CH_2Cl_2 absorbs 4–5 mmol of HCl and changes color from light to dark orange. On applying a vacuum, the color change is reversed and all of the HCl is released. Examination of the residue by ^1H NMR shows only II. It may also be that N (or O) protonation is occurring. The infrared spectrum of a solution of HCl and II at 25 °C contains new absorptions at 1615 and 1930 cm^{-1} which cannot be attributed to starting materials. Infrared experiments with DCl have thus far been inconclusive because of overlap.

The results of this work suggest that rhodium may be a poor catalyst for reactions of some substituted olefins with mechanisms which involve olefin insertion into an alkyl–rhodium bond. On the other hand it is a good catalyst for reactions involving alkylmetal formation such as the hydrogenation of 1,4-dicyano-2-butene.[12] In addition, a strong preference for linear alkyl formation was found.

Registry No. I, 59831-04-8; I-A, 59831-05-9; II, 52367-67-6; III, 12211-95-9; IV, 59831-06-0; IV-A, 59831-07-1; IV-B, 59831-08-2; V, 59831-09-3; VI, 52367-68-7; VII, 59831-10-6; VIII, 36312-12-6; IX, 59872-34-3; IX-A, 59831-11-7; IX-B, 59831-12-8; X, 36118-17-9; HCl, 7647-01-0.

Supplementary Material Available: Table II, showing elemental analyses of the new complexes (1 page). Ordering information is given on any current masthead page.

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Contribution No. 2359 from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Novel Triaryloxo- and Triaroyloxostannyl Transition Metal Complexes

D. Robert Coulson* and Linda P. Seiwell

Received February 24, 1976 AIC601434

Many transition metal complexes are known which have SnX_3^- as a monodentate ligand.[1-3] X is usually halogen, but several complexes are known where X is alkyl or aryl. In contrast, transition metal complexes with tin ligands of the type $Sn(OR)_3^-$ or $Sn(NR_2)_3^-$ are rare.[4] We now report the preparation and some properties of a novel series of platinum(II) and palladium(II) complexes which have either $Sn(OC_6H_5)_3^-$ or $Sn(O_2CC_6H_5)_3^-$ as ligands.

Table I. Melting Point and Infrared Data for *trans*-$L_2M(X)Y$ (L = PEt_3, $P(OC_6H_5)_3$; M = Pd, Pt)

X	Y	Mp, °C	ν_{PtX},[e] cm^{-1}
	trans-$(PEt_3)_2Pt(X)Y$		
Cl	$Sn(OC_6H_5)_3$	92–93	302
Cl	$SnCl_3$[a]		339,[c] 315[d]
Cl	$Sn(CH_3)_3$[a]		278[f]
Cl	$Sn(C_6H_5)_3$[a]		298[c]
Cl	$Sn(O_2CC_6H_5)_3$	141	280
Cl	$Sn(OC_6H_5)_3$[b]	151–152	288
Br	$Sn(OC_6H_5)_3$	90–91	187
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	152–153	
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$[b]	177–180	
	trans-$(PEt_3)_2Pd(X)Y$		
Cl	$Sn(OC_6H_5)_3$	94–95	*g*
Cl	$Sn(O_2CC_6H_5)_3$	144–146	286
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	141–142	

[a] Complex where PEt_3 is replaced by $P(C_6H_5)_3$. [b] Complex where PEt_3 is replaced by $P(OC_6H_5)_3$. [c] R. V. Parish and P. J. Rowbotham, *J. Chem. Soc., Dalton Trans.*, 38 (1973). [d] M. C. Baird, *J. Inorg. Nucl. Chem.*, 29, 367 (1967). [e] Duplicate determinations of the stretching frequencies on the new complexes gave values within 3–5 cm^{-1} of each other. [f] D. J. Cardin and M. F. Lappert, *Chem. Commun.*, 506 (1966). [g] Assignment uncertain due to interference by other absorptions.

