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Synthesis of the diphenylacetylene-based, tetra-amine ligand 1,2-bis(3,5-bis[(dimethylamino)methyl]phenyl)acetylene by palladium-catalysed cross-coupling: isolation and crystal structure of the catalyst *trans*-(3,5-bis[(dimethylamino)methyl]-phenyl)bis(triphenylphosphine)palladium(II) iodide

Marieke P.R. Spee [a], Bart Ader [a], Pablo Steenwinkel [a], Huub Kooijman [b], Anthony L. Spek [b,1], Gerard van Koten [a,*]

[a] *Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b] *Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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Abstract

Reaction of 3,5-bis[(dimethylamino)methyl]phenyl iodide with 3,5-bis[(dimethylamino)methyl]phenylacetylene in diethylamine in the presence of bis(triphenylphosphine)palladium(II) dichloride (3.6 mol%) and copper(I) iodide (3.0 mol%) gave 1,2-(bis(3,5-bis[(dimethylamino)methyl]phenyl)acetylene (**1**) in 82% yield. The palladium catalyst was recovered in 93% yield as *trans*-(3,5-bis-[(dimethylamino)methyl]phenyl)bis(triphenylphosphine)palladium(II) iodide (**2**). The crystal structure of **2** shows that the coordination geometry of the palladium is distorted square-planar. No inter- or intramolecular interactions between the N-donor atoms and the Pd are observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Catalysis; Sonogashira coupling; Tetraamine ligand; X-ray

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1. Introduction

The compound 1,2-(bis(3,5-bis[(dimethylamino)-methyl]phenyl)acetylene (**1**) (see Scheme 1), is a representative of a new class of ligand structures from which bimetallic compounds might be obtained in which the metal centres are connected by π-conjugation through a dianionic organic bridge [1]. We describe here its preparation via the palladium-catalysed cross-coupling of a terminal alkyne with the appropriate aryl halide, usually referred to as the Sonogashira coupling [2].

2. Results and discussion

3,5-Bis[(dimethylamino)methyl]phenylacetylene was reacted with 3,5-bis[(dimethylamino)methyl]phenyl iodide in a 1:1 molar ratio in diethylamine in the presence of catalytic amounts of bis(triphenylphosphine)palladium(II) dichloride and copper(I) iodide (Scheme 1). The cross-coupling product 1,2-(bis(3,5-bis[(dimethyl-amino)methyl]phenyl)acetylene (**1**) was isolated as a solid in 82% yield.

Interestingly, the palladium catalyst was recovered as *trans* - (3,5 - bis[(dimethylamino)methyl]phenyl)bis(triphenylphosphine)palladium(II) iodide (**2**), (see Scheme 1). The isolated yield of **2** was 93% based on the starting amount of $PdCl_2(PPh_3)_2$ catalyst. This points to a quantitative conversion of $PdCl_2(PPh_3)_2$. Although several *trans*-$Pd(X)(Ar)(PPh_3)_2$ complexes have been reported, mainly with $X = Cl$, or Br, and with

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* Corresponding author. Fax: +31-30-2523615.
E-mail address: g.vankoten@chem.uu.nl (G. van Koten)

[1] Crystallographic correspondence to this author.

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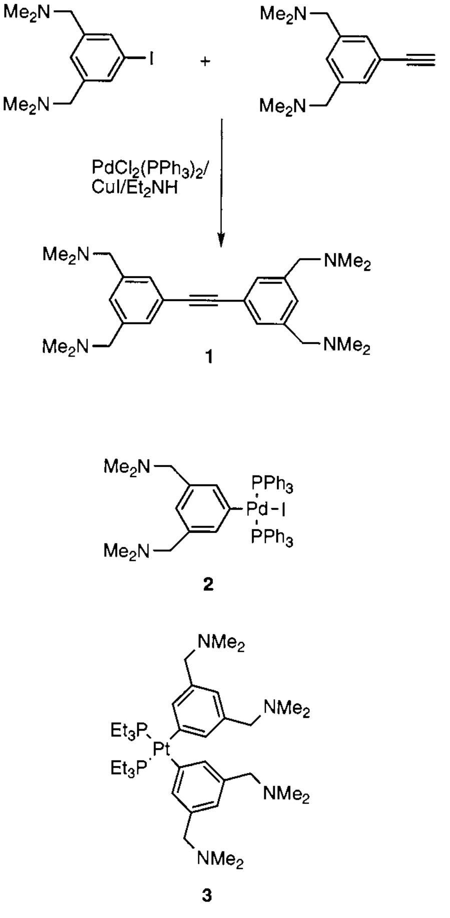
phenyl groups bearing substituents mainly at the *ortho*-position [3], little is known of such palladium complexes with X = I and *meta*-substituted phenyl groups. So far, only one complex is known, (*cis*-$[Pt(PEt_3)_2\{C_6H_3(CH_2NMe_2)_2\text{-}3,5\}_2]$ (**3**), in which the (dimethylamino)methyl-substituents of the 3,5-bis[(dimethylamino)methyl]phenyl anion are in a *meta* position to the metal–carbon bond [4]. Since the formation of **2** potentially opens pathways to multimetallic species via a 4-lithiation/transmetallation sequence, as has been demonstrated for **3**, its crystal structure has been elucidated.

