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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

The palladium(II) complexes trans-\([\text{PdCl}(L)(\text{PPh}_3)_2]\), 5, and cis-\([\text{PdI}_2(L)\text{PPh}_3]\), 7, (L = benzoxazol-2-ylidene) have been synthesized by treatment of the complexes trans-\([\text{PdX}_2(\text{PPh}_3)_2]\) (4: X = Cl, 6: X = I) with 2-(trimethylsiloxy)phenyl isocyanide 1, and subsequent hydrolysis of the Si-O bond. The crystal structures of 5 and 7 were established by X-ray diffraction. NMR and IR studies indicate, that the unexpected cis-configuration of 7 obtained from trans-\([\text{PdI}_2(\text{PPh}_3)_2]\) is not the result of a solution equilibrium between the cis- and the trans-isomers.

Key words: Carbene Complexes, Palladium, Crystal Structures

Introduction

We have reported that complexes with a coordinated 2-(trimethylsiloxy)phenyl isocyanide ligand (A) react after hydrolytic O-SiMe₃ bond cleavage to give a mixture of products containing either the 2-hydroxyphenyl isocyanide ligand (B) or a benzoxazol-2-ylidene ligand (C) (Scheme 1). The reaction A → B/C has been studied at various metal centers like Cr [1], W [2], Re [3], Pd [4], and Fe [5] and non-metal centers [6] and has been reviewed [7]. The equilibrium between the isocyanide complex B and the carbene complex C resides on the isocyanide side for electron-rich complex fragments MLₓ, where the isocyanide carbon atom is deactivated for an intramolecular nucleophilic attack by the hydroxyl oxygen atom by \((d \rightarrow \pi^*)\) backbonding. However, complexes of type B are spontaneously converted into type C if MLₓ is electron-poor [3]. The equilibrium between B and C can always be shifted to the carbene complex if the electronically disfavoured cyclization reaction is initiated by deprotonation of the hydroxyl function in B, thereby enhancing its nucleophilicity, and if the intermediate anionic ylide in D is subsequently alkylated to give the N-alkylated carbene complex E [8]. Species with the anionic ylide ligand like in D have been isolated [9] and additional methods for shifting the equilibrium between B and C have also been reported [1, 10]. More recently this type of carbene synthesis from \(\beta\)-functional phenyl isocyanides has been extended to include 2-aminophenyl isocyanide, thus leading to complexes with NH,NH heterocyclic carbene ligands [11, 12]. The N-alkylation of cationic, square-planar tetra (benzoxazol-2-ylidene) complexes of palladium(II) and platinum(II) (Scheme 2) proved difficult. For example, attempts to deprotonate complexes of type F.
lead to complexes with both protonated and unprotonated ylidene ligands [4], which are insoluble in all organic solvents, and the subsequent N-alkylation is therefore not possible.

In this contribution we report on attempts to N-alkylate the known dicarbene complex 3 [4] obtained by intramolecular cyclization from the diisocyanide complex 2 [13] (Scheme 3). In addition, we present the preparation of the palladium complexes trans-[PdCl(L)(PPh3)2]Cl 5 and cis-[PdI2(L)PPh3] 7 (L = benzoxazol-2-ylidene) containing only one ylidene ligand (Scheme 3).

Results and Discussion

Alkylation of trans-diiodo-bis(benzoxazol-2-ylidene)palladium(II) (3)

