Inorganica Chimica Acta, *76* (1983) L283–L284

Attempted Synthesis of a Tin–Platinum Heterocycle

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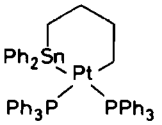
Received January 11, 1983

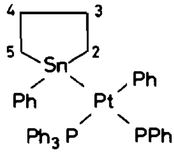
The study of metallacycloalkanes is of current interest because of their involvement as intermediates in many homogeneous catalytic reactions. Catalyst systems of transition metal complexes activated by tin compounds are known in olefine metathesis [1], hydrogenation [2] and hydroformylation [3]. Silaplatinacycloalkanes containing silicon and platinum bonded directly have been proposed as intermediates in the formation of silacycloalkanes by hydrosilation [4]. Bulten and Budding [5] have reported the formation of an unstable stannaferracyclohexane which could be characterized by spectroscopic methods. A prelimanry account of our own attempts to synthesize several stannaferracycloalkanes is given in Ref. [6]. Since the stability of tin–transition metal bonds increases when descending in the Periodic Table, we expected that stable tin–transition metal heterocycles could be formed with 5d metals like platinum. Recently, H. Weichmann [7] reported the synthesis of the first spirocyclic stannaplatinacycloalkanes, *cis-* and *trans-*$\{\overline{\mathrm{Pt}[\mathrm{PPh_2(CH_2)_n Sn}}\mathrm{Me_2}]_2\}$ (n = 2,3), which are stabilized by phosphine coordination.

Results and Discussion

When 1,1-diphenyl-1-stannacyclopentane is reacted with η^2-ethylene-bis(triphenylphosphine)-platinum(0) in benzene medium, slow evolution of ethylene takes place and a tin–platinum complex is precipitated as a white solid which decomposes without melting above 150 °C. However, the complex dissociates slowly in solution when redissolved. The elemental analysis and the mass spectrum (mol. peak at *m/e* = 1049, FD method, calc. for ^{195}Pt, ^{120}Sn) are in accordance with the composition $\mathrm{Ph_2Sn(CH_2)_4}$-$\mathrm{Pt(PPh_3)_2}$. The following structures are reasonable for the obtained product:



I



II

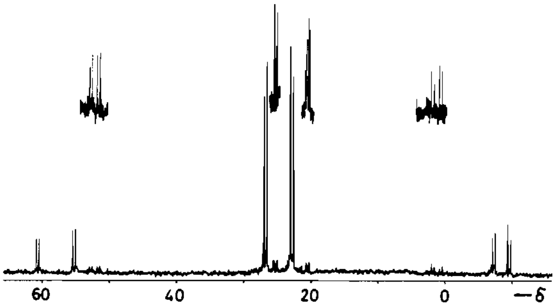


Fig. 1. ^{31}P{^{1}H} NMR spectrum of *cis*-$\mathrm{(PPh_3)_2Pt(Ph)}$-$\mathrm{Sn(Ph)(CH_2)_4}$ (in $\mathrm{C_6H_6/C_6D_6}$, ext. standard 85% $\mathrm{H_3PO_4/D_2O}$).

The ^{31}P{^{1}H} NMR spectrum (Fig. 1) reveals two doublets due to coupling between the two non-equivalent $\mathrm{PPh_3}$ ligands with ^{2}J(P–Pt–P) = 13.5 Hz§. The left doublet centred at δ +26.33 ppm is associated with satellites due to coupling with ^{195}Pt [^{1}J(Pt–P) 2182 Hz], ^{119}Sn [^{2}J(Sn–Pt–P) 1673 Hz] and ^{117}Sn [^{2}J(Sn–Pt–P) 1598 Hz]. This doublet is assigned to the $\mathrm{PPh_3}$ group *trans* to tin. The right doublet at δ +22.46 ppm shows a similar coupling pattern with smaller coupling constants [^{1}J(Pt–P) 2077 Hz, ^{2}J(^{119}Sn–Pt–P) 161 Hz and ^{2}J(^{117}Sn–Pt–P) 154 Hz] and, therefore, is assigned to the P atom *cis* to tin. It has been fairly well established that in tin-platinum complexes the *trans* Sn–Pt–P coupling is much larger than the *cis* coupling [8].

As expected, the ^{119}Sn{^{1}H} NMR spectrum shows a doublet of doublets with centre at δ = –0.3 ppm ($\mathrm{CDCl_3}$ solution, $\mathrm{Me_4Sn}$ standard) and Sn–Pt–P coupling constants identical to those in the ^{31}P spectrum. The platinum satellites could not be detected due to poor resolution. An additional singlet at δ = –1.1 ppm reveals that the parent stannacyclopentane is reformed in solution during longer recording times [9].

The ^{13}C{^{1}H} NMR spectrum ($\mathrm{CDCl_3}$ solution, TMS standard) shows two multiplets for aliphatic carbons at δ = 12.6 and 29.8 ppm. Two carbon atoms must be equivalent and thus the bimetallacyclic structure I is excluded. An additional singlet at δ = 9.9 ppm is due to decomposition as indicated above [9]; the second singlet of the reformed stannacyclo-

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§Absolute values are given for all coupling constants.

0020-1693/83/$3.00

pentane is overlapped by the 29.8 ppm multiplet. This multiplet can be assigned to C3,4 of complex II with an exocyclic Sn–Pt bond. The fine structure of the multiplet is explained by coupling with ^{195}Pt, ^{3}J(Pt–Sn–C–C) 16.6 Hz (overlapped with Sn satellites), and ^{31}P, ^{4}J(P–Pt–Sn–C–C) 1.5 Hz. The multiplet for C2,5 consists of a doublet of doublets by coupling with *trans*-P, ^{3}J(P–Pt–Sn–C) 9.7 Hz, and *cis*-P, ^{3}J(P–Pt–Sn–C) 2.3 Hz. The Pt satellites appear with ^{2}J(Pt–Sn–C) = 67.9 Hz which clearly favours structure II since direct Pt–C coupling constants are in the order of 300–600 Hz [10].

The formation of the desired tin-platinum bimetallacycle I is prevented by the higher polarizability of the tin-phenyl bonds which are more prone to electrophilic attack than tin-methylene bonds. As an examination of the molecular model shows, insertion of the bis(phosphine)platinum moiety into the stannacycle would afford a sterically highly-crowded molecule with eight phenyl groups closely neighboured. Thus, no overall release of the ring strain [5] can occur and the ring expansion is not favoured.

Acknowledgement

The grant of a visiting professorship to J. D. K. by DAAD (German Academic Exchange Service) and the gift of platinum salt by DEGUSSA (Hanau) is gratefully acknowledged. We are obliged to Dr. B. Mathiasch, Univ. of Mainz, for the registration of the Sn NMR spectrum and to Dr. P. Merbach, Univ. of Erlangen, for recording the mass spectrum.

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