Contribution from the Inorganic Chemistry Department,
The Queen's University, Belfast, N. Ireland.

Some Group IVb Complexes of Iridium

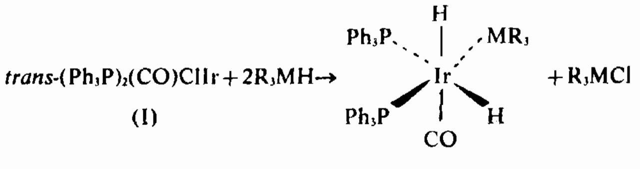
F. Glockling and J. G. Irwin

Received Jannuary 25, 1972

Trans-$(Ph_3P)_2(CO)ClIr$ *(I) adds* $HSiCl_3$, $HGeCl_3$ *and* Me_3SiH *yielding dihydridoiridium complex* $(Ph_3P)_2(R_3M)(CO)(H)_2Ir$ *(II). Exchange reactions between (II),* $(R_3M = Me_3Ge)$ *and silanes and stannanes favour reaction products in the order:* $Cl_3Si > Bu_3Sn \sim Me_3Sn > Me_3Ge > Me_3Si$ *and* $Cl_3Ge > Me_3Ge$. *A possible mechanism for these exchange reactions is discussed. Complex (II) hydrogenates hex-2-yne to hex-2-ene.*

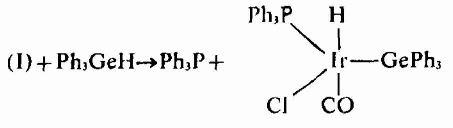
Introduction

Neutral iridium(I) complexes such as (I) combine readily with silanes[1,2,3] germanes[4] and stannanes[5,10] to yield iridium(III) products containing iridium-hydrogen and iridium-group IVb element bonds. In the case of trimethylgermane the reaction proceeds by a series of addition-elimination stages, and the stereochemistry of the product(II) $MR_3 = GeMe_3$ has been rigorously established by an X-ray crystal structure[6] and by its i.r. and high field p.m.r. spectra[4].



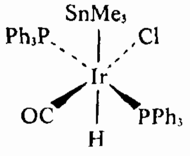
(II)

The analogous reactions of silanes produce octahedral adducts, $(Ph_3P)_2(R_3Si)(CO)HClIr$, which, under appropriate conditions, react with excess silane yielding dihydridoiridium complexes(II) with $M = Si$ and $R =$ alkyl, alkoxy.[1,2] By contrast triphenylgermane adds to (I) with elimination of 1 mol. of triphenylphosphine and formation of a 5-coordinate complex (III).

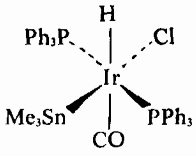


(III)

Triorganostannanes are reported to behave differently[5]: thus Ph_3SnH gives an octahedral adduct with (I) whereas Me_3SnH gives two isomeric octahedral adducts (IV) and (V) according to the ratio of reactants.



(IV)



(V)

The stereochemistry of (IV) and (V) was deduced from their i.r. spectra making the assumption that the phosphine ligands are *trans*. Although a high field Ir-H proton resonance was observed no coupling to the *cis* phosphorus atoms was reported.

The present work is concerned with comparing the chemical and physical properties of this class of compounds, and examining the exchange reactions between silanes, germanes and stannanes bonded to iridium.

Results and Discussion

Oxidative additions of R_3M-H compounds to (I) are highly sensitive to steric effects and electronegative substituents. For example, whereas Pr^i_3GeH and $(o\text{-tolyl})_3GeH$ are unreactive, $HSiCl_3$ and $HGeCl_3$ combine rapidly forming complexes of type (II). Trimethylsilane has not previously been studied and we find that it combines only slowly with (I) to give the dihydridoiridium complex(II). In our hands the addition of trialkylstannanes to (I) has proved more complex and temperamental than originally suggested. Using accurately equimolar ratios of (I) and Me_3SnH in benzene under the conditions reported by Lappert and Travers[5] gave only unreacted material although benzene solutions contained an infrared band at 2080 cm^{-1}, ascribable to ν(Ir-H). However with 2 mols. of Me_3SnH a white complex was isolated analysing as (IV) or (V), but its high field p.m.r. spectrum which, on the basis of either of these structures should have been a 1:2:1 triplet, was far more complex. Between 19 and 21.5τ 14 lines of varying intensity were observed, three pairs were indicative of *cis*-H-Ir-H coupling in dihydridoiridium compounds [^2J(H), 4-5 Hz]. It therefore

