Journal of Organometallic Chemistry, 63 (1963) 41–45

COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXXIII. THE COORDINATION CHEMISTRY OF DIMETHYL- AND DIPHENYLTHALLIUM(III) WITH TRIDENTATE LIGANDS

L. PELLERITO, R. CEFALÙ and G. RUISI
Istituto di Chimica Generale, Università di Palermo, 90123 *Palermo* (*Italia*)
(Received May 15th, 1973)

SUMMARY

Several novel complexes Na[Me_2TlL] and Na[Ph_2TlL] (L^{2-} = dianion tridentate ligands with S, N, and O donor atoms) were synthesized, and investigated by infrared spectroscopy in the solid state, and by electronic and PMR spectroscopy in solution. Suggestions for the configuration of the complex anions are advanced and the nature of species present in solution is discussed.

INTRODUCTION

Few anionic complexes of organothallium(III) compounds are presently known. The first literature reports concerned the preparation of complexes $K_2[(C_2H_5)_2TlF_4]$[1] and $K[C_6H_5Tl(CN)_3]$[2], the latter readily decomposing into $(C_6H_5)_2TlCN$. Complexes [M] [$(C_6F_5)_2TlX_2$] (M = Ph_4P^+, Et_4N^+; X = Cl, Br) were prepared, which are 1/1 electrolytes in acetone and methanol. The IR spectra of the chloro complexes were consistent[3] with the presence of the tetrahedral anion $(C_6F_5)_2TlCl_2^-$. Barbieri *et al.*[4] synthesized the compounds [Me_4N][$PhTlCl_3$] and $[Me_4N]_2$[$PhTlCl_4$], which, according to osmometric measurements, give the complex anions $PhTlCl_3^-$ and $PhTlCl_4^{2-}$ in anhydrous methanol. In addition, Ph_4As^+ and R_4N^+ salts of anionic halide and thiocyanate complexes of R_2Tl^{III} and $PhTl^{III}$ were obtained and investigated in anhydrous acetone, in which were formed the complex anions $Me_2Tl(SCN)_2^-$, $Ph_2TlX_2^-$ (X = Cl, Br, I, SCN) and $PhTlX_3^-$ (X = Cl, Br, I)[5]. These compounds were later investigated by IR spectroscopy in the solid state, as well as by conductivity in acetone and methanol, which showed that [R_4N][$PhTlCl_3$] and $[R_4N]_2$[$PhTlCl_4$] are 1/1 and 2/1 electrolytes respectively[6]. The formation of complexes between organothallium(III) cations and halide as well as thiocyanate ligands was investigated also in aqueous solution, by paper electrophoresis and anion exchange paper chromatography[7,8].

There seems to be no report of organothallium(III) anionic species other than complexes with monodentate ligands. We recently demonstrated the ability of tridentate dianionic ligands (L^{2-}) to coordinate to organothallium centres[9], and planned to investigate systems R_2Tl^{III}–L^{2-}, in which anions R_2TlL^- would presumably be formed. This paper deals with the synthesis and structural spectroscopic studies of novel compounds Na[R_2TlL] (R = Me, Ph), where L are tridentate ligands with sulphur, nitrogen and oxygen donor atoms.

EXPERIMENTAL

Reagents and solvents were analytical grade (C. Erba, Milano), and were purified and/or dried, where necessary, by standard procedures.

The ligands 4-(2-benzothiazolinyl)-2-pentanone, H_2Aat, and 2-(*o*-hydroxyphenyl)benzothiazoline, H_2Sat, were prepared as previously described[10]. The compounds Ph_2TlCl and Me_2TlCl were obtained by published methods[11,5]

The complexes Na[Ph_2TlL] and Na[Me_2TlL] (L^{2-} = Aat^{2-} and Sat^{2-}) were synthesized by mixing methanolic solutions of L^{2-}, Schiff base forms, with methanolic suspensions or solutions of Ph_2TlCl and Me_2TlCl, in the ratio 1/1. The stable solid crystalline compounds slowly precipitated at room temperature. Analytical data are reported in Table 1. Sodium analyses were carried out by flame photometry using a Beckman DK2A spectrometer, and thallium analyses gravimetrically, according to literature methods[12,13]

TABLE 1

MELTING POINTS AND ANALYTICAL DATA

Compound (colour)	*M p (°C)*	*Found (calcd) (%)*						
		C	*H*	*O*	*N*	*S*	*Tl*	*Na*
Na[Ph_2TlAat]	145–147	47 32	3.78	2 77	2 51	5 44	34 83	3 35
(yellow)		(47 07)	(3 61)	(2 73)	(2 39)	(5 46)	(34 82)	(3 92)
Na[Ph_2TlSat]	170–172	49 33	3 35	2 63	2.46	5 59	33.21	3 43
(yellow)		(49 32)	(3 15)	(2 63)	(2 30)	(5 27)	(33 57)	(3 78)
Na[Me_2TlAat]	144–146	34 01	3 82	3 32	3 00	6 82	43 93	5 10
(pale yellow)	(dec)	(33 75)	(3 70)	(3 46)	(3 03)	(6 92)	(44 18)	(4 97)
Na[Me_2TlSat]	92	37 03	3 08	3 30	2 90	6 61	42 38	4 70
(red orange)	(dec)	(37 17)	(3 12)	(3 30)	(2 89)	(6 60)	(42 17)	(4 74)

The IR spectra were recorded on Nujol and hexachlorobutadiene mulls in the range 4000–250 cm^{-1}, by a Perkin–Elmer 457 spectrometer, using CsI disks

The electronic spectra were measured in methanol at 25° using a Beckman DK 2A spectrometer with 1 cm optical path cells. The results are listed in Table 2.

