

Proceedings

Preparation and Crystal Structure of Metallated 2,4,6-Trimethylaniline Imines [†]

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Abstract: In a typical condensation reaction, Schiff Base ligands were synthesized from 2,4,6-trimethylaniline and the appropriate aldehydes. Treatment of the ligands with the corresponding palladium salt provided dinuclear cyclometallated compounds with bridging acetate moieties. The X-ray crystal structure analysis carried out was in agreement with the spectroscopic data. Herein we describe the preparation of the complexes; a brief discussion of the crystal structure is also given. The resulting dinuclear palladacycles are suitable for further ligand-exchange processes.

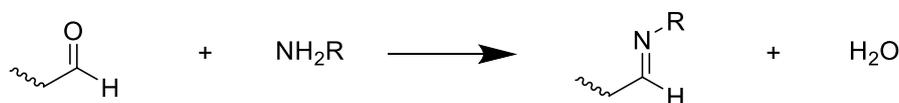
Keywords: Schiff base; aniline; palladacycle

1. Introduction

Schiff bases are compounds prepared by a condensation reaction between a primary amine and a carbonyl group from an aldehyde or a ketone, thus forming an imine bond [1]. These are adequate ligands for the synthesis of palladacycles. Palladacycles derived from N-donor ligands have been extensively studied in the last decade due to their properties and diverse applications [2], being one of the most used tools in organic synthesis [3], as catalysts in the Suzuki-Miyaura reaction [4]; in insertion reactions; or antiviral or antitumor applications.

2. Methods

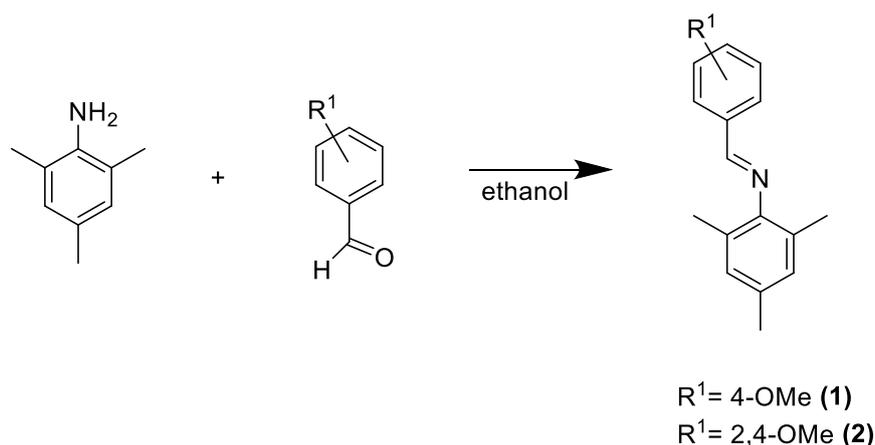
The synthesis of the Schiff bases ligands was carried out using an amine and two types of aldehydes, and the solvent used was ethanol.



Scheme 1. General scheme for the synthesis of a Schiff base.

2.1. Synthesis of (1) and (2)

Two different ligands were synthesized using 2,4,6-trimethylaniline as amine, and 4-methoxybenzaldehyde and 2,4-dimethoxybenzaldehyde to obtain the corresponding compounds (1) and (2), respectively.



Scheme 2. Scheme for the synthesis of ligands (1) and (2).

