Reactions of Silanes and Germanes with Iridium Complexes. Part I. Reactions with Vaska's Compound

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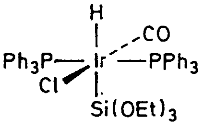
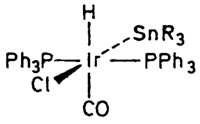
Vaska's compound, *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), reacts with SiH_3X (X = H, Cl, Br, I) and with GeH_4 in benzene at room temperature to give insoluble 1 : 1 adducts. With GeH_3Y (Y = Cl, Br, I) and with Ge_2H_6, initial reaction gives soluble 1 : 1 adducts, whose stereochemistries have been determined from their n.m.r. spectra; after 30—60 min, insoluble adducts precipitate. Reaction with Si_2H_6 is more complicated and the product is not homogeneous; in every other case addition involves the breaking of Si–H or Ge–H bonds. The i.r. spectra and some of the reactions of the adducts are described. On prolonged standing, under an excess of SiH_3Cl, Vaska's compound gives SiH_2Cl_2 and a soluble silyl complex of six-co-ordinated iridium containing two Ir–H bonds; with the other halides, prolonged reaction leads to halogen exchange and to decomposition.

OXIDATIVE addition by simple molecules to *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), Vaska's compound, has been extensively studied over the past ten years.[1,2] Trisubstituted silanes XYZSiH (X, Y, Z = Cl, R, OR) react to give equimolar adducts, and the reaction involves addition of Si and H to iridium;[3] the stability of the adduct formed is greatest when the other groups bound to silicon are electronegative, but with Me_3SiH or with Et_3SiH no adducts were isolated. Unfortunately, the products are almost all only sparingly soluble in common solvents, and their structures have in most cases to be deduced from i.r. spectra. The n.m.r. spectra that could be obtained from saturated solutions of the adduct of $HSi(OEt)_3$ were consistent with structure (I) below, with the two phosphine groups mutually *trans* and with H *trans* to Si.[4]



(I)



(II)

The i.r. spectra of the other adducts were consistent with structures of this general type, though it is not easy to distinguish with certainty between all possible isomers. A study of the reactions of R_3SnH with Vaska's compound and with the analogous complex of methyldiphenylphosphine led to the conclusion that the structures of the adducts formed were either of type (I) or of type (II); in one case a mixture of isomers was formed.[5]

When Vaska's compound or its adduct with XYZSiH was allowed to stand for a long time at room temperature in the presence of excess of the silane, a further reaction occurred.[4,6] Halogenosilane was evolved and a soluble silyl complex of iridium was formed in which there were two IrH bonds in each molecule and the Ph_3P-groups were mutually *cis*. Reaction of Vaska's compound with XYZGeH led exclusively to dihydrides of this type;[7] equimolar adducts of Vaska's compound were not isolated even when the reactants were taken in equimolar proportions. From these results it appears that in the formation of the equimolar adducts the *trans*-phosphine configuration of the starting material is preserved, but that the change in the relative positions of the phosphine ligands is associated with the substitution at iridium of Cl by H. The apparent difference between the reactions with Vaska's compound of silanes and of germanes led us to investigate the reactions with the simple molecules MH_3X (M = Si or Ge; X = H, Cl, Br, or I) and M_2H_6; we were also interested to see if there was any evidence for oxidative addition involving bonds other than MH.

TABLE 1

Analysis of adducts of Vaska's compound (V) with silyl and germyl compounds

	Analysis			
	Found		Equimolar adduct requires	
Reactants	C	H	C	H
V + SiH_4	54·9	4·1	54·9	4·1
V + $2SiH_3Cl$	52·9	3·9	54·7	4·2
V + SiH_3Cl	52·9	3·9		
V + $2SiH_3Br$	49·9	3·7	49·7	3·7
V + SiH_3Br	49·9	3·7		
V + $2SiH_3I$	47·6	3·5	47·4	3·5
V + SiH_3I	47·9	3·6		
V + GeH_4	51·5	3·7	51·9	4·0
V + GeH_3Cl	49·7	4·1	49·9	3·7
V + GeH_3Br	47·1	3·3	47·5	3·5
V + GeH_3I	45·2	3·5	45·2	3·4
V + Ge_2H_6	47·8	4·1	47·6	3·9
V + $2MeSiH_2Cl$	52·5	3·9	53·0	4·1
V + $MeSiH_2Cl$	53·0	4·1		

