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SOME NEW ASSOCIATED (PHENYLETHYNYL)METALLIC AND OCTYNYLMETALLIC COMPOUNDS

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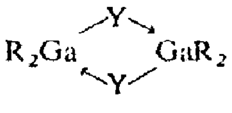
INTRODUCTION

Association of organometallic compounds through electro-negative atoms (Y) attached to the metal atoms (M) is an extremely widespread phenomenon. For example, a wide range of dimeric organogallium compounds (I) (R = an alkyl or aryl group; Y = halogen, OMe, SMe, NMe_2, etc.) is known[1,2]. Association through σ-bonded hydrocarbon groups is less common, and hitherto appears to have been restricted to the alkali metals, beryllium, magnesium (and possibly the alkaline earths), and aluminium.



(I)

The simple organic derivatives (R_2M) of zinc, cadmium and mercury are monomeric[3], as are the corresponding compounds (R_3M) of gallium, indium and thallium[3,4], with the exception of trivinylgallium[5], which is dimeric.

If association is regarded as a Lewis acid–Lewis base interaction, then the alkyl groups must be the least effective hydrocarbon bridging groups. Unsaturated hydrocarbon radicals have higher Lewis basicity and should be more effective (hence dimeric trivinylgallium). In particular, the claim that the phenylethynyl group provides an extremely strong bridge between aluminium atoms[6] has prompted a search for new associated (phenylethynyl)metallic compounds.

RESULTS AND DISCUSSION

Dimethyl(phenylethynyl)gallium and dimethyl(phenylethynyl)indium were prepared by reaction of phenylacetylene with trimethylgallium and trimethylindium, respectively. Reaction was more facile than in the case of trimethylaluminium. Ebullioscopic molecular weight determination in benzene showed each of the phenylethynyl compounds to be dimeric. The infra-red stretching frequencies of the triple bonds of the new compounds are given in Table 1, and PMR data is given in Table 2. The Tables also give data for dimethyl(phenylethynyl)aluminium, which is dimeric

TABLE 1

C≡C STRETCHING FREQUENCIES OF (PHENYLETHYNYL)METALLIC COMPOUNDS

Compound	*Frequency* (cm^{-1})		
	Nujol	*Benzene*[a]	*Tetrahydrofuran*
$Me_2PhCCAl$		2050	2110[b]
$Me_2PhCCGa$		2050	2120[b]
$Me_2PhCCIn$		2050	2110 (very weak)[b]
$(PhCC)_2Zn$	2060		
$(PhCC)_2Cd$	2050		

[a] The intensity in benzene was 5 to 10 times that in tetrahydrofuran. [b] Only one peak was observed despite disproportionation.

TABLE 2

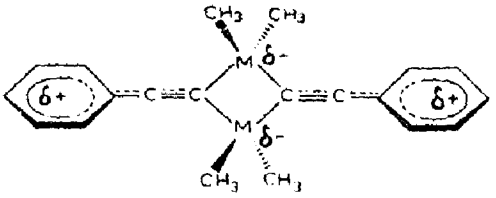
PMR CHEMICAL SHIFTS OF (PHENYLETHYNYL)METALLIC COMPOUNDS

Compound	*Solvent*	*Chemical shift* (δ, *ppm*[a])	
		Aryl protons	*Methyl protons*
$Me_2(PhCC)Al$	C_6D_6	7.2–7.4 (*o*)[b] 6.7–6.95 (*m*, *p*)[b]	0.00[c]
$Me_2(PhCC)Al$	THF	7.0–7.3	−0.83[d,e]
$Me_2(PhCC)Ga$	C_6D_6	7.25–7.45 (*o*) 6.7–7.0 (*m*, *p*)	+0.37
$Me_2(PhCC)Ga$	THF	7.0–7.4	−0.37[f]
$Me_2(PhCC)In$	C_6D_6	7.3–7.5 (*o*) 6.8–7.0 (*m*, *p*)	+0.29
$Me_2(PhCC)In$	THF	7.0–7.4	−0.35[g]
$(PhCC)_2Zn$	C_5D_5N	7.7–7.9 (*o*) 7.1–7.4 (*m*, *p*)	
$(PhCC)_2Cd$	C_5D_5N	7.7–7.9 (*o*) 7.1–7.4 (*m*, *p*)	

