

Synthesis and characterization of iminophosphorane palladacycles[†]

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Abstract: Herein we report on the synthesis and characterization of bisiminophosphoranes as potential tetradentate ligands. Treatment of the latter with palladium acetate gives tetranuclear structures with two ligand moieties linked by acetate-bridging ligands. The addition of ddp_m (4 equivalents) provides doubly metallated structures where the phosphine acts as a bidentate chelating ligand.

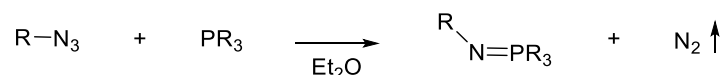
Keywords: Palladacycles; Iminophosphoranes; Phosphine.

1. Introduction

Recently research on palladacycles has come upon new findings employing tetradentate [C,N:C,N] ligands derived from Schiff bases [1]. The related iminophosphoranes are also adequate ligands for the synthesis of palladacycles [2]. Thus, the chemistry of iminophosphoranes seeks new compounds with reactivity and / or relevant structural characteristics which could be similar to the imine palladium complexes.

2. Methods

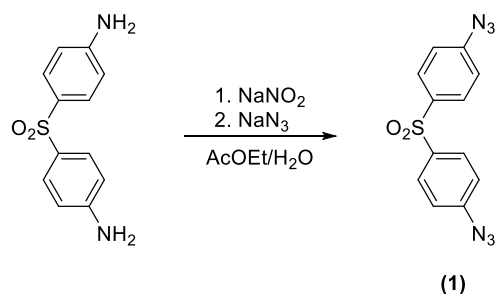
Synthesis of the iminophosphorane ligands were carried out by the Staudinger method using a mixture of an azide compound and a phosphine [3].



Scheme 1. General scheme for iminophosphorane synthesis by Staudinger method

2.1. Synthesis of (1)

First the corresponding azide compound was isolated by synthesis from the diamino compound using 4,4'-diaminodiphenylsulfone as is shown in Scheme 2.

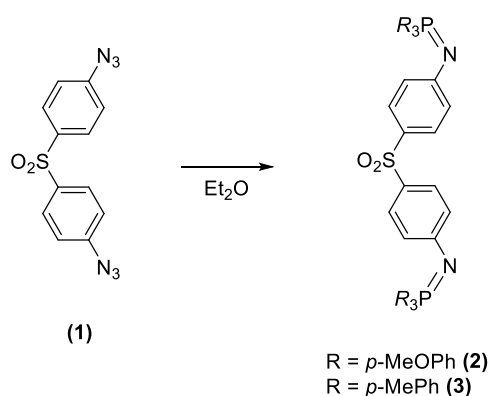


Scheme 2. General scheme for the synthesis of the diazide compound (1)

The synthesis of (1) was carried out in two steps: sodium nitrite was added and then the azide group was incorporated. The azide compounds are susceptible to spontaneous decomposition at relatively low temperatures, therefore these reactions were carried out below 5 °C.

2.2. Synthesis of (2) and (3)

Two different ligands were synthesized from azide (1) by the Staudinger method employing two different phosphines (Scheme 3)

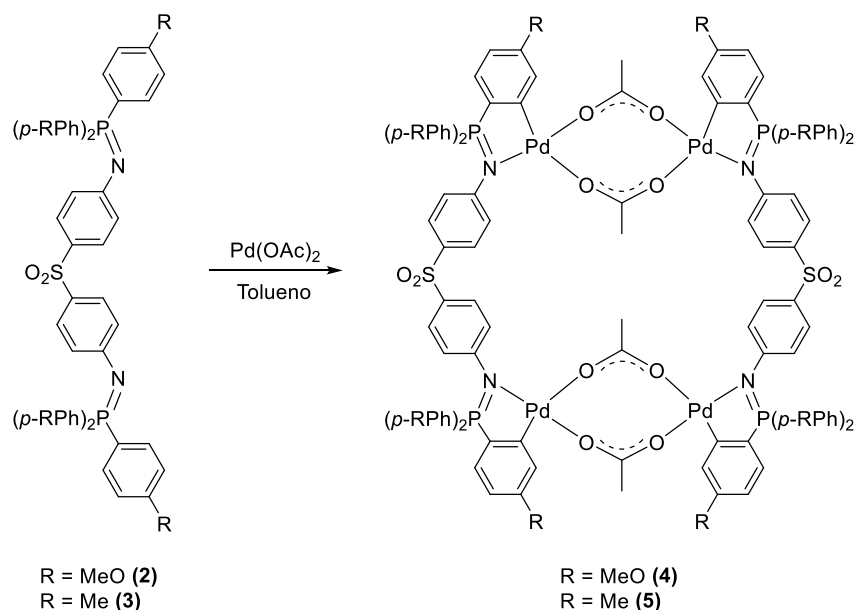


Scheme 3. General scheme for the synthesis of ligands (2) and (3)

