

Correspondence to: Professor B K Nicholson
Chemistry Department
University of Waikato
Private Bag 3105
Hamilton
New Zealand
Email: b.nicholson@waikato.ac.nz
Fax: 64 7 838 4219

COMMUNICATION:

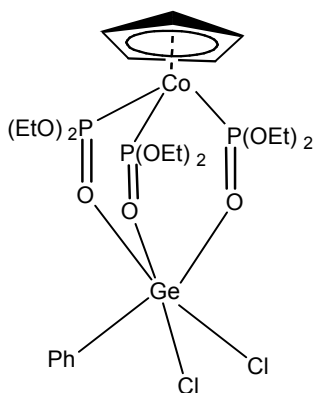
A six-coordinate aryl-germanium complex formed by the Kläui ligand

Kelly A. Davidson, Kelly J. Kilpin, Nicholas C. Lloyd and Brian K. Nicholson*

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand.

Synopsis

The first structurally-characterised six-coordinate aryl-germanium(IV) complex is described.



Abstract.

PhGeCl₃ reacts with Na{[OP(OEt)₂]₃CoCp} to give the six-coordinate complex PhCl₂Ge{[OP(OEt)₂]₃CoCp}, characterised spectroscopically and by an X-ray crystal structure determination which showed a firmly-attached tridentate ligand [Ge-O 1.973(2) Å].

Whilst six-coordinate organo-tin complexes are common [1], corresponding derivatives are rare in organo-germanium chemistry. There are some cyclometallated examples based on Ge-CH₂-heteroatom motifs [2], but there appear to be no structurally characterised aryl-germanium six-coordinate species [3]. We have recently reported some novel six-coordinate organo-tin complexes based on the Kläui ligand **1** (L^R) [4] which showed good stability even for the example incorporating the weak Lewis acid group Ph₃Sn⁺ [5]. We now report the synthesis and structure of a related compound of germanium, PhCl₂Ge{[OP(OEt)₂]₃CoCp} (**2a**). As far as we are aware, the only previous use of the Kläui ligand in germanium chemistry is the report from Filipou et al [6] of some inorganic Ge(II) and Ge(IV) compounds, of which (N₃)₃Ge{[OP(OEt)₂]₃CoCp} (**2b**) is the only six-coordinate example relevant to the present work.

PhGeCl₃ reacts smoothly with NaL^{Et} in CH₂Cl₂ to give crude **2a** as an oil in essentially quantitative yield. This can be crystallised to give yellow, air-stable crystals. The structure was determined by single-crystal X-ray methods and is illustrated in Figure 1. It shows true six-coordination, with only minor deviations from ideal octahedral geometry with the angles around germanium in the range 86-95°. There are no systematic

variations in the Ge-O distances despite the differences in the *trans* groups from the PhCl₂Ge moiety. Table 1 compares some bond parameters with those from the corresponding (N₃)₃GeL^{Et} (**2b**) [6] and PhCl₂SnL^{Me} [5] compounds. The Ge-O distances in **2a** are 1.973(2) Å, almost exactly as predicted from the sum of the covalent radii of Ge(IV) and O (1.21 and 0.74 Å respectively [7]) but are marginally longer than those in the (N₃)₃GeL^{Et} complex [1.893(5) Å]. This suggests the Kläui ligand is moderately strongly bonded to the Ge centre in both germanium examples. The Sn-O distances in the tin analogue of **2a** are longer by only 0.102(4) Å, which is less than expected given that the covalent radius of Sn(IV) is *ca* 0.17 Å larger than that of Ge(IV), based on a comparison of the E-E and E-C bonds in Ph₆E₂ (E = Ge, Sn) [8], indicating even stronger attachment of the Kläui ligand for tin.

