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Synthesis and characterization of electronically varied XCX palladacycles with functional arene groups

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Dedicated to Professor Gerard van Koten in celebration of a scientific career of remarkable breadth.

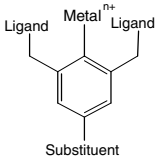
Abstract

X-ray crystallographic studies show that varying the nature of the S-aryl ligands in SCS-Pd(II) pincer complexes and the electronic nature of the aryl substituent *para* to the Pd(II) group in PCP-Pd(II) pincer complexes do not lead to structural changes in these palladacycles that can be correlated with the changing nature of the ligands. While the original C2 symmetry for the S-aryl groups in SCS-Pd(II) pincer complexes seen in the case of the 2,5-bis(thiophenylmethyl)phenylpalladium chloride pincer complex is also seen in other SCS-Pd(II) pincer complexes, the relative stereochemistry of the S-aryl rings is not consistently maintained in 2,5-bis((4-dimethylamino-thiophenyl)methyl)-phenylpalladium chloride.

Keywords: Pincer complexes; Palladacycles; Structure; Catalysis; Synthesis

1. Introduction

Pincer-type transition metal complexes like **1** containing 2,6-disubstituted arenes rings with a σ-bonded transition metal bonded to C1 of the substituted arene are by now well-known species [1–6]. These complexes are interesting as versatile examples of stable σ-bonded organometallic derivatives and can be prepared using a variety of different metals. Such complexes have useful applications as sensors [2,7], in materials chemistry [8–10], and in catalysis as catalysts or pre-catalysts [1,3–6,11–15]. Our interests in homogeneous catalysis and the many diverse examples, where pincer complexes facilitate Kharasch couplings [16], C–H activation [4,5,17], and various cross-coupling chemistry [11,12,18,19] originally attracted our attention to these species. This interest was heightened by the many successful examples, where pincer complexes were attached to dendrimers [20,21] as this chemistry suggested that pincer complexes could similarly be attached to linear polymers. Finally, our interest in palladacycles in particular was excited by a report by Milstein describing PCP-Pd(II) species that could be used in cross-coupling chemistry in air at elevated temperature [18]. While these species exact roles as either catalysts or pre-catalysts in various reactions are not always understood [12–15], their interesting chemistry, their high stability, and the structural diversity inherent in the pincer ligand framework of these palladacycles makes them a subject of continuing interest.



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As part of a broader program aimed at developing recyclable catalysts on soluble polymers [22,23], we have

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explored the synthesis of these complexes, preparing and structurally characterizing a series of SCS- and PCP-type Pd(II) complexes like **1** that contain a *para*-substituent to immobilize a preformed metal complex onto a support. An advantage of this approach is that we can fully structurally characterize the complexes before immobilization using X-ray crystallography. Here we describe some of our work detailing the synthesis and structural details of a selection of various SCS-Pd(II) and PCP-Pd(II) complexes like **1**. The ultimate goal of these studies was to eventually bind these complexes to soluble polymer and use them in catalysis and we have previously described that approach in a number of different studies [24–30]. Below we describe another aspect of these studies where we have prepared and structurally characterized a series of SCS-Pd(II) pincer complexes to study the effects of electronically varying S-aryl ligands on structure and the Pd(II) environment. We also prepared a series of PCP-Pd(II) complexes and structurally characterized them to probe how the electronic nature of substituents *para* to the σ-bonded Pd(II) species effect the structure of PCP palladacycles.

2. Experimental

2.1. General procedures

Reagents and solvents were obtained from commercial sources and were generally used without further purification. ^{1}H NMR spectra were recorded on Varian spectrometers at 300 or 500 MHz. Chemical shifts are reported in ppm using hexamethyldisiloxane (HMDS, 0.055 ppm) as the internal standard. ^{13}C NMR spectra were recorded at 75 or 125 MHz with $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5 ppm) as the internal reference. Infrared spectra were recorded as thin films between NaCl plates or as pressed KBr pellets using a Mattson Galaxy 4021 FT-IR spectrometer. Crystallographic data were collected on a Bruker SMART 1000 X-ray three circle diffractometer and rendered using Ortep for Windows. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and were uncorrected.

