Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTIONS OF THE *cis*-DICYANOETHYLENE-1,2-DITHIOLATE ION WITH MONO- AND TRISUBSTITUTED GROUP IVB ORGANOMETALLIC COMPOUNDS

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(Received November 7th, 1971)

SUMMARY

The reactions between disodium dicyanoethylene-1,2-dithiolate, Na_2Mnt**, and various Group IVB organometallic compounds, $R_{4-n}MX_n$ ($R=CH_3$, C_6H_5; $n=1, 3$; $M=Ge$, Sn, Pb) in the presence of tetraalkylammonium halides, have been investigated. With R_3MX species as the starting materials, complexes exhibiting the following stoichiometry have been prepared and characterized: $[R'_4N]^+[M\,MntR_3]^-$ ($M=Ge$, Sn, Pb; $R=C_6H_5$ and $M=$ Sn, Pb; $R=CH_3$). NMR measurements show that the alkyl pentacoordinate complexes undergo rapid rearrangement. When RMX_3 species were employed as starting materials, metal–carbon bond cleavage was observed at room temperature. NMR and IR spectra, X-ray powder pattern, and conductivity data are reported and discussed.

INTRODUCTION

Considerable information is available on the syntheses and properties of bis and tris complexes of transition metals with bidentate sulfur donor ligands, such as the dicyanoethylene-1,2-dithiolate (Mnt)** ion[1-4]. We have recently reported a series of Group IVB Mnt complexes[5]; Group IIIB Mnt complexes have also been reported[6,7]. The organometallic chemistry of the post-transition elements with bidentate sulfur donor ligands is limited. Complexes derived from organotin halides and saturated ligands such as the ethane-1,2-dithiolate ion are reported to be tetracoordinate monomers[8]. Unsaturated ligands, such as the toluene-3,4-dithiolate ion and the Mnt ion, have been reported to form complexes with organometallic species of Groups IIIB, IVB and VB[9,10]. Dithiocarbamato organotin complexes have been reported[11,12].

As part of our continuing investigation of the coordination chemistry of bidentate sulfur donor ligands with the post-transition elements, we report the interactions of the Mnt ion with mono- and trisubstituted Group IVB organometallic compounds. Due to the complexity of the systems, the corresponding study with

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** Mnt is an abbreviation of the trivial name maleonitrile dithiolate for the dicyanoethylene-1,2-dithiolate ion.

disubstituted Group IVB organometallic compounds will be reported in a separate communication.

EXPERIMENTAL

Materials

Disodium dicyanoethylene-1,2-dithiolate (Na_2Mnt)[13], phenyltin trichloride[14], and triphenyltin chloride[15] were prepared by previously reported procedures. Methyltin trichloride was provided through the courtesy of M&T Chemicals. The remaining organometallic reagents were purchased from Alfa Inorganics, Inc. The triphenyllead acetate was washed with diethyl ether to remove acetic acid. Spectral grade solvents were used for NMR spectra measurements. All other reagents and solvents were used without further purification.

Measurements

X-ray powder patterns were determined using film methods (Cu-K_{α}). Conductivity measurements were obtained at 25° using an Industrial Instruments model RC 1682 bridge with a cell calibrated with 0.01 *M* KCl solution. Infrared spectra were obtained with a Beckman IR 5A spectrophotometer (CsBr) using KBr disks and solution cells. NMR measurements were recorded on a Varian A-60 spectrophotometer with a Varian V-6040 variable temperature attachment.

Syntheses

The preparations of the complexes were all similar, so two typical reactions, one with and one without metal – carbon cleavage, will be described. The complete series of preparations is summarized in Table 1. The yields of the phenyl substituted complexes were high (80–90%). The yields for the methyl substituted complexes and the metal–carbon cleavage products were somewhat lower (60–80%).