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Elemental analyses were performed in house. Tin was determined by ASTM method E54-60T. An important starting material in this work, $Sn(OCH_3)_2$, was prepared from $SnCl_2$, $N(C_2H_5)_3$, and methanol following the procedure described by Morrison.[6] All NMR spectra were referenced to tetramethylsilane. The far-infrared spectra were taken in Nujol mulls between CsI plates. Molecular weights were determined cryoscopically in benzene under N_2.

Preparation of $NaSn(OC_6H_5)_3$·THF. Addition of 30 ml of tetrahydrofuran to a mixture of phenol (3.03 g, 32 mmol), $Sn(OCH_3)_2$ (2.84 g, 16 mmol), and $NaOC_6H_5$ (1.87 g, 16 mmol) produced a clear solution. Evaporation of volatiles under vacuum (10 mmHg) produced a white amorphous solid which was then dissolved in 25 ml of benzene. This mixture was filtered and 1 ml of tetrahydrofuran was added to the filtrate. Rapid addition of 40 cm^3 of hexane to the filtrate followed by 1 h of standing yielded 4.93 g (63% yield) of white crystals, mp 122.5–124 °C.

NMR (60 MHz, DMSO): δ (ppm) 1.60–1.90 and 3.50–3.75 (8 H, multiplet), 6.35–7.20 (15 H, aromatic, multiplet). Anal. Calcd for $C_{22}H_{23}O_4SnNa$: C, 53.58; H, 4.70; Sn, 24.05. Found: C, 53.75; H, 4.78; Sn, 22.67.

Preparation of $NaSn(O_2CC_6H_5)_3$·0.5THF. Following the procedure described for the preparation of $NaSn(OC_6H_5)_3$·THF the analogous $NaSn(O_2CC_6H_5)_3$·0.5THF was prepared in 80% yield. This material did not melt below 230 °C.

NMR (60 MHz, DMSO): δ (ppm) 8.05 and 7.50 (15 H, multiplet, $-C_6H_5$), 3.60 and 1.75 (4 H, multiplet, THF). Anal. Calcd for $C_{23}H_{19}O_{6.5}SnNa$: C, 51.11; H, 3.54; Sn, 21.96. Found: C, 51.57; H, 4.07; Sn, 21.58.

Preparation of *trans*-$(PEt_3)_2Pt[Sn(OC_6H_5)_3]Cl$. A solution of $NaSn(OC_6H_5)_3$·THF (4.93 g, 10.0 mmol) in 35 ml of THF was added to a solution of *trans*-$(PEt_3)_2PtCl_2$ (5.03 g, 10.0 mmol) in 20 ml of THF. A white precipitate formed on mixing. The mixture was filtered and the filtrate evaporated to dryness under vacuum (12 mmHg) to give an oily yellow residue. This residue was taken up in 10 ml of THF and then 50 ml of hexane was added. On standing of the mixture at 0 °C yellow needles formed (5.96 g); mp 90–91 °C. Recrystallization from 5 ml of THF and 7 ml of hexane gave 4.22 g (50% yield), mp 92–93 °C.

NMR (60 MHz, CD_2Cl_2): δ (ppm) 2.25 and 1.15 (30 H, multiplet, $-C_2H_5$), 7.05 (15 H, multiplet, $-C_6H_5$).

Tables I and II give the elemental analyses[15] and physical measurements for this complex and related ones prepared by this procedure.

Table II. Analytical Data for *trans*-$L_2M(X)Y$ (L = PEt_3, $P(OC_6H_5)_3$; M = Pd, Pt)

