

## LETTERS TO THE EDITOR

### MIXED-VALENT PALLADIUM (IV AND II) COMPLEXES OF TETRADENTATE SCHIFF BASES DERIVED FROM ACETYLACETONE AND DIAMINES—NOVEL EXAMPLES OF PALLADIUM(IV)-OXO- $\pi$ -ALLYLIC BONDING

#### Introduction

THE formation of  $\pi$ -allylic complexes is now recognized as a general feature of transition metals and several reviews on this subject have appeared in the literature<sup>1-5</sup>. Of all the metal ions palladium in its lower oxidation states, 0 and +2, are known to form maximum number of  $\pi$ -allylic complexes. However, there seems to be no report on similar type of bonding involving higher oxidation states of palladium. This communication reports the first examples of mixed-valent palladium complexes involving Pd(IV)-Oxo- $\pi$ -allylic bonding with bivalent tetradentate Schiff bases derived from acetylacetone and diamines.

#### Experimental

**Materials and Physical Measurements:** N, N'-diamine-bis(acetyl-acetoneimine)<sup>6</sup> and  $K_2PdCl_4$  (Ref. 7) were prepared by the reported methods.  $PdCl_2$  (Johnson-Mathey, Ltd.) was used as such. Organic solvents were of analar grade. The physico-chemical measurements of the complexes were made as described before<sup>8</sup>.

**Preparation of the Complexes:** The complexes  $[Pd^{IV}L][Pd^{II}Cl_4]$ , were prepared by adding ice-cold aqueous solution of an appropriate N, N'-diamine-bis(acetylacetoneimine) to an excess of  $PdCl_2$  or  $K_2PdCl_4$  in water which is also previously cooled to 0°C. The orange-red crystals obtained were collected by filtration, washed with water and recrystallized from a large volume of chloroform. The yields of the complexes were found to be temperature dependent, being maximum at 0°C (50-60%) and decreasing with increase in temperature. The formation of these complexes is very specific to the aqueous medium as well as the sequence of addition of the reagents. The latter condition is very critical since the addition of  $PdCl_2$  or  $K_2PdCl_4$  to the excess of ligand solution yielded yellow crystalline compounds, which were found to be identical with the already reported compounds<sup>6</sup>, having structure (B).

#### Results and Discussion

The orange red complexes gave satisfactory elemental analyses corresponding to the molecular formula  $[Pd^{IV}L][Pd^{II}Cl_4]$ . The complexes in contact with acetonitrile for several hours deposit metallic palladium

as a silver mirror. The reduction of the complexes to metallic palladium was found to be instantaneous in presence of hydrazine hydrochloride. The electrical conductivity of the complexes in acetone and acetonitrile (concentration  $\sim 10^{-3}$  M) shows that they are 1:1 electrolytes ( $\Lambda_M < 120 - 160 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ). The diamagnetic nature of the complexes is indicative of square-planar geometry around  $Pd^{IV}$  and  $Pd^{II}$ .

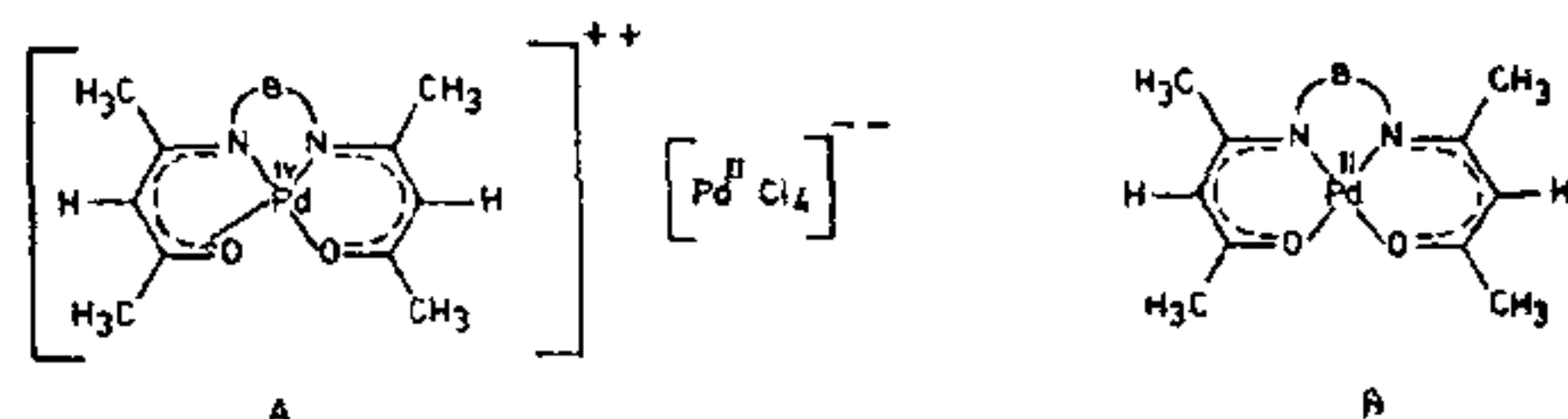
The electronic absorption spectra of the complexes in nujol mull show four bands in the ultraviolet region. The broad band centered at  $39,700 \text{ cm}^{-1}$  is due to the ligand transitions of  $[Pd^{IV}L]^{2+}$ , while the three bands occurring around 43,000, 30,000 and  $22,000 \text{ cm}^{-1}$  are characteristic of  $PdCl_4^{2-}$  ion<sup>9</sup>. The presence of  $PdCl_4^{2-}$  ion indirectly supports that the oxidation state of palladium in the cation is IV. This is further supported by the fact that the complexes liberate iodine from an acidified solution of KI. Although these results confirm the presence of Pd(IV) in the complexes, it is not clear how a portion of Pd(II) is oxidised to Pd(IV). It is probable that under the experimental conditions employed, water oxidises Pd(II) to Pd(IV), as even in an inert atmosphere the same product is obtained.