Reaction of Na_2Mnt with phenyltin trichloride. Phenyltin trichloride (3.00 g, ca. 0.01 mole) was added to a solution of 2.00 g (ca. 0.01 mole) of Na_2Mnt in 50 ml

TABLE 1

SYNTHESES

Organometallic species	*Ligand/metal ratio*[a]	*Cation*	*Product*
$(C_6H_5)_3GeCl$	1/1	$(C_4H_9)_4NCl$	$[(C_4H_9)_4N]GeMnt(C_6H_5)_3$
$(C_6H_5)_3GeCl$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]GeMnt(C_6H_5)_3$
$(C_6H_5)_3SnCl$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]SnMnt(C_6H_5)_3$
$(CH_3)_3SnCl$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]SnMnt(CH_3)_3$[b]
$(C_6H_5)_3PbCl$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]PbMnt(C_6H_5)_3$
$(CH_3)_3Pb(OAc)$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]PbMnt(CH_3)_3$[b]
$C_6H_5SnCl_3$	2/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]_2SnMnt_3$
$C_6H_5SnCl_3$	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]_2SnMnt_2Cl_2$
CH_3SnCl_3	1/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]_2SnMnt_2Cl_2$
CH_3SnCl_3	2/1	$(C_2H_5)_4NCl$	$[(C_2H_5)_4N]_2SnMnt_3$

[a] Except where noted, variation of the mole ratio employed did not change the product. [b] These compounds should be stored at reduced temperatures (0°) in order to prevent decomposition.

of ethanol. The mixture was stirred for several minutes and then 1.65 g (ca. 0.01 mole) of tetraethylammonium chloride was added. After several minutes of continued stirring, a precipitate formed. The solution was filtered and the precipitate was washed with acetone. The washings and the filtrate were combined and evaporated to dryness. The resulting solid was dissolved in acetone, filtered, and then ethanol was added. The solution was reduced to a volume of 10 ml, a yellow precipitate formed and was isolated by filtration. The product was shown to be $[(C_2H_5)_4N]_2SnMnt_2Cl_2$ by its melting point, elemental analyses, and conductivity data.

Reaction of Na_2Mnt with triphenyltin chloride. This reaction was analogous

TABLE 2

ANALYTICAL RESULTS FOR DICYANOETHYLENE-1,2-DITHIOLATO COMPLEXES[a]

Complex	*Found (calcd.) (%)*			
	C	*H*	*N*	*S*
$[(C_4H_9)_4N]GeMnt(C_6H_5)_3$	66.32	7.48	6.26	
	(66.46)	(7.50)	(6.12)	
$[(C_2H_5)_4N]GeMnt(C_6H_5)_3$	62.59	6.23		
	(62.72)	(6.15)		
$[(C_2H_5)_4N]SnMnt(C_6H_5)_3$	58.30	5.76	6.82	
	(57.89)	(5.67)	(6.77)	
$[(C_2H_5)_4N]SnMnt(CH_3)_3$	41.81	6.79		15.03
	(41.48)	(6.73)		(14.77)
$[(C_2H_5)_4N]PbMnt(C_6H_5)_3$	51.25	4.95	5.75	
	(50.82)	(4.98)	(5.92)	
$[(C_2H_5)_4N]PbMnt(CH_3)_3$	34.94	5.50	8.64	
	(34.45)	(5.78)	(8.30)	
$[(C_2H_5)_4N]_2SnMnt_3$	39.46	5.53		
	(39.93)	(5.81)		
$[(C_2H_5)_4N]_2SnMnt_2Cl_2$	42.17	5.08		
	(42.03)	(5.00)		

[a] Analyses by Robertson and Galbraith laboratories.

TABLE 3

PHYSICAL PROPERTIES OF DICYANOETHYLENE-1,2-DITHIOLATO COMPLEXES

Complex	*Conductivity*[a]	*Color*	*M.p. (°C)*[c]
$[(C_4H_9)_4N]GeMnt(C_6H_5)_3$	124	Yellow	163–164
$[(C_2H_5)_4N]SnMnt(C_6H_5)_3$	148	Yellow	136–137
$[(C_2H_5)_4N]SnMnt(CH_3)_3$	138	Yellow	116–117
$[(C_2H_5)_4N]PbMnt(C_6H_5)_3$	142	Brown	154–155
$[(C_2H_5)_4N]PbMnt(CH_3)_3$	185	Yellow	111–112
$[(C_2H_5)_4N]_2SnMnt_3$	107[b]	Yellow	162–163
$[(C_2H_5)_4N]_2SnMnt_2Cl_2$	157[b]	Yellow	119–120

[a] In cm^2/mole; 10^{-3} M solution in acetonitrile unless otherwise stated. Plots of $\sqrt{c}$ *vs.* equivalent conductance for the pentacoordinate complexes are linear and have slopes consistent with values calculated for 1/1 electrolytes in acetonitrile. [b] In nitromethane. [c] Uncorrected.

to the preceding one, except that 3.80 g (ca. 0.01 mole) of triphenyltin chloride was used in place of phenyltin trichloride. The yellow solid product was identified as $[(C_2H_5)_4N]Sn(C_6H_5)_3Mnt$ by elemental analyses and conductivity data.