RESULTS

Reaction of Vaska's Compound with SiH_3X.—No reaction occurred when Vaska's compound was kept at room temperature with an equimolar proportion of SiH_3Cl in the absence of solvent for two weeks. When the same starting complex was allowed to warm to room temperature with a 2 : 1 molar proportion of SiH_3X and a large excess of benzene, a white precipitate began to form almost at once from the yellow solution; after 5—10 min the yellow colour was discharged, and the reaction appeared complete. Half the amount of silyl compound initially taken was recovered, and analysis confirmed that the solids were equimolar adducts of Vaska's compound with SiH_3X (see Table 1). All the

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[1] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 5325.

[2] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[3] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

[4] A. J. Chalk, *Chem. Comm.*, 1969, 1207.

[5] M. F. Lappert and N. F. Travers, *J. Chem. Soc.* (*A*), 1970, 3303.

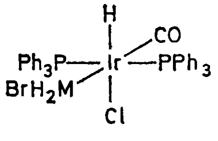
[6] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Canad. J. Chem.*, 1969, **47**, 2205.

[7] F. Glockling and M. J. Wilbey, *J. Chem. Soc.* (*A*), 1970, 1675.

adducts were effectively insoluble in all the solvents we tried; we therefore had to deduce what we could about their structures from their i.r. spectra. All the spectra could be interpreted satisfactorily in terms of the assumption that addition of H^- and XH_2Si^- to iridium has taken place; the increase in co-ordination of the metal accounts for the increase in ν(CO) from its value in the starting complex. Peaks of medium intensity near 2200 cm^{-1} can plausibly be assigned to ν(IrH), and the strong bands near 2100 cm^{-1} to ν(SiH). The frequencies of the bands observed, with tentative assignments, are given in Table 2.

Since the bands assigned to ν(CO) are single sharp peaks, we believe that these products are monoisomeric; therefore we have looked for a single structure to account for all the features in the spectra that can be used for structural diagnosis. Though the evidence is not conclusive, structures based on (III) below account best for our observations. The low values of ν(IrCl) imply that Cl is *trans* to a group of high *trans*-influence, probably silyl or hydride; the low values for ν(CO) suggest that carbonyl is also *trans* to one of these groups. On the other hand, ν(IrH) is relatively high, which indicates that H is *trans* to Cl. The insensitivity of ν(IrCl) to changes in X is also consistent with a structure in which SiH_2X is *cis* rather than *trans* to Cl. The only point apparently inconsistent with this arrangement is that ν(CO) is somewhat higher in the spectrum of $Cl(CO)IrD(PPh_3)_2SiD_2Br$ than it is in $Cl(CO)IrH(PPh_3)_2SiH_2Br$; this would normally be taken as implying that H is *trans* to CO, since coupling between ν(IrH) and ν(CO) is usually regarded as responsible for changes in ν(CO) on deuteriation and coupling between the two modes is supposed to be significant only when H and CO are mutually *trans*.[8] The shift on deuteriation, however, is relatively small, and may be due to coupling with ν(SiH). If all these deductions are correct, it follows that the phosphine groups are mutually *trans* [as in structure (III) below, M = Si]. However, the evidence cannot be regarded as conclusive.

Reactions between equimolar proportions of Vaska's compound and SiH_3X under the same conditions are much slower; precipitation occurs over about 24 h before the yellow colour of the starting complex is completely discharged. Analysis (Table 1) shows that the solid products are also equimolar adducts, and no SiH_3X was recovered. When X = H or Br, the i.r. spectra show that the products are the



(III)

same as those described above; when X = Cl or I, however, additional bands are present, which we associate with the presence of other isomers. When X = Cl, the frequencies of the new bands are consistent with a structure in which H is *trans* to SiH_2Cl, as in structure (I); when X = I, we believe that there has been some halogen exchange, which would lead to the formation of up to four possible products.

