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Nickel–Germanium Bonding in (η^5-Cyclopentadienyl)(trichlorogermyl)(triphenylphosphine)nickel(II) Hemibenzene Solvate, $C_{23}H_{20}Cl_3GeNiP.\frac{1}{2}C_6H_6$

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Abstract. $M_r = 604{\cdot}1$, monoclinic, $C2/c$, $a = 15{\cdot}080\,(3)$, $b = 11{\cdot}889\,(5)$, $c = 29{\cdot}113\,(11)$ Å, $\beta = 93{\cdot}38\,(1)^\circ$, $U = 5210$ Å^3, $Z = 8$, $D_m = 1{\cdot}52\,(2)$, $D_x = 1{\cdot}54$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 2{\cdot}59$ mm^{-1}, $F(000) = 2440$, $T = 295$ K, $R = 0{\cdot}051$ for 2862 observed reflections. The structure of the title complex, isolated as a benzene solvate, shows the presence of a short nickel–germanium bond, suggesting appreciable d_π–d_π interaction between the two metal atoms. The Ni, Ge, P and one of the Cl atoms are located in a plane approximately perpendicular to that of the distorted cyclopentadienyl ring. The Ni atom is bonded to the C_5H_5 ring, to Ph_3P and to Ge while the latter is also bonded to three Cl atoms and the benzene ring lies on the twofold axis.

Introduction. There has been significant interest in compounds containing metal–metal bonds over the last few years (Cotton & Walton, 1982) and although structures involving Group IV elements as one of the metal atoms have been extensively studied, structural data on compounds containing an Ni–Ge bond are limited to $Ph_3GeMNi(GePh_3)(\eta^5\text{-}C_5H_5)MNi(GePh_3)(\eta^5\text{-}C_5H_5)MGePh_3$ (M = Cd, Hg) (Titova, Bychkov, Domrachev, Razuvaev, Struchkov & Zakharov, 1980; Zakharov, Struchkov, Titova, Bychkov, Domrachev & Razuvaev, 1980). A series of compounds believed to contain Ni–Ge bonds have been prepared by the reaction

$$\eta^5\text{-}C_5H_5Ni(L)X + CsGeY_3 \longrightarrow \eta^5\text{-}C_5H_5Ni(L)GeY_3 + CsX$$

(L = tertiary phosphine or arsine, X and Y = halogen) and we have determined the structure of one member of this series, $\eta^5\text{-}C_5H_5Ni(PPh_3)GeCl_3$, isolated as the benzene solvate. A preliminary report of this structure has been published (Glockling, McGregor, Schneider & Shearer, 1970).

Experimental. Prepared by reaction of $\eta^5\text{-}C_5H_5Ni(PPh_3)Cl$ with $CsGeCl_3$; light green powder obtained was recrystallized from benzene as dark green needles (Glockling *et al.*, 1970); crystal $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}2$ mm had ill-defined faces; mounted in a thin-walled capillary tube under dry nitrogen, D_m by flotation in iodobenzene/bromobenzene; Hilger & Watts four-circle diffractometer, 3 standard reflections measured every 50 reflections, $\theta = 0$ to 26°; 5380 independent reflections measured, 2862 $[I \geq 3\sigma(I)]$ corrected for Lorentz and polarization factors and used in analysis (index range h 0–18, k 0–14, l −35–34); six heavy-atom positions found from Patterson function, carbon atoms by Fourier methods, atom parameters refined by least squares using block-diagonal approximation; for 2862 reflections observed, $R(wR) = 0{\cdot}051\,(0{\cdot}053)$; in final cycle of refinement with anisotropic thermal parameters, parameter shifts all $< \frac{1}{3}\sigma$, $w = 1{\cdot}0/(600 + |F_o| + 0{\cdot}0005|F_o|^2 + 0{\cdot}00002|F_o|^3)$; positions of the 24 H atoms calculated assuming D_{6h} symmetry for the benzene rings and D_{5h} for the cyclopentadienyl ring but these were not refined; residual electron density in final difference map within $-1{\cdot}2$ and $+0{\cdot}5$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1962); function minimized $\sum(w\Delta^2)$, where $\Delta = |F_o| - |F_c|$; computer programs supplied by Dr F. R. Ahmed and his associates.