The PMR spectra of Me_2Tl^{III} derivatives were obtained with a Jeol C 60 spectrometer operating at 25° in nearly saturated $CDCl_3$ or in deuterated DMSO, with TMS as internal standard. The chemical shifts and the coupling constants are listed in Table 3.

Owing to the very poor solubility of Na[R_2TlL] in common organic solvents, no osmometric or conductometric studies could be carried out.

DISCUSSION

Inspection of Table 1 clearly shows that the analytical data are fully consistent

TABLE 2

ELECTRONIC ABSORPTION SPECTRA OF $Na[R_2TlL]$ IN METHANOL[a]

Compound	λ	*log a*
$Na[Ph_2TlAat]$[b]	277	
	318	
	350 (sh)	
$Na[Ph_2TlSat]$[b]	256 (sh)	
	283 (sh)	
	315 (sh)	
	395	
$Na[Me_2TlAat]$	255 (sh)	3.64
	312	3.62
$Na[Me_2TlSat]$	280 (sh)	3.68
	310	3.62

[a] The wavelengths [λ (nm)] and absorptivities [a, (M^{-1} cm^2)] refer to the band maxima and shoulders (sh) Concentrations range between $5 \cdot 10^{-5}$ and $1.5 \cdot 10^{-4}$ *M* [b] Saturated solutions.

TABLE 3

PMR SPECTRA OF $Na[Me_2TlL]$ AND Me_2TlCl

Compound	*Solvent*	*(Tl)*CH_3	*(C)*CH_3	*CH*	*Arom*	$J(^{205}TlCH)$
$Na[Me_2TlAat]$	$CDCl_3$	1.02	1.84, 2.05	5.19	6.9–7.3	366
$Na[Me_2TlSat]$	$CDCl_3$	0.96		8.43	6.4–7.5	356
$Na[Me_2TlAat]$[b]	DMSO-d_6 + H_2O	0.70	1.95[c]		6.8–7.5	405
$Na[Me_2TlSat]$	DMSO-d_6 + H_2O	0.75			6.5–7.5	411
Me_2TlCl	DMSO-d_6 + H_2O	0.85				429

[a] δ(TMS) = 0, δ in ppm; *J* in Hz [b] The signals due to methylene protons[10] are obscured by H_2O signals, occurring at 3.2–3.5 δ [c] Integration corresponds to 6 protons

with 1/1 ligand/diorganothallium(III) stoichiometry, and imply the formation of R_2TlL^- anions.

The IR spectra of $Na[Ph_2TlL]$ and $Na[Me_2TlL]$ essentially coincide with those of $PhTlL$[9], R_2SnL[10] and R_2PbL[14], apart from bands associated with metal–organic radical vibrations, such as the strong absorption at 450 cm^{-1} in Ph_2TlL^-, which can be assigned to a Ph–Tl mode[9]. The strong broad bands occurring in the range 1605–1490 cm^{-1} for $Na[R_2TlAat]$, characteristic[10,14] of coordinated Aat^{2-}, may be assigned to C–C, C–N, C–O stretching vibrations[10,14]. The stretching frequencies for coordinated $>$C=N– in $Na[R_2TlSat]$ probably lie at 1600 cm^{-1}, s(R = Ph) and 1610 cm^{-1}, s(R = Me), in accord with previous assignments[10,13]. The attribution of experimental absorption bands to TlC_2 vibrational modes has been attempted by closely examining the spectra of the couples Me_2TlAat^-/Ph_2TlAat^- and Me_2TlSat^-/Ph_2TlSat^- in the 600–450 cm^{-1} region, where these modes are expected to occur[15,16] In Me_2TlAat^- there appears a medium intensity, rather broad band centered at 530 cm^{-1}, corresponding to a weak sharp band of Ph_2TlAat^-; furthermore, a weak absorption of Me_2TlAat^- at 485 cm^{-1} is missing in Ph_2TlAat^- Two weak bands, missing in Ph_2TlSat^-, occur at 515 and 470 cm^{-1} in Me_2TlSat^-

These two couples of Me$_2$TlL$^-$ bands are tentatively assigned to ν_{as}(TlC$_2$) and ν_s(TlC$_2$) modes, respectively[15,16].