The reaction of PdI2 with an excess of 2-(trimethylsiloxy)phenyl isocyanide and subsequent O-SiMe3 bond hydrolysis in the presence of a catalytic amount of nBu4NF yields the neutral complex trans-diiodo-bis(benzoxazol-2-ylidene)palladium(II) 3 [4] (Scheme 3). The N-alkylation of such coordinated benzoxazol-2-ylidenes has been described [1, 2, 5, 7, 10]. In analogy to the described methods, experiments were carried out to deprotonate complex 3 with various bases such as KOtBu or Et3N in DMF. Whilst evidence for the deprotonation of 3 could be obtained (for example Et3NH+ was detected in the 1H NMR spectrum upon reaction of 3 with Et3N, and the absorption for ν(NH) at 3200 – 3300 cm⁻¹ was absent in the IR spectrum), no alkylation products could be isolated upon treatment of deprotonated 3 with alkyl halides. Regardless of the method employed for deprotonation/alkylation, all reaction products showed a similar elemental composition and were insoluble in all organic solvents and in water. Elemental analyses indicated the loss of iodine from the reaction products. One possible explanation for this behavior might be a nucleophilic attack of the deprotonated ylidene ligand at a second palladium center. The coordination of deprotonated benzoxazol-2-ylidene ligands at a second metal center via the ring nitrogen atom has been described [10]. As a result of such an attack one would expect loss of coordinated iodine. The resulting product would have an oligomeric structure, which correlates well with the insolubility of the substances which were isolated. This insolubility prevented a further characterization of the reaction products.

In order to prevent the formation of insoluble oligomeric products upon deprotonation of complexes with benzoxazol-2-ylidene ligands we initiated a study to synthesize palladium(II) complexes with only one benzoxazol-2-ylidene ligand. Bulky triphenylphosphine ligands were introduced, which are poor leaving groups and which enhance at the same time the solubility of benzoxazol-2-ylidene complexes.

Reaction of 2-(trimethylsiloxy)phenyl isocyanide (1) with trans-[PdCl2(PPh3)2] (4)

trans-Dichloro-bis(triphenylphosphine)palladium(II) 4 was synthesized according to a method described in [14] from PdCl2 and PPh3 in acetonitrile. The 31P NMR spectrum of the product (in CDCl3) showed a singlet at δ = 24.46 ppm. This confirms that only one, namely the trans-isomer was obtained [14]. The reaction of trans-[PdCl2(PPh3)2] with two equivalents of 2-(trimethylsiloxy)phenyl isocyanide in THF at −40 °C and subsequent Si-O hydrolysis gave exclusively the monocarbene complex 5 (Scheme 4).
Fig. 1. Molecular structure of 5 (hydrogen atoms on calculated positions have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd-Cl1 2.3445(12), Pd-P1 2.3523(8), Pd-P2 2.3467(8), Pd-C1 1.961(2), O-C1 1.355(3), O-C2 1.405(3), N-C1 1.319(3), N-C3 1.400(3), C2-C3 1.363(4), C2-C7 1.398(4), C3-C4 1.388(4), N-HN 0.97(4), HN...Cl2 2.04(4) Å; Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), P2-Pd-C1 89.17(6), HN–Cl2 2.02(4); Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), HN–Cl2 2.02(4), Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), HN–Cl2 2.02(4), Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), HN–Cl2 2.02(4), Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), HN–Cl2 2.02(4). The presence of the benzoxazol-2-ylidene ligand in 5 was confirmed by the singlet at δ = 16.95 ppm for the N-H proton in the 1H NMR spectrum. The 31P NMR spectrum measured at low temperature showed just one resonance at δ = 13.84 ppm which clearly indicated that a uniform reaction product was obtained. No indications for a cis/trans isomer equilibrium in solution were found. Since no 31P NMR data for either the cis or the trans isomer have been published, we confirmed the trans configuration for 6 by determination of the lattice constants and space group of its dichloromethane solvate and compared the results with the published data for trans-[PdI2(PPh3)2]*2CH2Cl2 [ref. 15]: a = 11.922 [11.884], b = 20.432 [20.399], c = 8.35 [8.331] Å, β = 95.18 [94.896]°, space group P21/c [P21/c].