Azide (1) and the corresponding phosphine (tris(4-methoxyphenyl)phosphine or tri(*p*-tolyl)phosphine) in 1: 2 ratio were added in a round bottom flask in ethyl ether to obtain the corresponding compounds (2) and (3) as solids.

2.3. Synthesis of (4) and (5)

Palladium acetate was used as the metallating agent. This method provides cyclometallated compounds with acetate bridging ligands between two metal centers, with the bisiminophosphorane ligands as tetradentate [C,N:C,N] which resulted in tetranuclear compounds.

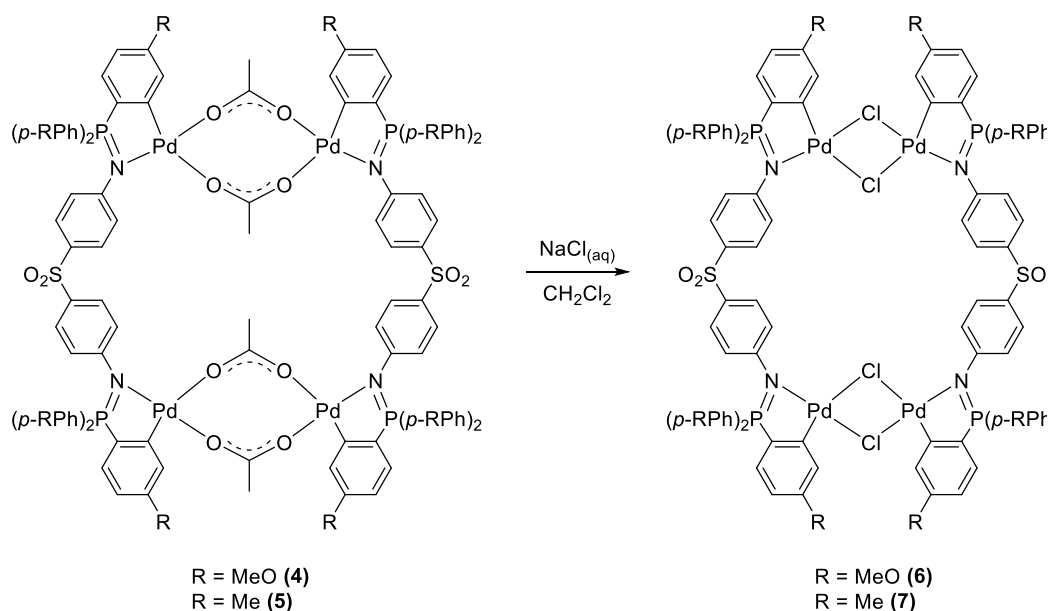


Scheme 4. General scheme for the synthesis of the tetranuclear cyclometallated compounds **(4)** and **(5)**

In a round bottom flask the ligand and palladium acetate (2 Eq) were added in toluene. The products obtained were presented as reddish solids.

2.4. Synthesis of **(6)** and **(7)**

Cyclometallated compounds bearing bridging ligands experiment ligand exchange reactions, in this case acetate-bridging ligands are exchanged for bridging chlorine ligands.