X	Y	C Calcd	C Found	H Calcd	H Found	P Calcd	P Found	Sn Calcd	Sn Found
			trans-$(PEt_3)_2Pt(X)Y$						
Cl	$Sn(OC_6H_5)_3$	41.66	41.88	5.24	5.41	7.16	7.14	13.72	12.00
Cl	$Sn(O_2CC_6H_5)_3$	41.77	41.37	4.78	4.88	6.53	6.70	12.51	11.98
Cl	$Sn(OC_6H_5)_3$[a]	51.92	51.98	3.63	3.88	4.96	4.85	9.50	10.98
Br	$Sn(OC_6H_5)_3$	39.62	39.47	4.99	4.97	6.81	6.85	13.05	12.04
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	46.97	46.44	4.93	5.02			19.34	18.46
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$[a]	53.65	53.28	3.76	3.85	3.84	2.79	14.73	14.33
			trans-$(PEt_3)_2Pd(X)Y$						
Cl	$Sn(OC_6H_5)_3$	46.41	46.20	5.84	5.82	7.98	7.74	15.29	12.50
Cl	$Sn(O_2CC_6H_5)_3$	46.10	47.17	5.27	5.37			13.75	13.99
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	50.63	48.64	5.31	5.82	5.44	5.71	20.85	18.69

[a] Complex where PEt_3 is replaced by $P(OC_6H_5)_3$.

Results and Discussion

The complexes described here are of the type *trans*-$L_2MX_{2-n}[Sn(OR)_3]_n$ (M = Pd, Pt) where X^- is Cl^- or Br^-, R is C_6H_5 or COC_6H_5, and L is PEt_3 or $P(OC_6H_5)_3$. These complexes were prepared from the appropriate dihalo complexes according to eq 1. The complexes prepared are listed

$$trans\text{-}L_2MX_2 + n\mathrm{NaSn(OR)_3} \rightarrow trans\text{-}L_2MX_{2-n}[\mathrm{Sn(OR)_3}]_n + n\mathrm{NaX} \quad (1)$$
$$(X = \mathrm{Br, Cl}; n = 1, 2)$$

in Table I along with associated physical data. All of the complexes with L = PEt_3 have ^1H NMR spectra characteristic of the trans configuration.[5]

The tin salts used in these preparations are also new compounds and were prepared from $Sn(OCH_3)_2$[6] as described by eq 2.

$$\mathrm{Sn(OCH_3)_2 + 2ROH + NaOR \rightarrow NaSn(OR)_3 + 2CH_3OH} \quad (2)$$

The preparations were carried out in tetrahydrofuran (THF) and the resulting salts were isolated as THF solvates. Interestingly, it was observed that the success of these preparations was critically dependent upon the nature of R. When R was aryl or aroyl, the reactions proceeded to completion immediately on mixing at room temperature. However, when this reaction was attempted with $NaOCH_3$, either in the presence or in the absence of methanol, no reaction was observed on stirring for 16 h at room temperature or on refluxing in methanol for 8 h. Lacking additional information we can offer no reasonable explanation for this reagent dependency.

The preparation of these transition metal complexes significantly increases the variety of tin-containing ligands bonded to the group 8 metals and affords an opportunity to examine the trans influence[7] of these ligands. Toward this end the far-infrared spectra of these complexes were examined and the absorptions attributable to the metal–halogen stretching frequencies, ν_{M-X}, were assigned by analogy to related complexes. Table I documents these and related assignments taken from the literature. The internal consistency of these assignments followed from a comparison of ν_{Pt-Cl} (280 cm^{-1}) in *trans*-$(PEt_3)_2Pt[Sn(O_2CC_6H_5)_3]Cl$ with ν_{Pd-Cl} (286 cm^{-1}) in the corresponding palladium complex. On the basis of the values of ν_{M-X} obtained, the tin ligands were arranged in the following order of *apparent* trans influence: $SnCl_3^- < Sn(OC_6H_5)_3^- \sim Sn(C_6H_5)_3^- < Sn(O_2CC_6H_5)_3^- \sim Sn(CH_3)_3^-$. This order was derived by assuming a negligible effect of the nature of the cis ligands, L, on ν_{M-Cl}.[7b]

