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Synthesis of Novel Bisiminophosphorane Palladacycles with Miscellaneous Bidentate Chelating Ligands †

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Abstract: Bisiminophosphorane palladacycles were synthesized efficiently through the cyclometallation process providing tetranuclear palladium species with macrocycle-type structures. The ensuing compounds were reacted with different bidentate ligands in a 1:4 ratio. The results showed that only bimetallic complexes with two chelating ligands were obtained. This puts forward that the chelate effect predominates in this process over the macrocycle effect.

Keywords: palladacycles; bisiminophosphoranes; chelation

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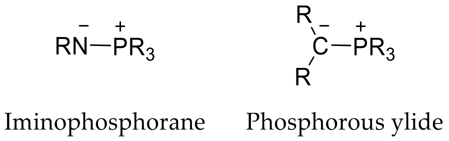
1. Introduction

Bisiminophosphoranes are compounds characterized by having two functional groups of the type P=N; this bond is polarized in a similar way to the case of phosphorus ylides.



Scheme 1. Comparative scheme of an iminophosphorane and a phosphorus ylide.

Due to their similarities with phosphorus ylides, iminophosphoranes are widely used as intermediates in ring formation processes through the aza-Wittig reaction for the synthesis of several products [1–3]. In this case, the formation of new bisiminophosphoranes is studied, those are characterized by having two P=N groups, these groups can be located in three different ways with respect to the skeleton that separates them (**Error! Reference source not found.**).

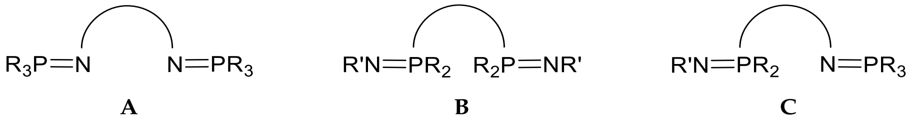
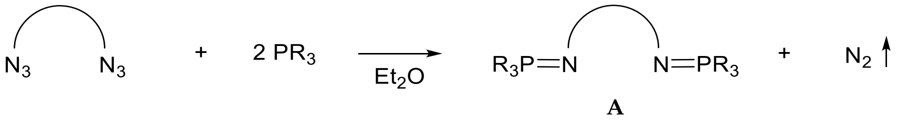


Figure 1. Types of bisiminophosphoranes compounds.

The compounds described in this work belong to type **A**, they are derived from a diamine and two equivalents of the same phosphine, which provides symmetric compounds with the same reactivity in both functional groups.

2. Methods

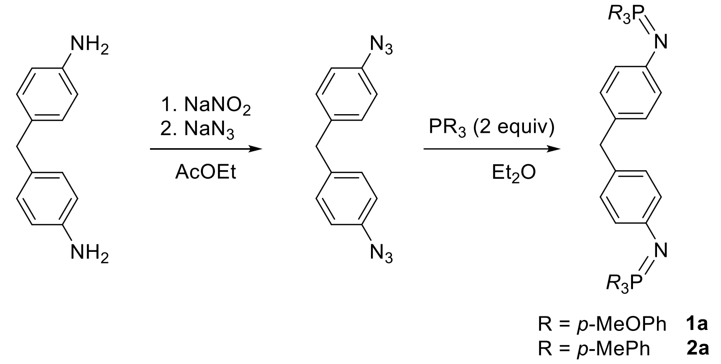
Bisiminophosphoranes were synthetized by using the Staudinger method [4] with a 1:2 mixture of 4,4′-diaminodiphenylmethane and tri(*p*-tolyl)phosphine (**1a**) or tris(4-methoxyphenyl)phosphine (**2a**).



Scheme 2. General scheme for bisiminophosphorane synthesis.

