



# Spectroscopic and solid state characterization of bimetallic terdentate [C,N,S] thiosemicarbazone Palladium(II) metallacycles with bridging and chelating [P,P] diphosphine ligands

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## ABSTRACT

Bimetallic cyclometallated palladium(II) complexes readily react with silver perchlorate and tertiary diphosphines to give dipalladium compounds with terdentate [C,N,S] thiosemicarbazones, and with bridging and chelating [P,P] ligands, of the type [Pd(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>-P,P){Pd[4-MeOC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NHMe](Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>-P,S)] [ClO<sub>4</sub>]<sub>2</sub>, **1a**. The crystal structures of complexes [PdCl<sub>2</sub>{Pd[2-MeOC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NHMe](Ph<sub>2</sub>PC(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>-P,S)] and [Pd(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>-P,P){Pd[3-MeOC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NHMe](Ph<sub>2</sub>PC(CH<sub>2</sub>)<sub>2</sub>P-Ph<sub>2</sub>-P,S)]-[ClO<sub>4</sub>]<sub>2</sub>, **6** and **4a**, respectively, are the first reported examples of palladacycles with the diphosphine Ph<sub>2</sub>PC(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, bis(diphenylphosphine)cyclopropane (dcpc), in the bridging mode. The short-bite diphosphines produce strained four-membered rings at the metal; the structures for **1a** and **4a** show the P–C–P carbon atom puckered away from the metal coordination plane.

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## 1. Introduction

The chemistry of cyclometallated compounds, and in particular that of palladacycles, has developed into one of the most noteworthy parts of modern organometallic chemistry, and a several reviews have appeared covering this issue [1]. They exhibit a good number of applications which range from the synthesis of new organic and organometallic compounds, to mesogenic species and catalytic materials [2]. Moreover, their use in the design of potential biologically active materials has also been put forward [3].

In the compounds, the bonds at the metal centre, namely the palladium–carbon and the palladium–donor atom bonds may undergo numerous conversions enhancing their varied reactivity, and to name but a few, insertion reactions [4] and reactions with nucleophiles [5] have been reported. More often than not thiosemicarbazone ligands produce tetranuclear compounds with an eight-membered Pd<sub>4</sub>S<sub>4</sub> core [6]; however, under the appropriate conditions a trinuclear complex with a six-membered Pd<sub>3</sub>S<sub>3</sub> ring has also been prepared [7]. In any case, the organic ligand binds

tightly to the metal as terdentate [C,N,S] through M–S<sub>chelating</sub> and M–S<sub>bridging</sub> bonds. The strength of the former bond is put forward in the reactivity with nucleophiles, where treatment even with strong chelating tertiary diphosphines only yields complexes with the ligand in a [C,N,S] fashion and a mono-coordinated diphosphine, to render bidentate P,S palladacycle metaloligands: they constitute the starting materials for the preparation of dinuclear assemblies [8].

Herein we report the preparation and characterization of new dinuclear palladium complexes derived from bidentate P,S palladacycle metaloligands, which include the first examples of structures that contain the bridging bis(diphenylphosphine)cyclopropane (dcpc) ligand. The crystal structures display hydrogen bonding and π–π interactions which are also described.