TABLE 2

Infrared spectra of silyl–iridium complexes

Reactants	Frequencies (cm^{-1}) and assignments								
	ν(SiH)	ν(IrH)	ν(CO)	δ(SiH)	δ(IrH)	δ(CO)	ν(SiX)	ν(IrSi)	ν(IrCl)
Vaska's compound (V)			1945vs			605s			
V + SiH_4				960m					
	2105vs	2130m	1980vs	945s	830m	604s		350w	255m
	2095vs			930vs					
V + $2SiH_3Cl$				980s					
	2120vs	2180m	1990vs	860s	835m	618vw		365w	265m
	2100vs								
V + SiH_3Cl				980s					
	2120vs	2180m	1995vs	970m	850m			365w	265m
	2110vs	2040m	1980vs	940s	830m	620vw		350w	250m
				860s					
V + $2SiH_3Br$	2120vs			975s					
	2100vs	2180m	1990vs	850vs	830s	618vw	405s	340m	265m
V + SiH_3Br	2120vs			975s					
	2100vs	2180m	1990vs	855vs	835m	618vw	405s	340m	265m
V + $2SiH_3I$	2120vs			965s					
	2100vs	2180m	1995vs	810s	830m	616vw	385s	305m	260m
V + SiH_3I				980m					
	2120vs	2170m	1990vs	970m	830m			356w	
	2100vs	2040m	1980vs	940m	810s	617vw	385m	305w	260w
	2080vs			860s					
V + SiD_3Br	1542s						401m		
	1480s	1583s	2010vs	640m	610m	618vw	393m	330m	265m
V + $2MeSiH_2Cl$				921m					
	2073vs	2143m	1976vs	800m	830m	620vw	465	350w	255m
V + $MeSiH_2Cl$	2082m	2140m		925m					
	2065vs	2020m	1975vs	890w	835m	618vw	465	345w	255m
				805m					
V (Br) + $2SiH_3Cl$ *	2110s	2165m	1993vs	980m					
	2100vs	2030m	1978vs	960m	830m	620vw	470s	372w	
				860s,br					

* V(Br) = *trans*-$(Ph_3P)_2Ir(CO)Br$.

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[8] L. Vaska, *J. Amer. Chem. Soc.*, **1966**, **88**, 4100.

Reaction with a 2 : 1 molar excess of SiH_3X over a period of 24 h also leads to the production of the additional isomers when X = Cl or I, and in roughly the same proportions.

Reaction of Vaska's Compound with GeH_3X.—Vaska's compound reacts with GeH_4 in much the same way as it reacts with SiH_3X. With an initial 2 : 1 excess of GeH_4, a white equimolar adduct is rapidly precipitated, whereas the same product is obtained very much more slowly from a mixture of the reactants in equimolar proportions. With GeH_3Y, however (Y = Cl, Br, or I), what happens is rather different. When equimolar proportions of the reactants are allowed to warm to room temperature in the presence of an excess of benzene, the yellow colour disappears at once; initially a clear solution is obtained, from which a white precipitate is slowly deposited over 30—60 min. Reactions with an initial molar excess of GeH_3Y of up to 2 : 1 are similar. The precipitates once formed could not be persuaded to redissolve; by analysis and from the amounts of GeH_3Y recovered they are shown to be equimolar adducts. The solubility of the initial products, though transient, means that we have been able to use ^1H n.m.r. spectroscopy to identify the compounds and to establish stereochemistries. In each case a resonance due to Ir*H* is observed, which establishes that addition has taken place as H^- and YH_2Ge^-. The Ir*H* chemical shifts (*ca.* τ 27) imply that H is *trans* to Cl. Since the Ir*H* and the Ge*H* resonances are both triplets, the phosphine groups are mutually *trans*, so that the initial products are of the form of (III) (M = Ge).