[a] To low field of tetramethylsilane; negative sign indicates a shift to high field. [b] The separation of the aryl absorption into two distinct groups of peaks appears to be more a function of the solvent chosen than of the structure of the solute alone; $Me_2(PhCC)Al$ shows two well separated groups of aryl resonances in C_5D_5N but not in hexane. [c] −0.43 ppm in hexane. [d] In equilibrium with disproportionation products, Me_3Al (−0.96 ppm) and $Me(PhCC)_2Al$ (−0.78 ppm); $K = [Me_2(PhCC)Al]^2/[Me_3Al] \cdot [Me(PhCC)_2Al] \sim 5$. [e] −0.32 ppm in C_5D_5N. [f] In equilibrium with disproportionation products, Me_3Ga (−0.48 ppm) and $Me(PhCC)_2Ga$ (−0.21 ppm); $K = [Me_2(PhCC)Ga]^2/[Me_3Ga] \cdot [Me(PhCC)_2Ga] \sim 50$. [g] In equilibrium with disproportionation products, Me_3In (−0.47 ppm) and $Me(PhCC)_2In$ (−0.25 ppm); $K = [Me_2(PhCC)In]^2/[Me_3In] \cdot [Me(PhCC)_2In] \sim 20$; the three methyl resonances are broadened due to exchange of methyl groups between the three species.

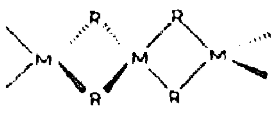
in hydrocarbon solvents and has been shown to be associated through its phenylethynyl groups[6,7,8]. The similarities in the spectroscopic data suggest strongly that the gallium and indium compounds are structurally akin to the aluminium compound.

The dimeric structures would, of course, be disrupted by donor solvents. The triple bond stretching frequencies exhibited in tetrahydrofuran are very close to those of phenylacetylene and of other compounds which are thought to have phenylethynyl groups simply σ-bonded to their metal atoms[9]. By contrast, the triple bond frequencies in benzene are shifted by about 60 cm^{-1} to lower wavenumber. This appears reasonable if the acetylenic group serves as a bridge in benzene solvent and is thus somewhat allenic in character [see structure (II)].



II

M = Al, Ga, In



III

$M = Zn, Cd; R = PhC \vdots C^-, C_6H_{13}C \vdots C^-$

Of the PMR data given in Table 2, most interest attaches to the singlet methyl resonances. Patterns of chemical shift behaviour are discernible, but the shifts are dependent on solvent and temperature. In tetrahydrofuran, each of the three compounds shows three methyl resonances. Similar behaviour was observed for dimethyl(phenylethynyl)aluminium in ether[7]. The behaviour may be interpreted in terms of reversible disproportionation according to equation (1) (M = Al, Ga, In; THF = tetrahydrofuran).

$$2\,Me_2(PhCC)M\cdot THF \rightleftharpoons Me_3M\cdot THF + Me(PhCC)_2M\cdot THF \qquad (1)$$

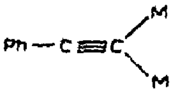
Random distribution of methyl and phenylethynyl groups on the metal atom would lead to an equilibrium constant, $K = 3$, for reaction (1). Approximate values for the equilibrium constants have been derived from the peak intensities (see Table 2). They indicate a small degree of stability towards disproportionation in tetrahydrofuran. The observation of only one methyl peak for each compound in deuterobenzene does not constitute reliable evidence against disproportionation, because of the occurrence of exchange reactions. Such stability is, however, suggested by the ease with which all the compounds may be obtained pure and crystalline from hydrocarbon solvents.

In view of the above results, association of phenylethynyl compounds of zinc and cadmium seemed possible. Bis(phenylethynyl)zinc has been prepared previously by reaction of phenylacetylene with diphenylzinc[10]. It has now been prepared by reaction of phenylacetylene with dimethylzinc, and bis(phenylethynyl)cadmium has been similarly prepared from phenylacetylene and dimethylcadmium. Both compounds decomposed without melting above 200°; bis(phenylethynyl)cadmium gave 1,4-diphenylbutadiyne in good yield. Poor solubility in a variety of organic solvents precluded purification by crystallization and led to difficulty in the determination of molecular weights. In pyridine, a molecular weight of 680 was found for the zinc compound (calcd. for monomer, 267.4) and of 410 for the cadmium compound (calcd. for monomer, 314.4). These values suggest that bis(phenylethynyl)zinc and bis(phenylethynyl)cadmium have associated structures, but the limitations of solubility prevented more meaningful molecular weight data being obtained in non-donor solvents.

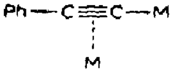
In order to obtain analogous compounds with better solubility characteristics, dimethylzinc and dimethylcadmium were reacted with 1-octyne. Di-1-octynylzinc was obtained as a crystalline solid and di-1-octynylcadmium as a wax. Both compounds were readily soluble in hot benzene, and a molecular weight of 1230 was determined for the zinc compound (calcd. 283.4) and of 1810 for the cadmium compound (calcd. 330.4).

It is therefore suggested that all four dialkynyl compounds are associated in linear polymers, as shown in structure (III).