---

(1) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, *87*, 16, (1965).
(2) A. J. Chalk, *Chem. Comm.*, 1207, (1969).
(3) J. F. Harrod and C. A. Smith, *Can. J. Chem.*, *48*, 870, (1970).
(4) F. Glockling and M. D. Wilbey, *J. Chem. Soc.* (A), *10*, 1675, (1970).
(5) M. F. Lappert and N. F. Travers, *J. Chem. Soc.* (A), *10*, 3303, (1970).
(6) M. L. Schneider and H. M. M. Shearer, IVth International Conference on Organometallic Chemistry, Bristol, (1969), A16.

appears that stannyliridium compounds such as (IV) isomerise and decompose to dihydridoiridium products when in solution. This behaviour is similar to that reported by Chalk[2] for the decomposition of $(Ph_3P)_2[(EtO)_3Si](CO)HClIr$ in dichloromethane. Experiments in which a large excess of Me_3SnH was used invariably gave complex high field p.m.r. spectra and in one case decomposition to iridium was observed.

Oxidative addition of tri-*n*-butylstannane to (I) is also complex. Preparative scale reactions yielded yellow viscous oils having complex high field p.m.r. spectra centred on 20.7τ but this reaction, examined in an n.m.r. tube, gave the high field p.m.r. spectrum shown in Fig. 1. Although not unambiguous this spectrum could be derived from structure (VI) or (VII) in which the two Ir-H hydrogen atoms are mutually *trans*, and the coupling $^2J(H\text{-}P)$ of 25 Hz is typical of the grouping H-Ir-(P-*cis*).

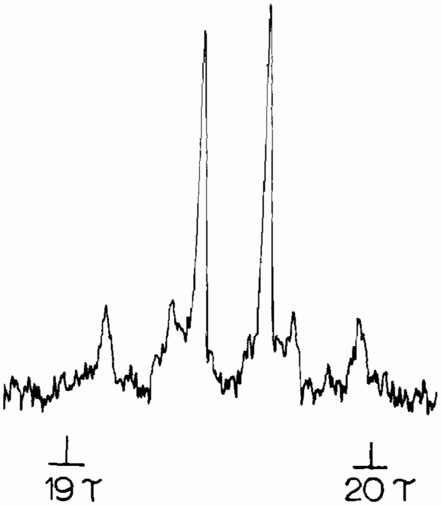
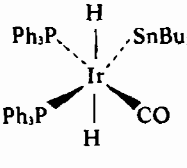
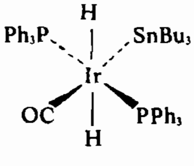


Figure 1. High field ^1H nmr spectrum from reaction: (1) $+Bu^n_3SnH$.


(VI)


(VII)

The reason (I) gives dihydrido complexes (II) in reactions with silanes and germanes rather than monohydrides may be due to successive addition-elimination reactions[4] although it has been suggested that the Ir-Cl is directly reduced by R_3MH.[5] If the latter suggestion were correct we would expect the 5-coordinate complex $(Ph_3P)(CO)(Ph_3Ge)HClIr$ to be reduced by trimethylgermane, but no reaction takes place in refluxing benzene.

The difficulty in preparing the trimethylstannyl derivative of (II) led us to examine exchange reactions of the type:

$$(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir + R_3MH \rightleftarrows (Ph_3P)_2(R_3M)(CO)(H)_2Ir + Me_3GeH$$

Whereas trimethylsilane does not undergo this reaction trichlorosilane and trichlorogermane react readily. Similarly trimethylstannane and tri-*n*-butylstannane will displace Me_3GeH. The high field part of the p.m.r. spectrum of (II) where $R_3M = Me_3Sn$ is shown in Figure 2.