2.1. Synthesis of **1a** *and* **2a**

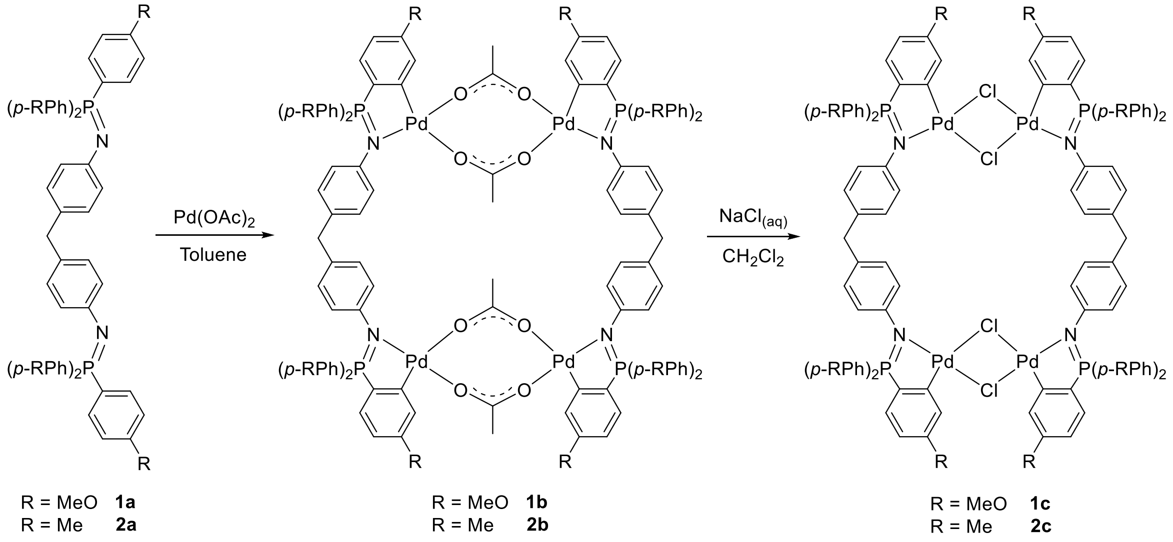
Ligands **1a** and **2a** were synthetized in two consecutive steps, first the formation of the corresponding azide and second the addition of the phosphine. The products were obtained as white solids.



Scheme 3. General scheme for the synthesis of **1a** and **2a**.

2.2. Synthesis of **1b-2b** *and* **1c-2c**

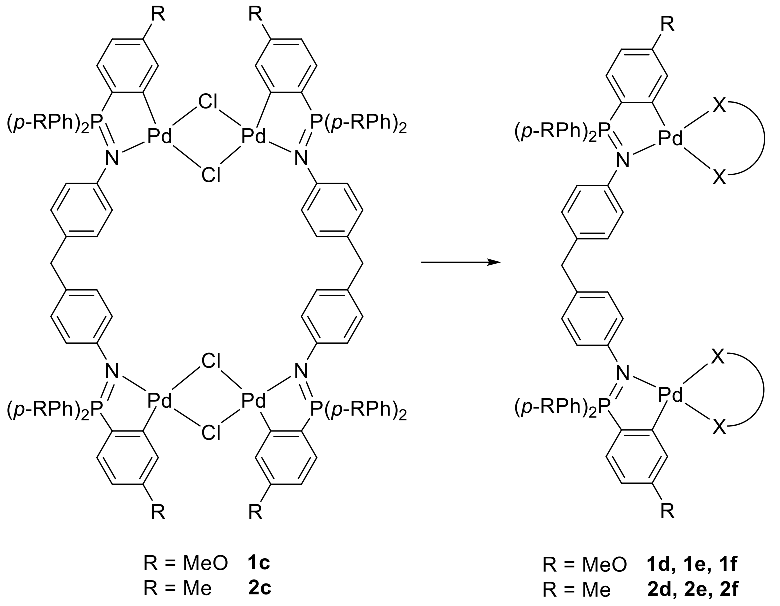
In the cyclometallation process palladium acetate was used and tetranuclear compounds **1b** and **2b** were obtained as red solids. Then an exchange ligand reaction was carried out and the acetate ligand was exchanged by a chloride ligand giving complexes **1c** and **2c**.