TABLE 3

Parameters from the HGe and HIr proton resonance spectra [a] of $GeH_3X{\cdot}Ir(CO)Cl(PPh_3)_2$

Adduct [b]	τ(Ge*H*) p.p.m.	^3J(*H*GeIr*P*) Hz	^4J(*H*GeIr*H*$_t$) [c] Hz	τ(Ir*H*) p.p.m.	^2J(*H*Ir*P*) Hz	Structure type
$V{\cdot}GeH_3Cl$	4·75 (t)	6		27·14 (t)	12	(III)
	5·78 [d]	6	3	17·77 [e]	15	(IV)
$V{\cdot}GeH_3Br$	5·40 (t)	7		27·10 (t)	12	(III)
$V{\cdot}GeH_3I$	6·52 (t)	8		26·97 (t)	11	(III)
$V(Br){\cdot}GeH_3Cl$	4·76 (t)	7		27·03 (t)	12	(III)
$V{\cdot}Ge_2H_6$	6·86 (t) (Ge*H*$_3$)	N.o.		27·6br (t)	12	(III)
	7·96 (t) (Ge*H*$_2$) [f]	6				

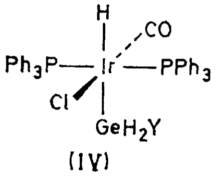
[a] All spectra measured in benzene relative to internal TMS (τ = 10·00). [b] V = *trans*-$(PPh_3)_2Ir(CO)Cl$. V(Br) = *trans*-$(PPh_3)_2$-Ir(CO)Br. [c] H_t = H *trans*. [d] Doublet of triplets. [e] Triplet of triplets. [f] Complex multiplet. N.o. = not observed.

TABLE 4

Infrared spectra (cm^{-1}) of germyl–iridium complexes (Nujol mulls)

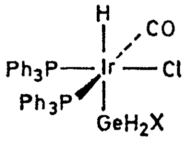
Reactants	ν(IrH)	ν(GeH)	ν(CO)	δ(GeH)	δ(IrH)	δ(CO)	ν(GeX)	ν(IrCl)	ν(IrGe)
V + $2GeH_4$	2225w 2120w	2010vs	1970s	900m 890s 830vs	?830vs	620vw		268m	240w
V + $2GeH_3Cl$	2200w 2100w	2020vs	1990s	875m	830w	620vw	350s	275m	N.o.
V + $2GeH_3Br$	2200m 2111m	2017vs	1997s	891m 870m	?850m	618vw	350m	260m	230w
V + $2GeH_3I$	2100w	2020vs,br		875m,br	?850m	618vw	345m,br	?240w	220w
V(Br) + $2GeH_4$	2210m 2110w	2006vs	1968vs,br	886m 837m	827m	615vw			280w
V(Br) + $2GeH_3Cl$	2185m 2100w	2017vs,br	1998vs,br	870m,br	N.o.	615vw	340m,br		N.o.
V + Ge_2H_6	2200w	2103sh 2072sh 2007vs	1970vs	875m	800m	617vw		266vw	230vw

When Y = Cl, resonances due to a second isomer are also observed. The Ge*H* resonance is a doublet of triplets; double irradiation shows that the doublet splitting is due to coupling with the Ir*H* proton, whose resonance, a triplet of triplets, appears at a chemical shift value consistent with structure (IV), like (I), in which H is *trans* to GeH_2Y. The resolution of ^3J(*H*GeIr*H*) in the spectrum of this isomer, but not in that of the other, is also consistent with the general observation that couplings involving protons are usually larger when the coupled atoms are *trans* than when they are *cis*. The relative proportions of the isomers do not depend on the time after mixing, nor on the proportions of reactants initially taken. Additional peaks were also observed in the spectra of the adducts when Y = Br or I. The intensities of these varied relative to the resonances associated with the predominant isomer, and from the parameters we believe that they are due to species in which halogen exchange has occurred. The n.m.r. parameters for all these soluble species are collected in Table 3.



