

## Preliminary communication

### Formation of platinum(IV) carbene complexes by oxidative addition

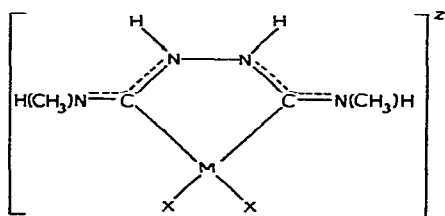
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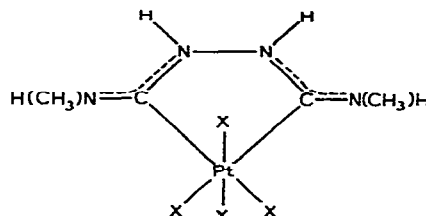
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The organometallic chemistry of Pt<sup>IV</sup> is largely, although not exclusively, limited to alkyl derivatives<sup>1</sup>. We now report on the preparation, via oxidative addition, of some Pt<sup>IV</sup> complexes containing ligands of the "carbene" type. Although oxidative addition to some Pt<sup>II</sup> alkyl complexes has been described<sup>2</sup>; the only preparation of a Pt<sup>IV</sup> carbene complex reported to date has involved construction of the carbene ligand at a Pt<sup>IV</sup> coordination site<sup>3</sup>.

Treatment of the planar complexes of the type I<sup>4</sup> with one equivalent of halogen



- Ia, M = Pt, X = I, z = 0  
Ib, M = Pt, X = Br, z = 0  
Ic, M = Pt, X = Cl, z = 0  
Id, M = Pt, X = CH<sub>3</sub>NC, z = +2  
Ie, M = Pd, X = I, z = 0  
If, M = Pd, X = Br, z = 0

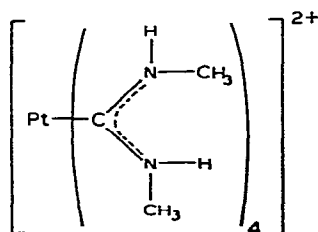


- IIa X = I  
IIb X = Br  
IIc X = Cl

in either aqueous acidic solution or in acetone solution results in the formation of the corresponding Pt<sup>IV</sup> complex II. In this way brown IIa (from Ia), deep yellow IIb (from Ib), and pale yellow IIc (from Ic) have been obtained. All of these Pt<sup>IV</sup> complexes have good stability towards moisture, oxygen, and heat. Their formulations are supported by satisfactory analytical data, infrared and PMR spectra, and conductivity measurements, which indicate that they are non-electrolytes. Consistent with oxidation at the metal center, the infrared spectra of the two series of complexes, I and II, in the 4000–600 cm<sup>-1</sup> region

are quite similar. For example Ia exhibits absorptions at 3320s, 3230s, 3125s, 3080s ( $\nu(\text{N-H})$ ); 2900w, 2850w, 2800w ( $\nu(\text{C-H})$ ); 1580s, 1520m, 1500s, ( $\nu(\text{N}\cdots\text{C}\cdots\text{N})$ ,  $\delta(\text{N-H})$ ); 1460w, 1425m, 1380w, 1370m, 1205m, 1155m, 1015  $\text{cm}^{-1}$  and IIa exhibits bands at 3280s, 3200s, 3150s, 3095s ( $\nu(\text{N-H})$ ); 2950w, 2800w ( $\nu(\text{C-H})$ ); 1600s, 1525m, 1495s ( $\nu(\text{N}\cdots\text{C}\cdots\text{N})$ ,  $\delta(\text{N-H})$ ); 1425s, 1375w, 1365m, 1190m, 1150m, and 1000m  $\text{cm}^{-1}$ . The PMR spectrum of Ia in acetonitrile- $d_3$  consists of a doublet at  $\tau$  7.16 ( $J(\text{H-C-N-H})$  5.5 Hz) due to the terminal methyl group of the chelating ligand; IIa in the same solvent consists of a corresponding resonance at  $\tau$  6.78 ( $J(\text{H-N-C-H})$  5.5 Hz). In both cases the N-H resonances, which are expected to be broad, could not be detected because of the low signal intensity caused by the limited solubility of the complexes. The H-C-N-H coupling constants are in the range found for similar complexes<sup>4</sup>.

In general we find that the carbene ligands in  $\text{Pt}^{\text{II}}$  complexes are quite resistant to oxidation. In addition to the above results, treatment of Id with moderately concentrated nitric acid results only in the precipitation of the nitrate salt of Id even after extended periods of time. Attempts to prepare  $\text{Pd}^{\text{IV}}$  complexes analogous to II have, not surprisingly, failed. Treatment of Ie with iodine resulted only in the recovery of starting material; whereas treatment of If with bromine led to the destruction of the complex. Attempts to perform oxidative-addition reactions on the carbene complex III<sup>5</sup> have been unsuccessful. This may be due to an intrinsic higher oxidation potential of III relative to I or to shielding



(III)

of the axial coordination sites in III by the rather bulky, planar carbene ligands. Such shielding is absent in the chelate complexes I where the carbene ligands are constrained to lie in the  $\text{PtC}_2\text{X}_2$  coordination plane.

#### ACKNOWLEDGEMENT

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