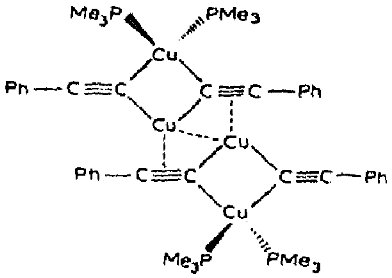
The triple-bond stretching frequencies of the bis(phenylethynyl) compounds are given in Table 1. They show the same shift (*ca.* 50 cm^{-1}) to low wavenumber and enhancement of intensity (compared with phenylacetylene) as do the dimeric dimethyl(phenylethynyl) compounds of aluminium, gallium, and indium. Di-1-octynylzinc and di-1-octynylcadmium likewise show triple-bond stretching frequencies enhanced in intensity and shifted by 30–40 cm^{-1} to low wavenumber as compared with 1-octyne (2110 cm^{-1}). Formation of a complex between a transition metal and an acetylene also results in a shift to low wavenumber[11,12]; in this case, the shift is of the order of several hundred cm^{-1}, and its magnitude appears to depend upon the nature of the bonding between the acetylene and the metal[13]. The small shift observed for the zinc and cadmium compounds suggests that their bridges are better represented by partial structure (IV) than by (V).



IV



V



VI

There are indications of the existence of a range of structures between the extremes represented by (IV) and (V). Corfield and Shearer[14,15] have recently reported X-ray crystallographic structures for polymeric (phenylethynyl)(trimethylphosphine)silver(I) and tetrameric (phenylethynyl)(trimethylphosphine)copper(I), and have regarded the phenylethynyl groups as σ-bonded to one metal atom and π-bonded to a second, and in some cases a third, metal atom. It is now suggested that structure (VI), in which each phenylethynyl group is σ-bonded to two copper atoms, more adequately represents the bonding in the copper compound, and that the silver compound has phenylethynyl groups bound to two silver atoms in a manner intermediate between the representations of partial structures (IV) and (V).

EXPERIMENTAL

Organometallic compounds were handled under a nitrogen atmosphere by dry-box techniques. Trimethylgallium and trimethylindium were prepared by reaction of dimethylmercury with gallium and indium respectively. Dimethylzinc and dimethylcadmium were obtained by the action of trimethylaluminium on zinc acetate and cadmium acetate. Dimethyl(phenylethynyl)aluminium has been described previously[7,8]. Molecular weights were determined (*ca.* 10^{-2} *M* concentration) using a Gallenkamp ebulliometer. PMR spectra were measured with a Varian A60 spectrometer at ambient temperature (37°). Melting points (uncorrected) were determined in evacuated capillaries.

Dimethyl(phenylethynyl)gallium

Trimethylgallium (225 mg) and phenylacetylene (239 mg) were heated together at 50° for 12 h in a sealed ampoule (*cf.* Eisch[16]). Gas was evolved. The resulting yellow oil was pumped at room temperature to remove volatile impurities, and the solid remaining was recrystallized from toluene/hexane to give dimethyl(phenylethynyl)gallium as a cream solid (160 mg) m.p. 114–117°. The formula was confirmed by the PMR chemical shifts and intensities (see Table 2), and by the C≡C stretching frequency in the IR spectrum (see Table 1). UV spectrometry showed the expected amount of phenylacetylene to be formed on hydrolysis. The ebullioscopic mol.wt. in benzene of 390 (calcd. for monomer, 200.7) indicated a dimeric structure.

Dimethyl(phenylethynyl)indium

Trimethylindium (101 mg) was warmed to 50° for ½ h with phenylacetylene (87 mg) in benzene (0.2 ml). Steady gas evolution occurred. Volatile impurities were removed *in vacuo* (1 mm Hg) at 40°, leaving dimethyl(phenylethynyl)indium as a pale cream solid (107 mg), m.p. 116–119°, soluble in hydrocarbon solvents. The formula was confirmed by the PMR spectrum (see Table 2) and by UV evidence for formation of the expected amount of phenylacetylene on hydrolysis. The ebullioscopic mol.wt. in benzene of 436 (calcd. 246) indicated a dimeric structure.

Bis(phenylethynyl)zinc

Dimethylzinc (191 mg) and phenylacetylene (385 mg) were heated together in a sealed ampoule for 16 h at 80°. A white solid resulted. The ampoule was opened (gas escaped), and the white solid was powdered. Volatile impurities were removed *in vacuo* at room temperature. The solid was insoluble in hot hydrocarbons, ether, anisole and tetrahydrofuran, but was slightly soluble in pyridine. The formula $(PhCC)_2Zn$ was established as follows: (*i*) titration against EDTA indicated one Zn atom per 260 mol.wt. (calcd. 267.4); (*ii*) no gas was evolved on hydrolysis; (*iii*) the PMR spectrum in pyridine-d_5 showed only aryl absorption; (*iv*) hydrolysis of a suspension in carbon tetrachloride and IR spectroscopy gave a spectrum identical with that of phenylacetylene; (*v*) hydrolysis of a suspension in cyclohexane and UV spectrometry gave a spectrum identical with that of phenylacetylene. The intensity of the 246 mμ peak was 92% of that expected from the assigned formula.

