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Journal of Organometallic Chemistry 692 (2007) 1871–1874
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Communication

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

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Received 20 November 2006; received in revised form 19 December 2006; accepted 10 January 2007
Available online 18 January 2007

Abstract

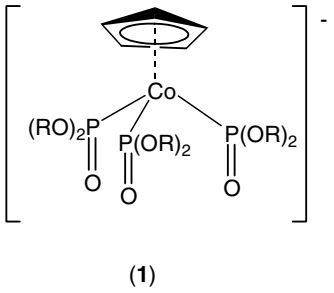
$PhGeCl_3$ reacts with $Na\{[OP(OEt)_2]_3CoCp\}$ to give the six-coordinate complex $PhCl_2Ge\{[OP(OEt)_2]_3CoCp\}$, characterised spectroscopically and by an X-ray crystal structure determination which showed a firmly-attached tridentate ligand [Ge–O 1.973(2) Å].

Keywords: Germanium; Six-coordination; Klaui ligand; X-ray crystal structure; NMR

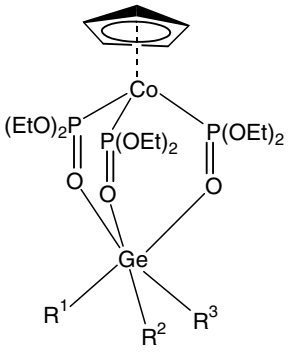
1. Introduction

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) [4] which showed good stability even for the example incorporating the weak Lewis acid group Ph_3Sn^+ [5]. We now report the synthesis and structure of a related compound of germanium, $PhCl_2Ge\{[OP(OEt)_2]_3CoCp\}$ (**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 $(N_3)_3Ge\{[OP(OEt)_2]_3CoCp\}$ (**2b**) is the only six-coordinate example relevant to the present work.

$PhGeCl_3$ reacts smoothly with NaL^{Et} in CH_2Cl_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 Fig. 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 $PhCl_2Ge$ moiety. Table 1 compares some bond parameters with those from the corresponding $(N_3)_3GeL^{Et}$ (**2b**) [6] and $PhCl_2SnL^{Me}$ [5] compounds. The Ge–O distances in **2a** are 1.973(2) Å, almost exactly as predicted from the sum



(**1**)



2a R^1 = Ph, R^2 = R^3 = Cl
2b R^1 = R^2 = R^3 = N_3

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doi:10.1016/j.jorganchem.2007.01.009

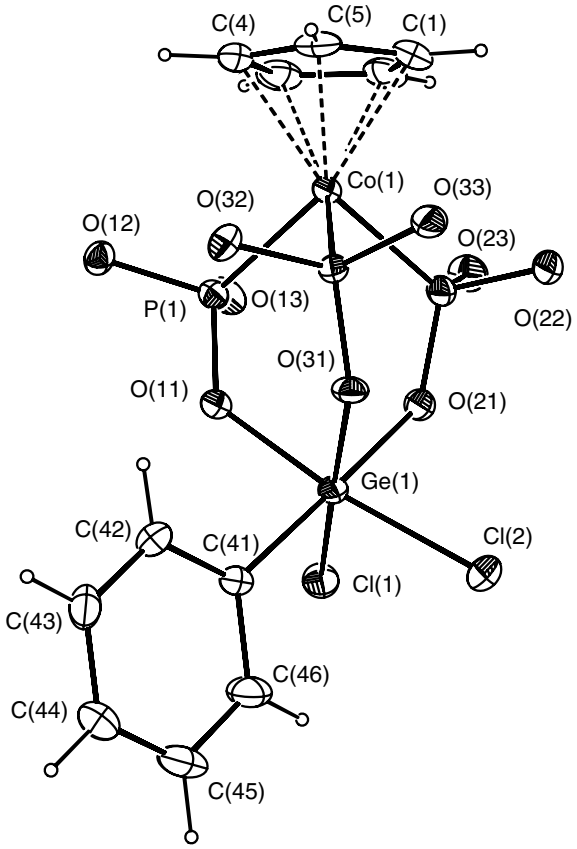

Fig. 1. The structure of complex **2a**, with the ethyl groups on the peripheral oxygen atoms omitted for clarity. Selected bond parameters include: Ge(1)–C(41) 1.994(3), Ge(1)–Cl(1) 2.3257(8), Ge(1)–Cl(2) 2.3292(8), Ge(1)–O(11) 2.010(2), Ge(1)–O(21) 1.938(2), Ge(1)–O(31) 1.970(2) Å; O–Ge(1)–O (avg)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

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 $(N_3)_3GeL^{Et}$ 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 Ph_6E_2 (E = Ge, Sn) [8], indicating even stronger attachment of the Kläui ligand for tin.