(IV)

The stereochemistries of the soluble complexes are established almost beyond doubt by the n.m.r. spectra; we have much less evidence as to the structures of the precipitates. Their i.r. spectra (see Table 4) are very like those of the solids obtained by evaporation of the solvent immediately after reaction, and also (as far as we could tell) like those of the soluble species in solution before precipitation has occurred. These observations suggest that precipitation is slow merely because of slow crystal growth, and that the solutions we have studied are supersaturated. Precipitation, however, is slow and prolonged rather than delayed and sudden; it is accelerated by warming, so such an explanation does not seem very plausible. Perhaps the insoluble material is an isomeric form, or even a polymer; in view of the isomerization in the extended reaction between Vaska's compound and R_3SiH, the possibility that precipitation is associated with a shift in the phosphine configuration from *trans* to *cis* must be considered, but we have no evidence to suggest that this is what happens. As for polymerization, it is hard to see how adducts like these could polymerize unless halogen bridges were formed; bridging would imply an increase in co-ordination number at either Si or Ir or both, and again there is no evidence to support this proposal. On balance we feel that isomerization is the most likely explanation, in which case the insoluble species would be of structure (V). The i.r. spectra could be reconciled with structures of this type. They agree rather better, if anything, however, with structures of type (III), if the insoluble species are of structure (III), isomerization has not occurred and some other explanation for precipitation must be found.

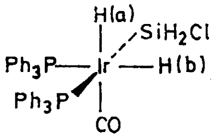


(V)

Reactions of Vaska's Compound with M_2H_6.—There is an immediate reaction when Vaska's compound is allowed to warm to room temperature with an equimolar proportion of Ge_2H_6 in benzene. The yellow colour fades within a few minutes, leaving a very pale yellow solution from which a white precipitate settles over about half an hour. The n.m.r. spectrum obtained from the solution shows that Ge_2H_6 has added as H⁻ and $Ge_2H_5^-$; the Ir*H* resonance, a triplet, is at τ 27·6, implying that H is *trans* to Cl and that the phosphine groups are mutually *trans*. The Ge*H* resonance consists of a triplet at τ 6·86, assigned to GeH_3, and a weaker triplet of quartets at τ 7·96. Irradiation at τ 27·6 does not affect either of these multiplets, implying that there is no detectable coupling between Ir*H* and Ge*H*, but irradiation at τ 6·86 caused the Ge*H* resonance at τ 7·96 to collapse to a broad triplet. The structure of this adduct is therefore of type (III). The i.r. spectrum of the ultimate precipitate is very like those of the other solid adducts; frequencies are given in Table 4, and n.m.r. parameters in Table 3.

The reaction between disilane and Vaska's compound does not follow the usual pattern. When equimolar proportions of the reactants were allowed to warm to room temperature in the presence of benzene, an insoluble white precipitate formed over about 20 min. No non-condensable gas was evolved, but about half of the disilane taken was recovered unchanged. The i.r. spectrum of the solid product suggested that addition of SiH to iridium had occurred, since a band at 2120 cm^{-1} could plausibly be assigned to ν(IrH); similarly, the Ir–Cl bond seems to have been retained. On pyrolysis, some Si_2H_6 was given off, so it seems that in at least some of the product there are Si–Si bonds. With an initial excess of disilane there was a similar reaction, though the proportion of Si_2H_6 consumed per mole of Vaska's compound taken was closer to 1 : 1. The i.r. spectra of the solid products in each case varied in detail from experiment to experiment, so we conclude that they are not homogeneous. It seems possible that at least some adducts containing iridium bound to each silicon atom in a disilane fragment have been formed, such as $ClIrH(CO)(PPh_3)_2SiH_2SiH_2IrHCl(CO)(PPh_3)_2$.

