Inorganica Chimica Acta, 28 (1978) L167–L168
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Derivatives of Bivalent Germanium, Tin and Lead. Part XXII*. Palladium and Platinum Complexes of Bivalent Tin Compounds

PAUL F. R. EWINGS and P. G. HARRISON**

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Received April 8, 1978

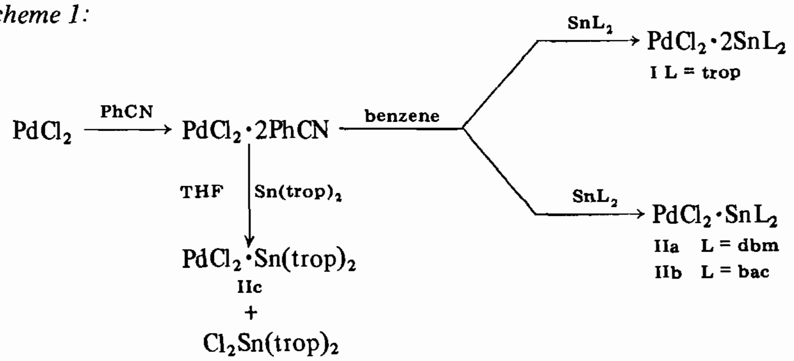
We have previously demonstrated that bis(1,2- and -1,3-ketoenolato)tin(II) compounds [1, 2] possess lone pairs which are stereochemically active [3] and which therefore are capable of functioning as two-electron donor ligands. Thus, photolysis of chromium, molybdenum and tungsten hexacarbonyls with these bivalent tin compounds in THF yields the expected stannio-Group VI metal pentacarbonyl complexes [4], whilst similar stannio-dicarbonyl-(methylcyclopentadienyl)manganese complexes were obtained from methylcyclopentadienylmanganesetricarbonyl [5]. With di-iron enneacarbonyl, however, dimerisation accompanies displacement of carbon monoxide yielding $[L_2SnFe(CO)_4]_2$ complexes, although dissociation occurs to varying extents in chloroform solution and is complete in strongly nucleophilic solvents such as pyridine [6]. The reaction with dicobalt octacarbonyl yields products of composition $\{Co(CO)_4\}_2SnL_2$, $Co_2(CO)_7(SnL_2)$, or $Co(CO)_4SnL$ depending on the nature of the ketoenolate residue [7]. In this Communication we report the syntheses of palladium(II) and platinum(II) complexes of these bivalent tin ligands.

The addition of benzene solutions of $Sn(dbm)_2$ or $Sn(bac)_2$ [8] to a benzene solution of $PdCl_2 \cdot 2PhCN$ also in benzene yielded the 1:1 complexes IIa and IIb, respectively (Scheme 1). A similar procedure using $Sn(trop)_2$ [8], however, afforded the 1:2 complex I in benzene, although a 1:1 complex IIc was obtained when THF was employed as the solvent. Some $Cl_2Sn(trop)_2$ was also obtained from the latter reaction.

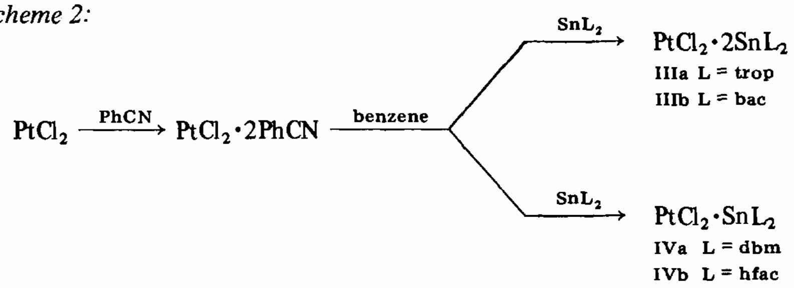
Analogous platinum(II) complexes were obtained similarly by initially dissolving $PtCl_2$ in a small amount of benzonitrile forming $PtCl_2 \cdot 2PhCN$ *in situ*, dilution with benzene, and addition of the bivalent tin ligand also in benzene (Scheme 2).

The complexes I–IV usually precipitated readily upon the addition of the solution of the bivalent tin ligand to the solution of the metal chloride, although slow dropwise addition of pentane was employed to induce the crystallisation of the perfluorinated derivative IVb. The products obtained were

Scheme 1:



Scheme 2:



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*Part XXI. P. G. Harrison and E. W. Thornton, *J. Chem. Soc. Dalton*, in press.

**Address all correspondence to this author.

TABLE I. Tin-119*m* Mössbauer Data for the Complexes (mm s^{-1})[a].

Complex	I.S.[b]	Q.S.
$PdCl_2 \cdot Sn(dbm)_2$	1.70	1.75
$PdCl_2 \cdot Sn(bac)_2$	1.82	1.62
$PtCl_2 \cdot 2Sn(bac)_2$	1.51	2.02
$PtCl_2 \cdot Sn(hfac)_2$	1.49	2.13
$PtCl_2 \cdot Sn(dbm)_2$	1.50	2.10

[a] Recorded at 77 K *vs.* a Ba $^{119m}SnO_3$ source. [b] Relative to SnO_2 = 0.

either dark brown (Pd) or orange (Pt) amorphous solids, which were moderately hygroscopic, and which did not readily redissolve in common organic solvents. The ^{119}Sn Mössbauer spectra of the complexes consisted of quadrupole split doublets, and typical data are listed in Table I. The isomer shifts of both palladium and platinum complexes are lower than those of the free ligands [1, 2], indicative of substantial removal of 5*s* electron density away from tin and/or increased shielding of the tin nucleus resulting from (d → p)π retrodative bonding from palladium or platinum to tin.

The stoichiometry adopted by the complexes appears to be largely controlled by steric factors. Thus, the bulky $Sn(dbm)_2$ and $Sn(bac)_2$ ligands form 1:1 complexes with palladium, whereas $Sn(trop)_2$ forms both 1:1 and 1:2 complexes. Similarly, in the case of platinum, 1:1 complexes are formed by $Sn(dbm)_2$ and $Sn(hfac)_2$ [8], but 1:2 complexes are formed by $Sn(trop)_2$ and $Sn(bac)_2$, the larger size of platinum allowing the formation of the latter.

Acknowledgement

We thank the Science Research Council for support.

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8 bac = OCMeCHCOPh; dbm = OCPhCHCOPh; trop = O_2-C_7H_5; hfac = $OC(CF_3)CHCO(CF_3)$.