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Synthesis and spectroscopic characterization of σ-bonded phenothiazinonepalladium complexes

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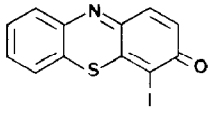
Abstract

Treatment of 4-iodo-3*H*-phenothiazin-3-one with tetrakis(triphenylphosphine)-palladium(0) in boiling benzene yields *trans*-iodo(3*H*-phenothiazin-3-one-4-yl)bis (triphenylphosphine)palladium(II) by oxidative addition. 5*H*-Benzo[*a*]phenothiazin-5-one-6-yl complex is prepared in a similar manner. The σ-bonded iminoquinone structure of the complexes has been elucidated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Introduction

The palladium-catalyzed coupling reaction of organic halides with alkynes has been employed for the preparation of a wide variety of substituted alkynes [1]. However, any attempt to couple 4-iodo-3*H*-phenothiazinone (**1**) with terminal acetylenes under the conditions usually used led to negligible yields of the expected products, and diacetylenes were obtained as major products (eq. 1). Column-chromatographic purification of the reaction mixture gave traces of the phenothiazinone palladium complex (**2**).



(1)

$$+\ R{-}{\equiv}{-}H \xrightarrow[\text{amine}]{PdCl_2(PPh_3)_2,\ CuI} R{-}{\equiv}{-}{\equiv}{-}R \qquad \text{(Eq. 1)}$$

We have now investigated the reaction of **1** with tetrakis(triphenylphosphine)palladium(0), and found that the oxidative addition of **1** to $Pd(PPh_3)_4$ yields the palladium complex **2** in good yield. Although a number of transition metal complexes containing a π-bonded quinone ligand have been reported, there has been

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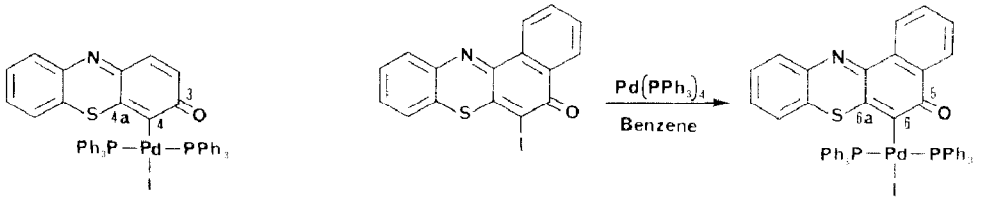
only one report of a σ-bonded quinone complex [2], and the structure was not fully characterized. To the best of our knowledge, compound **2** is the first palladium complex with the σ-bonded iminoquinone moiety to be isolated.

Results and discussion

The palladium catalyzed reaction of **1** with terminal acetylenes did not give the alkyne-substituted phenothiazinones, and only the deep color of **1** disappeared within 1 h. The ^1H NMR spectrum of the reaction mixture indicates that **1** had undergone reduction to 3-hydroxy-4-iodophenothiazine. Therefore, it was concluded that terminal acetylenes are oxidized to diacetylenes by iminoquinone in the presence of Pd^{II} and CuI.

The palladium-complex, **2**, was obtained from the reaction of equimolar amounts of the iodo-compound, **1**, and $Pd(PPh_3)_4$ in benzene, in 81% yield. The ^{13}C $\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ showed three triplets due to the coupling with two ^{31}P nuclei. The lowest field signal was assigned to the carbonyl carbon (184.7 ppm, J 2.5 Hz). The triplets at δ 164.0 and 136.1 ppm were assignable to C-4 and C-4a, respectively. The signal from the carbon (C-4) bonded to the palladium atom, was shifted 44 ppm downfield compared to that from 3*H*-phenothiazin-3-one. A similar deshielding effect on a palladium substituent was observed for iodophenylbis(triethylphosphine)palladium(II) [3]. These NMR parameters clearly indicate the σ-bonded structure of the iminoquinone complex. In the ^{31}P $\{^1H\}$ NMR spectrum one singlet was observed for the two triphenylphosphine ligands. The ^1H NMR spectrum showed an AB quartet (δ 6.458 and 5.901, J 9.6 Hz), which was assigned to the olefinic protons. From the comparison of the chemical shifts with those of the corresponding protons of 3*H*-phenothiazin-3-one (δ 7.611 and 6.928 ppm), it was clear that the chemical shifts of the olefinic protons in **2** are affected by the magnetic anisotropy of the aromatic rings of the triphenylphosphine ligands.



(2) (3) (4)

These spectroscopic properties suggest a square planar structure for the complex, the two triphenylphosphine ligands are in a *trans* configuration, and the plane of the phenothiazinone moiety bisects the plane of the complex.

Analogous treatment of 6-iodo-5*H*-benzo[*a*]phenothiazin-5-one (**3**) with $Pd(PPh_3)_4$ gave the palladium complex (**4**) as red needles in 75% yield.

Some 5*H*-benzo[*a*]phenothiazinones are magenta dyes [4]. The electronic absorption spectra of the phenothiazinones consist of six bands in the 220–600 nm region. In the spectra of the palladium complexes, the lowest-energy transition bands are shifted to longer wavelength by ca. 40–50 nm, and the positions of the remaining bands vary only slightly with palladium substituents.