Products of Long-term Reactions.—On standing for 1—2 weeks under an equimolar excess of SiH_3Cl in the presence of benzene, the adduct of Vaska's compound with SiH_3Cl slowly dissolved to give a colourless solution. The volatile products of the reaction consisted of SiH_2Cl_2 containing traces of SiH_4 and SiH_3Cl. From the solution a solid was recovered, whose i.r. spectrum contained no band that could reasonably be assigned to ν(IrCl). In the ^1H n.m.r. spectrum of the solution, the Si*H* resonance at τ 4·84 was split into a doublet of doublets, with small further splittings that were only partly resolved; the Ir*H* resonance, best observed at 220 MHz, consisted of two doublets of doublets of doublets, each of equal intensity. From the magnitudes of the splittings, we conclude that the compound is a dihydride of six-co-ordinated iridium. Since irradiating across the Ir*H* resonances did not affect the main doublet splittings in the Si*H* resonance, we conclude that these splittings are due to coupling with two non-equivalent P atoms, one *cis* and the other *trans* to Si. Since one of the couplings ^2J(HIrP) is of the order of 100 Hz, it appears that one Ir*H* is *trans* to Ph_3P. It follows that the compound has structure (VI) below; as found in related systems.[4,6]



(VI)

The n.m.r. parameters are given in the Experimental section. Reaction over a similar period of a 2 : 1 molar excess of $MeSiH_2Cl$ with Vaska's compound gives a soluble species which may well have a similar structure; unfortunately the n.m.r. spectrum was too weak to allow us to establish this.

Reaction between an excess of the other silyl or germyl compounds we have studied and Vaska's compound led to halogen exchange with iodides or bromides, and to disproportionation or other form of decomposition; no other well defined soluble species was detected.

Reactions with $BrIr(CO)(PPh_3)_2$.—We undertook some preliminary studies of the reactions between *trans*-$BrIr(CO)(PPh_3)_2$ and MH_3X, in the hope of obtaining adducts that were more soluble. With SiH_3Cl, GeH_4, or GeH_3Cl, however, precipitation occurred either immediately or in so short a time that we could not obtain useful n.m.r. spectra. From the i.r. spectra of the solids and of the volatile material recovered we conclude that addition occurs with some halogen exchange. We have not characterized the adducts further.

DISCUSSION

All the silanes or germanes we have studied add to Vaska's compound as H⁻ and M⁻; this is true even with molecules like GeH_3I or Ge_2H_6, in which other bonds appear to be thermodynamically much weaker than the GeH bond. Only with disilane is there any possibility that addition may have involved breaking a different type of bond. The contrast with the reactions of methyl iodide is interesting.[9] There are good thermodynamic

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[9] R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2796.

reasons why CH_3I adds as CH_3 and I rather than as H and CH_2I, and why GeH_3Cl adds as H and GeH_2Cl rather than as GeH_3 and Cl; however, thermodynamic arguments make the latter mode of addition more appropriate for GeH_3I. We had no difficulty in isolating 1 : 1 adducts of the usual type from Vaska's compound and germanium hydrides, despite the rather different reaction between Vaska's compound and triorganogermanes; indeed, we could not obtain germyliridium dihydrides by this reaction, even on prolonged standing. This may reflect the generally rather low thermal stabilities of the germyl complexes we have studied. However, despite the well defined reactions between XYZSiH and Vaska's compound to give silyliridium dihydrides, we were only able to obtain such compounds in this study from Vaska's compound and SiH_3Cl or $MeSiH_2Cl$. It is surprising that SiH_4 does not give a dihydride of this type by this reaction. In a subsequent paper we shall describe the preparation of a range of these dihydrides by a different method.[10]

The transient solubility of the adducts of GeH_3Y and Ge_2H_6 is remarkable, and we do not understand it; however, it has enabled us to assign stereochemistries to the soluble species with considerable confidence. We have no means of deciding whether the distribution of isomers we find in the soluble products reflects the relative importance of initial *cis* and *trans* addition, or whether it results from rapid rearrangement to an isomer pattern that is determined by thermodynamics. If we are right to believe that final precipitation is associated with isomerization, then it seems more likely that isomerization in these systems is generally slow, and so that the isomer pattern reflects pathways rather than thermodynamics. In any case, the observation of distinct resonances for different isomers rules out rapid fluxional behaviour.

It is not surprising to find some halogen exchange between iridium and silicon or germanium. In related compounds of platinum[11] such exchange is chemically fast and gives products in which the heavier halogen is bound to platinum; here exchange is much slower, and it is not clear that equilibrium always favours the species with the heavier halogen bound to iridium.