Scheme 4. General scheme for the synthesis of the tetranuclear species.

2.3. Synthesis of **1d-2d**, **1e-2e** *and* **1f-2f**

Tetranuclear complexes, **1c-2c**, give dinuclear compounds by reaction with different bidentate ligands in 1:4 ratio. The reaction conditions were acetone, room temperature and NH_4PF_6 (4 equiv) for compounds bearing dppma (**1d-2d**) and dppp (**1e-2e**); and dichloromethane, room temperature and thallium acetylacetonate for **1f-2f** complexes. The products were obtained as yellow solids in all cases.



Scheme 5. General synthesis scheme for compounds with dppma (**1d-2d**), dppp (**1e-2e**) and acac (**1f-2f**).

3. Results and Discussion

3.1. Discussion for Compounds **1a-2a**

^1H NMR and ^{31}P-{^1H} NMR spectra were recorded for compounds **1a-2a.** In the ^1H NMR spectra four signals were observed in the aromatic area, two apparent doublets that correspond to the aa′bb′ protons, and two double doublets corresponding to the phosphine ring protons (7.0 ppm: *H3H5* and 7.7 ppm: *H2H6*). Additionally, two singlets corresponding with the methoxy (**1a**), methyl (**2a**) or the methinic group were observed in the aliphatic region. In the ^{31}P-{^1H} NMR spectra one singlet was observed in both cases ca. 2 ppm.

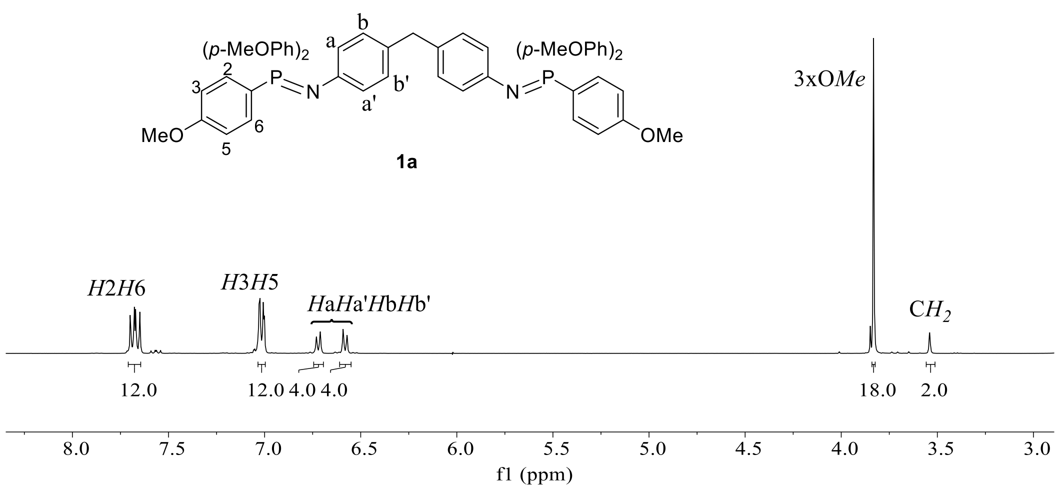


Figure 2. ^1H NMR spectra (400 MHz, acetone-d_6) for compound **1a**.

3.2. *Discussion for Compounds* **1b-2b** *and* **1c-2c**

Numerous signals were observed in the aromatic region in the ^{1}H NMR spectra for compounds **1b-2b** and **1c-2c**. In the aliphatic region the signals corresponding to the methyl and methinic groups could be unequivocally assigned.

