COMMUNICATION:

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

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Synopsis

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

\[
\begin{align*}
\text{Co} & \quad \text{P(OEt)}_2 \quad \text{Cl} \\
\text{Ph} & \quad \text{Cl} \\
\end{align*}
\]
Abstract.

PhGeCl$_3$ reacts with Na{[OP(OEt)$_2$]$_3$CoCp} to give the six-coordinate complex PhCl$_2$Ge{[OP(OEt)$_2$]$_3$CoCp}, 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-CH$_2$-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$_R^R$) [4] which showed good stability even for the example incorporating the weak Lewis acid group Ph$_3$Sn$^+$ [5]. We now report the synthesis and structure of a related compound of germanium, PhCl$_2$Ge{[OP(OEt)$_2$]$_3$CoCp} (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 (N$_3$)$_2$Ge{[OP(OEt)$_2$]$_3$CoCp} (2b) is the only six-coordinate example relevant to the present work.

PhGeCl$_3$ reacts smoothly with NaL$_{Et}$ in CH$_2$Cl$_2$ 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)₃GeL²E (2b) [6] and PhCl₂SnL¹Me [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)₃GeL²E 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 Ph₂ClGeL²E 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$_3$GeCl with NaLEt gave no indication that a stable complex forms, with Ph$_3$GeOGePh$_3$ the only species isolated from the reaction mixture. This suggests that Ph$_3$Ge$^+$ has a significantly lower tendency towards six-coordination than does Ph$_3$Sn$^+$ [5].

**Experimental**

**General.**

The Kläui ligand was purchased from Strem Chemicals, and PhGeCl$_3$ from Gelest. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded at 303 K on a Bruker Avance DRX300 instrument ($^1$H 300.1 MHz, $^{13}$C 75.5 MHz, $^{31}$P 121.5 MHz).

*Preparation of PhCl$_2$Ge{[OP(OEt)$_2$]$_3$CoCp}, (PhCl$_2$GeLEt, 2a).*

(a) NaLEt (0.650 g, 1.17 mmol) was dissolved in dry CH$_2$Cl$_2$ (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$_2$Cl$_2$/petroleum spirits at -20°C to give yellow crystals of 2a. Found: C 36.54, H 5.41 %; C$_{23}$H$_{40}$Cl$_2$CoGeO$_9$P$_3$ requires C 36.54, H 5.33%; NMR (CDCl$_3$): $^1$H: 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); $^{13}$C { $^1$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); $^{31}$P { $^1$H} (290 K): δ 112.4 br s; (220 K) 113.9 (2$^{nd}$ order doublet, $^3$J$_{p,p}$ 114 Hz), 115.0 (2$^{nd}$ order triplet, $^3$J$_{p,p}$ 114 Hz).

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

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures and software. An empirical absorption correction was applied
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\(_2\)Cl\(_2\) solution of the compound.

**Crystal data:** C\(_{23}\)H\(_{40}\)Cl\(_2\)CoGeO\(_9\)P\(_3\).CH\(_2\)Cl\(_2\), M = 840.81, monoclinic, space group Pc, a = 11.821(1), b = 17.951(2), c = 9.386(1) Å, β = 112.45(5)°, U = 1840.8(7) Å\(^3\), T = 93 K, Z = 2, D\(_{calc}\) = 1.517 g cm\(^{-3}\), μ(Mo-K\(_{α}\)) = 1.731 mm\(^{-1}\), F(000) = 860; 35843 reflections collected with 1° < θ < 33°, 13285 unique (R\(_{int}\) 0.0928) used after correction for absorption (T\(_{max, min}\) 0.724, 0.423). Crystal dimensions 0.60 x 0.25 x 0.20 mm\(^3\).

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 > 2σ (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).
Acknowledgements

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

References.


3. Cambridge Crystallographic Database, October 2006 release.


10. G. M. Sheldrick, SHELX97 Programs for the solution and refinement of crystal structures, University of Göttingen, Germany, 1997.

\[ (1) \]

2a \( R^1 = \text{Ph}, R^2 = R^3 = \text{Cl} \)

2b \( R^1 = R^2 = R^3 = \text{N}_3 \)
Table 1

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

<table>
<thead>
<tr>
<th></th>
<th>PhCl$<em>2$GeL$</em>{Et}$ (M = Ge)</th>
<th>PhCl$<em>2$SnL$</em>{Me}$ (M = Sn [5])</th>
<th>(N$_3$)$<em>3$GeL$</em>{Et}$ (M = Ge[6])</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)-C(41)</td>
<td>1.994(3)</td>
<td>2.111(5)</td>
<td></td>
</tr>
<tr>
<td>M(1)-Cl(avg)</td>
<td>2.327(1)</td>
<td>2.385(2)</td>
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<tr>
<td>M(1)-O(11)</td>
<td>1.973(2)</td>
<td>2.075(3)</td>
<td>1.893(5)</td>
</tr>
<tr>
<td>O-M(1)-O(avg)</td>
<td>87.9(1)</td>
<td>84.9(1)</td>
<td>89.9(3)</td>
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<td>Cl(1)-M(1)-Cl(2)</td>
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<td>97.40(5)</td>
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</tr>
<tr>
<td>C(41)-M(1)-Cl(1)</td>
<td>95.37(9)</td>
<td>99.3(1)</td>
<td></td>
</tr>
<tr>
<td>C(41)-M(1)-Cl(2)</td>
<td>94.83(9)</td>
<td>95.5(1)</td>
<td></td>
</tr>
</tbody>
</table>
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 $^{31}$P{1H} NMR spectrum of 2a at 220 K. showing the distorted doublet ($\delta$ 113.9) and triplet ($\delta$ 115.0) in a 2:1 ratio, $^3J_{P,P}$ 114 Hz.
Figure 1
Figure 2