EXPERIMENTAL

Volatile compounds were manipulated in conventional glass vacuum apparatus fitted either with greased glass or with greaseless polytetrafluoroethylene (Rotaflo or Sovirel) taps. Involatile solids were handled under dry nitrogen in an evacuable glove-box or Polythene bag. I.r. spectra were recorded using Perkin-Elmer 457 (4000—250 cm^{-1}) or 225 (4000—200 cm^{-1}) spectrometers. ^{1}H N.m.r. spectra were obtained using a Varian Associates HA 100 spectrometer or the HR 220 spectrometer in the Petrochemical and Polymer Laboratory of I.C.I. at Runcorn. Silyl and germyl compounds were prepared by standard methods. Vaska's compound was synthesized using the method of Collmann and Kang;[12] it was converted into *trans*-bromocarbonylbis(triphenylphosphine)iridium(I) with lithium bromide.

Representative Experiments.—Reaction of Vaska's compound (a) with SiH_3Cl *(1 : 2 molar ratio).* Vaska's compound (0·1 mmol) was sealed in a glass tube with benzene (1 ml) and SiH_3Cl (0·2 mmol). After 10—15 min a white precipitate formed and the yellow colour of Vaska's compound was completely discharged. Silyl chloride (0·1 mmol) was recovered as the sole volatile material apart from benzene. The white solid residue was identified by analysis (see Table 1) and by its i.r. spectrum (see Table 2) as an equimolar adduct of SiH_3Cl with Vaska's compound. Reactions with SiH_4, GeH_4, SiH_3Br, SiH_3I, and $MeSiH_2Cl$ proceeded similarly.

(*b*) *With* SiH_3Cl *(1 : 1 molar ratio).* Silyl chloride (0·1 mmol) was sealed with benzene (1 ml) and Vaska's compound (0·1 mmol) in a glass tube and kept at room temperature. A white precipitate formed slowly. After 24 h the colour of Vaska's compound was completely discharged. Benzene was the only volatile material recovered. The product was shown by analysis to be an equimolar adduct of SiH_3Cl with Vaska's compound, though there were some differences between the spectrum of this material and that of the adduct prepared as in (*a*). Reactions between equimolar proportions of Vaska's compound and SiH_4, GeH_4, SiH_3Br, SiH_3I, and $MeSiH_2Cl$ were studied similarly.

(*c*) *With* GeH_3Cl *(1 : 1).* GeH_3Cl (0·1 mmol) was allowed to react with GeH_3Cl (0·1 mmol) in benzene at room temperature. The yellow colour of Vaska's compound faded almost at once, and a white precipitate formed over 1 h. Benzene was the only volatile material recovered, and the white solid residue was shown by analysis to be the adduct $GeH_3Cl{\cdot}Ir(CO)Cl{\cdot}(PPh_3)_2$. With an excess of GeH_3Cl, precipitation was somewhat faster but the i.r. spectrum of the solid product was the same. Reactions of Vaska's compound with GeH_4, GeH_3, or GeH_3I took a similar course.

(*d*) *With* Ge_2H_6. Treatment of Vaska's compound (0·1 mmol) with Ge_2H_6 (0·1 mmol) in benzene at room temperature gave a pale yellow solution from which a white solid precipitated after 30 min. No volatile compound other than benzene was recovered. The white solid was identified by analysis (see Table 1) as the equimolar adduct $Ge_2H_6{\cdot}Ir(CO)Cl(PPh_3)_2$; its spectroscopic properties are given in Tables 2 and 3.

(*e*) *With* Si_2H_6. Treatment of Vaska's compound (0·1 mmol) with disilane (0·1 mmol) in benzene at room temperature (20 min) gave a colourless solution, Si_2H_6 (0·05 mmol) and an insoluble white precipitate (Found: C, 55·7; H, 4·0. $C_{37}H_{36}ClIrP_2Si_2$ requires C, 52·7; H, 4·3. $C_{74}H_{66}Cl_2Ir_2O_2P_2Si_2$ requires C, 58·4; H, 4·3%). Reaction of Vaska's compound (0·1 mmol) with disilane (0·2 mmol) in benzene (30 min) gave a white solid and Si_2H_6.

