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Preliminary communication

Rhodium–germanium complexes

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Relative stabilities and reactivities of transition metal–Group IVb complexes depend on the particular pair of elements and on the steric and electronegativity effects of other ligands present. For Co, Rh and Ir the only unknown combination in examples of bonding to Si, Ge and Sn is that between rhodium and germanium. We wish to report a wider range of Rh^{I} and Rh^{III} complexes than have so far been observed for silicon or tin.

Rhodium(I) and rhodium(III) complexes have been isolated by the following reactions:

$$(Ph_3E)_3\,RhCl + R_3GeH \rightarrow (Ph_3E)_2Rh(H)\,(GeR_3)\,Cl + Ph_3E$$

(I)

(E = P, As; R = Me, Et, Cl)

$$(Ph_3P)_3\,RhCl + 6HGeCl_3 \rightarrow [Ph_3PH]_3\,[Rh(GeCl_3)_6] + H_2 + HCl$$

(II)

$$RhCl_3{,}3H_2O + 3(Me_3NH)GeCl_3 + HCl \rightarrow [Me_3NH]_3\,[Rh(GeCl_3)_3Cl_3]$$

(III)

$$[(1{,}5\text{-cyclooctadiene})RhCl]_2 + 2HGeCl_3 \rightarrow 2(COD)Rh(H)\,(GeCl_3)Cl$$

(IV)

$$[(Ph_3P)_2Rh(CO)_2]Na + Et_3GeBr \rightarrow (Ph_3P)_2Rh(CO)_2GeEt_3$$

(V)

Compounds of type I (E = P, As; R = Me, Et) are formed at 20° in the presence of excess germane and a small amount of benzene as solvent. Like the silyl analogues[1,2] the complexes dissociate extensively in solution. Trichlorogermane combines rapidly with $(Ph_3P)_3RhCl$ and the trichlorogermyl compound I(E = P, R = Cl) is only isolable by the slow addition of a 1/1 ratio of reactants. With excess trichlorogermane the phosphonium salt of the octahedral anion(II) is formed. Rhodium trichloride also yields an octahedral anion(III) with trichlorogermyl salts. The salt crystallises as bright orange needles from aqueous hydrochloric acid.

Compound(IV) is believed to be the first example of a Rh^{III} cyclooctadiene complex. It separates as small crystals when trichlorogermane (2 mol.) is added to a benzene solution of $[(COD)RhCl]_2$ (1 mol.). Olefin complexes such as $[(C_2H_4)_2RhCl]_2$ are

TABLE 1

INFRARED DATA (cm^{-1})

s = strong, m = medium, br = broad, (sh) = shoulder.

All infrared data refer to the solid state, KBr or CsI.

Compound	Colour	ν(Rh-H)	Other bands	
$(Ph_3P)_2RhH(GeMe_3)Cl$	yellow	2080 m, 2035 m	816 s, ρ(MeGe);	296 s, 290(sh), ν(Rh–Cl)
$(Ph_3P)_2RhH(GeEt_3)Cl$	yellow	2107 m, 2062(sh)		306 s, 284 s, ν(Rh–Cl)
$(Ph_3P)_2RhH(GeCl_3)Cl$	orange-yellow	2123(sh), 2098 m		372 s, $\nu(GeCl_3)$
$(Ph_3As)_2RhH(GeMe_3)Cl$	green	2057 m, 2025 (sh)	815 s, ρ(MeGe);	334(sh), 322 s, ν(Rh–Cl)
$(Ph_3As)_2RhH(GeEt_3)Cl$	green	2114 m, 2042 m		331 s, 318(sh), νRh–Cl)
$(COD)RhH(GeCl_3)Cl$	orange	2000 m		370 s, br, $\nu(GeCl_3)$
$(Ph_3P)_2Rh(CO)_2GeEt_3$	yellow		1973 s, 1922 s ν(CO)	
$(Ph_3PH)_3[Rh(GeCl_3)_6]$	yellow		2389 m, ν(P-H);	881 s, (P-H bend), 1111 s, 720 s, 370 s,br, $\nu(GeCl_3)$.
$(Me_3NH)_3[Rh(GeCl_3)_3Cl_3]$	orange			360 s,br, $\nu(GeCl_3)$.

effective catalysts for the hydrosilation of olefins and a mechanism involving an intermediate containing both Rh—SiR_3 and Rh—H bonds has been suggested[3], although no complex of this type has been isolated. Cyclooctadienerhodium complexes are less effective hydrosilation catalysts, and the isolation of the compound (IV) demonstrates that the higher oxidation state can be stabilised. Unlike tin where only rhodium(I) compounds have been reported, all of the Rh—$GeCl_3$ compounds contain rhodium in the +3 oxidation state. All of the Rh—Ge compounds described are air-stable solids with the exception of I (E = P, R = Me) which, over 2–3 months, turned brown.

Infrared data are given in the table. Compounds of the type (I) show two bands due to ν(Rh—H); this could be a crystallographic effect or it could be due to the existence of isomers. Although the compounds are formally five-coordinate it has been shown that in the analogous complex $(Ph_3P)_2RhH(SiCl_3)Cl$ an *ortho* hydrogen atom of a phenyl group occupies the sixth coordinate site[4]. Compounds containing $(GeCl_3)^-$ show a strong broad band in the region 360–380 cm^{-1}.

^1H NMR studies on the complexes(I) have been restricted by extensive dissociation or low solubility in inert solvents but signals characteristic of the R_3Ge grouping are found and a weak Rh—H signal has been observed for the complex I (E = P, R = Et). This consists of an overlapping doublet of triplets centred at τ 25.4 due to splitting by ^{103}Rh (100%, $I = ½$, J(Rh-H) 19Hz), and two *cis* phosphorus nuclei ^{31}P (100%, $I = ½$, J(P–Rh–H) 15Hz). The Rh^I complex (V) gives a signal centred on τ8.76 due to the Et_3Ge grouping.

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