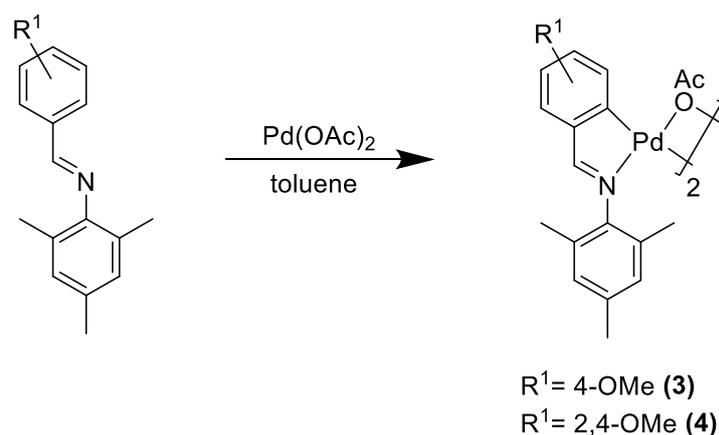
Synthesis: 10 cm³ of ethanol are added to the appropriate amounts amine and the corresponding aldehyde, and the sample was stirred for 3 h at room temperature [5].

1: Yield: 96%. Elemental Anal. Calc.: C 80.06, H 7.56, N 5.53, O 6.32%. Found: C 79.56, H 7.60, N 5.47, O 6.33%. IR (ATR, ν/cm^{-1}): 1633.40 (C=N). ¹H NMR (400 MHz, acetone) δ_{H} (ppm): 8.15 (s, 1H, Hi); 7.88 (da, 2H, H2H6, $N = 7.8$ Hz); 7.03 (da, 2H, H3H5, $N = 7.8$ Hz); 6.83 (s, 2H, H9H11); 3.84 (s, 3H, OMe); 2.21 (s, 3H, CH₃); 2.04 (s, 6H, 2xCH₃).

2: Yield: 92%. Elemental Anal. Calc.: C 76.30, H 7.47, N 4.94, O 11.29%. Found: C 73.25, H 7.38, N 4.76, O 11.31%. IR (ATR, ν/cm^{-1}): 1602.54 (C=N). ¹H NMR (400 MHz, acetone) δ_{H} (ppm): 8.47 (s, 1H, Hi); 8.10 (da, 1H, H6, $N = 8.3$ Hz); 6.81 (s, 2H, H9H11); 6.64 (s, 1H, H3); 6.62 (da, 1H, H5, $N = 8.3$ Hz); 3.86 (s, 6H, 2xOMe); 2.20 (s, 3H, CH₃); 2.04 (s, 6H, 2xCH₃).

2.2. Synthesis of (3) and (4)

Palladium acetate was used as the metallating agent, providing cyclometallated compounds with acetate bridging ligands between two metal centers, with the Schiff base ligands as bidentate [C,N] which resulted in dinuclear compounds.



Scheme 3. Scheme for the synthesis of the cyclometallated compounds (3) and (4).

Schiff bases (1) and (2) and palladium acetate in 1:1 ratio were added in a round bottom flask under nitrogen. Then, dry toluene was added and the reaction was stirred at room temperature for 24 h to obtain the corresponding binuclear compounds (3) and (4).

3. Elemental Anal. Calc.: C 54.62, H 5.07, N 3.35, O 11.49%. Found: C 52.98, H 5.01, N 3.38, O 11.44%. IR (ATR, ν/cm^{-1}): 1610.34 (C=N), 1563.13 $\nu_{\text{as}}(\text{COO})$, 1415.52 $\nu_{\text{s}}(\text{COO})$. ¹H NMR (400 MHz,

acetone) δ (ppm): 7.81 (s, 1H, *H*₁); 7.31 (d, 1H, *H*₂, $^3J(\text{H}_2\text{H}_3) = 8.1$ Hz); 6.84–6.50 (m, 3H, *H*₃*H*₉*H*₁₁); 6.17 (s, 1H, *H*₅); 3.75 (s, 3H, OMe); 2.79 (s, 3H, CH₃); 2.24 (s, 3H, CH₃); 2.06 (s, 3H, CH₃).