On the other hand, more information could be obtained from the ^{31}P-{^{1}H} NMR spectra, one singlet ca. 50 ppm was observed in all cases. This result was consentient with the formation of the cyclometallated product.

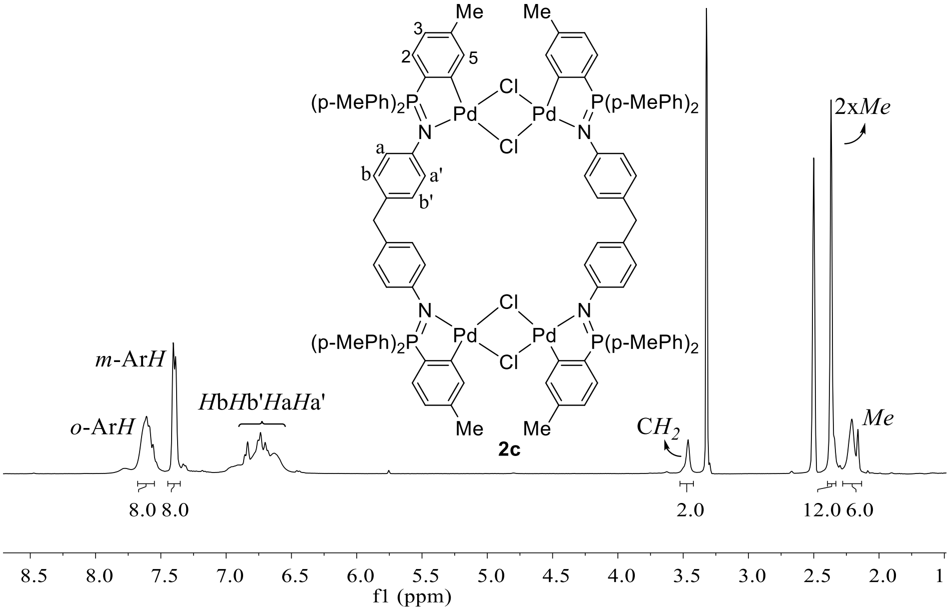


Figure 3. ^{1}H NMR spectra (400 MHz, dmso-d$_6$) for compound **2c**.

3.3. *Discussion for Compounds* **1d-2d**, **1e-2e** *and* **1f-2f**

The ^{1}H NMR spectra for compounds **1d-2d** and **1e-2e** present several multiplets in the aromatic area, in spite of which all signals were assigned. The different signals for the methinic and methyl groups were also assigned.

