CERTAIN TRIPHENYLGERMANIUM(IV) COMPLEXES OF STERICALLY CONGESTED HETEROCYCLIC β-DIKETONES: SYNTHETIC AND STRUCTURAL CONSIDERATIONS

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Abstract

Some new triphenylgermanium(IV) complexes of composition, $Ph_3Ge[RCOC:CON(C_6H_5)N:CCH_3]$ (where R = CH_3, C_2H_5, C_6H_5 and p-ClC_6H_4) have been synthesised by the interaction of triphenylgermanium (IV) chloride with the sodium salt of sterically congested heterocyclic β-diketones in a 1:1 molar ratio in dry THF solution. Osmometric molecular weight measurements of these derivatives in chloroform solution reveal their monomeric nature. The plausible structures of these complexes have been proposed with the help of physico-chemical and spectral studies.

Introduction

The chemistry of organogermanium (IV) complexes derived from organic ligands[1-2] has received significant attention. The conjugated bases of heterocyclic β-diketones are the potential organic ligands which have aroused tremendous interest because of their bonding patterns[3-5], structural features[6-7] and potential biological applications[8-9] of their metal complexes.

In our earlier publications, we have reported the synthesis and structural features of the complexes of group 4[10], 13[11] and 14[12-7] elements with this class of ligand. A survey of the literature reveals that no such triorganogermanium (IV) complexes have been reported so far. We now report the preparation, physico-chemical and spectral studies of the triphenylgermanium (IV) complexes derived from sterically congested conjugated base of the heterocyclic β-diketones in the present communication.

Results and Discussion

The reaction of sodium salt of 4-acyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, with triphenylgermanium (IV) chloride in a 1:1 molar ratio in benzene solution yield yellow coloured complexes of composition,

$$Ph_3Ge\,[RCOC{:}CON\,(C_6H_5)\,N{:}CCH_3]$$

at room temperature. The sodium salts of the diketones have been prepared in situ by treating them in methanol/benzene solution with an equimolar amount of metallic sodium.

$$R\,COC{:}\,C(OH)N(C_6H_5)\,N{:}CCH_3 + Na \rightarrow Na\,[R\,COC{:}CON(C_6H_5)N{:}\,CCH_3] + 1/2\,H_2 \uparrow$$

$$Na[R\,COC{:}\,CON(C_6H_5)N{:}CCH_3] + Ph_3GeCl \rightarrow Ph_3Ge\,[RCOC{:}\,CON(C_6H_5)N{:}\,CCH_3] + NaCl \downarrow$$

where R = CH_3, C_2H_5, C_6H_5 and p-ClC_6H_4.

The above reactions are facile and were completed on refluxing the reaction mixture for a period of ca. 6 h. The resulting complexes are found to be yellow solids, soluble in common organic solvents and can be recrystallised from benzene/hexane mixture in 68-80% yield. The vapor pressure molecular weight measurements in chloroform solution at 45°C show their monomeric nature.

Spectral Data and Structure

A broad band is observed at 3300-3200 cm^{-1} in the IR spectra of parent diketones due to νOH. This band is found to be absent in the spectra of the corresponding triphenylgermanium(IV) complexes indicating the deprotonation of the OH group. This is further supported by the appearance of a new band at 650-600 cm^{-1} due to the Ge—O stretching which indicates the bonding of the germanium atom with ligand moiety through the oxygen of the OH group.

The band observed at 1090-1000 cm^{-1} has been assigned to νGe--C[14]. The C=O band that appeared in the diketones at ~ 1545 cm^{-1} was shifted towards a lower wave number (1525±5 cm^{-1}) in the corresponding triphenylgermanium (IV) complexes. This indicates the involvement of the carbonyl oxygen of the diketones in chelation. The absorption bands observed at 1585±10 and 1575±5 cm^{-1} may be assigned to νC_6H_5 and ν C=C / C=N-modes, respectively.