4. Elemental Anal. Calc.: C 53.64, H 5.18, N 3.13, O 14.29%. Found: C 52.27, 5.15, N 3.10, O 12.31%. IR (ATR, ν/cm^{-1}): 1587.43 $\nu(\text{C}=\text{N})$, 1558.12 $\nu_{\text{as}}(\text{COO})$, 1420.23 $\nu_{\text{s}}(\text{COO})$. ^1H NMR (400 MHz, acetone) δ (ppm): 7.83 (s, 1H, *H*₁); 7.20 (d, 1H, *H*₂, $^3J(\text{H}_2\text{H}_3) = 7.8$ Hz); 7.14 (d, 1H, *H*₃, $^3J(\text{H}_3\text{H}_2) = 7.8$ Hz); 6.23 (s, 1H, *H*₅); 3.79 (s, 3H, OMe); 3.73 (s, 3H, OMe); 2.80 (s, 3H, CH₃); 2.28 (s, 3H, CH₃); 2.06 (s, 3H, CH₃).

3. Results and Discussion

3.1. Discussion for Compounds (1) and (2)

In the ^1H NMR spectra for compounds (1) and (2), a singlet at lowfield was observed, which corresponds to the imine proton. The signals for *H*₉ and *H*₁₁ appeared as one singlet, integrating for two protons. The signal for the methyl group at C4 appeared as a singlet (3H) slightly overlapping the acetone signal, clearly downfield from the methyl signals of the nitrogen phenyl ring.

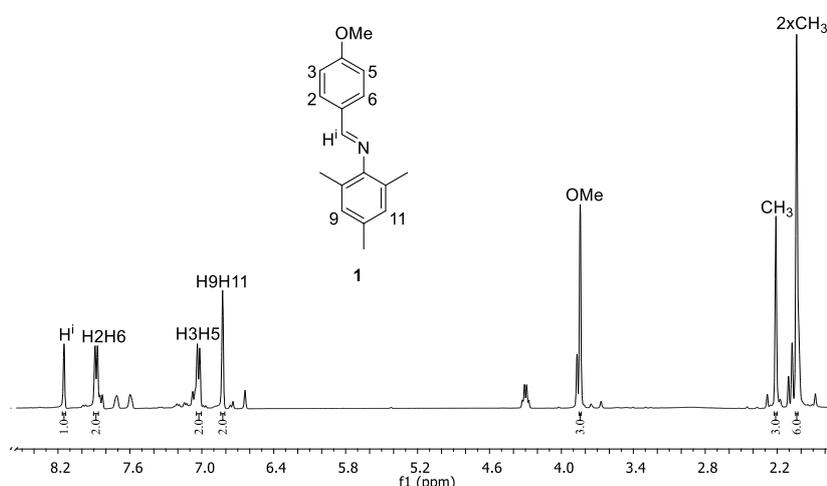


Figure 1. ^1H NMR spectrum (400 MHz, acetone) of the compound (1).

3.2. Discussion for Compounds (3) and (4)

Cyclometallation was confirmed by the absence of the *H*₆ proton resonance as compared to compounds (1) and (2), thus modifying the multiplicity of the *H*₅ proton. The signal for the *HC=N* proton was also highfield shifted as compared to the parent ligand. In the spectrum of compound 3, the signals for the *H*₃, *H*₉ and *H*₁₁ signals appeared as a multiplets in the range 6.84–6.50 ppm. Three singlets were assigned to the three inequivalent methyl groups. The presence of only one singlet *ca.* 2.4 ppm was in agreement with coordination of the acetate ligand as a bridging ligand between the two metal centers in an *anti* arrangement.