The ¹H and ¹³C NMR spectra gave the expected signals for the Ph and Cp groups, with those of the OCH₂CH₃ groups on the ligand appearing as single broad lines with no resolved splitting, despite their inequivalence and expected ¹H and ³¹P coupling. Obviously at room temperature fluxional averaging is much faster for the germanium complex than for the tin one, where the ¹H and ¹³C spectra of the analogous complex gave resolved signals from the three conformationally distinct OCH₂CH₃ groups, further complicated by virtual coupling [5]. The ³¹P spectrum of **2a** gave a broad singlet at room temperature through averaging; at 220 K an overlapping doublet and triplet, strongly distorted by second-order effects, was clearly resolved for the A₂B spin system with very similar δ values (113.9 and 115.0 ppm) (Figure 2).

Spectroscopic evidence suggested that Ph₂ClGeL^{Et} could also be synthesised by the same route, but this product has so far only been isolated as an impure oil which we have

been unable to crystallise. On the other hand the reaction of Ph_3GeCl with NaL^{Et} gave no indication that a stable complex forms, with $\text{Ph}_3\text{GeOGePh}_3$ the only species isolated from the reaction mixture. This suggests that Ph_3Ge^+ has a significantly lower tendency towards six-coordination than does Ph_3Sn^+ [5].

Experimental

General.

The Kläui ligand was purchased from Strem Chemicals, and PhGeCl_3 from Gelest. ^1H , ^{13}C and ^{31}P NMR spectra were recorded at 303 K on a Bruker Avance DRX300 instrument (^1H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz).

*Preparation of $\text{PhCl}_2\text{Ge}\{[\text{OP}(\text{OEt})_2]_3\text{CoCp}\}$, ($\text{PhCl}_2\text{GeL}^{\text{Et}}$, **2a**).*

(a) NaL^{Et} (0.650 g, 1.17 mmol) was dissolved in dry CH_2Cl_2 (10 mL). To this a solution of PhGeCl_3 (0.19 mL, 3.0 g, 1.17 mmol) was added and the mixture was stirred for 30 min. The solution was filtered and the solvent evaporated to leave a yellow oil that was crystallised from CH_2Cl_2 /petroleum spirits at -20°C to give yellow crystals of **2a**. Found: C 36.54, H 5.41 %; $\text{C}_{23}\text{H}_{40}\text{Cl}_2\text{CoGeO}_9\text{P}_3$ requires C 36.54, H 5.33%; NMR (CDCl_3): ^1H : δ 1.24 (br s, CH_3), 4.15 (br s, CH_2), 5.13 (s, Cp), 7.15 (m, H-3, Ph), 7.56 (m, H-4, Ph), 7.98 (m, H-2, Ph); $^{13}\text{C}\{^1\text{H}\}$: δ 16.5 (br s, CH_3), 63.1 (br s, CH_2), 89.6 (s, Cp), 126.4 (C-3), 126.9 (C-4), 132.2 (C-2); $^{31}\text{P}\{^1\text{H}\}$ (290 K); δ 112.4 br s; (220 K) 113.9 (2nd order doublet, $^3\text{J}_{\text{P-P}}$ 114 Hz), 115.0 (2nd order triplet, $^3\text{J}_{\text{P-P}}$ 114 Hz).

*X-ray crystal structure of $\text{PhCl}_2\text{Ge}\{[\text{OP}(\text{OEt})_2]_3\text{CoCp}\} \cdot \text{CH}_2\text{Cl}_2$ (**2a**· CH_2Cl_2)*

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures and software. An empirical absorption correction was applied

(SADABS [9]). The structure was solved by direct methods and developed and refined on F^2 using the SHELX programmes [10] operating under WinGX [11]. Hydrogen atoms were included in calculated positions. Yellow needle crystals of **2a** were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the compound.

