Reaction of Chloroplatinic Acid with 1,1-Dimethylcyclopropane: Formation of an Unusual Cyclobutenium Cation

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Summary A novel cyclobutenium cation has been isolated from the reaction of chloroplatinic acid and 1,1-dimethylcyclopropane: the structure and spectral properties of this cation are discussed.

THE reaction of cyclopropane with chloroplatinic acid in Ac_2O yields $PtCl_2(C_3H_6)$ which has a tetrameric structure in which Pt^{IV} achieves six-co-ordination through chloride bridges.[1,2] The anionic moiety is formally present as trimethylene dianion, and not as an intact 3-membered ring.[3] In order to clarify the nature of the bonding in such adducts, and to explain the formation of cyclopropane upon their decomposition, we have examined the interaction of chloroplatinic acid with various alkyl-substituted cyclopropanes. We report here the unusual and unexpected product obtained with 1,1-dimethylcyclopropane.

The reaction of chloroplatinic acid and 1,1-dimethylcyclopropane in Ac_2O yields a dark brown powder (*ca.* 43%), which upon recrystallization from MeOH or CH_2Cl_2 gives orange crystals which analyse correctly for $C_{18}H_{26}O_2PtCl_6$. The presence of $PtCl_6{}^{2-}$ anion was confirmed by precipitation of $Pt(NH_3)_4PtCl_6$ with $Pt(NH_3)_4Cl_2$ in MeOH solution. This is consistent with the high Cl/Pt ratio and the absence of any ^{195}Pt–H coupling in the adduct (*vide infra*). Conductivity measurements in MeCN are consistent with a 2 : 1 electrolyte. The n.m.r. spectrum of the adduct (CD_3CN solution) can be interpreted in terms of structure (I): δ 7·6 (s, 2H, ring H), 2·7 (q, 2H, J 7·5 Hz, $COCH_2Me$), 2·6 (s, 6H, CMe_2), and 1·0 p.p.m. (t, 3H, J 7·5 Hz, $COCH_2Me$). Strong deshielding of the ring protons to δ 7·58 p.p.m. is consistent with a delocalized positive charge in the ring. The presence of an ethyl group, and the *absence of any other coupling* can only be accounted for by structure (I). The strongest band in the i.r. spectrum, at 1630 cm^{-1}, although of rather low frequency, is consistent with a conjugated carbonyl group in (I). In addition, the methylene protons adjacent to this function undergo rapid exchange with D_2O. Interestingly, when the reaction is run in propionic anhydride, ^1H n.m.r., i.r., and elemental analyses of one of the products are consistent with (II). This indicates that R^2 and R^3 in (I) and (II) probably originate from the solvent, and not the dimethylcyclopropane moiety; this is consistent with the apparent formation of (I) from *cis*-1,2-dimethylcyclopropane as well as from 1,1-dimethylcyclopropane. Further, the fact that R^1 does not vary when the solvent is changed from acetic to propionic anhydride may mean that it originates, in part, from the ring. Due to the large number of species potentially present in the reaction solution it would be premature to postulate a mechanism. The reaction appears to be specific for methylcyclopropanes, as both cyclopropane[1] and 1,1-diethylcyclopropane give the simple platinum insertion compound. The nature of the apparently similar products obtained with other methyl-substituted cyclopropanes is under investigation. Although unusual, the suggested structures are not without precedent. The reaction of 3,4-dibromotetraphenylcyclobutene with an excess of $SnCl_4$ yields (III).[4]

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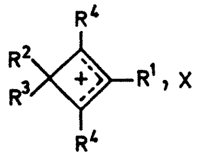

(I) $R^1 = COCH_2Me$; $R^2 = R^3 = Me$; $R^4 = H$; $X = PtCl_6^{2-}$

(II) $R^1 = COCH_2Me$; $R^2 = R^3 = Et$; $R^4 = H$; $X = PtCl_6^{2-}$

(III) $R^1 = R^2 = R^4 = Ph$; $R^3 = Cl$; $X = SnCl_5^-$

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