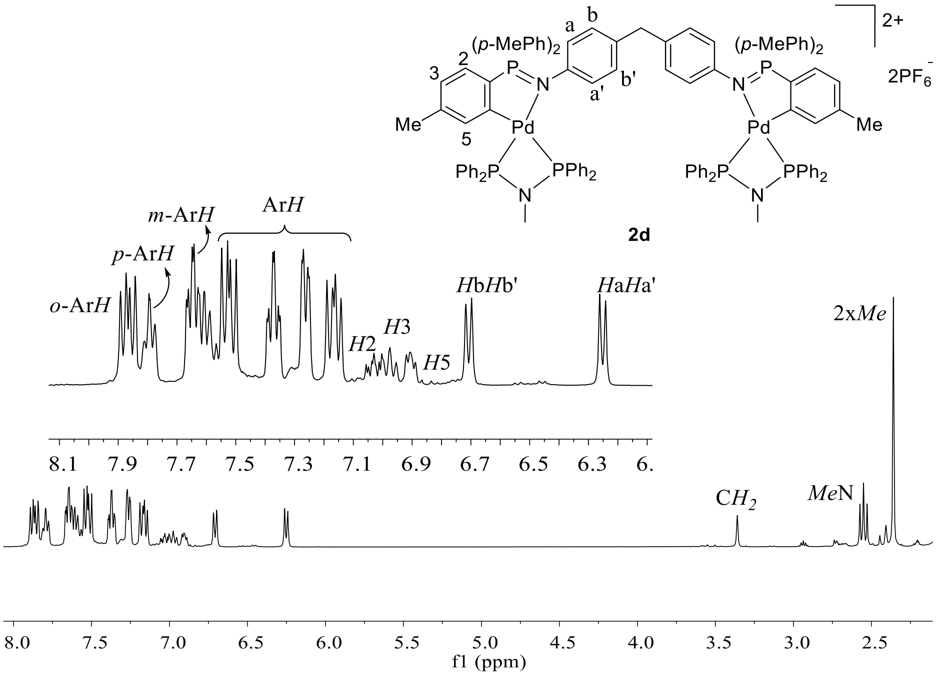


Figure 4. ^{1}H NMR spectra (400 MHz, acetone-d$_6$) for compound **2d**.

Information from the ^{31}P-{^{1}H} NMR spectra allowed to determine the phosphine ligand coordination mode. For the compounds with dppma (**1d-2d**) and with dppp (**1e-2e**) four signals were observed, three double doublets and one septet. Each double doublet corresponds to one phosphorous coupled to the other two remaining ^{31}P nuclei and the septet is related to the hexafluorophosphate ion as is shown in **Error! Reference source not found.**

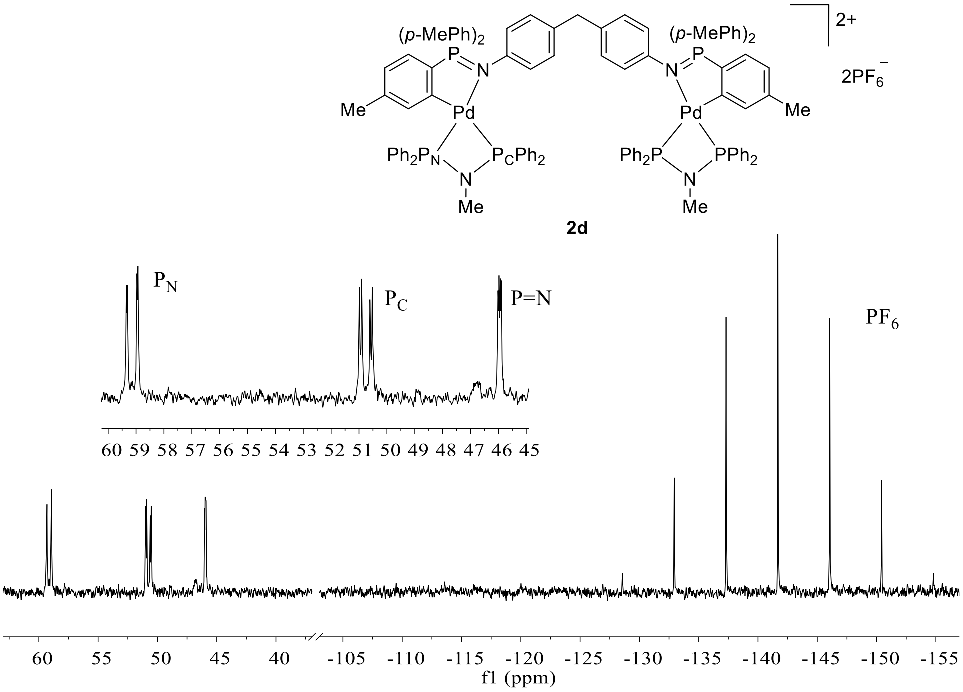


Figure 5. ^{31}P-{^{1}H} NMR spectrum (400 MHz, acetone-d$_6$) for compound **2d**.

A different arrangement was observed for the signal corresponding to the P=N phosphorous nucleus due to the *trans* effect produced in each case. For compounds with dppma (**1d-2d**) signals appeared ca. 50 ppm, however for compounds with dppp (**1e-2e**) the signal related to the phosphorous *trans* position to the nitrogen (P_N) appears ca. 24 ppm and the signal related to the phosphorous *trans* position to the metallated carbon (P_C) is ca. 2 ppm.