The ir spectra of the complexes in nujol mull show bands due to  $\pi$ -CH,  $\delta$ -CH and coordinated  $\nu$ CN, respectively around 760, 1190 and  $1575 \text{ cm}^{-1}$ . Two intense bands are observed around 1520 and  $1630 - 1650 \text{ cm}^{-1}$  region. The former band is due to coordinated  $\nu$ CO. The occurrence of the latter indicates that the second carbonyl group of the coordinated ligand is not conventionally bonded through oxygen. However, the position of this band is too low for it to be a non-coordinated acetyl carbonyl, which generally absorbs around  $1700 \text{ cm}^{-1}$  (Ref. 10). Their data could be accounted for by postulating Pd<sup>IV</sup>-oxo- $\pi$ -allylic bonding as shown in structure A. Bonding of this type has been assigned to di- $\mu$ -chloro-bis(2-phenyl-3-chloro- $\pi$ -oxapropenyl) dipalladium(II)<sup>11</sup>. The possibility of Pd<sup>IV</sup>- $\gamma$ -carbon bonding is ruled out since the model building shows considerable strain for such structures.

The complexes readily react with  $\pi$ -acids like triphenyl-phosphine and triphenylarsine, giving diamagnetic penta-coordinated adducts. These complexes show the absence of the band around  $1630 \text{ cm}^{-1}$  indicating the conventional coordination of the carbonyl oxygen to Pd<sup>IV</sup>. Hence, in presence of  $\pi$ -acids, the oxo- $\pi$ -allylic bond is weakened and the latter



coordination is favoured. The results of these studies along with reactions of A with primary amines and nitrosating reagents will be published elsewhere.



- (I) B = -CH<sub>2</sub>CH<sub>2</sub>-  
(II) B = -CH<sub>2</sub>CH(CH<sub>3</sub>)-  
(III) B = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-

Although four methyl proton signals are expected for the structure of the type A, the pmr spectrum of A(I) in CDCl<sub>3</sub> shows only three signals at 8.42, 8.00 and 7.94  $\tau$  with integrated intensities of 6:3:3, which are assignable respectively to  $[-(\text{CH}_3)\text{C}(=\text{N})-]$ , COCH<sub>3</sub> (Oxygen-bonded ring) and COCH<sub>3</sub> ( $\pi$ -allylic bonded ring). The merging of the methyl proton signals in the vicinity of the ethylene skeleton may be attributed to their identical shielding parameters. The  $\gamma$ -CH proton gives a broad singlet at 5.12  $\tau$ . The complex multiplet centered at 6.52  $\tau$  is due to ethylene protons. The pmr spectrum of A(II) shows spectral features analogous to that of A(I).

In conclusion, at present,  $[\text{Pd}^{\text{IV}} \text{L}]$   $[\text{PdCl}_4]^-$  are the only known mixed-valent palladium complexes, in which Pd<sup>IV</sup> shows oxo- $\pi$ -allylic bonding.

