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Preliminary communication

PREPARATION OF MONOBROMODIMETHYLPLATINUM(IV) COMPOUNDS

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Summary

Reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous Ag^+ yields an acidic solution apparently containing $[Pt(CH_3)_2Br(H_2O)_3]^+$, and neutralization of this solution produces $[Pt(CH_3)_2BrOH]_n$; both species react with a variety of ligands to produce monobromodimethylplatinum(IV) compounds.

Reaction of $[Pt(CH_3)_2Br_2]_n$ [1,2] with a one mol ratio of aqueous Ag^+ produces a single water-soluble species according to ^1H NMR. This species is presumably $[Pt(CH_3)_2Br(H_2O)_3]^+$ but the solutions are slightly acidic, indicating the presence of Pt—OH bonds. On neutralization of the solution with NaOH a yellow solid analysing for $Pt(CH_3)_2BrOH$ precipitates from solution. Both $[Pt(CH_3)_2Br(H_2O)_3]^+$ in aqueous solution and $[Pt(CH_3)_2BrOH]_n$ which is soluble in methanol and acetone, prove to be useful starting materials for the preparation of a variety of monobromodimethylplatinum(IV) compounds as shown in Scheme 1.

Reaction of $[Pt(CH_3)_2BrOH]_n$ with 3,5-lutidine or addition of 3,5-lutidine to the solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ gives $[Pt(CH_3)_2BrOHLut_2]$ which is the first example of a terminal OH group in methylplatinum(IV) systems. Treatment of $[Pt(CH_3)_2Br(H_2O)_3]^+$ with aqueous solutions of NaX (X = I, Br, Cl and SCN) gives solutions apparently containing $[Pt(CH_3)_2BrX_3]^{2-}$ since addition of lutidine to these solutions precipitates complexes of formulae $Pt(CH_3)_2BrXLut_2$ all of which according to ^1H NMR contain Lut groups *trans* to CH_3. Reaction with $NaNO_2$ produces the nitrito species $[Pt(CH_3)_2Br(ONO)Lut_2]$ as identified by IR (ν(N=O) 1511 cm^{-1}, ν(N—O) 960 cm^{-1}). This compound converts to the nitro isomer on heating (ν_{asym}(N—O) 1420 cm^{-1}, ν_{sym}(N—O) 1332, 1322 cm^{-1}.

Reaction of $[Pt(CH_3)_2Br(H_2O)_3]^+$ with acetylacetone yields a solid analysing for $Pt(CH_3)_2AcacBr$ and containing O-bonded acetylacetonate

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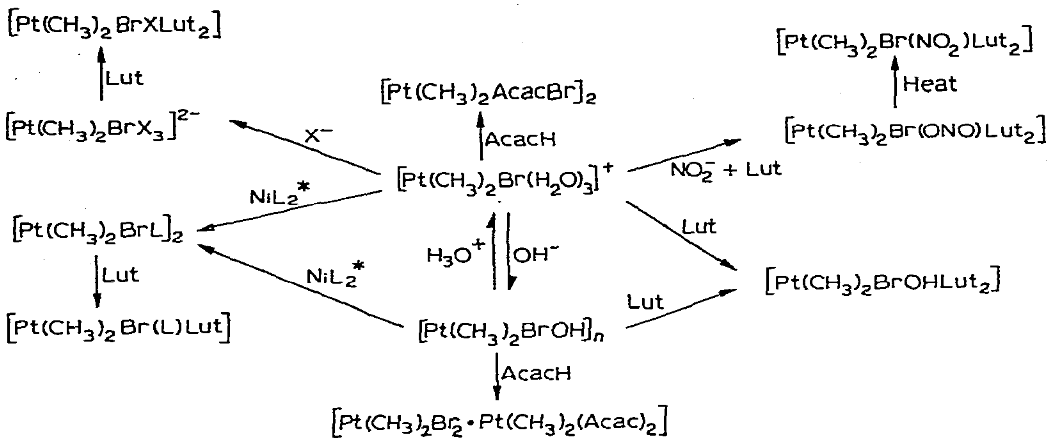

*L = Sal=N—R or thio-β-diketonate

SCHEME 1

groups, while $[Pt(CH_3)_2BrOH]_n$ dissolves in boiling acetylacetone to yield the isomeric species $[Pt(CH_3)_2Br_2 \cdot Pt(CH_3)_2(Acac)_2]$, which contains both O- and C-bonded Acac groups as previously reported [3]. Reactions of either $[Pt(CH_3)_2Br(H_2O)_3]^+$ or $[Pt(CH_3)_2BrOH]_n$ with nickel complexes NiL_2 where L is a salicylaldiminate or a thio-β-diketonate produce compounds of formulae $[Pt(CH_3)_2BrL]_2$ which react with lutidine to produce $[Pt(CH_3)_2Br(L)Lut]$.

The above compounds are presently being investigated in detail by ^1H NMR and IR spectra.

References

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