Crystal data: $\text{C}_{23}\text{H}_{40}\text{Cl}_2\text{CoGeO}_9\text{P}_3 \cdot \text{CH}_2\text{Cl}_2$, $M = 840.81$, monoclinic, space group Pc , $a = 11.821(1)$, $b = 17.951(2)$, $c = 9.386(1)$ Å, $\beta = 112.45(5)^\circ$, $U = 1840.8(7)$ Å³, $T = 93$ K, $Z = 2$, $D_{\text{calc}} = 1.517$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.731$ mm⁻¹, $F(000) = 860$; 35843 reflections collected with $1^\circ < \theta < 33^\circ$, 13285 unique ($R_{\text{int}} 0.0928$) used after correction for absorption ($T_{\text{max, min}} 0.724, 0.423$). Crystal dimensions $0.60 \times 0.25 \times 0.20$ mm³. Refinement was on F^2 .

Towards the end of the refinement, racemic twinning was indicated and was included using the TWIN/BASF options of SHELXL-97. This converged with a 0.71/0.29 twinning ratio and final agreement indices of $R_1 0.0432$ [$I > 2\sigma(I)$] and $wR_2 0.1176$ (all data), GoF 1.013.

The structure of **2a** is illustrated in Figure 1, with selected bond parameters summarised in the caption.

5. Supplementary material.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 627741. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

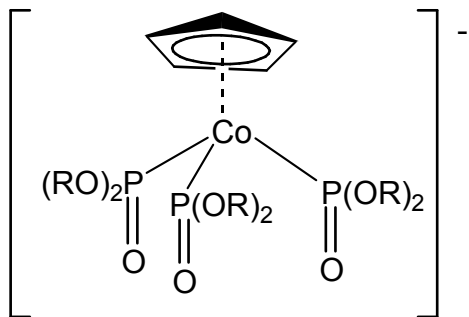
Acknowledgements

We thank Dr Tania Groutso, University of Auckland, for collection of X-ray intensity data.

References.

1. J. A. Zubieta, J. J. Zuckerman, *Progr. Inorg. Chem.*, 24 (1978) 251; A. G. Davies, *Organotin Chemistry*, VCH, Germany, 1997; C. E. Holloway, M. Melnik, *Main Group Metal Chem.*, 23 (2000) 1
2. S.A. Artamkin, V. N. Sergeev, Y. I. Baukov, A O. Mozzhukhin, M. Y. Antipin, Y. T. Struchkov, *Metalloorg. Khim.*, 4 (1991) 1024; Y. E. Ovchinnikov, S. A. Pogozhikh, V. N. Khrustalev, S. Y. Bylikin, V. V. Negrebetsky, A. G. Shipov, Y. I Baukov, *Izv. Akad. Nauk SSSR* (2000) 1799; S. Mahboob, M. Parvez, M. Mazhar, S. Ali *Acta Cryst.*, E61 (2005) m358.
3. Cambridge Crystallographic Database, October 2006 release.
4. W. Kläui, *Angew. Chem. Int. Ed. Eng.*, 29 (1990) 627.
5. N. C. Lloyd, B. K. Nicholson, A. L. Wilkins, *J. Organometal. Chem.*, 691 (2006) 2757.
6. A. C. Filippou, P. Portius, G. Kocok-Köhn and V. Albrecht, *J. Chem. Soc., Dalton Trans.*, (2000) 1759.
7. *SI Chemical Data*, G. Aylward and T. Findlay, 5th Ed, Wiley, Australia, 2002.
8. R. E. Marsh, *Acta Cryst*, B55 (1999) 931; D. Dakternieks, F. S. Kuan, A. Duthie, E. R. T. Tiekink, *Main Group Metal Chem.*, 24 (2001) 65.
9. R. H. Blessing, *Acta Cryst.*, A51, (1995) 33.

10. G. M. Sheldrick, SHELX97 Programs for the solution and refinement of crystal structures, University of Göttingen, Germany, 1997.
11. L. J. Farrugia, WinGX, Version 1.70.01, University of Glasgow, UK; L. J. Farrugia, *J. Appl. Cryst.*, 32 (1999) 837.



