Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A convenient synthesis for a variety of methyl- and trifluoromethylplatinum complexes

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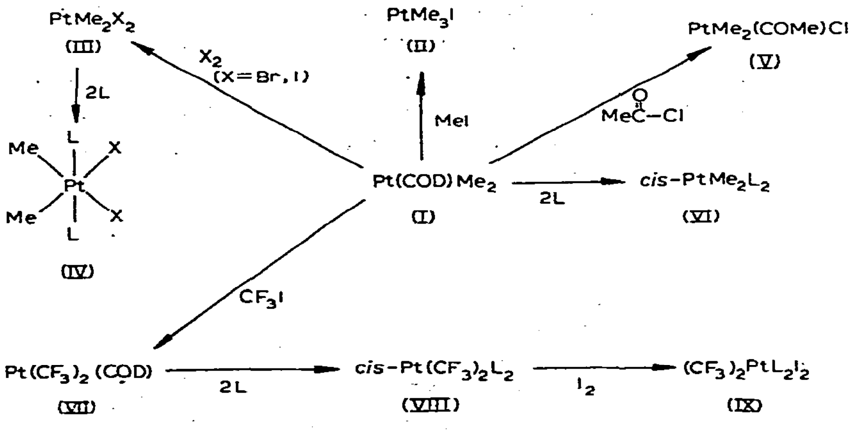
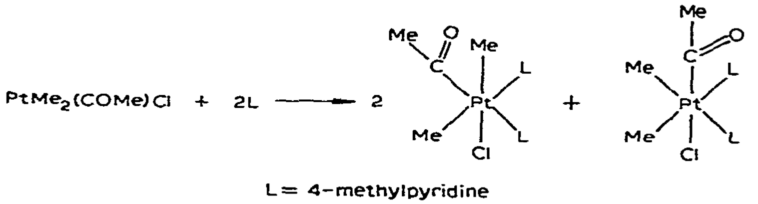
(Received March 7th, 1972)

Since the preparation of $[PtMe_3I]_4$ [1] an extensive chemistry of platinum(IV) has been developed[2]. Similar work with dimethylplatinum(IV) compounds has been very limited due to the difficulty of preparation[3] rather than any inherent instability. We now give a preliminary report of some reactions (see Scheme 1) of (COD)$PtMe_2$ (COD = 1,5-cyclooctadiene)[4] which indicates its versatility in the facile preparation of Pt^{IV} complexes, including the first bis(perfluoroalkyl) complexes of platinum.

(COD)$PtMe_2$, I, reacts with iodomethane to give $PtMe_3I$, II, and with iodine or bromine to give the dimethylplatinum(IV) compounds, III, in quantitative yields. The reaction of neutral ligands with III yields a variety of octahedral complexes of configuration IV. The NMR spectrum of IV, L = CNEt, X = Br is very interesting. The ethyl resonance shows the usual triplet and quartet pattern as well as triplet fine structure from spin–spin interaction with the ^{14}N nucleus ($I = 1$, $^3J(^{14}N–^1H) = 3.86$ Hz and $^2J(^{14}N–^1H) = 1.44$ Hz) indicating slow quadrupolar relaxation[5].



At present only three basic types of platinum(IV) complexes which do not contain stabilizing, π-bonding ligands, have been prepared[2], namely $PtEt_3X$, $PtMe_2X_2$, and $PtMe_3X$, where X is a variety of anionic ligands. We have now prepared another member of this series, $PtMe_2(COMe)Cl$, V, by the oxidative addition of acetyl chloride to I. This compound which may well have the same type of tetrameric structure as $PtMe_3X$ [2] reacts readily with a variety of ligands to give two isomers in the 2/1 ratio (eqn. 1), expected for cleavage of such a tetrameric unit.



(1)

Displacement reactions of COD from I have previously been reported[4,6] and we have now extended these. Of particular interest are the complexes VI where L = alkyl or aryl isocyanides and bipyridyl. We are also examining oxidative addition reactions of these isocyanide complexes.

The most interesting and complex reaction of $(COD)PtMe_2$ is with CF_3I, which gives a mixture of $(COD)Pt(CF_3)_2$, VII, and $PtMe_3I$ (eqn. 2).

$$3(COD)PtMe_2 + 2CF_3I \xrightarrow{CH_2Cl_2} (COD)Pt(CF_3)_2 + 2PtMe_3I + 2COD \qquad (2)$$

The reaction proceeds smoothly in dichloromethane and VII is easily separated from $PtMe_3I$ which is insoluble in dichloromethane. The 1,5-cyclooctadiene is very labile in VII and readily displaced by many ligands (*e.g.* PMe_2Ph, $AsMe_3$, NC_5H_5, CN—R, bipy, $SbPh_3$, $AsPh_3$) to form *cis*-$Pt(CF_3)_2L_2$, VIII. The coupling constant ^2J(Pt—F) varies with the *trans*-influence of L, ranging from 627 Hz to 793 Hz for L = PMe_2Ph and 4-NC_5H_4—CH_3 respectively. The bis(trifluoromethyl) complexes are very stable compared to their methyl platinum analogues and are quite soluble in polar solvents.

The platinum(II) complexes VIII are readily oxidized by iodine and preliminary results indicate that the stereochemistry of IX is dependent on the *trans*-influence of L.

We are currently investigating similar reactions with $(COD)PtPh_2$ and $(COD)PtEt_2$ and these results along with full details of the work outlined above will be reported shortly.

Satisfactory analytical, as well as ^1H and ^{19}F NMR spectroscopic data have been obtained for all of the complexes described.

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