A comparative study of the ^{1}H NMR spectra of the triphenylgermanium (IV) complexes with their parent diketones' shows the absence of OH signal indicating the deprotonation of OH group and the formation of a Ge--O bond.

The signal for the terminal protons in the complex where R = CH_3, has been observed at δ 2.32 whereas in the complex where R = C_2H_5, the signals for terminal protons CH_2 and CH_3 have been observed at δ 2.70 as a quartet and δ 1.24 as a triplet, respectively. In the complex where R = C_6H_5 and p-ClC_6H_4, the terminal protons are found to be merged with the ring phenyl and phenyl protons of triphenylgermanium and are observed at δ 7.07-8.23 and 7.07-7.99 ppm, respectively as a complex pattern.

In the complex where R = CH_3 and C_2H_5, the phenyl protons attached to germanium are observed in the range of δ 7.07 - 8.12 ppm as a complex pattern and are found to be merged with phenyl protons of the ligand.

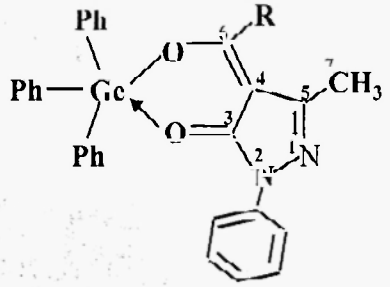
A comparison of the ^{13}C NMR spectra (Table I) of these complexes with those of the corresponding diketones shows a small shift of 2-4 ppm in the position of the carbonyl carbon C6 (observed in the range δ194.92-196.25 in the complexes) and the enolic carbon C3 (observed in the range δ 161.4 -161.8 in the complexes). This indicates that the carbonyl oxygen participates in bonding. The shift in the position of C3 and C6 signals may be explained by assuming the delocalisation of electrons in quasi-aromatic chelate ring formed by the chelation of the ligand moiety with the central germanium atom. The position of the ring methyl carbon signal C7 (observed in the range δ 16.2 - 15.8 ppm in the complexes) also shows a shift when compared with its position in the parent diketone. In the complex where R= CH_3 and C_2H_5, signals for phenyl carbon attached to the germanium atom have been observed in the range δ128.7-139.4 ppm and δ 29.3-140.5 ppm, respectively. However, in the complex where R=C_6H_5, and p-ClC_6H_4, the phenyl carbon signals are found to be merged with terminal and p-ClC_6H_4 group signals.

Table 1: ^{13}C NMR data of germanium(IV) complexes of heterocyclic β-diketones:

S.	*Complexes*	*Types of C atoms (ppm)*							*Ge-phenyl**	
No.		C3	C4	C5	C6	C7	CH_2	CH_3		
1.	Ph_3Ge(OPPMA)	161.4	104.1	138.9	191.8	16.0	-	27.6	139.4	135.2
									128.7	130.6
2.	Ph_3Ge(OPPMP)	161.8	103.9	137.5	196.2	16.2	32.9	8.7	140.5	134.3
									127.9	129.3
3.	Ph_3Ge(OPPMB)	161.6	103.6	137.7	190.8	15.8	-	-	127.8-140.8**	
4.	Ph_3Ge(OPPMC)	161.1	103.0	138.7	189.1	15.2	-	-	127.1-140.2**	

* Values are given in i, o, m and p carbon, respectively.
** Phenyl carbons give a complex pattern.

In view of the monomeric nature of triphenylgermanium (IV) complexes and the bidentate nature of the ligands, conjugated bases of the heterocyclic β-diketones, the following structure in which the central germanium atom acquires a trigonal bipyramidal geometry is proposed.