(1)

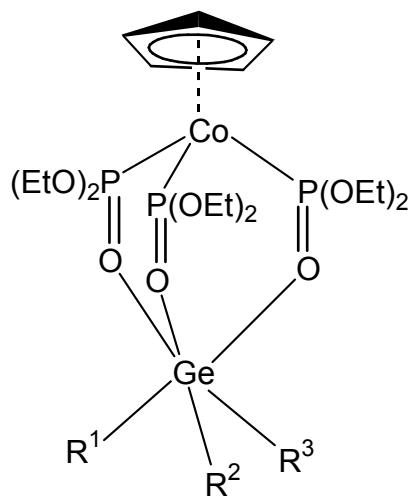
**2a** R¹ = Ph, R² = R³ = Cl**2b** R¹ = R² = R³ = N₃

Table 1

Selected bond lengths(Å) and angles (°) for **2a** and related complexes

	PhCl ₂ GeL ^{Et}	PhCl ₂ SnL ^{Me}	(N ₃) ₃ GeL ^{Et}
	(M = Ge)	(M = Sn [5])	(M = Ge[6])
M(1)-C(41)	1.994(3)	2.111(5)	
M(1)-Cl(av)	2.327(1)	2.385(2)	
M(1)-O(11)	1.973(2)	2.075(3)	1.893(5)
O-M(1)-O(av)	87.9(1)	84.9(1)	89.9(3)
Cl(1)-M(1)-Cl(2)	94.35(3)	97.40(5)	
C(41)-M(1)-Cl(1)	95.37(9)	99.3(1)	
C(41)-M(1)-Cl(2)	94.83(9)	95.5(1)	

Caption to Figures:

Figure 1. The structure of complex **2a**, with the ethyl groups on the peripheral oxygen atoms omitted for clarity. Selected bond parameters include: Ge(1)-C(41) 1.994(3), Ge(1)-Cl(1) 2.3257(8), Ge(1)-Cl(2) 2.3292(8), Ge(1)-O(11) 2.010(2), Ge(1)-O(21) 1.938(2), Ge(1)-O(31) 1.970(2) Å; O-Ge(1)-O (avg) 87.9(1)°, Cl(1)-Ge(1)-Cl(2) 94.35(3)°, C(41)-Ge(1)-Cl(1) 95.37(9)°, C(41)-Ge(1)-Cl(2) 94.83(9)°.

Figure 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** at 220 K. showing the distorted doublet (δ 113.9) and triplet (δ 115.0) in a 2:1 ratio, $^3J_{\text{P-P}}$ 114 Hz.

