

aqueous reaction solution was brought to pH 2, taken to dryness *in vacuo* and extracted with ether, leading to an oil residue, β -acetoxy- β -phenylpropionic acid, 0.212 g. (1.0 mmole), 84% yield, α_{obsd} 0.00°, 3.1% in chloroform. A portion of this (0.165 g., 0.80 mmole) in 10 ml. of ether was added to 0.224 g. of 1,3-bis-(*p*-dimethylaminophenyl)-carbodiimide in 15 ml. of ether,

boiled under reflux for 3 hours, and cooled, leading to 1-(3-phenyl-3-acetoxypropionyl)-1,3-bis-(*p*-dimethylaminophenyl)-urea, 0.342 g. (0.70 mmole), 88% yield, α_{obsd} 0.00°, 1.8% in chloroform, m.p. 178–179° from ether.

Anal. Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_4\text{N}_4$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.40; H, 6.73; N, 11.81.

COMMUNICATIONS TO THE EDITOR

HOMOGENEOUS HYDROGENATIONS WITH PLATINUM-TIN CHLORIDE COMPLEXES

Sir:

Although several metal ions and complexes that catalyze the homogeneous hydrogenation of unsaturated compounds have been described,¹ none is reported to be effective for ethylene² and acetylene. We wish to report the facile homogeneous hydrogenation of these two compounds at room temperature and atmospheric pressure with a complex platinum-tin chloride catalyst. This complex was shown earlier to catalyze the carbonylation of a variety of unsaturated compounds.³

A typical catalyst solution was prepared (with exclusion of oxygen) by dissolving stannous chloride dihydrate (10.0 mmoles) and chloroplatinic acid (1.0 mmole) in 120 ml. of methanol. When a 1:1 mixture of ethylene and hydrogen at a pressure of 1 atm. was admitted to the stirred catalyst solution, rapid and essentially quantitative hydrogenation occurred. Similarly, a 1:1 mixture of acetylene and hydrogen gave ethane and ethylene in about a 3:1 molar ratio.

Preliminary studies indicate that the hydrogenation of ethylene is first order in platinum. At constant platinum concentration, maximum rates are observed at tin:platinum molar ratios above about 5:1.

Pertinent to the catalytic activity of the complex is the ability of stannous chloride to promote the coordination of ethylene to platinum. Thus, reaction of ethylene at atmospheric pressure with a solution of K_2PtCl_4 containing 5 mole % of stannous chloride in 1.5 *M* HCl gave a quantitative conversion to Zeise's salt, $\text{KPtCl}_3\text{C}_2\text{H}_4\cdot\text{H}_2\text{O}$, within 1.5 hr. In the absence of stannous chloride, no Zeise's salt formed in 16 hr. Furthermore, solutions of stannous chloride and chloroplatinic acid (6:1) in CH_3OD containing an excess of ethylene show a single n.m.r. absorption attributable to ethylenic protons that is appreciably shifted downfield compared to the absorption for ethylene in CH_3OD . This suggests an extremely rapid exchange between coordinated and free ethylene in the platinum-tin system. Since higher olefins are more difficult to hydrogenate with the complex catalyst, it appears that the ease of hydrogenation parallels the ability of the olefin to complex with platinum.

A second function of the stannous chloride is to stabilize the platinum against reduction to metal by hydrogen. Used catalyst solutions were shown to be devoid of colloidal particles by a variety of optical

methods. This is in marked contrast to the behavior of simple platinum salts.

To better understand their catalytic activity, we are also examining the chemistry of the platinum-tin chloride complexes. Meyer and Ayres⁴ suggested that the predominant species formed in 3 *M* hydrochloric acid is a cationic complex, $\text{Pt}(\text{SnCl}_4)^{+4}$, whereas Shukla⁵ demonstrated the presence of anionic species in both the platinum-tin and rhodium-tin systems in dilute hydrochloric acid by electrophoresis. In the ruthenium-tin system, the precipitation of complexes with cations and anions was recently reported by Okuno, *et al.*⁶ In none of these studies, however, were any discrete compounds fully characterized. In our work, we have established the existence of at least two complex anions and have also isolated neutral complexes as their triphenylphosphine derivatives.⁷

Addition of methyltriphenylphosphonium chloride to a deep red solution of chloroplatinic acid and stannous chloride (molar ratio 1:6) in methanol gave a quantitative yield of red, crystalline $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_3[\text{Pt}(\text{SnCl}_3)_6]$ (*Anal.* Calcd.: Cl, 24.7; Pt, 9.1; Sn, 27.6. Found: Cl, 24.2; Pt, 9.0; Sn, 27.5), soluble in acetone and nitromethane. Evaporation of the filtrate gave one mole of $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_2\text{SnCl}_6^8$ for each mole of Pt(IV) used, indicating that no reduction below Pt(II) occurs. The same red compound was obtained by reaction of phosphonium chloride, stannous chloride and K_2PtCl_4 in a molar ratio of 3:5:1 in 3 *M* hydrochloric acid.

