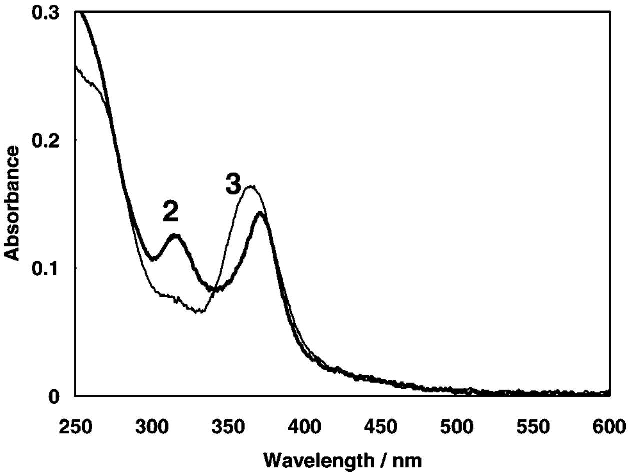

**Figure 3.** Absorption spectra of **2** (1 × $10^{-2}$ mM) and **3** (1 × $10^{-2}$ mM) in $CH_2Cl_2$ at room temperature.

The present data indicate that the arsine in the bimetallic complex of **1** is a better acceptor compared to the arsine in the monometallic complex of **1**. This may be due to some electron interaction thorough the ethylene bridges between the two arsines in **1**.

We studied the catalytic activities of **2** and **3** in a Heck reaction between 4-bromoacetophenone and *n*-butyl acrylate.[9] Although no reaction proceeded at 100 °C in *N*,*N*-dimethylacetamide (DMA) in the case of **3**, the product was obtained by the Heck reaction with **2** in a yield of 41%. It should be noted that the Heck olefination proceeded to yield the products without any reduction of catalytic activity even in air because the arsine ligand is stable to oxidation, which usually leads to deactivation of the catalyst. Detailed studies on the catalytic activities of the complexes are currently underway.

In conclusion, we have demonstrated that the bimetallic complex $[Pd_2Cl_4(\mathbf{1})_2]$ (**2**) and the monometallic complex $[PdCl_2(\mathbf{1})_2]$ (**3**) were synthesized by stoichiometric addition of $PdCl_2(PhCN)_2$ to 1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis-(methoxycarbonyl)-1,4-diarsinine (**1**) in toluene. The rigidity of the ring structure of the 1,4-dihydro-1,4-diarsinine provided well-defined complexes. Since **1** can be synthesized with no volatile toxic intermediates such as arsenic chlorides and arsenic hydrides, the 1,4-dihydro-1,4-diarsinine could provide a possible building block for supramolecular structures.

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**Supporting Information Available:** Text, figures, tables, and CIF files giving synthetic details, $^1$H NMR data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Pyrex tubes were filled with NaOAc (0.0237 g, 0.29 mmol), 4-bromoacetophenone (0.0501 g, 0.25 mmol), *n*-butyl acrylate (0.05 mL, 0.35 mmol), **2** (0.0007 g, 0.55 $\mu$mol), and DMA (0.25 mL), degassed, and filled with argon via freeze−pump thawing before heating to 100 °C for 26 h. The products were analyzed by $^1$H NMR spectroscopy.