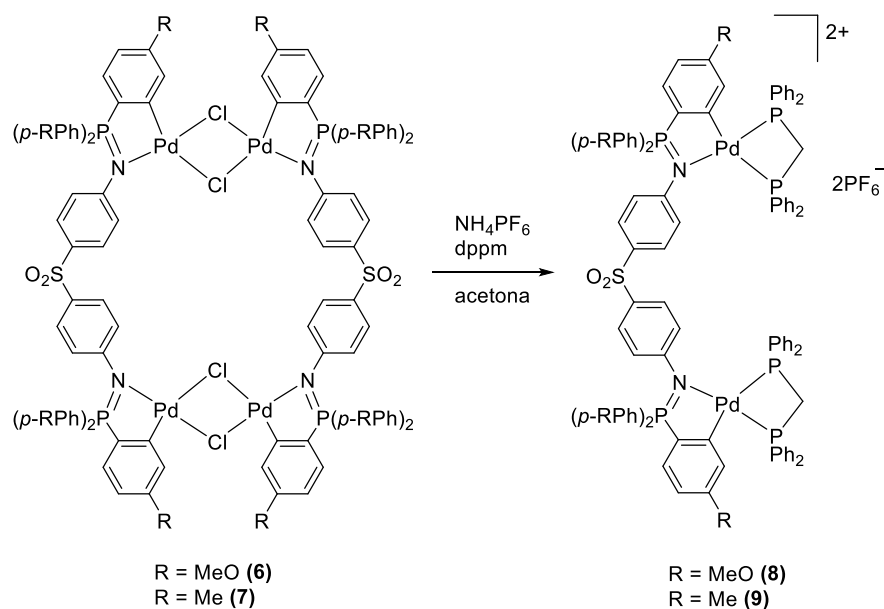


Scheme 5. General scheme for the synthesis of the tetranuclear compounds **(6)** and **(7)**

To compounds **(4)** and **(5)**, as appropriate, in dichloromethane aqueous sodium chloride was added. Subsequently, the organic and aqueous phases were separated and compounds **(6)** or **(7)** were obtained from the organic phase.

2.5. Synthesis of (8) and (9)

Compounds (6) and (7) react with bidentate ligands such as diphosphines to give dinuclear structures bearing one bisiminophosphorane ligand. This behavior differs from that found in the case of the analogous Schiff base compounds.



Scheme 6. General scheme for the synthesis of the tetranuclear compounds (8) and (9)

To compound (6) or (7) in acetone ammonium hexafluorophosphate and the diphosphine dppm were added. The products were obtained as yellow solids in both cases.

3. Results and Discussion

3.1. Discussion for compound (1)

In the ^1H NMR spectra of azide (1) two apparent doublets were observed that correspond to the aromatic system of type AA'BB'.

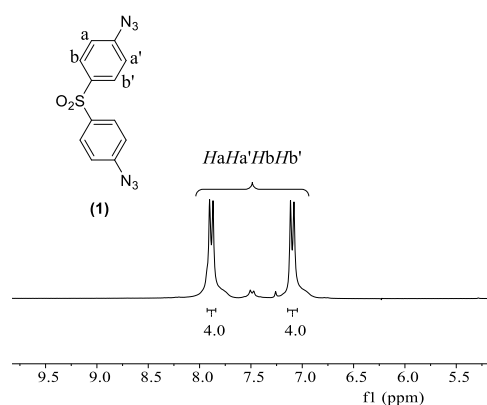


Figure 1. ^1H NMR spectrum (250 MHz, CDCl_3) of the compound (1)

3.2. Discussion for compounds (2) and (3)

In the ^1H NMR spectra of the bisiminophosphorane ligands (2) and (3), two apparent doublets were observed that correspond to the AA'BB' aromatic system and the signals corresponding to the protons of the phosphine rings appear *ca.* 7.7 ppm (H2H6) and *ca.* 7.0 ppm (H3H5).

Signals at 3.8 ppm and for (2) and at 2.4 ppm for (3) were assigned to the MeO and Me groups respectively.

