

## Monomeric Derivatives of Bivalent Germanium: Keto-Enolate and Related Chelate Compounds

By ALEX RODGERS and STEPHEN R. STOBART\*†

(Department of Chemistry, Queen's University, Belfast BT9 5AG)

**Summary** Keto-enolato- and tropolonato-derivatives of bivalent germanium,  $[\text{Ge}(\text{chel})_2]$  or  $[\text{Ge}(\text{chel})\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ), have been synthesised from  $\text{Ge}^{\text{II}}$  halide species; their physical and spectroscopic properties are consistent with monomeric character.

THAT relatively little is known about the chemistry of germanium in its bivalent state is conspicuously illustrated in relation to molecular, monomeric compounds (germyl-

enes). Only two such species having significant lifetimes under ambient conditions appear to have been fully characterised, bis(cyclopentadienyl)germanium(II) (which however auto-polymerizes at 20 °C)<sup>1</sup> and bis-(*N*-*t*-butyl-*N*-trimethylsilylamido)germanium(II).<sup>2</sup> A substantial advance in this area resulting from the use of chelating oxygen-donor ligands is reported.

Refluxing (3 h) either  $\text{GeI}_2$  or  $\text{CsGeCl}_3$  with  $\text{Na}(\text{acac})\ddagger$  in anhydrous THF provides a route (45–65% yields) to the

\* Present address: Department of Chemistry, University of Victoria, Victoria, B.C., Canada V8W 2Y2.

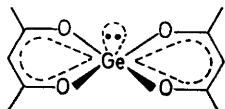
† The following abbreviations have been adopted throughout this communication: acac, acetylacetonato; dpm, dipivaloylmethanato; bza, benzoylacetonato; dbm, dibenzoylmethanato; tfa, trifluoroacetylacetonato; hfa, hexafluoroacetylacetonato; trop, tropolonato; thuj,  $\beta$ -thujaplicinato; and THF, tetrahydrofuran.

TABLE

Compound <sup>a</sup>	Colour (m.p./°C)	M		$\nu(\text{C}=\text{O})/\text{cm}^{-1}$
		Calc.	Found	
[Ge(acac) <sub>2</sub> ]	Pale yellow liquid	272	272 <sup>b</sup>	1580s, 1540s
[Ge(acac)Cl]	White (64–66)	208	208 <sup>b</sup>	1550s, 1520s sh
[Ge(acac)I]	Bright yellow (49–51)	300	300 <sup>b</sup>	1565m sh, 1555s, 1545s
[Ge(trop) <sub>2</sub> ]	Bright yellow (178, decomp.)	315	282 <sup>c</sup>	1590s, 1570m, 1510vs
[Ge(thuj) <sub>2</sub> ]	Yellow (137–139, decomp.)	399	361 <sup>c</sup>	1585m, 1569s, 1520s

<sup>a</sup> Satisfactory C, H, and halogen analyses have been obtained in each case. <sup>b</sup> Mass spectroscopically for <sup>74</sup>Ge; calc. value assumes monomeric formulation. <sup>c</sup> Osmometrically in CHCl<sub>3</sub> solution.

extremely air- and moisture-sensitive compounds [Ge(acac)X] (X = acac, Cl, or I). Physical data are given in the Table; the absence from mass spectra of ions at higher *m/e* than those appropriate for the molecular ion in each case is consistent with a monomeric representation (*e.g.*



FIGURE

Figure) involving four- or three-co-ordinate germanium. High volatility (sublime <40 °C at 10<sup>-3</sup> mmHg) supports this. I.r. spectra exhibit the characteristic lowering of  $\nu(\text{C}=\text{O})$  associated with chelating behaviour of the acac ligand (Table), and <sup>1</sup>H n.m.r. spectra show singlet resonances due to acac methyl protons.

The crystalline halogeno-derivatives, [Ge(acac)X] (X = Cl or I), melt without decomposition and are unchanged after over 100 days at 20 °C when sealed *in vacuo*. Addition

of Br<sub>2</sub>, I<sub>2</sub>, or MeI to a solution of [Ge(acac)<sub>2</sub>] yields the appropriate [Ge(acac)<sub>2</sub>(Y)(Z)] derivative, consistent with oxidation from Ge<sup>II</sup> to Ge<sup>IV</sup>. Some corresponding products to those of the Table have been obtained in varying yields using sodium dpm, bza, dbm, tfa, and hfa salts.

Addition of NEt<sub>3</sub> to 2-hydroxycyclohepta-2,4,6-trienone (tropolone) and [CsGeCl<sub>3</sub>] (2:1 mol ratio) in THF gives quantitatively the compound [Ge(trop)<sub>2</sub>] and an analogous product is formed with 2-hydroxy-4-isopropylcyclohepta-2,4,6-trienone (Table). I.r., <sup>1</sup>H n.m.r., and mass spectroscopic data for these tropolonato-germanium(II) compounds correspond to those for the keto-enolates, and further evidence for monomeric character is provided by solution molecular weight determinations. A similar reaction with a 1:1 mol ratio affords the cream, sublimable (70 °C) [Ge(trop)Cl].

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<sup>2</sup> D. H. Harris and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 895.