

Preliminary communication

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PREPARATION AND REACTIONS OF DIMETHYLPLATINUM(IV)  
HYDROXO AND AQUA COMPLEXES

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Summary

The preparations of  $[\text{Pt}(\text{CH}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]_n$  and the ion  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  are described. Their reactions with a variety of ligands are outlined.

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$[\text{Pt}(\text{CH}_3)_2\text{Br}_2]_n$  [1,2] dissolves readily in hot, concentrated NaOH to produce a colourless solution which, according to the  $^1\text{H}$  N.M.R. spectrum ( $\tau$  8.79,  $^2J(^{195}\text{Pt}-\text{CH}_3)$  76.5 Hz) contains a single species, presumably  $[\text{Pt}(\text{CH}_3)_2(\text{OH})_4]^{2-}$ . Neutralization of this solution with perchloric acid produces a fine white precipitate which analyses for  $\text{Pt}(\text{CH}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2$ , and is insoluble in all common solvents. The structure of the compound is unknown but it is probably polymeric with bridging OH groups. Attempts to remove the water from the compound resulted in decomposition to metallic platinum. The hydroxide is amphoteric, dissolving in NaOH solution to regenerate  $[\text{Pt}(\text{CH}_3)_2(\text{OH})_4]^{2-}$  (according to  $^1\text{H}$  N.M.R. spectra) and in acids such as  $\text{H}_2\text{SO}_4$  to give solutions containing a single species ( $\tau$  8.01,  $^2J(^{195}\text{Pt}-\text{CH}_3)$  75.2 Hz) tentatively described as  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$ . Evaporation of such solutions

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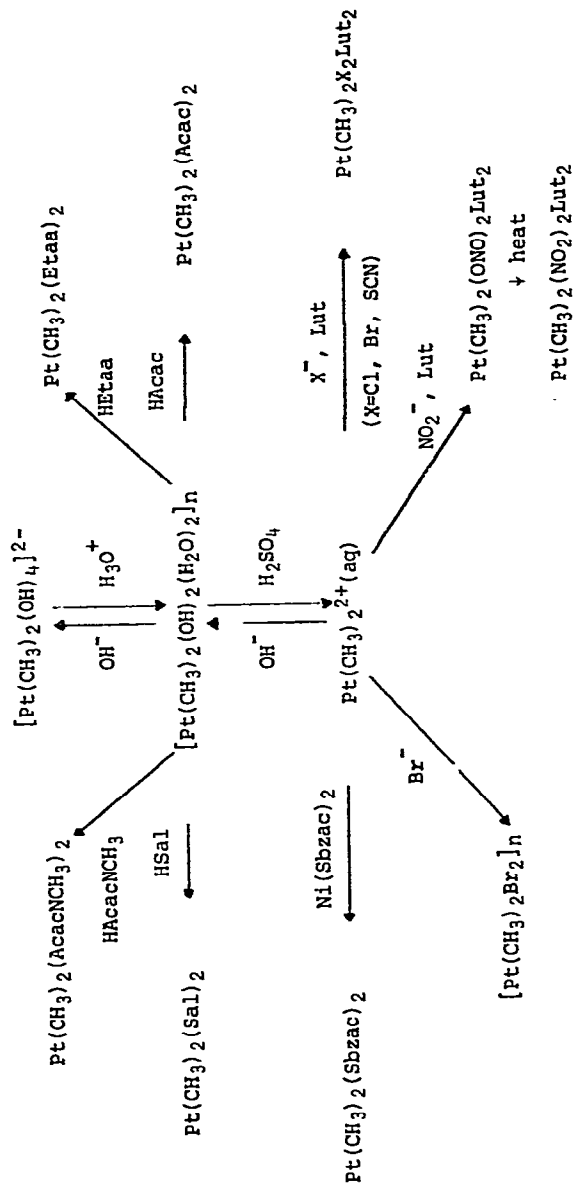
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yields a deliquescent white solid, soluble in water and alcohols but insoluble in acetone and chloroform. Both  $[\text{Pt}(\text{CH}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]_n$  and solutions of  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  are useful starting materials for the preparation of a range of dimethylplatinum(IV) compounds. Scheme 1 illustrates some representative reactions of these compounds.