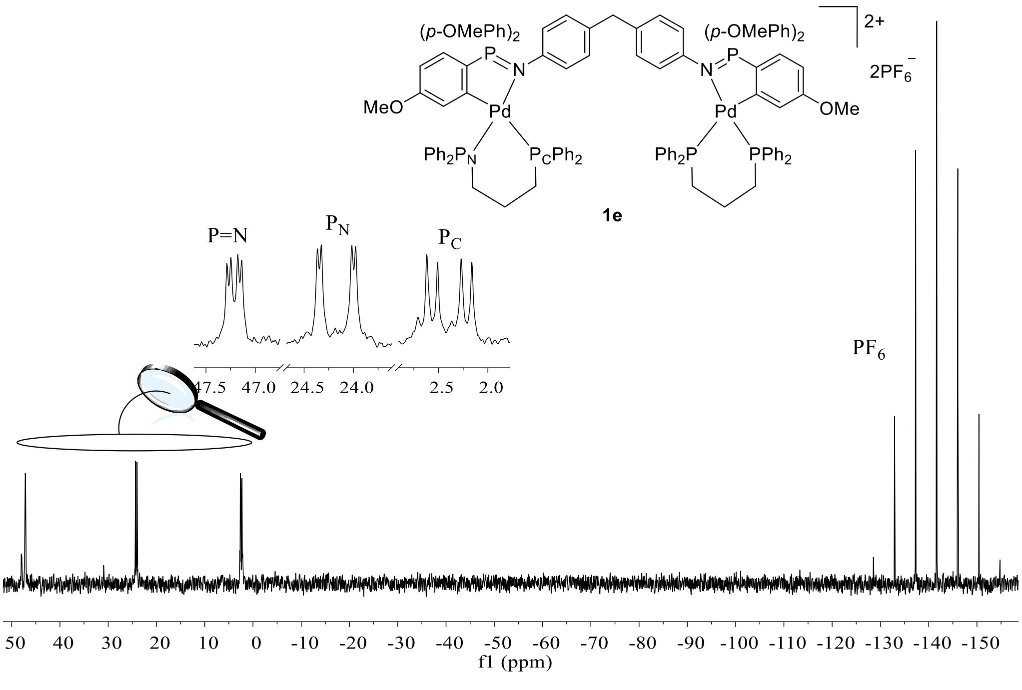


Figure 6. ^{31}P-{^{1}H} NMR spectrum (400 MHz, acetone-d$_6$) for compound **1e**.

The ^{1}H NMR spectra for compounds **1f-2f** is simplified owing to the absence of any phosphine phenyl rings, the signal corresponding to *H*5 could be unequivocally assigned. In the aliphatic area it was possible to observe the different signals for all the methinic and methyl groups.