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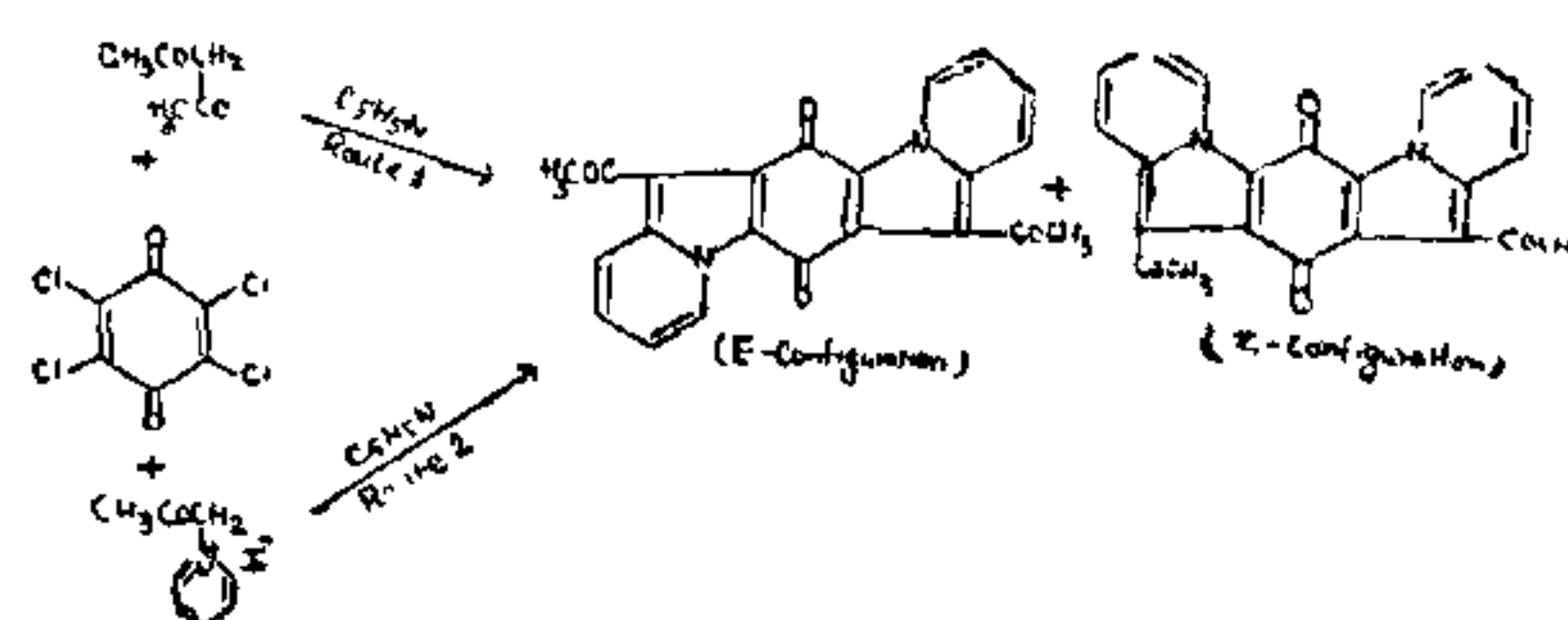
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## A NEW PROCEDURE FOR THE SYNTHESIS OF SUBSTITUTED PYRROCOLINE QUINONES

### Introduction

THE synthesis of a number of 5:11 disubstituted and 5:7 disubstituted pyrrocoline quinones has been reported by Tilak *et al.*<sup>1</sup>; by the oxidative condensation of chloranil with pyridine and active methylene compounds, like acetyl acetone, acetoacetic ester or malonic ester. That both malonic ester and acetoacetic ester gave the same products was explained on the basis that in the final stage the more electron withdrawing group was cleaved.

It was therefore thought logical to use some other compounds like acetonil pyridinium iodide ( $\text{CH}_3\text{CO-CH}_2\text{-N}^+\text{C}_5\text{H}_5\text{I}^-$ ) and its analogues in which an active methylene group is situated between a carbonyl group and a strongly electron withdrawing  $\text{N}^+$  group (quaternary nitrogen). It should be the strongly electron withdrawing  $\text{N}^+$  group which should be cleaved at the final stage. The resulting product in this particular case should be identical with the product obtained by the condensation of chloranil with acetyl acetone and pyridine as shown in the scheme below:



It may be seen that the use of acetonil pyridinium iodide or acetonil quinolinium iodide should give the same products and it is actually observed that the products of reaction (i) and (ii) are the same as verified through T.L.C. The nature of Z and E isomers of pyrrocoline quinones is ascertained through their characteristic colour reaction with sulphuric acid. In reaction (ii), if we take quinoline or isoquinoline instead of pyridine as the base, only E configuration benzo dibenz pyrrocoline quinone is obtained and is found to be identical with the compounds reported earlier<sup>2</sup>. The formation of compounds of Z configuration seems to be sterically hindered. The identity of the compounds prepared by both the routes was ascertained through T.L.C.