Complex **2** was obtained as a deep-red crystalline material from a pentane solution. The crystals could be kept in air for several months without any observable degradation. The crystal structure of **2** shows that the coordination geometry of the palladium is distorted square-planar (see Fig. 1) with P(1)–Pd–P(2) and C(1)–Pd–I bond angles of 174.93(2) and 173.40(7)°, respectively. The Pd–P(1) and Pd–P(2) distances (2.3262(7) and 2.3238(7) Å, respectively) are in the range expected for *trans*-positioned triphenylphosphine ligands (2.319–2.342 Å) [5]. Both the Pd–I distance (2.6968(4) Å) and the Pd–C(1) distance (2.025(2) Å) agree well with those reported for *trans*-iodo(methylthiomethylphenyl)bis(triphenylphosphine)palladium(II) [3e] (Pd–I (2.692(1), Pd–C 2.029(6) Å) in which likewise the Pd–I bond is *trans* to a C sp^2 donor atom of high *trans* influence. No inter- or intramolecular interactions between the N-donor atoms and Pd were observed.



Scheme 1.

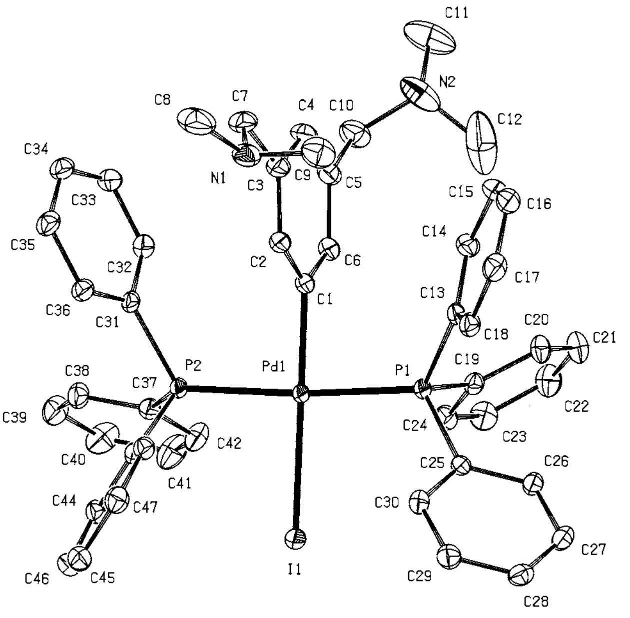


Fig. 1. ORTEP drawing (50% probability atomic displacement ellipsoids) of **2**. Hydrogen atoms have been omitted for clarity.

Compound **2** is probably formed by oxidative addition of 3,5-bis[(dimethylamino)methyl]phenyl iodide to a catalytically active 14-electron complex $Pd(PPh_3)_2$. In a separate experiment, **2** was obtained quantitatively from the reaction of 3,5-bis[(dimethylamino)methyl]phenyl iodide with $Pd(PPh_3)_4$ in toluene. It is known that $Pd(PPh_3)_2$ can be formed from $PdCl_2(PPh_3)_2$ by reduction with in situ generated copper(I) acetylide [2a,6]. In the present catalytic cycle $Pd(PPh_3)_2$ will be regenerated by reductive elimination of **1** from an aryl-alkynyl palladium(II) derivative. The stability of the reaction mixture with respect to separation of zerovalent palladium metal may arise from the presence of alkynyl groupings in both starting and product compounds. This stability then allows the recovery of the palladium as the iodide salt **2** from the reaction medium.

3. Experimental

3.1. General

All reactions and handling were performed under an inert atmosphere of dinitrogen. Melting points were determined in sealed capillaries. NMR spectra were recorded on Varian Inova 200 and 300 spectrometers. Elemental analyses were performed by Dornis und

Kolbe, Mikroanalytisches Laboratorium (Mühlheim, Germany). All chemicals were purchased from Acros. Kieselgel 60 was purchased from Merck. CuI and $PdCl_2(PPh_3)_2$ were prepared according to literature procedures [4,5]. Dry solvents were freshly distilled from sodium sand under a dinitrogen atmosphere.