R = CH_3, C_2H_5, C_6H_5, p-ClC_6H_4

AMPPOH = $CH_3COC{:}C(OH)NC_6H_5\ N{:}C\ CH_3$;

PMPPOH = $C_2H_5COC{:}C(OH)N(C_6H_5)N{:}C\ CH_3$;

BMPPOH = $C_6H_5\ COC{:}C(OH)N\ C_6H_5\ N{:}C\ CH_3$;

CMPPOH = p-$ClC_6H_5COC{:}C(OH)N(C_6H_5)N{:}C\ CH_3$;

A similar mode of bonding has been observed in the analogous triorganotin (IV) complexes', synthesised earlier using these diketones.

Experimental Section

All the reactions were carried out under anhydrous conditions. Triphenylgermanium chloride was distilled before use. All solvents were dried before use. The diketones were synthesized by a reported method[12]. Melting points were determined in sealed capillaries. Molecular weight measurements were carried out on a Knauer Vapour Pressure Osmometer in chloroform solutions at 45°C. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer using cesium iodide plates or as nujol mulls. ^{1}H and ^{13}C NMR spectra have been recorded in $CDCl_3$ solutions on a JEOL FX-90Q (90 MHz) spectrometer using TMS as an internal reference. All the complexes were synthesized by similar procedures and therefore, the synthesis of one of these derivatives is described below.

Synthesis of [4-acetyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato]triphenylgermanium(IV)

A benzene solution of 4-acetyl-2,4 dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (0.83g, 3.85 mMl) was added to the sodium methoxide solution, prepared in situ by reacting sodium (0.08g) with methanol (5ml) and refluxed for ca.3h. After cooling, a benzene solution of triphenylgermanium (IV) chloride (1.30g, 3.85mM) was added with constant stirring. The reaction mixture was further refluxed for ca.12h. Sodium chloride, thus formed, was filtered off and the excess solvent from the filtrate was removed under reduced pressure to afford a yellow colored solid product that was recrystallized from chloroform/hexane in 68% yield.

The yield, melting point, molecular weight and ^{1}H NMR chemical shift of the complexes Ph_3Ge[OPPMA], Ph_3Ge[OPPMP], Ph_3Ge[OPPMB] and Ph_3Ge[OPPMC] are summarised hereunder.

1. Ph_3Ge [OPPMA]; Yield* 68%; M.P. 172-173°
   Analysis : Found (Calcd.), NaCl : 0.20 (0.22); Mol.Wt : 508 (518.8).
   ^{1}H NMR ($CDCl_3$), δ 2.04 (s) ring methyl; δ 6.99-8.04(m) ring phenyl; δ 2.32(s) CH_3;
   δ 7.07-7.89(m) germanium phenyl.
2. Ph_3Ge [OPPMP]; Yield* 70% M.P. 186-187°
   Analysis : Found (Calcd); NaCl : 0.31 (0.33); Mol.Wt. : 528 (532.9);
   ^{1}H(NMR), δ 2.49(s) ring methyl; δ 7.10-8.04(m) ring phenyl; δ 2.70(q)CH_2;
   δ 1.24(t)CH_3; δ 7.15-8.12(m) germanium phenyl.
3. Ph_3Ge[OPPMB]; Yield* 80%; M.P. 182-183°;
   Analysis; Found (Calcd.); NaCl : 0.25 (0.27); Mol.Wt. : 595 (580.8);
   ^{1}H NMR: δ 2.57(s) ring methyl; δ 7.15-8.00(m) ring phenyl; δ 7.07-8.23(m) germanium phenyl.
4. Ph_3Ge[OPPMC]; Yield* 75%; M.P. 178-179;
   Analyses Found (Calcd.); NaCl : 0.54 (0.57); Mol.Wt. : 602 (615.4);
   ^{1}H NMR: δ 2.49(s) ring methyl; δ 7.39-8.12(m) ring phenyl; δ 7.07-7.99(m) germanium phenyl.

* Recrystallised yield, s = single, t = triplet, q= quartet, satisfactory elemental analysis have been obtained for all the compounds. The ^{1}H NMR data of the diketones (4-acyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one) have been reported earlier[3].

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