Upon interaction with Na_2Mnt, all organosilicon, trialkyl germanium, and monoorganogermanium compounds yielded complex reaction mixtures which appear to result from ligand degradation, possibly due to solvolysis of the germanium–sulfur and silicon–sulfur bonds by ethanol.

Analytical data and physical properties for the products are reported in Tables 2 and 3.

RESULTS AND DISCUSSION

The reaction of Na_2Mnt with monoalkyl or aryltin trichlorides leads in all cases to tin–carbon bond cleavage at room temperature. Depending on the ligand/metal ratio either of the previously characterized[5] $SnMnt_3^{2-}$ or $SnMnt_2Cl_2^{2-}$ species were isolated. Reactions carried out at 0° gave similar results. This observation is surprising in that monoalkyl- and monoaryltin complexes of bidentate oxygen donor ligands, such as the tropolonates[16] and acetylacetonates[17], are readily formed. Furthermore, tin–carbon bond cleavage in complex formation normally occurs at 100° or higher[18].

The reaction of Na_2Mnt with organometallic germanium, tin and lead monohalides (or acetates) gives rise to a new series of pentacoordinate complexes, R_3MMnt^- where $R = CH_3$ (except for germanium) or C_6H_5 and $M = Ge$, Sn, or Pb. The stoichiometry of these complexes was established by the analytical and conductivity data reported in Tables 2 and 3. The X-ray powder patterns (Table 4) show that the triphenyltin and -lead complexes are isomorphous as are the trimethyltin and -lead complexes.

Infrared spectral data for the pentacoordinate complexes may be found in Table 5. Three lead–carbon stretching modes are observed for the trimethyllead complex; one tin–carbon stretching frequency is observed for the trimethyltin complex. The region in which the second band would be expected ($\approx 520\ cm^{-1}$) is masked by the ligand modes. The assignment of the metal–carbon bands is con-

TABLE 4

X-RAY POWDER PATTERNS

Complex	*Interplanar spacings of the prominent peaks (d/A°)*
$[(C_2H_5)_4N]GeMnt(C_6H_5)_3$	5.43m, 3.97s, 3.73m, 3.30w, 3.09w, 2.86w, 2.68w, 2.46w, 2.32m, 2.21m, 2.04w, 1.92w, 1.81w, 1.65m, 1.44m.
$[(C_2H_5)_4N]SnMnt(C_6H_5)_3$	10.15vw, 8.53s, 6.60w, 5.81m, 5.35m, 4.85m, 4.53s, 3.89m, 3.32w, 3.05w, 2.55m, 2.47m, 2.16m, 1.93w.
$[(C_2H_5)_4N]PbMnt(C_6H_5)_3$	10.29vw, 8.61s, 6.51w, 5.79m, 5.32m, 4.52s, 4.33w, 3.84m, 3.40w, 3.21w, 2.99w, 2.35m, 2.16w, 2.06w.
$[(C_2H_5)_4N]SnMnt(CH_3)_3$	10.21s, 7.73w, 6.60w, 5.83s, 5.12m, 4.82w, 4.43w, 3.88w, 3.67w, 3.43w, 3.13w, 2.93m, 2.71m, 2.59w, 2.47w.
$[(C_2H_5)_4N]PbMnt(CH_3)_3$	10.00s, 7.83w, 6.62w, 5.81s, 5.12m, 4.81w, 4.59m, 3.85w, 3.70w, 3.52m, 3.35w, 2.93m, 2.74m.