*3.2. Synthesis of 1,2-(bis(3,5-bis[(dimethylamino)-methyl]phenyl)acetylene (**1**) and isolation of trans-(3,5-bis[(dimethylamino)methyl]phenyl)bis-(triphenyl-phosphine)palladium(II) iodide (**2**)*

3,5-Bis[(dimethylamino)methyl]phenyl iodide (4.99 g, 15.7 mmol) and 3,5-bis[(dimethylamino)methyl]phenylacetylene (3.40 g, 15.7 mmol) were dissolved in diethylamine (100 ml). CuI (0.08 g, 0.44 mmol) and $PdCl_2(PPh_3)_2$ (0.40 g, 0.57 mmol) were added to this solution. After 6 days of stirring at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in a diethyl ether–diethylamine (v/v = 95/5) mixture and then filtered over a short column of Kieselgel 60. After evaporation of the solvent from the filtrate in vacuo the resulting residue was dissolved in pentane (100 ml). Immediately a small amount of black precipitate was formed. This mixture was allowed to stand for 3 days at room temperature, after which red crystals of **2** had formed from the deep-red solution. Yield of **2**: 0.5 g (0.53 mmol, 93% of Pd). ^{1}H-NMR (CD_2Cl_2, 300 MHz): δ 7.57–7.50 (m, 12H, *ortho*-H PPh_3), 7.40–7.27 (m, 18H, *meta*/*para*-H PPh_3), 6.55 (s, 2H, *ortho*-ArH), 6.24 (s, 1H, *para*-ArH), 2.72 (s, 4H, $ArCH_2$), 1.95, (s, 12H, NMe_2). ^{31}P-NMR ($CDCl_3$, 80 MHz), 200 MHz): δ 24.0 (PPh_3). ^{13}C-NMR (CD_2Cl_2, 75 MHz): δ 135.2–134.8 (m, PPh_3), 130.0–130.2 (d, PPh_3), 128.2–127.6 (m, PPh_3), 134.7, 130.4, 123.8 (Ar), 64.5 ($ArCH_2$), 45.2 (NMe_2). Anal. Calc. for $C_{48}H_{49}N_2P_2PdI$: C, 60.74; H, 5.20; N, 2.95. Found: C, 60.86; H, 5.28; N, 2.88%.

The remaining solution was decanted and filtered over a short alumina column. The solvent was evaporated in vacuo after which methanol (50 ml) was added. To this solution a solution of HBF_4 in water (25 ml, 35%) was added. The mixture was stored at −30°C for a day, after which a yellow–white solid had precipitated. The solid was isolated and washed first with cold methanol (25 ml) and then with diethyl ether (15 ml). The resulting white solid was dissolved in aqueous NaOH (100 ml, 2 M) and extracted with dichloromethane (3 × 50 ml). The combined extracts were dried over $MgSO_4$. After evaporation of the solvent a light-yellow oil was obtained which was crystallised from pentane. After removal of the pentane, **1** was obtained as a light-yellow solid. Yield 2.49 g (6.1 mmol, 82%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38 (s, 4H, *ortho*-ArH), 7.26 (s, 2H, *para*-ArH), 3.43 (s, 8H, $ArCH_2$), 2.27, (s, 12H, NMe_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 139.2, 130.9, 129.6, 123.0 (Ar), 89.3 ($ArC\equiv CAr$), 63.9 ($ArCH_2$), 45.4 (NMe_2).

*3.3. Crystal structure determination of **2***

Crystallographic data: $C_{48}H_{49}IN_2P_2Pd$, space group $P\bar{1}$, $a = 11.9594(12)$, $b = 13.9118(18)$, $c = 14.2892(18)$ Å, $\alpha = 90.511(5)$, $\beta = 96.737(8)$, $\gamma = 96.951(7)°$, $V = 2343.0(5)$ Å^3, $Z = 2$, $D_{calc.} = 1.345$ g cm^{-3}, $M_w = 949.20$, μ (Mo–K$_\alpha$) = 1.16 mm^{-1}, $T = 150$ K, deep-red crystal, 0.2 × 0.2 × 0.3 mm. X-ray data were collected on a Nonius Kappa CCD [Mo–K$_\alpha$, Rotating anode, $\Theta_{max} = 27.5°$]. The structure was solved using SHELXS-86/PATT and refined on F^2 with SHELXL-97-2. Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. The structure was found to contain a void at an inversion centre with poorly defined electron density. The contribution of this density was taken into account using the PLATON/SQUEEZE procedure. The integrated density in the solvent area amounts to 45 electrons, probably due to the presence of one disordered pentane molecule of crystallisation per unit cell. Convergence was reached at $R = 0.0330$ (9082 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0721$ (10363 unique reflections), 491 parameters, $S = 1.073$, $-0.71 < \Delta\rho < 0.54$ electron Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis of **2** have been deposited with the Cambridge Crystallographical Data Centre, CCDC no. 133325.

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