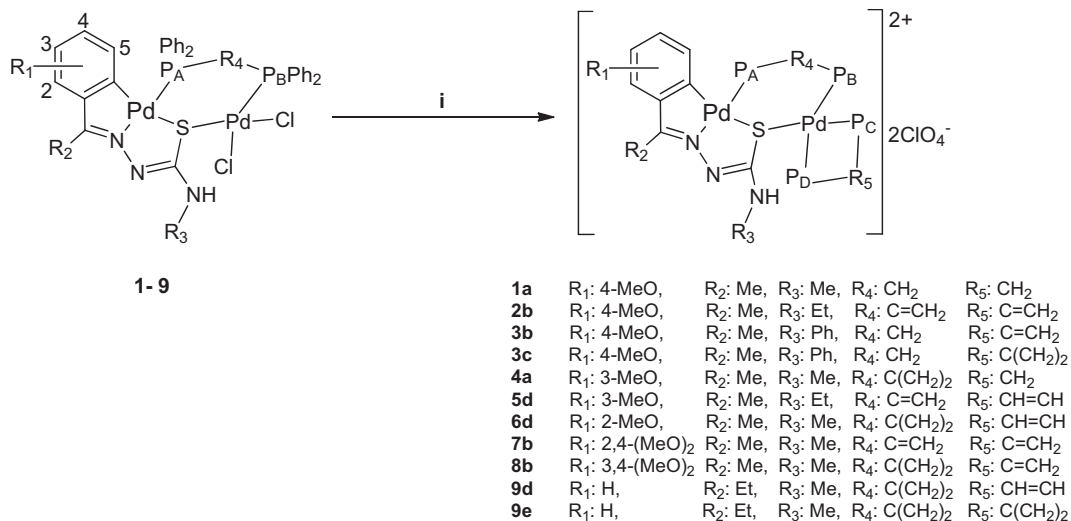
## 2. Results and discussion

### 2.1. Synthesis and characterization

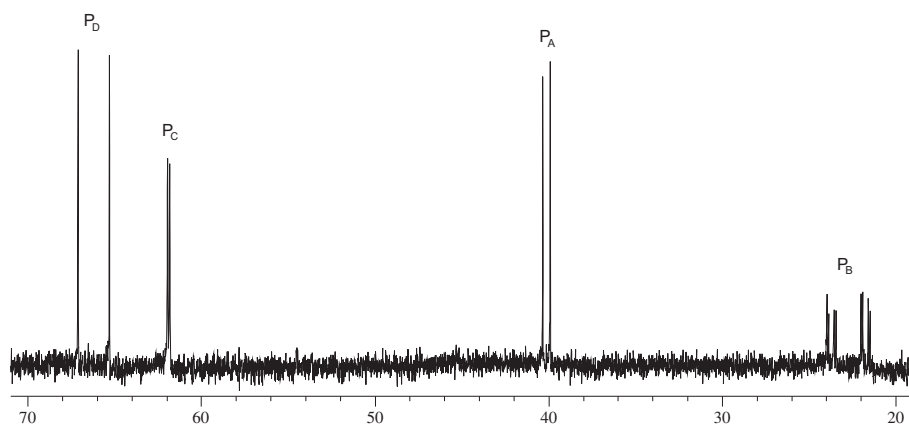
The new homobimetallic palladium complexes **1–9** used as starting materials were prepared following the synthetic route described by us in a previous paper [8]; the final stages of the

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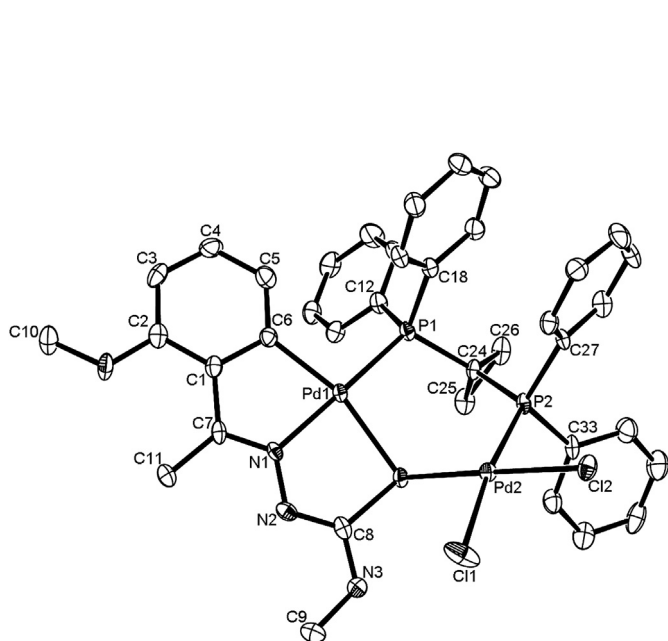
E-mail address: [josemanuel.vila@usc.es](mailto:josemanuel.vila@usc.es) (J.M. Vila).



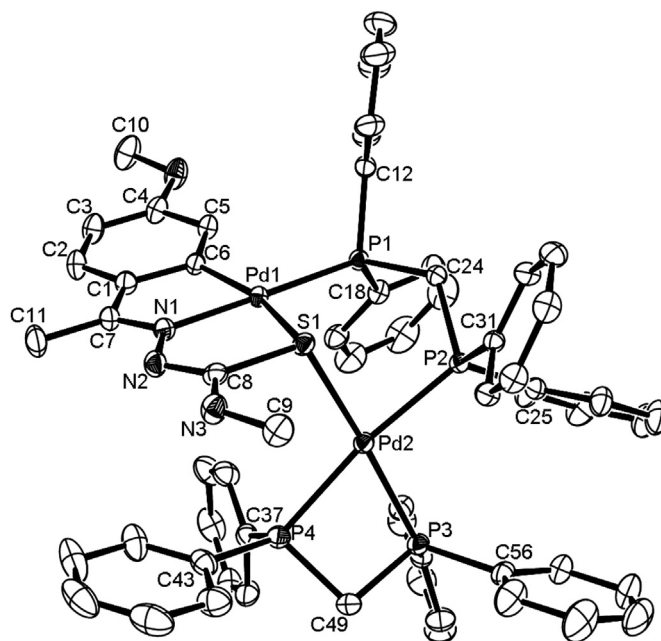
**Scheme 1.** i) In acetone, 2 equiv. AgClO<sub>4</sub>, 2 h; followed by 1 equivalent of diphosphine ligand.



**Fig. 1.** <sup>31</sup>P-{<sup>1</sup>H} NMR spectra of **5d**.



**Fig. 2.** Crystal structure of compound **6** (Ellipsoids probability: 50%). Hydrogen atoms have been omitted for clarity.



**Fig. 3.** Molecular structure of **1a**. (Ellipsoids probability: 30%). Hydrogen atoms and counterions have been omitted for clarity.

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