It can be concluded that Na[R$_2$TlL] complexes, in the solid state, contain L^{2-} (Schiff base form) coordinating R$_2$Tl^{III} through the S, N, and O donor atoms, and that the CTlC skeletons of Me$_2$TlL$^-$ seem to display a bent configuration In the light of previous studies[10,14,15], we thus suggest a trigonal bipyramidal configuration for R$_2$TlL$^-$, in which the bent CTlC moieties could be located in the trigonal plane (Fig. 1). The true structure may, of course, diverge from that idealized in Fig 1, especially in view of the tendency of R$_2$Tl^{III} moieties to maintain a linear arrangement[3] On the other hand, Mössbauer studies on R$_2$SnL[17], as well as preliminary X-ray data for Me$_3$SbL[18] and R$_2$SnL[19], tend to indicate that the coordinated L^{2-} maintains a more or less planar structure, from which a bent configuration has to be inferred for CTlC in R$_2$TlL$^-$ containing a five-coordinated Tl atom

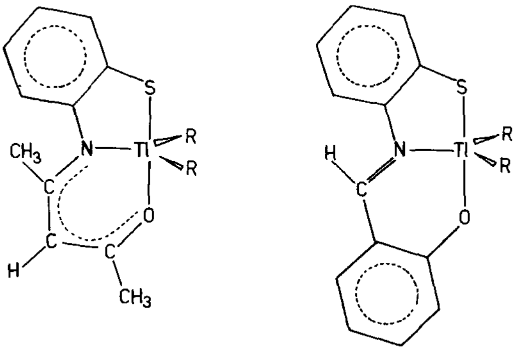

Fig 1. Idealized structures for [R$_2$TlL]$^-$ with L^{2-} = Aat^{2-} and Sat^{2-}

The electronic spectra of Na[Ph$_2$TlL] suggest that chelation occurs also in methanol, as indicated by the appearance of new bands at longer wavelengths (Table 2) in comparison with the absorption bands of the free ligands[10]. The electronic spectra of Na[Me$_2$TlL], in methanol solution, on the other hand, are very similar to those of the free ligands[10] (Table 2). This could imply the dissociation of Me$_2$TlL$^-$ into Me$_2$Tl$^+$ and L^{2-}, the latter reacting with the solvent, or with traces of water contained in it, to give H$_2$Aat and H$_2$Sat. That coordinating solvents probably dissociate Me$_2$TlL$^-$ into Me$_2$Tl$^+$ and L^{2-}, and that protolytic agents may induce the formation of H$_2$L in these conditions, is indicated by PMR spectra of Na[Me$_2$TlL] in dimethyl sulfoxide-d_6 containing water, (Table 3), where no vinyl or formimidoyl protons[10] appear This does not seem the case for solutions in non-coordinating solvents such as CDCl$_3$, where the formimidoyl and vinyl protons, respectively, occur in Me$_2$TlSat$^-$ and Me$_2$TlAat$^-$ (Table 3), implying the presence of Aat^{2-} and Sat^{2-}, Schiff base forms[10]. The ^{205}Tl–H coupling constant values increase with the increasing donor strength of the solvents, as expected[16].

ACKNOWLEDGEMENTS

The authors acknowledge financial support by C N.R. (Roma).

REFERENCES

1 E Krause, *Ber Deut Chem Ges*, 51 (1918) 1447
2 F Challenger and O V Richards, *J Chem Soc*, (1934) 405
3 G B Deacon, J H S Green and R S Nyholm, *J Chem Soc*, (1965) 3411
4 G Faraglia, L Roncucci Fiorani, B C L Pepe and R Barbieri, *Inorg Nucl Chem Lett*, 2 (1966) 277
5 G Faraglia, L Roncucci Fiorani, B C L Pepe and R Barbieri, *J Organometal Chem*, 10 (1967) 363
6 A G Lee, *J Organometal Chem*, 22 (1970) 537
7 G Faraglia, L Roncucci Fiorani, B C L Pepe and R Barbieri, *Ric Sci*, 37 (1967) 3
8 G Faraglia, A Cassol and R Barbieri, *Proc Journées Hellénes de Séparation Immédiate et de Chromatographie* (*III J S I C*), Ass Greek Chem Ed, Athens, 1966, p 271
9 L Pellerito, R Cefalù and G Ruisi, *J Organometal Chem*, 44 (1972) 243
10 R Cefalù, R Bosco, F Bonati, F Maggio and R Barbieri, *Z Anorg Allg Chem*, 376 (1970) 180; and references therein
11 F Challenger and B Parker, *J Chem Soc*, (1931) 1464
12 A I Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longman, London, 3rd Ed, 1971, p 884
13 W M T Smith, *Anal Chem*, 20 (1948) 937
14 R Bosco and R Cefalù, *J Organometal Chem*, 26 (1971) 225
15 I R Beattie and P A Cocking, *J Chem Soc*, (1965) 3860
16 G D Shier and R S Drago, *J Organometal Chem*, 5 (1966) 330
17 R H Herber and R Barbieri, *Gazz Chim Ital*, 101 (1971) 149
18 J G Noltes, personal communication
19 F Huber, personal communication