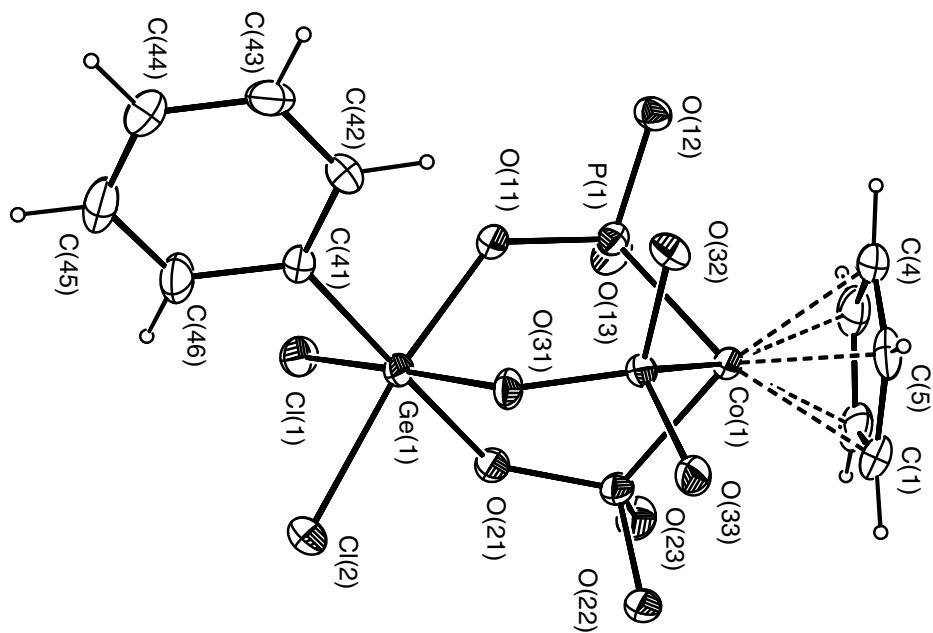


Figure 1

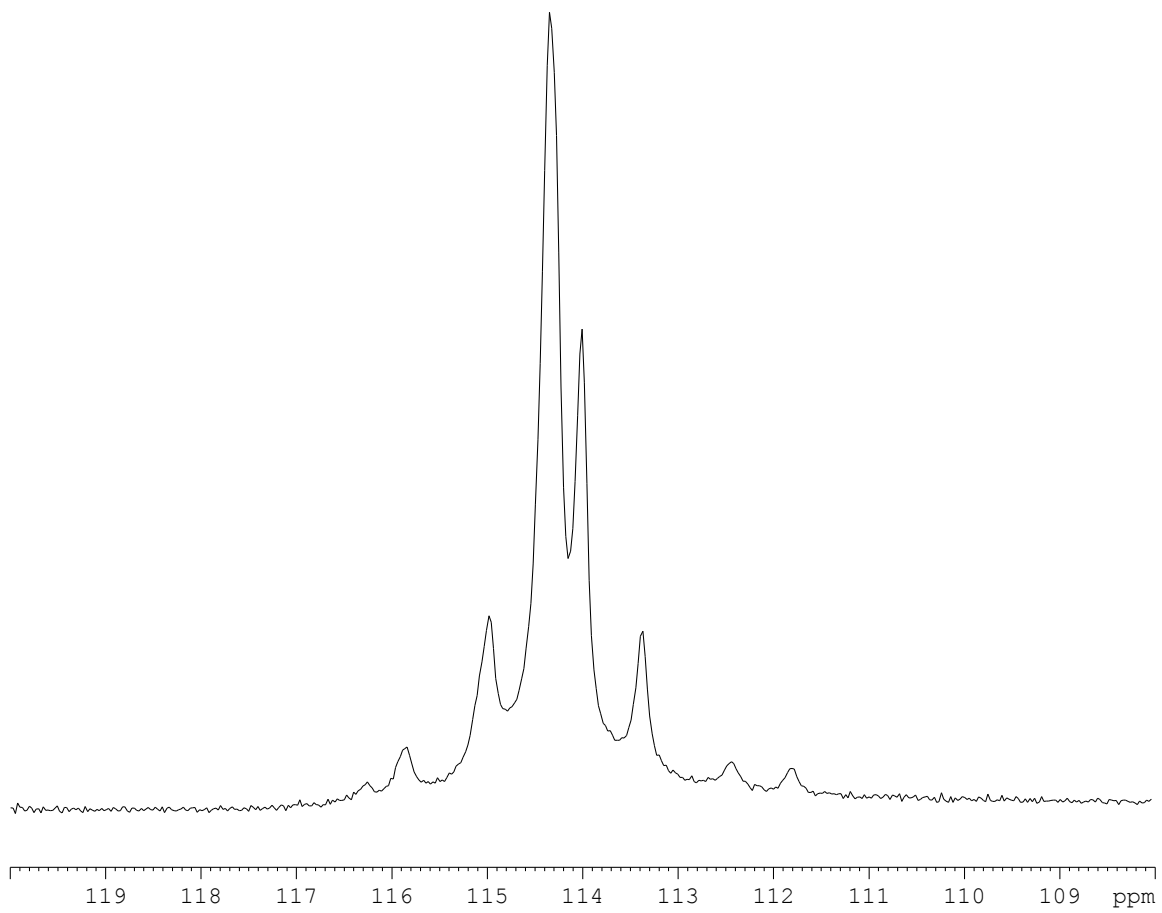


Figure 2