Recent discussions of the trans influence have indicated its dependence on both σ- and π-bonding properties of the trans ligands. With regard to σ-bonding properties, the trans influence has been generally found[7,9] to increase with decreasing ligand electronegativity among ligands possessing similar π-bonding properties. In the systems examined here, because of the constancy of the ligating atom, the ligand electronegativities might be expected to be primarily dependent upon the electronegativities of the atoms bonded to tin. On this basis the oxygen-containing ligands studied here should show a lesser trans influence than, for example, the $SnCl_3^-$ ligand.[10] In fact, the opposite was apparently found to be true; vide supra. A possible explanation[11] for this anomaly came from cryoscopic molecular weight determinations on *trans*-$(PEt_3)_2Pt(Cl)Sn(OC_6H_5)_3$. It was found that this complex was significantly associated at concentrations as low as 0.86 wt % in benzene. At this concentration an average molecular weight, $\bar{M}_n$, of 1094 was obtained (monomer mol wt 864.8). However, due to the presence of traces of THF, this value probably represents an underestimate of the true extent of association. The nature of this association is unknown but may involve the formation of a SnO→Sn coordinate bond as has been observed[12] for related tin alkoxides. It seems reasonable to expect this association to be more pronounced in the solid state and that the far-infrared measurements performed on these complexes are influenced by this association. Furthermore, the "effective" electronegativities[13] of these tin ligands would be expected to decrease as a result of electron donation from a coordinated oxygen. Thus, a major effect of this association phenomena might well be to cause the observed reversal in the expected trans-influence order. If this interpretation is correct, then the observed ordering is less meaningful since ligands of differing coordination numbers are being compared. Thus, the trans influences observed here for the oxostannyl ligands should be considered as representing their maximum values with the most probable values being significantly less than these. These observations also illustrate another of the pitfalls associated with interpreting infrared stretching frequencies in terms of trans-influence properties and suggest that similar solid-state effects might be responsible for other reported anomalies.[7b]

Acknowledgment. Helpful discussions with Dr. C. A. Tolman of this department are gratefully acknowledged. We thank Ms. N. E. Schlichter for the measurements of the far-infrared spectra of the complexes.

Registry No. *trans*-$(PEt_3)_2Pt(Cl)Sn(OC_6H_5)_3$, 59982-26-2; *trans*-$(PEt_3)_2Pt(Cl)Sn(O_2CC_6H_5)_3$, 59982-34-2; *trans*-$(P(OC_6H_5)_3)_2Pt(Cl)Sn(OC_6H_5)_3$, 59982-35-3; *trans*-$(PEt_3)_2Pt(Br)Sn(OC_6H_5)_3$, 59982-36-4; *trans*-$(PEt_3)_2Pt(Sn(OC_6H_5)_3)Sn(OC_6H_5)_3$, 59982-37-5; *trans*-$(P(OC_6H_5)_3)_2Pt(Sn(OC_6H_5)_3)Sn(OC_6H_5)_3$, 59991-81-0; *trans*-$(PEt_3)_2Pd(Cl)Sn(OC_6H_5)_3$, 59982-38-6; *trans*-$(PEt_3)_2Pd(Cl)Sn(O_2CC_6H_5)_3$, 59982-39-7; *trans*-$(PEt_3)_2Pd(Sn(OC_6H_5)_3)Sn(OC_6H_5)_3$, 59982-40-0; $NaSn(OC_6H_5)_3$, 59982-41-1; $NaSn(O_2CC_6H_5)_3$, 59982-42-2; *trans*-$(PEt_3)_2PtCl_2$, 13965-02-1.

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Contribution from the Department of Chemistry,
The Pennsylvania State University, Shenango Valley Campus,
Sharon, Pennsylvania 16146