$[\text{Pt}(\text{CH}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]_n$  reacts with weakly acidic liquids such as acetylacetone (HAcac), ethylacetoacetate (HEtaa), salicylaldehyde (HSal) and 4-methyliminopent-3-en-2-one (HAcacNCH<sub>3</sub>) when these are heated to boiling. In each case the product isolated has the formula  $\text{Pt}(\text{CH}_3)_2(\text{ligand})_2$  and contains two bidentate ligands as confirmed by <sup>1</sup>H NMR spectra. Although more than one isomeric form is possible for all of these compounds except  $\text{Pt}(\text{CH}_3)_2(\text{Acac})_2$ , in each case only one isomer is obtained from the above reaction according to <sup>1</sup>H NMR spectra. For  $\text{Pt}(\text{CH}_3)_2(\text{Etaa})_2$  the CH<sub>3</sub> groups are *trans* to the ester carbonyl groups; for  $\text{Pt}(\text{CH}_3)_2(\text{Sal})_2$  the CH<sub>3</sub> groups are *trans* to the phenolic oxygen atoms; and for  $\text{Pt}(\text{CH}_3)_2(\text{AcacNCH}_3)_2$  the CH<sub>3</sub> groups are *trans* to the N atoms. A significant feature of the <sup>1</sup>H NMR spectrum of  $\text{Pt}(\text{CH}_3)_2(\text{Sal})_2$  is the presence of a very large coupling (J 120 Hz) between <sup>195</sup>Pt and the aldehydic protons of the Sal ligands. The value is similar to that found for coupling between <sup>195</sup>Pt and *trans* protons in alkenylplatinum(II) compounds [3].

$[\text{Pt}(\text{CH}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]_n$  dissolves in acids such as HBr and HCl to produce the anions  $[\text{Pt}(\text{CH}_3)_2\text{X}_4]^{2-}$  [2]. Similar anions are formed on reaction of  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  with concentrated solutions of NaX (X=Cl, Br, SCN). Addition of NaNO<sub>2</sub> to a solution of  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  apparently produces the anion  $[\text{Pt}(\text{CH}_3)_2(\text{ONO})_2(\text{NO}_2)_2]^{2-}$  (CH<sub>3</sub> *trans* NO<sub>2</sub>) since addition of 3,5-lutidine precipitates  $\text{Pt}(\text{CH}_3)_2(\text{ONO})_2\text{Lut}_2$  [ $\nu(\text{N}=\text{O})$  1512,  $\nu(\text{N}-\text{O})$  945 cm<sup>-1</sup>]. This isomerizes to  $\text{Pt}(\text{CH}_3)_2(\text{NO}_2)_2\text{Lut}_2$  on heating [ $\nu_{\text{asym}}(\text{NO}_2)$  1428,  $\nu_{\text{sym}}(\text{NO}_2)$  1338, 1328 cm<sup>-1</sup>] [2].

Addition of a one mole ratio of NaBr to aqueous  $\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  produces in solution an equimolar mixture of  $\text{Pt}(\text{CH}_3)_2\text{Br}_2(\text{H}_2\text{O})_2$  and



SCHEME 1

$\text{Pt}(\text{CH}_3)_2^{2+}(\text{aq})$  according to  $^1\text{H}$  NMR spectra.  $[\text{Pt}(\text{CH}_3)_2\text{Br}_2]_n$  precipitates from this solution on standing.

Reaction of  $[\text{Pt}(\text{CH}_3)_2(\text{H}_2\text{O})_4]^{2+}$  with  $\text{Ni}(\text{Sbzac})_2$  (Sbzac = 3-mercapto-1-phenyl-2-buten-1-one) yields initially  $\text{Pt}(\text{CH}_3)_2(\text{Sbzac})_2$  with bis bidentate Sbzac groups ( $\text{CH}_3$  *trans* S). This slowly changes to the isomer with  $\text{CH}_3$  *trans* to O according to  $^1\text{H}$  NMR spectra.

#### References

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3. B.E. Mann, B.L. Shaw and N.I. Tucker, *Chem. Commun.*, (1970) 1333.