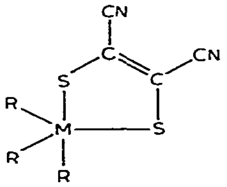
TABLE 5

SELECTED IR DATA FOR DICYANOETHYLENE-1,2-DITHIOLATO COMPLEXES[a]

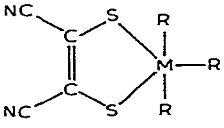
Complex	$\nu(M\text{–}C)$	$\nu(Ligand)$	$\nu(M\text{–}S)$	y^b	t^b
$[(C_4H_9)_4N]GeMnt(C_6H_5)_3$		531 m	327 ms	457 s	337 m
		521 s	319 m	419 m	
		493 w	300 w(sh)		
$[(C_2H_5)_4N]SnMnt(C_6H_5)_3$		528 sh	305 m	465 s	
		509 ms	290 ms		
		495 sh			
$[(C_2H_5)_4N]PbMnt(C_6H_5)_3$		529 sh		437 s	
		513 ms			
$[(C_2H_5)_4N]SnMnt(CH_3)_3$	542 m	532 m			
		513 s			
		491 sh			
$[(C_2H_5)_4N]PbMnt(CH_3)_3$[c]	481 s	531 m			
	471 sh	521 s			
	451 m				

[a] In cm^{-1}; obtained from KBr disks unless otherwise noted. [b] Metal sensitive phenyl modes; for nomenclature see ref. 21. [c] Obtained in methylene chloride solution.

sistent with other systems[11,19] and is reinforced by comparison with the spectra of the triphenyl complexes. The observation of more than one metal–carbon stretching mode eliminates formulation in which all methyl groups are in the equatorial plane of a trigonal bipyramid, *i.e.*, a polymeric species with bridging ligands. Therefore, structures (I) and (II) represent reasonable configurations for the lead complex.



(I)



(II)

Structure (I) is the most favorable in that the S–M–S bond angles are approximately 90° which is consistent with the observed structural chemistry of Mnt complexes[1-3]. There is considerable ring strain in structure (II)[20]. A similar structure for the tin complex is reasonable in view of the fact that the tin and lead complexes are isomorphous compounds.

The substituent-sensitive phenyl modes[21] in the triphenyl complexes are assigned by comparison to the literature values[22,23]. The vibration y involves phenyl bending with contribution from metal–carbon bending. This band often occurs as a doublet[22]. The observation that the germanium complex has two y vibrations, while the tin and lead complexes only have one, may indicate that the germanium species has a different structure from the tin and lead complexes. The fact that the tin and lead complexes are isomorphous, but are not isomorphous with the germanium complex, is consistent with this proposal. The vibration *t* is a ring deformation with contribution from metal–carbon stretching and is sensitive to the symmetry about the metal[22]. However, this band is only observed in the germanium complex at 337 cm^{-1}; any other *t* bands would be masked by the germanium–sulfur bands or below the range of the instrument.

The infrared spectra show tin–sulfur modes above 285 cm^{-1} for the triphenyl- but not the trimethyltin complex. The greater group electronegativity of the phenyl over the methyl group[24] apparently results in a greater positive charge on the tin atoms and hence a stronger tin–sulfur interaction. The greater metal–sulfur stretch for the germanium compared to the tin complex reflects, in part, the mass difference between germanium and tin.

The near constancy of the ligand mode throughout the range of complexes prepared, and the fact that the range above 600 cm^{-1} is essentially invariant outside of the changes in the organic group attached to the metal, indicates that the internal structure of the ligand is not significantly perturbed upon complexation. This is consistent with previous observations on Group IVB Mnt complexes[5].

TABLE 6

NMR DATA FOR METHYL SUBSTITUTED DICYANOETHYLENE-1,2-DITHIOLATO COMPLEXES

Complex	*Solvent*	*J* (^{119}Sn–*H*) (*Hz*)	*J* (^{117}Sn–*H*) (*Hz*)	τ (*ppm*)
$[(C_2H_5)_4N]SnMnt(CH_3)_3$	CH_3NO_2	56.0	53.5	9.64
	$(CH_3)_2CO$	56.5	53.5	9.63
	CH_2Cl_2	56.5	54.0	9.62
$[(C_2H_5)_4N]PbMnt(CH_3)_3$	CH_3NO_2	67.5[a]		8.77

[a] *J* (^{207}Pb–H).