Properties of the Adducts.—The adducts are all white or pale yellow solids. They are stable under nitrogen for periods of hours to days at room temperature, the GeH-compounds being appreciably less stable than the SiH derivatives. The i.r. spectra of the adducts of the silyl halides are almost unchanged even after the compounds have been kept in air for some days.

Reactions of the Adducts with an Excess of MH_3X.—When SiH_3Cl (0·2 mmol) was kept with Vaska's compound (0·1

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mmol) in benzene at room temperature the adduct precipitated initially was found to redissolve over about 10 days; benzene and $\mathrm{SiH_2Cl_2}$ (0·1 mmol) were the sole volatile products recovered. Evaporation of the solvent left an unstable white gelatinous solid, but solutions were stable for several weeks at room temperature. Analysis of the n.m.r. spectrum gave the following parameters: $\tau(\mathrm{Si}H)$, 4·54; $\tau(\mathrm{Ir}H_\mathrm{a})$, 19·58; $\tau(\mathrm{Ir}H_\mathrm{b})$ = 20·6 p.p.m. $^2J(H_\mathrm{a}\mathrm{Ir}P)$ = 16, 20; $^2J(H_\mathrm{b}\mathrm{Ir}P_\mathrm{a})$ = 110; $^2J(H_\mathrm{b}\mathrm{Ir}P_\mathrm{b})$ = 20; $^2J(\mathrm{H_a}\mathrm{Ir}H_\mathrm{b})$ = 4; $^3J(H\mathrm{SiIr}P_\mathrm{a})$ = 12; $^3J(H\mathrm{SiIr}P_\mathrm{b})$ = 24 Hz. The i.r. spectrum in benzene gave bands at 2095s,br (νSiH), 1980s,br (νCO), 950w, and 850w (δSiH), 830w (δIrH), 620 vw (δCO) $\mathrm{cm^{-1}}$ besides those due to $\mathrm{Ph_3P}$-groups; in Nujol, bands were observed at 2100vs and 2080vs (νSiH), 1990vs (νCO), 962vs, and 960vs (δSiH), 830s and 782s (δIrH), 620 vw (δCO), 452s (νIrSi) and 350w (νIrSi) $\mathrm{cm^{-1}}$. A similar product was obtained from the reaction (10 days) of Vaska's compound with a 2 : 1 molar excess of $\mathrm{MeSiH_2Cl}$. The n.m.r. spectrum was very complex, but contained resonances at τ 4·78 (complex multiplet; Si*H*), 8·43 and 8·63 ($\mathrm{C}H_3$) and 19·77 (t) and 20·2 p.p.m. (doublet of doublets, Ir*H*). Approximate coupling constants of $^2J(H_\mathrm{b}\mathrm{Ir}P_\mathrm{a})$ *ca.* 110, ^2J-$(H_\mathrm{b}\mathrm{Ir}P_\mathrm{b})$ *ca.* 18, and $^2J(H_\mathrm{a}\mathrm{Ir}P)$ *ca.* 20 Hz were measured. The i.r. spectrum in Nujol, besides bands due to $\mathrm{Ph_3P}$ groups, included peaks at 2100vs and 2080vs (νSiH), 1980vs (νCO), 905s and 885s (δSiH), 830s, 790s, and 770m (δIrH and $\rho\mathrm{CH_3}$), 618m (δCO), 345m, and 325m (νIrSi). No further reaction was observed between $\mathrm{SiH_4}$ and $\mathrm{SiH_4{\cdot}Ir(CO)Cl(PPh_3)_2}$ even after prolonged standing. Treatment of Vaska's compound with $\mathrm{SiH_3I}$ or $\mathrm{SiH_3Br}$ under these conditions did not give soluble products; when Vaska's compound was allowed to stand with an excess of $\mathrm{GeH_4}$ or germyl halides, decomposition began after 2—3 days.

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