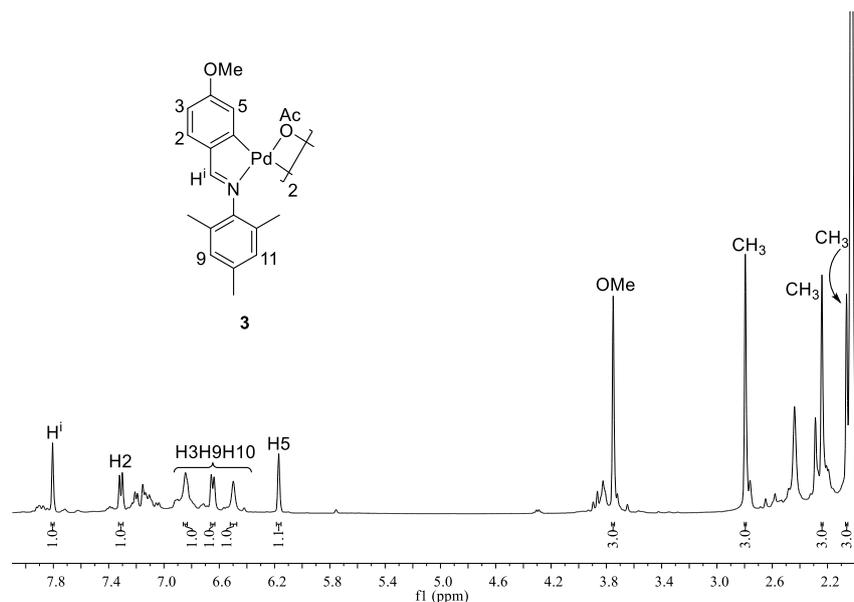


Figure 2. ^1H NMR spectrum (400 MHz, acetone) of the compound (3).

4. X-ray Discussion

The bond lengths and angles are within the expected values. The structures show the typical open-book arrangement, with both in the *anti* form, confirming the spectroscopic results.

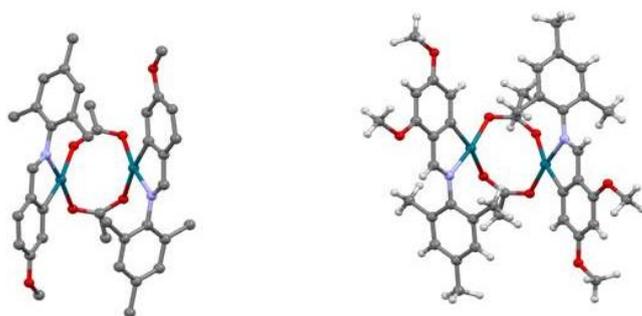


Figure 3. X-ray structure of the compounds (3) and (4).

There seems to be some type of interaction as is shown by the distance between the methyl group and the phenyl ring, 3.392\AA . This would be in agreement with the presence of inequivalent methyl groups on the *N-Ph* ring. [6]

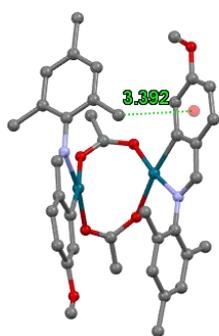


Figure 4. X-ray analysis of the compound (3).

The angles at palladium are close to 90° , with allowance for the somewhat reduced C-Pd-N angle, 81.72° (3) and 81.89° (4), consequent upon chelation of the imine ligand. The sum of angles about palladium is *ca.* 360° .

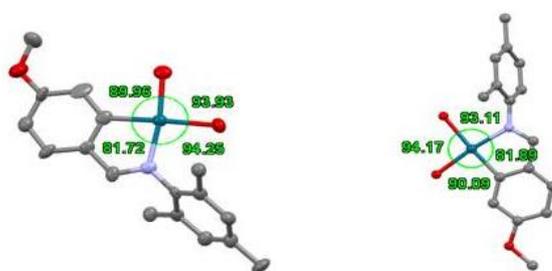


Figure 5. Angles around the two metal atoms of compound (3).

5. Conclusions

Schiff bases ligands were successfully synthesized. They yield dinuclear cyclometallated complexes with the ligands as bidentate [C,N] with acetate bridging ligands between the two metal centers. The X-ray crystal structural analysis shows that the complexes are in the *anti* arrangement.

Conflicts of Interest: The authors declare no conflict of interest.

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