Discussion. Final positional parameters and equivalent isotropic temperature factors are listed in Table 1.§ The structure is shown in Fig. 1 and the bond lengths and angles, together with their e.s.d.'s, are listed in Table 2. The Ni, Ge and P atoms are located in a plane which is approximately perpendicular to that of the mean plane of all five atoms in the cyclopentadienyl (Cp) ring, the

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§ Lists of structure factors, anisotropic thermal parameters, calculated H-atom parameters, mean-plane calculations and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39103 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional positional parameters* (Ni, P, Ge, Cl $\times 10^5$; C $\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

B_{eq} defined according to Willis & Pryor (1975).

	x	y	z	B_{eq}(Å^2)
Ni	1796 (6)	954 (9)	10811 (3)	3·74 (4)
P	14797 (13)	−6164 (17)	12250 (7)	2·15 (7)
Ge	4772 (6)	19362 (8)	11777 (3)	3·94 (3)
Cl(1)	17962 (16)	26618 (21)	12929 (11)	5·9 (1)
Cl(2)	−334 (22)	29639 (25)	5925 (10)	7·0 (2)
Cl(3)	−1657 (20)	27504 (27)	17458 (11)	7·0 (2)
C(1)	−501 (6)	−960 (10)	599 (4)	6·2 (5)
C(2)	−835 (6)	116 (10)	543 (3)	6·2 (5)
C(3)	−1155 (6)	431 (10)	987 (4)	6·3 (5)
C(4)	−1073 (6)	−483 (10)	1282 (4)	6·2 (6)
C(5)	−628 (6)	−1320 (9)	1060 (4)	6·0 (5)
C(6)	1523 (5)	−2089 (7)	1064 (3)	3·2 (3)
C(7)	1250 (6)	−2923 (7)	1357 (3)	3·9 (4)
C(8)	1210 (6)	−4042 (8)	1223 (3)	4·4 (4)
C(9)	1436 (6)	−4336 (7)	787 (4)	5·0 (4)
C(10)	1702 (6)	−3523 (8)	481 (3)	5·0 (4)
C(11)	1758 (6)	−2407 (8)	620 (3)	4·2 (4)
C(12)	2328 (5)	47 (6)	891 (3)	11·2 (3)
C(13)	3223 (5)	50 (9)	1037 (3)	5·0 (4)
C(14)	3823 (6)	555 (10)	756 (4)	7·9 (5)
C(15)	3562 (7)	1057 (9)	345 (4)	5·8 (5)
C(16)	2673 (7)	1040 (8)	205 (3)	5·0 (4)
C(17)	2062 (6)	553 (7)	475 (3)	3·9 (4)
C(18)	1898 (5)	−573 (7)	1827 (3)	3·7 (3)
C(19)	2560 (6)	−1315 (8)	1988 (3)	4·3 (4)
C(20)	2883 (6)	−1232 (8)	2448 (3)	5·1 (5)
C(21)	2567 (7)	−432 (9)	2728 (3)	5·4 (5)
C(22)	1919 (7)	309 (8)	2570 (3)	5·6 (5)
C(23)	1581 (6)	237 (7)	2113 (3)	4·3 (4)
C(24)	0	−2044 (18)	2500	12·1 (15)
C(25)	−655 (9)	−2588 (15)	2295 (6)	11·2 (10)
C(26)	−675 (9)	−3733 (15)	2279 (5)	10·5 (9)
C(27)	0	−4301 (15)	2500	9·9 (12)

dihedral angle between these two planes being 86·5 (8)° and Cl(1) is almost coplanar with the Ge, Ni, P plane. Although to a first approximation Ni may be considered to be trigonally coordinated, there is considerable distortion about the central metal. In particular, the P—Ni—Ge and P—Ni—Cp angles of 100·7 (1) and 134·4 (4)° are worthy of note being significantly distorted from the ideal value of 120°.

The cyclopentadienyl ring is non-planar, and although in general the C_5H_5 moiety bonds to the metal in the normal manner, it is interesting to note that there may be a small degree of localized bonding as exemplified by: (i) The non-planarity of the C_5H_5 ring in which the ring is composed of two planes, one passing through C(1), C(2), C(3), C(5) and the other through C(3), C(4), C(5), the dihedral angle being 174·1 (9)°. (ii) Although not significantly different, there appear to be two sets of C—C distances; C(1)—C(5) and C(2)—C(3) have a mean value of 1·44 (2) Å and C(1)—C(2), C(3)—C(4) and C(4)—C(5) have a mean of 1·38 (1) Å, the mean of all five bond lengths being 1·41 (1) Å. This is reflected in there being two sets of C—Ni—C angles formed by adjacent C atoms in the ring, ranging from 38·1 (4) to 40·7 (4)° with those located along the longer C—C bonds being the larger. (iii) Two sets of Ni—C distances; those between Ni and C(1), C(2) and C(4) have a mean of 2·12 (1) Å and those from Ni to C(3) and C(5) have a mean of 2·06 (1) Å.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code: (i) $-x, y, 0{\cdot}5-z$

