

### Preliminary communication

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## SIX-MEMBERED CYCLOMETALLATED COMPOUNDS OF METHYLBENZALAZINES WITH Pd—C(ALIPHATIC) BONDS\*

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### Summary

The preparation of mono- and di-cyclometallated compounds with six-membered rings containing Pd—C(*sp*<sup>3</sup>) bonds is reported. These are obtained from [2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=N—]<sub>2</sub> and Pd(AcO)<sub>2</sub>, or by ligand exchange reactions.

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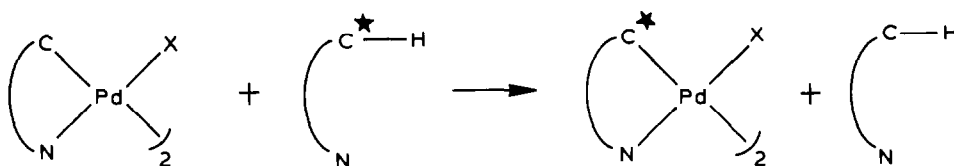
Activation of C—H bonds of alkyl groups by transition-metal complexes is one of the most important topics in organometallic chemistry. There have been many reports of the activation of the alkyl groups by cyclopalladation and cycloplatination of bulky tertiary alkylphosphines [1], but only a few on the cyclopalladation of alkyl groups of nitrogen ligands. Nearly all of them involve five-membered metallocycles [2], which are specially favoured in cyclometallation processes [3]. To date, only a few examples of six-membered cyclometallated compounds of *N*-donor ligands containing Pd—C(*sp*<sup>3</sup>) bonds have been reported. To the best of our knowledge these are (i) a derivative of 2-neopentylpyridine [4], and (ii) a derivative of 2-[1,1-bis(methoxycarbonyl)propyl]pyridine [5].

In continuation of our investigations of cyclometallation reactions of *N*-donor ligands [6], we report here the preparation of the first dicyclopalladated compound with six-membered rings containing Pd—C(*sp*<sup>3</sup>) bonds.

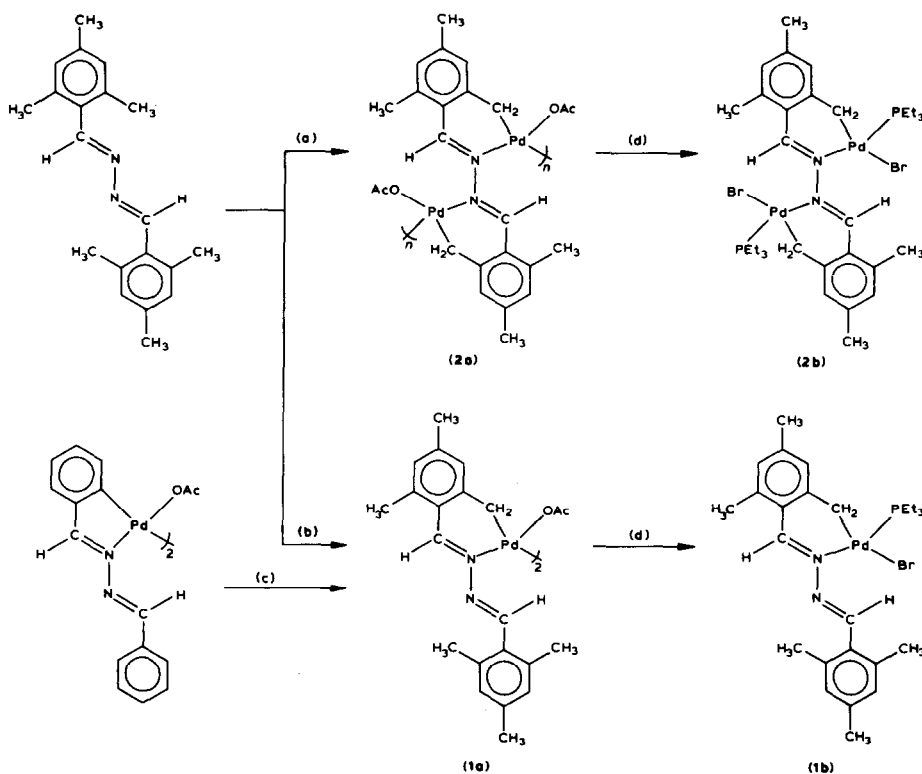
The action of Pd(AcO)<sub>2</sub> on the azine [2,4,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CH=N—]<sub>2</sub> in anhydrous acetic acid under reflux leads to the new cyclometallated compounds **1a** and **2a** (~70%) (see Scheme 1), depending on the amounts of reactants used and the reaction time. The cyclometallated compounds obtained react with PEt<sub>3</sub> to give monomeric species.

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\*Dedicated to Professor R. Usón on the occasion of his 60th birthday.



Recently, ligand exchange reactions have been used in a novel procedure for obtaining cyclopalladated compounds [7, 8]. This reaction involves the interaction of a soluble cyclopalladated dimeric compound and a *N*-donor ligand, which is able to form the chelate ring with the palladium-carbon bond to afford a new palladocycle. We have found that the monometallated complex **1a** can be obtained from  $[(\text{AcO})\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_5)]$  [6] and the free trimethylbenzalazine ligand in refluxing acetic acid during 10 h (70% yield). This is the first example of formation of a six-membered metalocycle containing Pd-C(*sp*<sup>3</sup>) bonds from a five-membered compound containing Pd-C(*sp*<sup>2</sup>) bonds. These results suggest that the six-membered metalocycles containing Pd-C(aliphatic) bonds are more stable than expected. The dicyclopalladated



**SCHEME 1.** (a)  $[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}=\text{N}-]_2/\text{Pd}(\text{AcO})_2$  (1/2), HAcO reflux, 5 h. (b)  $[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}=\text{N}-]_2/\text{Pd}(\text{AcO})_2$  (1/1), HAcO reflux, 30 min. (c) excess of  $[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}=\text{N}-]_2$ , HAcO reflux, 10 h. (d) excess of  $\text{PET}_3$  and  $\text{LiBr}$ , acetone reflux, 30 min.

compound  $[(\text{AcO})\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{N})]_n$  does not undergo this reaction, probably because of its great insolubility in acetic acid.

Elemental analyses and IR spectra were found to be satisfactory. The proton NMR spectra (80 MHz,  $\text{CDCl}_3$  solutions) of **1b** shows two azomethine signals, one at  $\delta$  8.57 ( $^4J(\text{P}-\text{H})$  9.6 Hz), shifted to upper fields, as is usual for the methinic protons belonging to a metallocycle, and another at  $\delta$  10.03 at lower fields than for the free azine (8.96). This downfield shift is due to the paramagnetic anisotropy of the metal and shows the proximity of this proton H' to the Pd atom. Compound **2b** shows only one signal, at  $\delta$  9.31 [ $^4J(\text{PH})$  9 Hz], from the two azomethine protons. The intermediate shift of these protons results from the two opposing effects mentioned previously, the proximity to the Pd atom and the fact that the proton belongs to the metallocycle.

The Pd-CH<sub>2</sub> protons appears as a singlet at  $\delta$  3.19 ( $^3J(\text{H}-\text{P})$  4.0 Hz) and  $\delta$  2.87 ( $^3J(\text{PH})$  4.5 Hz) for **2b** and **1b** respectively, shifted to lower fields than for the free azine.

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