Table 1
Selected bond lengths (Å) and angles (°) for **2a** and related complexes

	$PhCl_2GeL^{Et}$ (M = Ge)	$PhCl_2SnL^{Me}$ (M = Sn [5])	$(N_3)_3GeL^{Et}$ (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)	

The ^1H and ^{13}C NMR spectra gave the expected signals for the Ph and Cp groups, with those of the OCH_2CH_3 groups on the ligand appearing as single broad lines with no resolved splitting, despite their inequivalence and expected ^1H and ^{31}P coupling. Obviously at room temperature fluxional averaging is much faster for the germanium complex than for the tin one, where the ^1H and ^{13}C spectra of the analogous complex gave resolved signals from the three conformationally distinct OCH_2CH_3 groups, further complicated by virtual coupling [5]. The ^{31}P 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 A_2B spin system with very similar δ values (113.9 and 115.0 ppm) (Fig. 2).

Spectroscopic evidence suggested that Ph_2ClGeL^{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 $Ph_3GeOGePh_3$ 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].

2. Experimental

2.1. 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).

2.2. Preparation of $PhCl_2Ge[OP(OEt)_2]_3CoCp$, ($PhCl_2GeL^{Et}$, **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**. *Anal.* Calc. for $C_{23}H_{40}Cl_2CoGeO_9P_3$: C, 36.54; H, 5.33. Found: C, 36.54; H, 5.41%. 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); $^{13}C\{^1H\}$: 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); $^{31}P\{^1H\}$ (290 K); δ 112.4 br s; (220 K) 113.9 (2nd order doublet, $^3J_{P-P}$ 114 Hz), 115.0 (2nd order triplet, $^3J_{P-P}$ 114 Hz).

2.3. X-ray crystal structure of $PhCl_2Ge\{[OP(OEt)_2]_3CoCp\}.CH_2Cl_2$ (**2a**, CH_2Cl_2)

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures

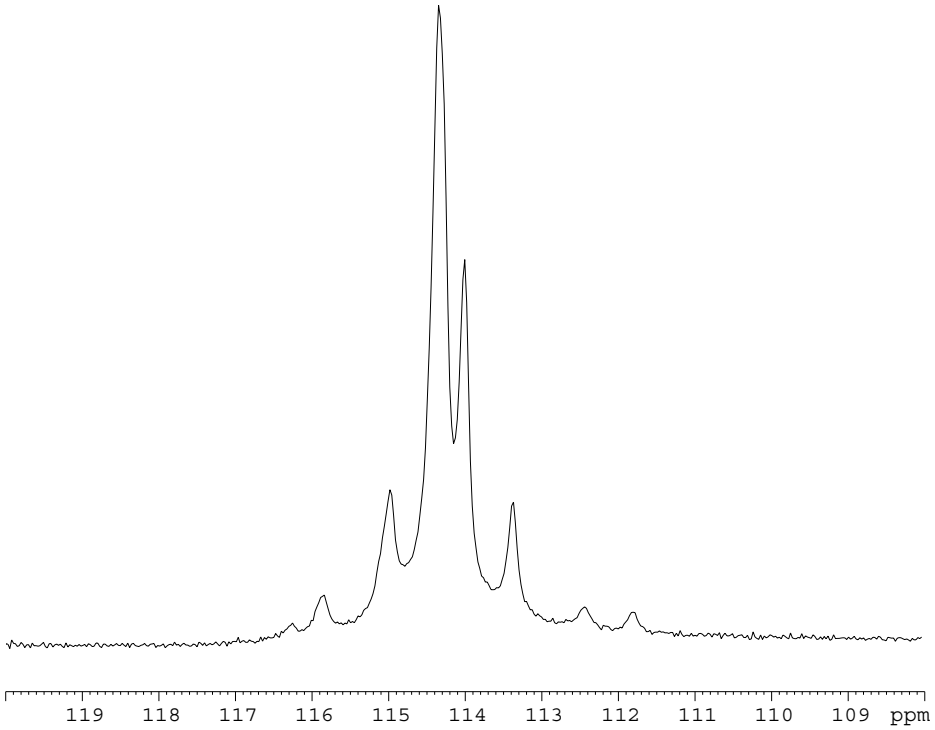

Fig. 2. The ^{31}P ^{1}H NMR spectrum of **2a** at 220 K, show the distorted doublet (δ 113.9) and triplet (δ 115.0) in a 2:1 ratio, $^{3}J_{P-P}$ 114 Hz.

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: $C_{23}H_{40}Cl_2CoGeO_9P_3 \cdot CH_2Cl_2$, $M = 840.81$, monoclinic, space group Pc, $a = 11.821(1)$, $b = 17.951(2)$, $c = 9.386(1)$ Å, $\beta = 112.45(5)°$, $U = 1840.8(7)$ Å^3, $T = 93$ K, $Z = 2$, $D_{calc} = 1.517$ g cm^{-3}, μ(Mo Kα) = 1.731 mm^{-1}, $F(000) = 860$; 35 843 reflections collected with $1° < \theta < 33°$, 13 285 unique (R_{int} 0.0928) used after correction for absorption ($T_{max,\,min}$ 0.724, 0.423). Crystal dimensions $0.60 \times 0.25 \times 0.20$ 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 [$I > 2\sigma$ (I)] and wR_2 0.1176 (all data), Goodness-of-fit 1.013.

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

Acknowledgements

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

Appendix A. Supplementary material

CCDC 627741 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.009.

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