Ni—Ge	2·248 (1)	C(6)—C(7)	1·39 (1)
Ni—P	2·154 (2)	C(7)—C(8)	1·39 (1)
Ni—C(1)	2·104 (11)	C(8)—C(9)	1·38 (1)
Ni—C(2)	2·124 (10)	C(9)—C(10)	1·39 (1)
Ni—C(3)	2·054 (9)	C(10)—C(11)	1·39 (1)
Ni—C(4)	2·123 (10)	C(11)—C(6)	1·41 (1)
Ni—C(5)	2·076 (10)	C(12)—C(13)	1·39 (1)
Ge—Cl(1)	2·176 (3)	C(13)—C(14)	1·39 (1)
Ge—Cl(2)	2·198 (3)	C(14)—C(15)	1·38 (1)
Ge—Cl(3)	2·191 (3)	C(15)—C(16)	1·38 (1)
C(1)—C(2)	1·38 (2)	C(16)—C(17)	1·37 (1)
C(2)—C(3)	1·46 (1)	C(17)—C(12)	1·39 (1)
C(3)—C(4)	1·39 (2)	C(18)—C(19)	1·39 (1)
C(4)—C(5)	1·38 (1)	C(19)—C(20)	1·40 (1)
C(5)—C(1)	1·43 (2)	C(20)—C(21)	1·36 (1)
P—C(6)	1·814 (8)	C(21)—C(22)	1·37 (1)
P—C(12)	1·830 (7)	C(22)—C(23)	1·40 (1)
P—C(18)	1·827 (8)	C(23)—C(18)	1·38 (1)
		C(24)—C(25)	1·30 (2)
		C(25)—C(26)	1·36 (3)
		C(26)—C(27)	1·35 (2)
P—Ni—Ge	100·7 (1)	C(7)—C(6)—C(11)	118·1 (7)
P—Ni—Cp*	134·4 (4)	C(8)—C(7)—C(6)	121·4 (8)
Ge—Ni—Cp*	124·7 (4)	C(9)—C(8)—C(7)	119·6 (8)
Cl(1)—Ge—Cl(2)	100·0 (1)	C(10)—C(9)—C(8)	120·6 (8)
Cl(2)—Ge—Cl(3)	100·9 (1)	C(11)—C(10)—C(9)	119·6 (9)
Cl(3)—Ge—Cl(1)	98·6 (1)	C(6)—C(11)—C(10)	120·6 (8)
Cl(1)—Ge—Ni	125·4 (1)	C(13)—C(12)—C(17)	119·3 (7)
Cl(2)—Ge—Ni	112·7 (1)	C(14)—C(13)—C(12)	118·4 (8)
Cl(3)—Ge—Ni	115·5 (1)	C(15)—C(14)—C(13)	122·5 (10)
C(5)—C(1)—C(2)	108·7 (9)	C(16)—C(15)—C(14)	118·3 (10)
C(1)—C(2)—C(3)	105·7 (9)	C(17)—C(16)—C(15)	120·8 (9)
C(2)—C(3)—C(4)	109·0 (9)	C(12)—C(17)—C(16)	120·8 (8)
C(3)—C(4)—C(5)	107·8 (9)	C(19)—C(18)—C(23)	120·3 (8)
C(4)—C(5)—C(1)	108·4 (9)	C(20)—C(19)—C(18)	118·7 (8)
C(6)—P—C(12)	104·0 (3)	C(21)—C(20)—C(19)	120·6 (9)
C(12)—P—C(18)	106·5 (3)	C(22)—C(21)—C(20)	121·1 (9)
C(18)—P—C(6)	105·1 (3)	C(23)—C(22)—C(21)	119·4 (9)
C(6)—P—Ni	112·0 (3)	C(18)—C(23)—C(22)	119·9 (8)
C(12)—P—Ni	112·6 (3)	C(24)—C(25)—C(26)	121·9 (15)
C(18)—P—Ni	115·7 (3)	C(25)—C(26)—C(27)	117·9 (14)
		C(26)—C(27)—C(26^{i})	120·1 (12)

* Cp is the centre of the cyclopentadienyl ring.