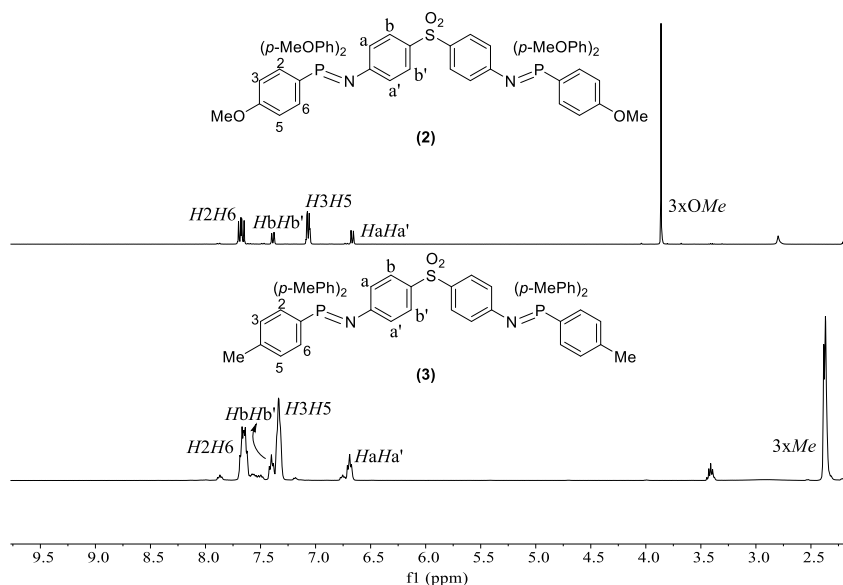


Figure 2. ^1H NMR spectra (400 MHz, acetone- d_6) for compounds (2) and (3)

3.3. Discussion for compounds (4) and (5)

In the ^1H NMR spectra several multiplets *ca.* 6.0–8.0 were assigned to the aromatic protons.

Signals *ca.* 3.7 ppm were assigned to the methoxy groups on the metallated rings and on the phosphine phenyl rings. The OAc and OAc* resonances *ca.* 1.2 ppm were also correctly assigned.

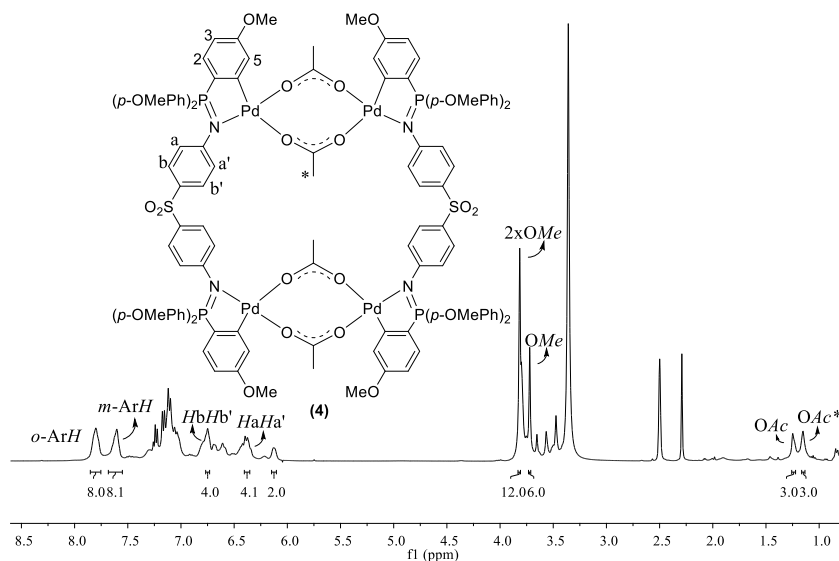
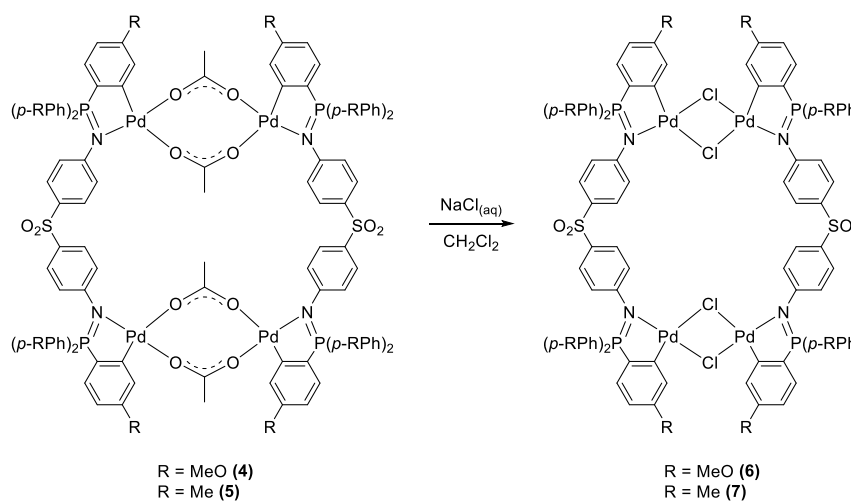


Figure 3. ^1H NMR spectrum (400 MHz, $\text{dms-}d_6$) for compound (4)

3.4. Discussion for compounds (6) and (7)

In the ^1H NMR spectra the resonances could be adequately assigned. The most salient difference with respect to (4) and (5) was the absence of the signals corresponding to the acetate ligands.



