

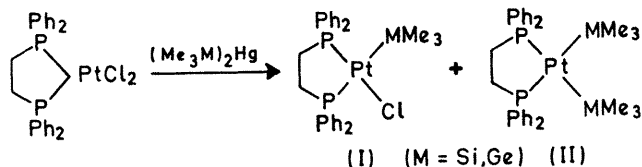
Silyl-, Germyl-, and Stannyl-exchange Reactions of Platinum(II) Complexes: Isolation of Octahedral Platinum-Tin Intermediates

By A. F. CLEMMIT and F. GLOCKLING*

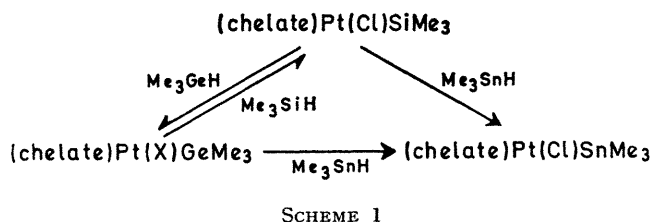
(Department of Inorganic Chemistry, The Queen's University, Belfast BT9 5AG)

Summary Exchange reactions between trialkyl-silanes, -germanes, and -stannanes and complexes (I) and (II) have led to the isolation of the two octahedral platinum-tin compounds (III) and (IV).

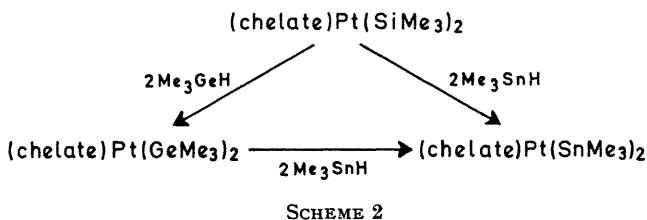
MANY silyl-, germyl-, and stannyl-derivatives of Pt^{II} and Pt^{IV} have been reported;¹⁻³ all examples with platinum in its +2 oxidation state are four-co-ordinate, whilst the Pt^{IV} compounds are all six-co-ordinate. Most reactions involving cleavage of a Pt—M bond (*e.g.* with H₂ or HCl) have been interpreted in terms of an addition-elimination mechanism, although with one exception⁴ definitive evidence for octahedral adducts has hitherto been lacking.^{5,6}



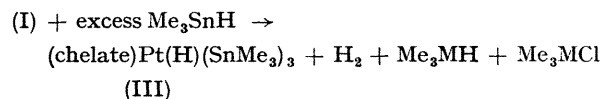
We have isolated two series of *cis*-complexes (I) and (II) and have examined their exchange reactions with Me_3MH compounds ($\text{M} = \text{Si, Ge, Sn}$). These are equilibrium reactions of low activation energy (typically 12 h at 40°) and for both series of compounds the position of equilibrium



favoured R_3M -products in the order: $\text{R} = \text{Sn} > \text{Ge} > \text{Si}$ (Schemes 1 and 2).



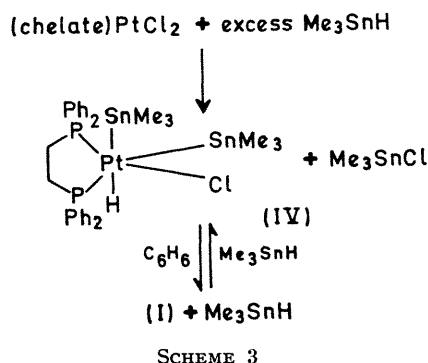
None of the stoichiometric reactions of Schemes 1 or 2 produced direct evidence of octahedral adducts but the reaction of (I) ($\text{M} = \text{Si or Ge}$) with an excess of trimethylstannane yielded the white crystalline complex (III) together with hydrogen, Me_3MH , and Me_3MCl .



Complex (III) showed $\nu(\text{Pt-H})$ at 1960 cm^{-1} (consistent with *trans*- H-Pt-SnMe_3) but its ^1H n.m.r. spectrum gave only a broad resonance centred on τ 15.25 attributable to the Pt-H proton. The broadness is probably due to the proton being coupled to Pt, both P atoms, and both magnetic isotopes of the three tin atoms. In this reaction the Si-H n.m.r. of the displaced Me_3SiH molecule showed 8 of the expected 10 lines [$J(\text{H-Si-CH}_3)$ 3.5 Hz] whereas the Sn-H resonance of the excess of Me_3SnH was not resolved. This implies rapid exchange of free trimethylstannane with (III) and would also broaden the Pt-H resonance. In the absence of platinum compounds $J(\text{H-Sn-CH}_3)$ 3.63 Hz. Compound (III) is air-stable in the solid state but in solution it is stable only in the presence of an excess of stannane; in its absence Me_3SnH and $(\text{chelate})\text{Pt}(\text{SnMe}_3)_2$ are formed.

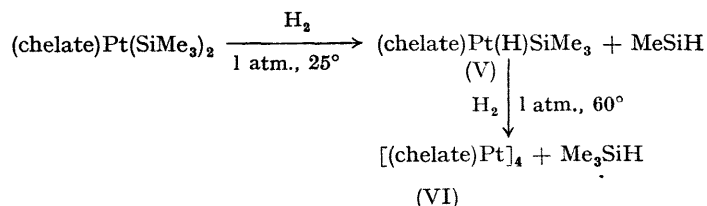
A similar octahedral hydride (IV) was isolated from the reaction between $(\text{chelate})\text{PtCl}_2$ and trimethylstannane. This also shows $\nu(\text{Pt-H})$ at 1960 cm^{-1} , consistent with the

grouping *trans*-Me₃Sn-Pt-H, and is stable in solution only with an excess of trimethylstannane present; its decomposition to (I; M = Sn) is reversible (Scheme 3).



The ¹H n.m.r. spectra of the methyl protons of complexes (I) and (II) consist of 1:1:4:4:1:1 sextets owing to the coupling *trans*-Me₃M-¹⁹⁵Pt-³¹P when M = Si and Ge. However, for trimethylstannyl groups in (I) and (II) coupling to *trans*-phosphorus was not observed, but only a 1:4:1 triplet resulting from *J*(Me₃Sn-¹⁹⁵Pt) 9.3 Hz, together with satellites due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn isotopes. The absence of observable long range coupling to the *trans*-phosphorus atom is probably due to the high *trans*-influence of the Me₃Sn group producing reversible breaking of the *trans*-Pt-P bond.

Compound (I; M = Si) is cleaved by hydrogen (25°, 1 atm.) to yield (chelate)Pt(H)Cl and Me₃SiH. At 25° one Me₃Si group was cleaved from the bis(trimethylsilyl) complex (II) yielding (V) in a reaction which was first order with respect to hydrogen and (II). However, at 60° both Pt-Si bonds are cleaved by hydrogen to yield Me₃SiH and a platinum(0) complex, tentatively formulated as (VI).



(Received, April 22nd, 1970; Com. 591.)

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