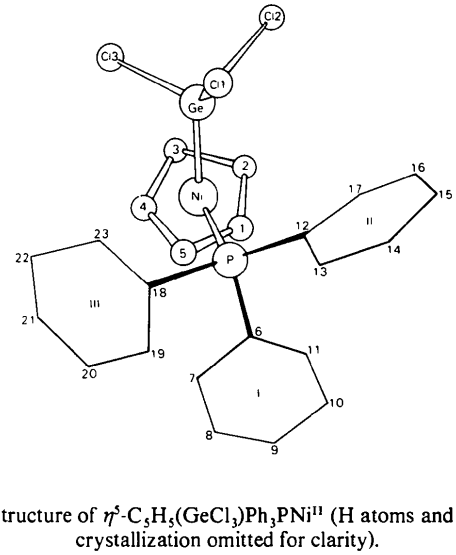

Fig. 1. Structure of η^5-$C_5H_5(GeCl_3)Ph_3PNi^{II}$ (H atoms and C_6H_6 of crystallization omitted for clarity).

Thus, Ni could have a distorted tetrahedral-type configuration to relieve steric crowding with a Ge—Ni—P angle of 100·7 (7)° and with C(3), C(4), C(5) being considered as a π-allyl system and the rather short C(1)—C(2) bond as a double bond. Although the C_5H_5 ring in $(C_5H_5)_2Ni$ is irregular, the rings still maintain planarity (Seiler & Dunitz, 1980).

The Ge—Cl bonds have an average length of 2·189 (3) Å and, whereas Ge—Cl(2) and Ge—Cl(3) are the same within experimental error, Ge—Cl(1) is shorter. The angles at Ge are distorted, the Cl—Ge—Cl angles varying from 98·6 (1) to 100·9 (1)° and the Ni—Ge—Cl angles from 112·7 (1) to 125·4 (1)°. In all cases the length and angles involving Cl(1) deviate the most and this is the atom which is almost coplanar with P, Ge and Ni and is located opposite to the C_5H_5 ring.

The Ni—Ge bond length [2·248 (1) Å] is shorter than those in the only other two compounds for which this is known [2·308 (3) and 2·329 (4) Å] (Titova *et al.*, 1980; Zakharov *et al.*, 1980) and the sum of the covalent radii (2·61 Å) (Pauling, 1960). This short bond length, the small Cl—Ge—Cl angles and the closeness of the Ge—Cl distance to the sum of the covalent radii (2·21 Å) (Pauling, 1960) suggest appreciable d_π–d_π bonding between Ni and Ge rather than d_π–p_π bonding with the Cl atoms.

The benzene molecule lies on the twofold axis located at 0, y, $\frac{1}{4}$. The surrounding groups are phenyl(III) and the C_5H_5 ring.* There is no evidence for disorder, but the thermal parameters are large and the refinement of the atomic parameters was slow, which could explain the rather short C(24)—C(25) bond length of 1·30 (2) Å.

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* A packing diagram has been deposited. See deposit footnote.

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Carbonyldihydrido(trimethylgermyl)bis(triphenylphosphine)iridium(III) Hemibenzene Solvate, $C_{40}H_{41}GeIrOP_2.\frac{1}{2}C_6H_6$

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Abstract. $M_r = 903·5$, monoclinic, $P2_1/c$, $a = 13·63$ (1), $b = 11·044$ (5), $c = 26·07$ (1) Å, $\beta = 92·52$ (3)°, $U = 3920·5$ Å^3, $Z = 4$, $D_m = 1·54$ (2), $D_x = 1·53$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 4·10$ mm^{-1}, $F(000) = 1796$, $T = 295$ K, $R = 0·052$ for 3560 observed reflections. The structure of $H_2(Me_3Ge)CO(Ph_3P)_2Ir$, isolated as a benzene solvate, has distorted octahedral coordination round iridium. The two phosphine groups are *cis* to each other, one being *trans* to a hydride hydrogen atom and the other *trans* to the germyl group.

Introduction. Addition of R_3GeH (R = Me, Et) to *trans*-$(Ph_3P)_2CO(Cl)Ir$ unexpectedly results in the slow formation of the six-coordinate dihydrido complexes $H_2(R_3Ge)CO(Ph_3P)_2Ir$ (Glockling & Wilbey, 1970). This contrasts markedly with analogous hydrosilation (Chalk & Harrod, 1965; Hazeldine, Parish & Parry, 1967) and hydrostannation (Lappert & Travers, 1968) where addition of R_3MH results in the formation of monohydrido complexes $H(R_3M)CO(Cl)(Ph_3P)_2Ir$ (M = Si or Sn; R = alkyl, alkoxy or halide).

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