From similar reactions at Sn:Pt of about 2:1, we have isolated yellow, crystalline $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_2[\text{PtCl}_2(\text{SnCl}_3)_2]$ (*Anal.* Calcd.: Cl, 22.4; Pt, 15.4; Sn, 18.5. Found: Cl, 22.6; Pt, 15.0; Sn, 18.8). This compound was also prepared by treating a suspension of $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_2\text{PtCl}_4^9$ in acetone with two molar equivalents of stannous chloride.

Addition of triphenylphosphine in ethyl alcohol to a solution of K_2PtCl_4 and stannous chloride (molar ratio 1:10) in 3 *M* HCl gave orange $[(\text{C}_6\text{H}_5)_3\text{P}]_2[\text{Pt}(\text{SnCl}_3)_2]$ (*Anal.* Calcd.: Cl, 18.2. Found: Cl, 18.1.) Solutions of this compound in acetone rapidly precipitated $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2$. However, dissolution of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2$ in an acetone solution of stannous chloride afforded pale yellow, crystalline $[(\text{C}_6\text{H}_5)_3\text{P}]_2[\text{PtCl}_2(\text{SnCl}_3)]$ (*Anal.* Calcd.: Cl, 14.5; Pt, 19.9. Found: Cl, 14.8; Pt, 19.4). Both the red and yellow anionic complexes also reacted with triphenylphosphine in acetone to give $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2$.

(1) See, for example, (a) J. Kwiatek, I. L. Mador and J. K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962); (b) J. Halpern, J. F. Harrod and B. A. James, *ibid.*, **83**, 753 (1961); (c) M. F. Sloan, A. S. Matlack and D. S. Breslow, paper presented at the Delaware Science Symposium, University of Delaware, Newark, Delaware, February 23, 1963, abstracted in the DEL-CHEM Bulletin, **19** (5), 24 (1963).

(2) The data presented by J. H. Flynn and H. M. Hulburt, *J. Am. Chem. Soc.*, **76**, 3393 (1954), may, however, be interpreted as a homogeneous hydrogenation of ethylene in the presence of $(\text{PtCl}_2\text{C}_2\text{H}_4)_2$ at temperatures below -10° .

(3) E. L. Jenner and R. V. Lindsey, Jr., U.S. Patent 2,876,254, March 3, 1959.

(4) A. S. Meyer, Jr., and G. H. Ayres, *J. Am. Chem. Soc.*, **77**, 2671 (1955).

(5) S. K. Shukla, *Ann. Chim. (Paris)*, [13] **6**, 1432 (1961).

(6) H. Okuno, H. Yamatera, T. Ishemoric and K. Mezumachi, Abstract 4E3, 7th International Conference on Coordination Chemistry, 1962.

(7) Similar results have been obtained by A. G. Davies, G. Wilkinson and J. F. Young, *J. Am. Chem. Soc.*, **85**, 1692 (1963).

(8) Identical with a sample prepared from $(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Cl}$ and SnCl₄ in 3 *M* HCl, m.p. 294° after recrystallization from methanol-3 *M* HCl (*Anal.* Calcd.: Cl, 24.1; Sn, 13.4. Found: Cl, 24.4; Sn, 13.8).

(9) A. Michaelis and K. v. Soden, *Ann. Chem.*, **229**, 310 (1885).

The structure of these complexes is under investigation. Tin-metal bonding has recently been proposed by Gorsich¹⁰ for the related compounds $\text{Mo}(\text{CO})_5\text{SnCl}_3$ and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnCl}_3$. The platinum-tin complexes may contain $(\text{SnCl}_3)^-$ ligands attached through platinum-tin bonds.

Acknowledgments.—R. V. L. wishes to acknowledge many helpful discussions with Professors Dietmar Seyferth and J. W. Irvine, Jr., during that part of this investigation conducted at the Massachusetts Institute of Technology.

(10) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

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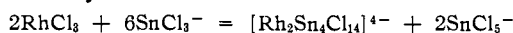
TIN(II) CHLORIDE COMPLEXES OF PLATINUM METALS

Sir:

It has been known for decades¹ that certain platinum metal halides or halide complex ions in aqueous solution or in solvents such as ethanol or ethyl acetate give colored species when treated with tin(II) chloride. The platinum chloride-tin(II) chloride system is also known to be a carbonylation and hydrogenation catalyst.²

Although Ayres³ considered the platinum species to be cationic, *viz.*, $[\text{PtSn}_4\text{Cl}_4]^{4+}$, Shukla¹ showed by electrophoresis measurements that the rhodium and platinum species are anionic in hydrochloric acid solution, an observation we have confirmed by ion exchange study. Recently⁴ a ruthenium complex (Ru:Sn ratio 1:4-5) was shown to be anionic and to be precipitated by large cations.