Reaction of Hexachlorocyclotriphosphazene with Amides to Form Nitriles

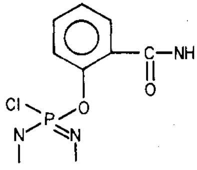
E. J. Walsh* and J. Smegal

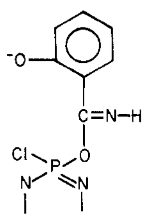
Received February 11, 1976 AIC60108X

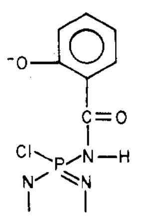
Hexachlorocyclotriphosphazene, $N_2P_3Cl_6$, is known to act as a reagent for the formation of nitriles when heated with salts of organic acids.[1-3] $N_3P_3Cl_6$ has also been shown to act as an activator for the formation of amides in the reaction between organic acids and amines.[4] Both of these reactions were believed to involve an initial step which resulted in an unstable phosphazene–carboxylate adduct which either rearranged to the nitrile or was displaced by an amine to form an amide. Recently, such an adduct was isolated by forming a stable spiro compound using salicylic acid as a reagent.[5] Isolation of this compound led us to attempt isolation of an analogous spiro compound for salicylamide. The product obtained was not the spiro derivative predicted but rather a phosphazene derivative which had the amide group rearranged to a nitrile.

Caglioti et al. had reported the synthesis of salicylamide in high yields from the reaction between salicylic acid, ammonia, and $N_3P_3Cl_6$.[4] The reaction times utilized were relatively short, 5–10 min, and no nitrile products were reported. The proposed initial step in this reaction was on attack by the carboxylate anion on a phosphorus atom followed by a rapid nucleophilic attack on the carboxyl carbon atom by the amine to yield the amide. Our work would seem to indicate that the aryloxy group of the salicylamide may be the initial attacking group.

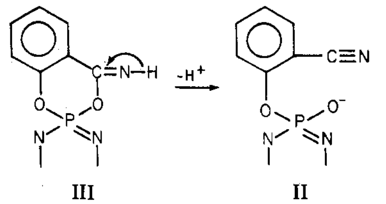
There are three possible products from the initial attack by salicylamide on a phosphazene: Ia, Ib, and Ic.


Ia

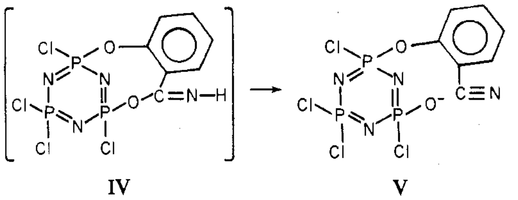

Ib


Ic

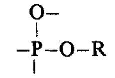
None of these compounds could be isolated or detected in the reaction mixture. However, the first product which could be isolated is shown as II. From the structure of II the most probable intermediate would be III, and III could only arise from Ia or Ib. At this time there is no physical evidence to distinguish which of these two compounds is the correct intermediate.


III II

It was possible that the intermediate was of an "Ansa"[6,7] type, IV to yield V. However, the ^{31}P NMR spectrum of the


IV V

product is an AB_2 type which indicates that II is the correct structure and not V. The doublet centered at −6.9 ppm



$$-\overset{\displaystyle O-}{\underset{|}{\overset{|}{P}}}-O-R$$

and the triplet at +18.55 ppm (PCl_2) were intergrated at 1:2 respectively and are within the range of phosphazene–phosphorus absorptions.[8]

Although there are no previously reported examples of carbonyl oxygen attack on phosphazenes to yield products such as Ib and III, this mode of attack has been well documented in the formation of spiro phosphoranes.[9,10] Also this mode of attack has been hypothesized for the mechanism of the reaction of amino acid esters with $N_3P_3Cl_6$.[11]

The intermediate III is the same type as that proposed by Cherbuliez et al. for the alcoholysis of a phosphate derivative which begins as a nitrile and yields an amide.[12]

Further support for the intermediate Ib is that the times necessary for the preparation of phenoxy phosphazene esters are very long, 1–4 days, compared to the times of reactions involving carboxylate groups, 15–30 min.[8-13]

If more than 1 equiv of salicylamide was reacted with $N_3P_3Cl_6$, the product which could be isolated had the structure VI. Neither an increase in temperature, an increase in the concentration of salicylamide, nor changing solvents resulted in the addition of more than two salicylamide groups to a phosphazene. The reasons for this limitation to substitution are unclear. Solubility is not a factor, as the reaction results in the precipitation only of triethylammonium chloride. Steric factors would seem to be the only explanation at this time. The