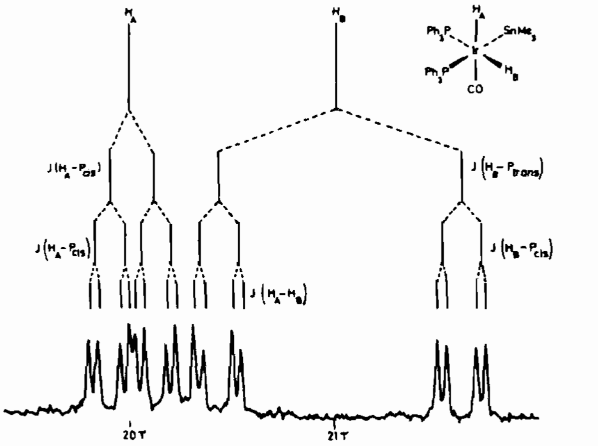
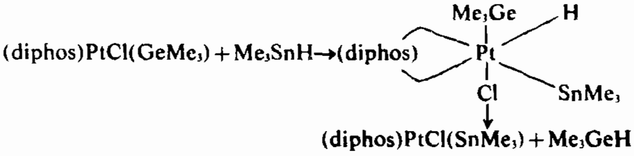


Figure 2. High field ^1H nmr spectrum of $(Ph_3P)_2(Me_3Sn)$-$(CO)(H)_2Ir$ at 100 MHz.

The position of equilibrium in these reactions appears to favour the products in the order $Cl_3Si > Bu_3Sn \sim Me_3Sn > Me_3Ge > Me_3Si$ and $Cl_3Ge > Me_3Ge$, and in all cases the stereochemistry remains unaltered. A factor contributing to this « stability order » could be the low solubility of the trichlorosilyl and trichlorogermyl complexes, but it is agreement with that found for platinum complexes of the type (diphos)-$PtCl(MMe_3)$[7] though a different mechanism seems likely. For platinum addition - elimination reactions occur e.g.



These iridium complexes are already 6-coordinate and we favour a mechanism involving reversible dissociation of trimethylgermane from (II) followed by a reversible oxidative addition stage. This view is based on a study of the reaction of (II) with trimethyldeuterostannane in which Me_3GeH and Me_3GeD are formed and both Ir-H protons in the product are equally deuterated.

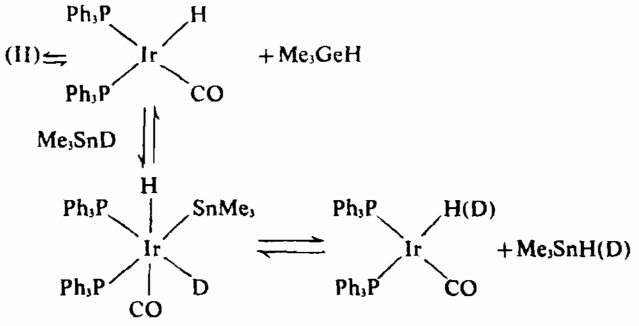


Table I. Infrared Spectra.

Complex	ν(C≡O) ν(Ir-H) cm^{-1} (KBr)	ν(C≡O) ν(Ir-H) cm^{-1} (cyclohexane)	ν(M-Cl) cm^{-1} (CsI)
$(Ph_3P)_2(Me_3Si)(CO)(H)_2Ir$	2085(sh), 2070, 1966	2094, 2082, 1978	
$(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$[4]	2123(sh), 2071, 1956	2114(sh), 2076, 1969	
$(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$	2112(sh), 2084, 1975	2098(sh), 2063, 1974	
$(Ph_3P)_2(Cl_3Si)(CO)(H)_2Ir$	2150(sh), 2128, 2018	2148, 2128, 2018 [a]	524, 508, 493
$(Ph_3P)_2(Cl_3Ge)(CO)(H)_2Ir$	2084(sh), 2065, 2055	2082, 2058, 2051(sh) [b]	388, 370, 364.

[a] nujol mull; [b] in C_6H_6

Table II. ^1H n.m.r. data (in C_6D_6)*

Complex	MR$_3$ group τ(CH$_3$)	Iridium Hydrides τ	J[H-P$_{trans}$]	J[H-P$_{cis}$]	J[H-H]
$(Ph_3P)_2(Me_3Si)(CO)(H)_2Ir$	9.37	19.36	116	24, 16	3.6
		20.39		20	3.6
$(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$	9.20	19.50	117	19,15	3.5
		20.50		18	3.5
$(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$	9.44	20.06	116	22, 15	4.7
		21.04		18	4.7
$(Ph_3P)_2(Bu_3Sn)(CO)(H)_2Ir$		19.43		25	
		19.65			

* τ values relative to internal TMS; coupling constants in Hz.