Scheme 7. General scheme for the synthesis of compounds (6) and (7)

3.4. Discussion for compounds (8) and (9)

The good solubility of compounds (8) and (9) allows full assignment of the ^1H NMR spectra, inclusive of the diphosphine methylene groups.

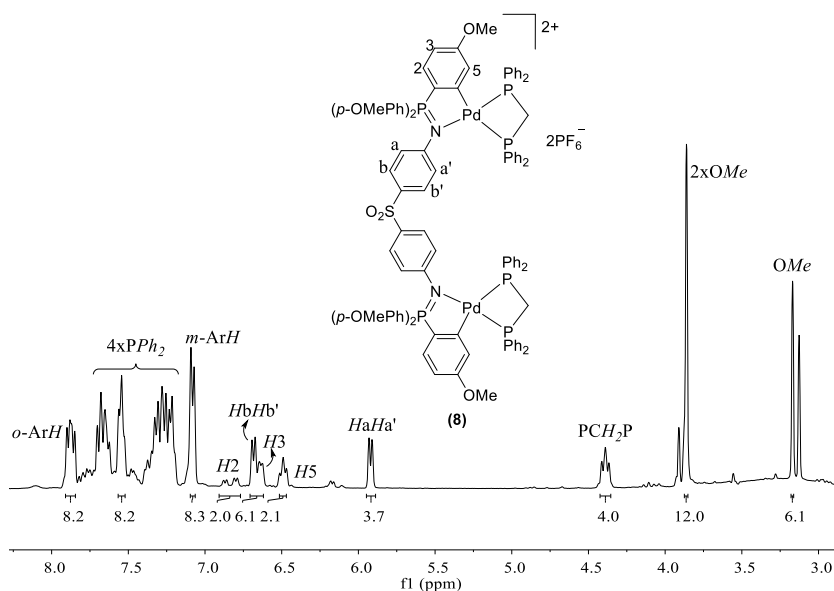


Figure 4. ^1H MR spectrum (400 MHz, acetone- d_6) of the compound (8)

Four signals were observed in the ^{31}P NMR spectra: a doublet *ca.* 50 ppm, P=N; two double doublets *ca.* -10 ppm and -32 ppm for $\text{P}_{\text{trans-N}}$ and $\text{P}_{\text{trans-C}}$ respectively; and that for the PF_6 anion.

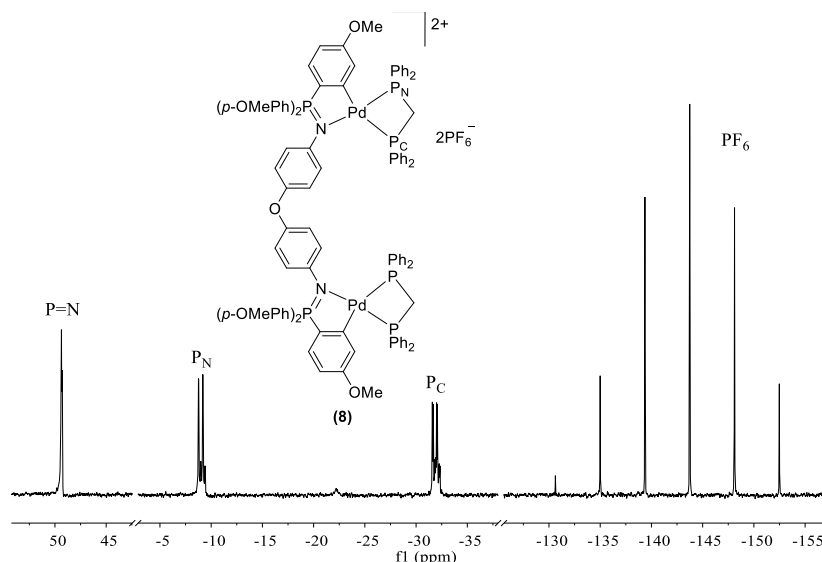


Figure 5. $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (400 MHz, acetone- d_6) for compound (8)

4. Conclusions

- Symmetric bisiminophosphorane ligands could be synthesized by the Staudinger method reaction.
- Bisiminophosphorane ligands provide cyclometallated compounds with tetranuclear structures.
- Cyclometallated compounds derived from bisiminophosphorane ligands undergo ligand exchange reactions.

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

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