

# Oxygen insertion into palladium–arene bonds by iodosylbenzene

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## Abstract

The regiospecific hydroxylation of the naphthyl ring at the C(2) position of unsymmetrical 1-(phenylazo)naphthalene **1** was achieved via oxygen atom insertion into the palladium–naphthyl bond of **2** with iodosylbenzene, followed by demetallation. The insertion of oxygen atom into the Pd–C(phenyl) bond of the cyclopalladated azobenzenes **5** was also achieved with iodosylbenzene.

**Keywords:** Palladium; Oxygen insertion

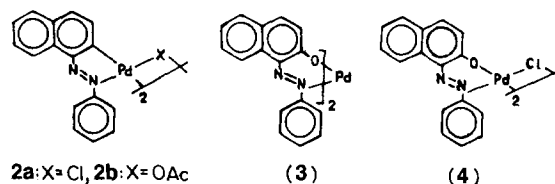
## 1. Introduction

The activation of carbon–hydrogen bonds in hydrocarbons by transition metal ions often leads to selective functionalization under remarkably mild conditions [1–3]. We have explored the aromatic metaloxylation (Ar–M → Ar–O–M) reactions [4–6] of species containing Pd–C(aryl) bonds via cyclometallation reactions [7] using iodosylbenzene to achieve regiospecific aromatic hydroxylation [8–11]. Iodosylbenzene is well known for its use as a source of oxygen atom in wide variety of studies, especially in metal-catalysed oxygenation reactions [12–15]. Here we report the regiospecific hydroxylation of the naphthyl group of 1-(phenylazo)naphthalene and the regiospecific metaloxylation of the phenyl group of 1-phenylazobenzene [4] using iodosylbenzene.

## 2. Results and discussion

Unsymmetrical 1-(phenylazo)naphthalene (**1**) is known [16] to undergo an *ortho*-palladation reaction to form compounds **2**. It has been established [16–18] that

the palladium–carbon(aryl)  $\sigma$ -bond formation in **2** occurs exclusively at C(2) of the naphthyl ring.



The cyclopalladated complex **2a** reacts slowly with suspended iodosylbenzene in acetonitrile medium at room temperature and complexes **3** and **4** have been isolated from the reaction mixture using a chromatographic technique according to



Complex **4** is of limited stability and gradually, produces complex **3** and palladium(II) dichloride:



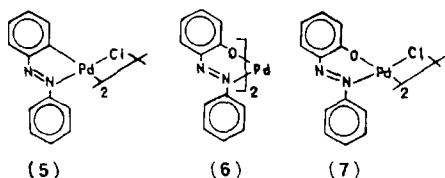
Complex **2b** also reacts with iodosylbenzene at room temperature in acetonitrile medium and only complex **3** has been isolated from the reaction mixture.

The elemental analysis data for complexes **3** and **4** are in full agreement with the above formulations. Complexes **3** and **4** have  $\nu(\text{CO})$  at 1144 and 1147  $\text{cm}^{-1}$ , respectively [19]. Complex **3** exhibits a strong absorption band at 542 nm ( $\epsilon = 12\,700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in dichloromethane and complex **4** shows an intense absorption band at 495 nm ( $\epsilon = 6300 \text{ dm}^3 \text{ mol}^{-1}$ )

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$\text{cm}^{-1}$ ) in acetonitrile. The demetallation of complex **3** by reducing the palladium(II) centre with hydrazine hydrate in dichloromethane medium [20] produces 1-(phenylazo)-2-naphthol [21] and palladium metal. The identity of the complex **3** has also been established by comparing its analytical and spectral data with those of the authentic complex, independently prepared by reaction of 1-(phenylazo)-2-naphthol and palladium(II)acetate. The formation of complex **3** following a non-oxidative route conclusively proves that aromatic hydroxylation has occurred at C(2) of the naphthyl group of 1-(phenylazo)naphthalene. Reports of the regioselective hydroxylation of a naphthyl group are rare [22]. Reaction (2) in the solid state suggests the presence of a palladium(II)-bound 1-(phenylazo)-2-naphtholato fragment in complex **4**.

We have also investigated the reactivity of iodosylbenzene with a compound having a palladium(II)–C(phenyl) bond. At room temperature, complex **5** [23] reacts with iodosylbenzene in acetonitrile medium and produces complexes **6** and **7**. The spectral and elemental analysis data for complexes **6** and **7** are in full agreement with those reported elsewhere [4,19]. This reaction shows that iodosylbenzene regioselectively metaloxylates at C(2) of the phenyl ring of azobenzene.



### 3. Experimental

#### 3.1. Instrumentation

IR spectra, electronic spectra and elemental analysis data were obtained using a Perkin-Elmer Model 983 spectrophotometer, Shimadzu UV-240 spectrophotometer and Carlo Erba Model 1106 elemental analyser, respectively.

#### 3.2. Syntheses

Iodosylbenzene [24], 1-(phenylazo)naphthalene [16], 1-(phenylazo)-2-hydroxynaphthalene [24], di( $\mu$ -chloro)bis[1-(phenylazo)naphthyl-C(2), $N_\beta$ ]dipalladium(II) [16], di( $\mu$ -acetato)bis[1-(phenylazo)naphthyl-C(2), $N_\beta$ ]dipalladium(II) [16] and di( $\mu$ -chloro)bis[1-(phenylazo)phenyl-C(2), $N$ ]dipalladium(II) [23] were synthesized following reported methods.