NMR data for the trimethyltin and -lead complexes are reported in Table 6. Only one methyl peak and one set of metal–methyl coupling constants are observed for the complexes down to −50° (in deuterioacetone). The observed metal–methyl coupling constants are around the range normally observed for tetracoordinate containing the trimethyltin[25,26,27] or -lead[25,27] moieties. In fact, the observed coupling constants are around the range normally observed for tetracoordinate species. The observation that the coupling constants are essentially constant in solvents ranging from dichloromethane to nitromethane rules out dissociation in solution. The possibility of the Mnt unit acting as a unidentate ligand exists; however, this does not appear to be likely in view of the known coordination chemistry of the ligand[1–7]. The literature values for these coupling constants are reported for monodentate adducts of the trimethyltin (or -lead) halides and in these cases the methyl groups are all in the equatorial plane. However, in the systems considered in this work, there are both axial and equatorial methyl groups. A reasonable model for the bonding in pentacoordinate tin complexes involves, as a first approximation, an sp^2 hybrid tin orbital for the equatorial plane and a *pd* hybrid orbital for the axial sites. The tin–methyl coupling constant for the axial position would be expected to be low due to the low *s*-character in this bond[28]. The single methyl peak (and set of coupling constants) can be taken as indicating averaging of axial and equatorial positions via a rapid intramolecular isomerization mechanism. Related phosphorus systems[29] remain stereochemically non-rigid to temperatures below −100°. Thus the observed coupling constants represent a weighted average of the values for the axial and equatorial methyl groups.

ACKNOWLEDGEMENT

We thank Drs. D. B. Brown and J. H. Waters for helpful discussions, and M&T Chemicals for the gift of methyltin trichloride.

REFERENCES

1 H. B. Gray, *Transition Metal Chem.*, 1 (1965) 239.
2 J. A. McCleverty, *Progr. Inorg. Chem.*, 10 (1968) 49.
3 G. N. Schrauzer, *Transition Metal Chem.*, 4 (1968) 299.
4 G. N. Schrauzer, *Accounts Chem. Res.*, 2 (1969) 72.
5 E. S. Bretschneider, C. W. Allen and J. H. Waters, *J. Chem. Soc. A*, (1971) 500.
6 R. O. Fields, T. J. Bergendahl and J. H. Waters, *Inorg. Chem.*, 10 (1971) 2808.
7 D. G. Tuck and M. K. Yang, *J. Chem. Soc. A*, (1971) 214.
8 R. C. Poller and J. A. Spillman, *J. Chem. Soc. A*, (1966) 958.
9 M. Wieber and M. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 3 (1968) 657.
10 E. W. Abel and C. R. Jenkins, *J. Chem. Soc. A*, (1967) 1344.
11 T. A. George, K. Jones and M. F. Lappert, *J. Chem. Soc.*, (1965) 2157.
12 M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, 30 (1968) 3231.
13 G. Bähr and G. Schleitzer, *Chem. Ber.*, 90 (1957) 438.
14 H. Gilman and L. A. Grist Jr., *J. Org. Chem.*, 22 (1957) 368.
15 H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 74 (1952) 5580.
16 E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 86 (1964) 5132.
17 R. Ueeda, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Organometal. Chem.*, 5 (1966) 194.
18 W. H. Nelson and D. F. Martin, *J. Organometal. Chem.*, 4 (1965) 67.
19 R. J. H. Clark, A. G. Davies and R. J. Puddephatt, *J. Amer. Chem. Soc.*, 90 (1968) 6923.
20 F. H. Westheimer, *Accounts Chem. Res.*, 1 (1968) 70.
21 D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).
22 K. M. Mackay, D. B. Sowerby and W. C. Young, *Spectrochim. Acta, Part A*, 24 (1968) 611.
23 J. R. Durig, C. W. Sink and J. B. Turner, *Spectrochim. Acta, Part A*, 25 (1969) 629.
24 J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, 84 (1962) 540.
25 N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, 3 (1964) 337.
26 M. L. Maddox, N. Flitcroft and H. D. Kaesz, *J. Organometal. Chem.*, 4 (1965) 50.
27 W. Kitching, C. J. Moore and D. Doddrell, *Aust. J. Chem.*, 22 (1969) 1149.
28 J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83 (1961) 3903.
29 F. Ramirez, O. P. Madan and S. R. Heller, *J. Amer. Chem. Soc.*, 87 (1965) 731.