The reaction of trans-[PdI2(PPh3)2] with two equivalents of 1 in chloroform at −40 °C and the subsequent Si-O bond cleavage yielded exclusively cis-diodo(benzoxazol–2–ylidene)–(triphenylphosphine) 7.
Fig. 2. Molecular structure of 7 (hydrogen atoms on calculated positions have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd-C1 1.962(5), Pd-P 2.2797(14), Pd-I 2.6500(9), Pd-I 2.6562(9), O-C 1.375(7); dihedral angle between planes made up from N 108.0(4), C3-C2-O 108.3(4), C7-C2-O 127.9(5), C2-C3-C3 111.6(4), Pd-C1-O 121.9(3), Pd-C1-N 130.1(3), O-C1-C1 85.79(13), P-Pd-C1 90.45(13), C1-O-C2 107.9(4), C1-N-P 91.05(4), I1-Pd-C1 177.69(13), I2-Pd-P 171.71(4), I2-Pd-C2-C7 1.367(7), C3-C4 1.375(7); I1-Pd-I2 92.50(3), I1-Pd-I1 1.392(6), N-C1 1.305(6), N-C3 1.394(6), C2-C3 1.364(7), Pd-I1 2.6500(9), Pd-I2 2.6562(9), O-C1 1.346(5), O-C2 1.346(5); the dihedral angle between the two possible stereoisomers. Palladium(II) complexes with benzoxazol-2-ylidene ligands 199

Table 1. Crystal and data collection details for 5 and 7\textsubscript{cis}CH\textsubscript{2}Cl\textsubscript{2}.

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<th>Compound</th>
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<tr>
<td>5CH\textsubscript{2}Cl\textsubscript{2}</td>
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Experimental Section

All experiments were carried out in an argon atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and distilled prior to use. Correct elemental analyses were obtained for all reported compounds using a Vario EL elemental analyzer. NMR spectra were recorded on Bruker AM 250 and Jeol \(\lambda\) 400 instruments. Mass spectra were measured with Finnigan MAT 112 and MAT 711 spectrometers. Ligand 2 and complexes 2 and 3 were prepared according to published methods.

Preparation of trans-dichlorobis(triphenylphosphine)palladium(II). (4): A sample of 299 mg (1.686 mmol) of PdCl\textsubscript{2} was suspended in 40 ml of warm acetonitrile. A solution of 890 mg (3.39 mmol) of triphenylphosphine in 20 ml of acetonitrile was added at room temperature and the mixture was stirred for one hour. The yellow precipitate formed...
was isolated by filtration, washed with small amounts of acetonitrile and dried in vacuo. Yield 1.10 g (1.567 mmol, 93%). \( ^{1}H \) NMR (250 MHz, CDCl\(_3\)): \( \delta = 7.3 - 7.1 \) (m, 22 H, Ar-H), 7.80 (m, 12 H, Ar-H). \( ^{31}P \) NMR (161 MHz, CDCl\(_3\)): \( \delta = 21.18 \). FAB-MS (positive ions, CHCl\(_3\)/nitrophenol): \( m/z = 768(8) + \text{[PdCl(PPh}_3\text{)(L)]}^+ \), 748 (9) + \text{[PdCl(PPh}_3\text{)]}^+, 630 (2) + \text{[Pd(PPh}_3\text{)]}^+, 524 (4) + \text{[PdCl(PPh}_3\text{)]}^+, 489 (16) + \text{[Pd(PPh}_3\text{)]}^+. Suitable crystals were selected and mounted on a CAD-4 diffractometer equipped with a sealed Mo X-ray tube (\( \lambda = 0.71073 \) Å) and a nitrogen cooling device for data collection at 153(2) K. Both structures were solved by standard Patterson and Fourier methods. All non hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms (except HN in 5) were located by Fourier procedures and its positional parameters were refined with isotropic displacement parameters. Selected crystallographic data are listed in Table 1. ORTEP [20] plots are presented in Figures 1 and 2. All calculations were carried out using the SHELX-97 [21] programs.

**Acknowledgement**

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 206018 & 206019. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.ac.uk).