Bis(phenylethynyl)cadmium

Dimethylcadmium (183 mg) and phenylacetylene (265 mg) were heated together in a sealed ampoule at 90° for 2½ h to give a white solid. The formula $(PhCC)_2Cd$ was established in the same way as that of the zinc compound. In particular titration against EDTA showed one Cd atom per 305 mol.wt. (calcd. 314.4), and hydrolysis of a suspension of the solid in cyclohexane gave 84% of the expected amount of phenylacetylene. Bis(phenylethynyl)cadmium decomposed at 220°, and could not be sublimed *in vacuo*. At 220°, 1,4-diphenylbutadiyne, m.p. 86–87.5°, characterized by its UV spectrum[17], sublimed and a dark residue remained.

Di-1-octynylzinc

Dimethylzinc (70 mg) and 1-octyne (162 mg) were heated in a sealed tube at 95° for $3\frac{1}{2}$ h to give di-1-octynylzinc (120 mg) as a white, crystalline solid, from which volatile impurities were removed *in vacuo* at room temperature. The solid decomposed, without melting sharply, at 200° and was characterized in the following manner: (*i*) titration against EDTA showed one zinc atom per 291 mol.wt. (calcd. 283.4); (*ii*) the PMR spectrum was broadly similar to that of 1-octyne, showing multiplets at 1.0 ppm (CH_3), 1.4 ppm (4 CH_2 groups), and 2.7 ppm ($C{\equiv}C{-}CH_2$). The sharp triplet due to the $C{\equiv}CH$ proton was absent, and no other absorption was observed; (*iii*) the IR spectrum (nujol) showed a $C{\equiv}C$ stretching frequency at 2080 cm^{-1}; (*iv*) after a suspension of the solid in carbon tetrachloride was hydrolysed by aqueous HCl, the IR spectrum of the hydrolysate was indistinguishable from that of a solution of 1-octyne in carbon tetrachloride.

Di-1-octynylcadmium

Dimethylcadmium (139 mg) and 1-octyne (222 mg) were heated to 95° for 2 h. The gelatinous solid thus generated was pumped at 1 mm Hg at room temperature for several hours to leave a pale yellow wax (280 mg), which was identified as di-1-octynylcadmium in the same way as the corresponding zinc compound. In particular, titration against EDTA indicated one zinc atom per 324 mol.wt. (calcd. 330.4), and the $C{\equiv}C$ stretching frequency (nujol) was observed at 2070 cm^{-1}

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SUMMARY

Dimethyl(phenylethynyl)gallium and dimethyl(phenylethynyl)indium have been prepared and are dimeric. They are considered to be associated through the phenylethynyl groups. Bis(phenylethynyl)zinc, bis(phenylethynyl)cadmium, di-octynylzinc, and dioctynylcadmium appear to be polymeric.

REFERENCES

1 P. G. Perkins and M. E. Twentyman, *J. Chem. Soc.*, (1965) 1038.
2 O. T. Beachley, G. E. Coates and G. Kohnstam, *J. Chem. Soc.*, (1965) 3248 and ref. quoted therein.
3 W. Strohmeier, K. Hümpfner, K. Miltenberger and F. Seifert, *Ber. Bunsenges. Phys. Chem.*, 63 (1959) 537.
4 N. Muller and A. L. Ottermat, *Inorg. Chem.*, 4 (1965) 296.
5 J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, 24 (1962) 953.
6 E. A. Jeffery, T. Mole and J. K. Saunders, *Aust. J. Chem.*, in press.
7 T. Mole and J. R. Surtees, *Aust. J. Chem.*, 17 (1964) 1229.
8 T. Mole and J. R. Surtees, *Chem. Ind. (London)*, (1963) 1727.
9 M. L. H. Green and T. Mole, unpublished.
10 R. Nast, O. Künzel and R. Müller, *Chem. Ber.*, 95 (1962) 2155.
11 K. Nakamoto, *IR Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, p. 228.
12 G. E. Coates and C. Parkin, *J. Inorg. Nucl. Chem.*, 22 (1961) 59.
13 J. P. Collman and J. W. Wang, *J. Amer. Chem. Soc.*, 89 (1967) 844.
14 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 20 (1966) 502.
15 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 21 (1966) 957.
16 J. Eisch, *J. Amer. Chem. Soc.*, 84 (1962) 3830.
17 J. B. Armitage, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, (1954) 150.