2.2. Synthesis of N-acetyl-3,5-bis((p-dimethylaminophenyl)-thiomethyl)aniline (*6b*)

A 200-mL flask and attached condenser was purged with nitrogen. Acetone (50 mL) was bubbled through with nitrogen for 15 min. Dimethylaminothiophenol (590 mg, 3.85 mmol), K_2CO_3 (604 mg, 4.38 mmol), and bis(benzyl chloride) (**5**) (407 mg, 1.75 mmol) were combined in the 200 mL flask and dissolved in 100 mL acetone. The reaction was protected from light and refluxed for 48 h. The reaction was filtered and the solvent removed. The residue was dissolved in chloroform and washed with water and brine. The solvent was evaporated and the residue purified by chromatography on silica gel (ethyl acetate: CH_2Cl_2, 1:9) to yield 574 mg (70%) of a white solid: m.p. 115–116.5 °C; ^{1}H NMR (DMSO-d^6) 1.99 (s, 3H), 2.83 (s, 12H), 3.90 (s, 4H), 6.60 (dd, 4H), 6.78 (s, 1H), 7.17 (dd, 4H), 7.39 (s, 2H), 9.84 (s, 1H); ^{13}C NMR (DMSO-d^6) 24.0, 39.9, 40.4, 112.7, 117.8, 119.8, 124.1, 133.2, 138.6, 139.2, 149.7, 168.2; IR (KBr, cm^{-1}) 3292, 1664, 1594; HRMS (*m*/*z*) [$M + H^+$] Calcd. for $C_{24}H_{21}O_5NS_2$, 466.1987; Found, 466.1984.

2.3. 4-N-Acetyl-3,5-bis((p-dimethylaminophenyl)-thiomethyl)phenylpalladium trifluoroacetate (*10b*)

In a 50-mL round-bottomed flask, dimethyl amino SCS ligand **6b** (100 mg, 0.215 mmol) was dissolved in 10 mL acetone. $Pd(TFA)_2$ (75 mg, 0.225 mmol) was dissolved in 10 mL acetone and added to the reaction via pipette. The reaction stirred at room temperature for 4 h. The reaction was filtered, the solvent removed and the resulting brownish-red solid dried under vacuum (150 mg > 99%): m.p. 185 °C (dec.); ^{1}H NMR (DMSO-d^6) 1.99 (s, 3H), 2.95 (s, 12H), 4.6 (s, 4H), 6.78 (dd, 4H), 7.20 (s, 2H), 7.66 (dd, 4H), 9.83 (s, 1H); ^{13}C NMR (DMSO-d^6) 24.6, 40.4, 52.1, 113.2, 114.2, 115.8, 134.4, 137.5, 150.5, 152.2, 168.9; HRMS (*m*/*z*) (the spectrum was obtained using a dilute acetic acid solution and compound was detected with an acetate ligand) [$M + H_2O + H^+$] Calcd. for $C_{28}H_{36}O_4N_3S_2Pd$, 648.1182; Found, 648.1085. Crystals were grown by the slow diffusion of hexane into an acetone solution of **10b**.

2.4. Synthesis of N-Acetyl-3,5-bis(dicyclopentylphosphinomethyl)aniline-borane (*26*)

A solution of 4.0 g (21.76 mmol) of dicyclopentylphosphine-borane in 40 mL of freshly distilled THF under N_2 was prepared and then cooled to −78 °C. Slow addition of 20 mL of 1.6 M *n*-BuLi using a syringe formed a solution of the lithiated phosphine after stirring 2 h at −78 °C and then additional 2 h at room temperature. The reaction solution was again cooled down to −78 °C and 10 mL of a THF solution of 2.32 g (10 mmol) of *N*-acetyl-3,5-bis(chloromethyl)aniline was added using a syringe. After 2 h of stirring at −78°, the reaction mixture was allowed to warm to 25 °C and to continue stirring for 10 h. The solution was then concentrated to ca. 1/3 of its original volume. A 100 mL of CH_2Cl_2 was added and the solution was washed with 2 N NaOH (10 mL) and brine (2 × 30 mL), dried over $MaSO_4$, and the organic solvent was removed at reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc, 1/1) to yield 4.0 g of light yellow, air-stable crystals (76% yield): ^{1}H NMR (300 MHz, $CDCl_3$) 0.23–0.60 (br, m, 6H), 1.55–2.13 (m, 36H), 2.18 (s, 3H), 2.98 (d, J = 11.4 Hz, 4H), 6.91 (s, 1H), 7.26 (s, 1H), 7.38 (s, 1H); ^{31}P NMR ($CDCl_3$) 31.3; ^{13}C NMR ($CDCl_3$) 24.88, 26.10 (d, J = 8.07 Hz), 26.50 (d, J = 9.13 Hz), 28.10 (d, J = 9.05 Hz), 30.88 (d, J = 29.19 Hz), 32.78 (d, J = 33.79 Hz), 119.16, 126.73, 134.67, 137.99, 168.26.