Experimental

All reactions were carried out under nitrogen. ^1H (270 MHz), ^{13}C (67.9 MHz), and ^{31}P (109.4 MHz) NMR spectra were recorded on a JEOL GX-270 spectrometer. Infrared spectra were recorded on a JASCO IRA-1 spectrometer. Electronic spectra were measured on a Shimadzu UV-300 spectrophotometer.

Starting materials

The iodophenothiazinones **1** and **3** were prepared from the corresponding phenothiazinones by iodination with *N*-iodosuccinimide in acetonitrile. The ^1H NMR spectra of the iodo compounds are consistent with published spectra [5,6]. $Pd(PPh_3)_4$ was purchased from Aldrich Chemical Co.

Dimerization of phenylacetylene

A mixture of phenylacetylene (210 mg 2.1 mmol), **1** (170 mg, 0.5 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (5 mg, 0.026 mmol) in *N*-methylpiperidine (5 ml) was stirred at room temperature for 12 h. After removal of the solvent, the residue was triturated with ether. The ether layer was washed with hydrochloric acid (pH 4) and dried over Na_2SO_4. Evaporation of the solvent, and chromatography on silica gel (hexane solvent) gave 1,4-diphenyl-1,3-butadiyne (152 mg, 0.75 mmol). The ^1H NMR, MS and IR spectra were identical with those of authentic material. A trace amount of the palladium complex **2** was separated from the ether-insoluble fraction by column chromatography. Its ^1H NMR spectrum was identical with that of the authentic sample described below.

trans-Iodo(3H-phenothiazin-3-one-4-yl)bis(triphenylphosphine)palladium(II)

A solution of the iodo-compound **1** (68 mg, 0.2 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) in benzene (10 ml) was heated under reflux for 12 h. After cooling, the reaction mixture was purified by passing it through a short silica gel column. Elution of a violet band with dichloromethane followed by recrystallization from dichloromethane/hexane gave the complex (158 mg, 81%) as dark violet microcrystals. Anal. Found: C, 55.97; H, 3.55; P, 5.81. $C_{48}H_{36}INOP_2PdS \cdot CH_2Cl_2$ calcd.: C, 55.78; H, 3.63; P, 5.87%. The presence of the solvating dichloromethane was confirmed by ^1H NMR spectroscopy. IR(KBr) ν(CO) 1605 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.458 and 5.901 (AB quartet, 2H, J 9.6 Hz), 7.21–7.31 (m, 21H), 7.58 (m, 1H), 7.71–7.78 (m, 12H); ^{13}C {^1H} NMR ($CDCl_3$/TMS) δ 124.6, 125.1, 126.8, 127.6 (t, J 5.1 Hz, *m*-C of Ph), 129.6, 130.2 (*p*-C of Ph, 131.7 (t, J 24.3 Hz, *ipso*-C of Ph), 132.2, 134.4, 135.0 (t, J 6.4 Hz, *o*-C of Ph), 136.1 (t, J 4.7 Hz, C-4a), 137.4, 139.7, 146.3, 164.0 (t, J 4.7 Hz, C-4) 184.7 (t, J 2.5 Hz, C-3); ^{31}P {^1H} NMR ($CDCl_3$/external 85% H_3PO_4) δ 24.0; EPS (CH_2Cl_2) λ_{max} 540 nm (log ϵ, 3.71), 380 (sh, 3.89), 360 (sh, 4.08), 320 (sh, 4.21), 276 (4.58), 235 (4.74).

trans-Iodo(5H-benzo[a]phenothiazin-5-one-6-yl)bis(triphenylphosphine)palladium(II)

Analogous treatment of 6-iodo-5*H*-benzo[a]phenothiazin-5-one (**3**) with Pd $(PPh_3)_4$ gave the palladium complex **4** as red needles in 75% yield. Anal. Found C, 60.98; H, 3.65; P, 5.81. $C_{52}H_{38}INOP_2PdS$ calcd.: C, 61.22; H, 3.75; P, 6.07%. IR (KBr) ν(C=O) 1600 cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.15 (m, 18H), 7.25–7.29 (m, 3H), 7.35 (m, 1H), 7.42 (m, 1H), 7.62–7.65 (m, 2H), 7.75–7.78 (m, 12H), 8.28 (m, 1H);

^{13}C {^1H} NMR ($CDCl_3$) δ 124.2, 125.0, 126.7, 127.5 (t, J 5.1 Hz, *m*-C of Ph), 128.4, 128.6, 128.7, 129.1, 130.0(*p*-C of Ph), 131.6 (t, J 24.1 Hz, *ipso*-C of Ph), 131.7, 132.1, 133.1, 133.9, 134.9 (t J 6.4 Hz, *o*-C of Ph), 138.7 (t, J 4.7 Hz, C-6a), 139.3, 144.6, 166.0 (t, J 4.2 Hz, C-6), 182.3 (t, J 2.3 Hz, C-5); ^{31}P {^1H} NMR ($CDCl_3$/external 85% H_3PO_4) δ 23.9; EPS(CH_2Cl_2) λ_{max} 520 nm (log ϵ, 3.85), 380 (sh, 3.94), 360 (sh, 4.12), 328 (4.30), 262 (4.70), 238 (4.77).

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