Our studies on the rhodium(III) chloride-tin(II) chloride system provided the first evidence for what we now consider to be the true nature of these tin-containing platinum metal complexes. Thus in ethanolic or in 3 *M* hydrochloric acid solution (main species SnCl_3^-) the Job method using the visible absorption spectrum showed that in both media the ratio Rh:Sn required for the formation of the red complex was 1:3. Addition of tetramethylammonium chloride to the solutions gave orange-yellow precipitates. The analysis corresponds to $[(\text{CH}_3)_4\text{N}]_4[\text{Rh}_2\text{Sn}_4\text{Cl}_{14}]$ [*Anal.* Calcd. C, 13.0; H, 3.2; Cl, 33.7; N, 3.8; Sn, 32.2. Found: C, 13.1; H, 2.9; Cl, 34.0; N, 3.7; Sn, 32.0] so that the interaction in 3 *M* acid may be written



We have prepared similar diamagnetic tetraalkylammonium salts (shown to be 2:1 electrolytes in dimethylformamide) of the ions $[\text{Ru}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$, $[\text{Ir}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ and $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$. While the latter ion can be obtained from PtCl_4^{2-} by chloride ion displacement, it is also formed by direct replacement by tin(II) chloride of the ligands in complexes such as $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$ and mesityloxydeplatinum(II) chloride.⁵

(1) For references see S. K. Shukla, *Ann. Chim. (Paris)*, [13] **6**, 1383 (1961).

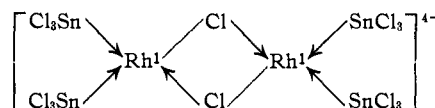
(2) E. L. Jenner and R. V. Lindsey, Jr., U.S. Pat. 2,876,254, March 3, 1959; R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(3) G. H. Ayres, B. L. Tuffy and J. S. Forester, *Anal. Chem.*, **27**, 1742 (1955); A. S. Meyer and G. H. Ayres, *J. Am. Chem. Soc.*, **77**, 2671 (1955).

(4) H. Okuno, H. Yamatera, T. Ishimori and K. Mizumachi, Abstract 4E3, 7th International Conference on Coordination Chemistry, 1962.

(5) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

Although numerous examples of transition metal to tin bonds are known from the work of Hieber and more recently Gorsich,⁶ these are best regarded as derivatives of tin(IV). However, we believe that the present complexes are best formulated as complexes of tin(II). Thus, for example, the rhodium and platinum species can be considered as square planar complexes of Rh^I and Pt^{II} , respectively, in which either SnCl_3^- (in the complex anions) or solvated tin(II) chloride (in neutral species) act as donor ligands using the lone-pairs known to be present.⁷ The ion $[\text{Rh}_2\text{Sn}_4\text{Cl}_{14}]^{4-}$ thus can be regarded as



and the other species can be similarly formulated. Support for this view is provided by the direct replacement, from the Ru, Rh, Ir and Pt complexes, of tin(II) chloride—which can be characterized by standard tests—by ligands such as pyridine, triphenylphosphine and carbon monoxide, in the latter case the rhodium complex giving $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. In these studies we have also isolated an orange complex which can be formulated $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2\text{SnCl}_3$ and there appear to be similar complexes of rhodium, iridium and ruthenium. It may be noted that Dwyer and Nyholm⁸ have reported compounds of rhodium containing methyl diphenylarsine and stannous chloride which they formulated as bridged species containing combinations of Sn-Cl-Rh, Sn-Cl-Sn and Rh-Cl-Rh bridges; we believe that Rh-Sn bonds probably are present here also.

(6) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962), and references therein.

(7) D. Grdenić and B. Kamenar, *Proc. Chem. Soc.*, 304 (1961); *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962).

(8) F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **76**, 129 (1942).

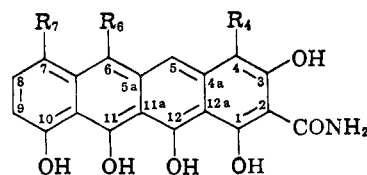
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BIOSYNTHESIS OF THE TETRACYCLINES. V.¹ NAPHTHACENIC PRECURSORS

Sir:

We wish to report the biological conversion of 1,3-, 10,11,12-pentahydroxynaphthacene-2-carboxamide² (2) and some related compounds to tetracycline antibiotics. These naphthacenic precursors, which can be represented by the general formula 1, were prepared by degradation of tetracycline antibiotics.³



- 1
2 $R_4, R_6, R_7 = \text{H}$
3 $R_4, R_7 = \text{H}; R_6 = \text{CH}_3$
4 $R_4 = \text{N}(\text{CH}_3)_2; R_6 = \text{CH}_3; R_7 = \text{H}$
5 $R_4 = \text{N}(\text{CH}_3)_2; R_6 = \text{H}; R_7 = \text{Cl}$

(1) Paper IV: J. R. D. McCormick, P. A. Miller, S. Johnson, N. Arnold and N. O. Sjolander, *J. Am. Chem. Soc.*, **84**, 3023 (1962).

(2) We propose the name "pretetramid" for this tetracyclic amide which is the parent of the family of precursors reported here.

(3) The preparation of compound 2 from 6-demethyltetracycline is described in the accompanying communication [J. R. D. McCormick, J. Reichenthal, S. Johnson and N. O. Sjolander, *J. Am. Chem. Soc.*, **85**, 1694 (1963)]. Compound 3 was prepared from tetracycline by the method of A.