#### Reaction of di( $\mu$ -chloro)bis[1-(phenylazo)naphthyl-C(2), $N_\beta$ ]dipalladium(II) (**2a**) with iodosylbenzene

Solid iodosylbenzene (0.450 g, 2.046 mmol) was added to complex **2a** (0.100 g, 0.134 mmol) suspended

in acetonitrile (20  $\text{cm}^3$ ) and the mixture was stirred for 160 h. The filtrate and the dichloromethane washings of the residue were evaporated to dryness and the residue was washed with hexane ( $4 \times 5 \text{ cm}^3$ ). The residue was then extracted with dichloromethane (60  $\text{cm}^3$ ), the volume of the solution was reduced and the resulting solution was chromatographed on silica gel (mesh size 60–120). A pink–violet band was eluted with benzene and evaporation of the eluent in vacuo yielded complex **3** as deep-violet crystals, yield 0.032 g, 0.053 mmol (ca. 40%). Found: C, 63.86; H, 3.65; N, 9.28. Calc. for  $\text{C}_{32}\text{H}_{22}\text{O}_2\text{PdN}_4$ : C, 63.95; H, 3.66; N, 9.32%. A mixture of benzene and acetonitrile (9:1) was then used to elute a red–violet band containing complex **4**, which was isolated after removal of solvent in vacuo, yield 0.032 g, 0.041 mmol (ca. 30%). Found: C, 49.20; H, 2.82; N, 7.08. Calc. for  $\text{C}_{32}\text{H}_{22}\text{O}_2\text{Cl}_2\text{Pd}_2\text{N}_4$ : C, 49.37; H, 2.82; N, 7.19%.

#### Reaction of di( $\mu$ -acetato)bis[1-(phenylazo)naphthyl-C(2), $N_\beta$ ]dipalladium(II) (**2b**) with iodosylbenzene

Solid iodosylbenzene (0.450 g, 2.046 mmol) was added to a solution of complex **2b** (0.100 g, 0.126 mmol) in acetonitrile (25  $\text{cm}^3$ ) and the mixture was stirred for ca. 120 h. Complex **3** was isolated from the reaction mixture following the method for **2a**, yield 0.027 g, 0.045 mmol (ca. 35%). Found: C, 63.89; H, 3.66; N, 9.28. Calc. for  $\text{C}_{32}\text{H}_{22}\text{O}_2\text{PdN}_4$ : C, 63.95; H, 3.66; N, 9.32%.

#### Reaction of di( $\mu$ -chloro)bis[1-(phenylazo)phenyl-C(2), $N$ ]dipalladium(II) (**5**) with iodosylbenzene

To a suspension of compound **5** (0.150 g, 0.232 mmol) in acetonitrile (20  $\text{cm}^3$ ), solid iodosylbenzene (0.500 gm, 2.274 mmol) was added and the mixture was stirred for 72 h. The filtrate and dichloromethane washings of the residue were collected and evaporated to dryness. The solid mass was washed with hexane ( $4 \times 5 \text{ cm}^3$ ) and dissolved in dichloromethane (45  $\text{cm}^3$ ). The solution was chromatographed on silica gel (mesh size 60–120). A pink–violet band was eluted with benzene, which on evaporation of the eluent in vacuo yielded complex **6**, yield 0.047 g, 0.093 mmol (ca. 40%). Found: C, 57.50; H, 3.58; N, 11.0. Calc. for  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{PdN}_4$ : C, 57.55; H, 3.59; N, 11.19%. Complex **7** was isolated using a mixture of benzene and acetonitrile (9:1) as eluent, yield 0.024 g, 0.035 mmol (ca. 15%). Found: C, 42.39; H, 2.62; N, 8.12. Calc. for  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{Cl}_2\text{Pd}_2\text{N}_4$ : C, 42.49; H, 2.65; N, 8.26%.

#### Reaction of complex **3** with hydrazine monohydrate

Hydrazine monohydrate ( $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ , 98%) (0.064 g, 1.260 mmol) was added to a suspension of complex **3** (0.051 g, 0.085 mmol) in dichloromethane (35  $\text{cm}^3$ ) and the mixture was stirred at room temperature for 96 h. The yellow dichloromethane layer was

separated from metallic palladium. The solvent was removed and the solid mass was extracted with methanol. The shining crystals of 1-(phenylazo)-2-hydroxynaphthalene were collected from the solution, yield 0.021 g, 0.085 mmol (ca. 50%).

*Bis[1-(phenylazo)-2-naphtholato-N<sub>β</sub>,O]palladium(II)*  
(3)

Complex 3 was prepared by reaction of palladium(II)acetate (0.100 g, 0.445 mmol) with 1-(phenylazo)-2-hydroxynaphthalene (0.220 g, 0.887 mmol) in chloroform (30 cm<sup>3</sup>). The mixture was stirred for 12 h and the deep-violet crystals of complex 3 were collected by filtration, washed with ethanol and dried in vacuo, yield 0.188 g, 0.313 mmol (ca. 70%). Found: C, 63.92; H, 3.66; N, 9.28. Calc. for C<sub>32</sub>H<sub>22</sub>O<sub>2</sub>PdN<sub>4</sub>: C, 63.95; H, 3.66; N, 9.32%.

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