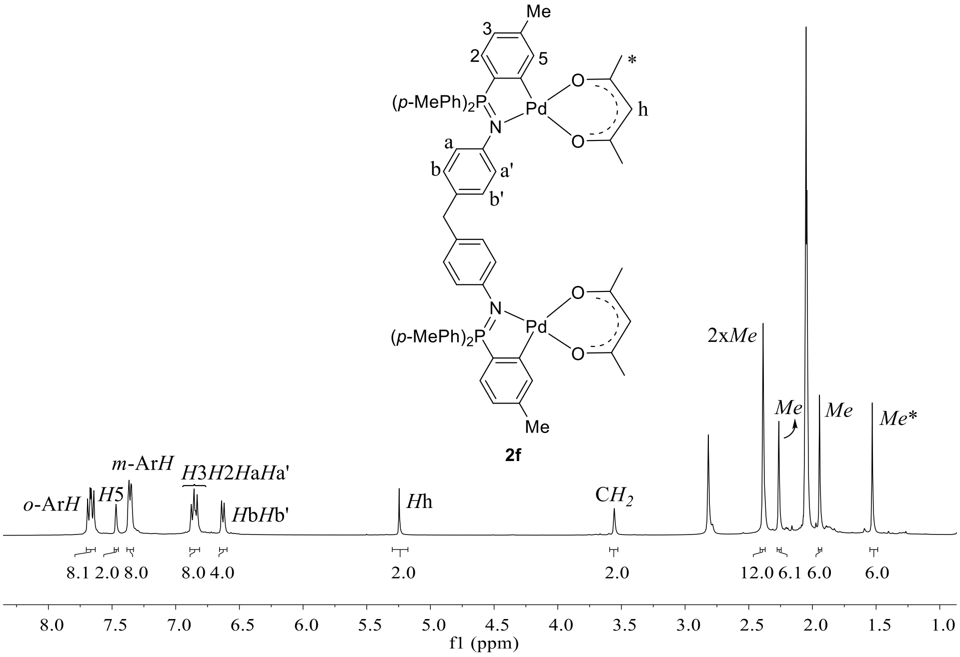


Figure 7. ^{1}H NMR spectra (400 MHz, acetone-d$_6$) for compound **2f**.

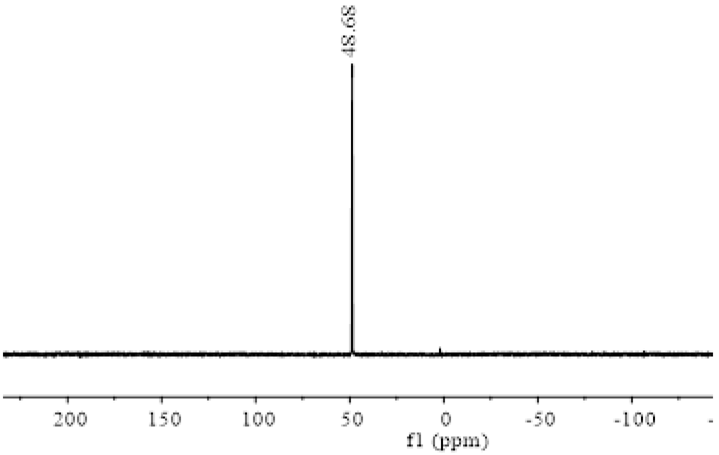


Figure 8. ^{31}P-{^{1}H} NMR spectrum (400 MHz, acetone-d$_6$) for compound **2f**.

In the ^{31}P-{^{1}H} NMR spectra for compounds **1f-2f** one singlet signal was observed, in accordance with equivalent ^{31}P nuclei. The position of this signal is similar to the previous result for the compounds with diphosphine ligands, ca. 50 ppm.

These compounds showed a preference to form dinuclear complexes with chelating ligands coordinated to the metal center.

4. Conclusions

- Bisiminophosphorane ligands gave symmetrical cyclometallated compounds with four palladium atoms.
- Complexes derived from bisiminophosphorane ligands react with different donor atom bidentate ligands in 1:4 molar ratio to give species with two bidentate ligands.

- The resulting cyclometallated compounds gave as result dinuclear palladium complexes with two different size chelated moieties, of four and six membered rings.

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

References

1. Luo, J.; Zhao, A.; Zheng, C.; Wang, T. *Phosphorus Sulfur Silicon Relat. Elem.* **2017**, *192*, 1124.
2. Ramazani, A.; Ahmadi, Y.; Fattahi, N.; Ahankar, H.; Pakzad, M.; Aghahosseini, H.; Rezaei, A.; Fardood, S.T.; Joo, S.W. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1057.
3. Krawczyk, H.; Dziegielewski, M.; Deredas, D.; Albrecht, A.; Albrecht, L. *Chem. Eur. J.* **2015**, *21*, 10268.
4. Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.