Since both H-Ir-P and H-Ir-H couplings are observed in the high field p.m.r. spectra these dissociation processes must be slow on the n.m.r. time scale.

The ionic complex $[(Ph_2PCH_2CH_2PPh_2)_2Ir]Cl$ reacted with trimethylgermane in ethanol to yield the known cationic dihydride[8,9], $[(diphos)(H)_2Ir]^+$ rather than an Ir-Ge complex. The reaction of (II), $R_3M = Me_3Ge$, with ethylene has previously been reported[4], and we find that hex-2-yne behaves in the same way producing hex-2-ene and the iridium (I) compound, $(Ph_3P)_2(Me_3Ge)(CO)Ir$. By contrast the trichlorogermyl analogue was not dehydrogenated by ethylene. This may have been due to its insolubility in benzene, though Cl_3Ge appears to stabilise the +3 oxidation state of iridium more effectively than Me_3Ge.

Infrared and p.m.r. spectra. Table I lists the assignable stretching modes for the dihydrido complexes. Since the group IVb substituent is *trans* to phosphorus, changes in ν(CO) and ν(Ir-H) are minor throughout the series. The p.m.r. spectra (Table II) are also similar with only small changes in chemical shifts and coupling constants. It is interesting that τ values for the Me_3Mprotons do not show a progressive change from silicon to tin. In the trimethyltin complex the methyl protons couple to the magnetic isotopes of tin with among the smallest coupling constants so far reported for trimethyltin complexes, [$^2J(H-^{119}Sn)$, 45.2 Hz, $^2J(H-^{117}Sn)$, 42.1 Hz].

Experimental

All experiments were carried out under nitrogen, solvents being dried and deoxygenated. Reaction products such as R_3GeH, R_3SiCl were identified by their i.r., ^1H n.m.r., mass spectra or vapour phase chromatography.

Dihydrido (carbonyl) trimethylsilylbis (triphenylphosphine) iridium (III).

Trimethylsilane (0.5 ml.) and benzene (8 ml.) were condensed onto *trans*–$(Ph_3P)_2(CO)ClIr$ (512 mg) in an evacuated tube equipped with a break-seal and refluxed for 12 days, during this time the original yellow solution became colourless. Removal of benzene and crystallisation of the residue from cyclohexane yielded the complex. (420 mg., 79%) m.p. 136-138° (Found: C, 59.69; H, 4.71. $C_{40}H_{41}IrOP_2Si$ requires C, 58.59; H, 5.00%). The mother liquors contained Me_3SiCl together with unreacted Me_3SiH.

Dihydrido (carbonyl) trichlorosilylbis (triphenylphosphine) iridium (III). Trichlorosilane (2 ml.) and benzene (20 ml.) were condensed onto *trans* $(Ph_3P)_2(CO)ClIr$ (1.2 g.). At room temperature a grey solution formed and on standing overnight an off-white solid precipitated. At 40° the solution turned pale yellow and small white crystals formed. Work up of the reaction volatiles gave $SiCl_4$. Recrystallisation from a large volume of benzene gave the complex. (630 mg., 47%). identified by i.r. comparison with material prepared by an exchange reaction (Table I).

Reaction of (I) with trimethylstannane. Trimethylstannane (29 cc.at S.T.P.) was condensed onto *trans*-$(Ph_3P)_2(CO)ClIr$ (505 mg.) and benzene (10 ml.) in an evacuated flask, (2:1 molar ratio). The solution was stirred and quickly became almost colourless. The volatiles were removed and the product recrystallised from benzene, yielding unreacted material and white crystals of $(Ph_3P)_2(Me_3Sn)(CO)HClIr$. (128 mg., 21%). ν(Ir-H) ν(C-O) 2104, 1986 cm^{-1}. ν(Ir-Cl) 294 cm^{-1}. (Found: C, 50.32; H, 4.10; Cl, 3.73. C_{40}-

---

(7) A. F. Clemmit and F. Glockling, *J. Chem. Soc.*, (A), *11*, 1164, (1971).
(8) J. F. Harrod and C. A. Smith, *J. Am. Chem. Soc.*, *92*, 2699 (1970).
(9) L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, *88*, 5324, (1966).
(10) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, *5*, 20 (1966).

$H_{40}ClIrOP_2Sn$ requires C, 50.84; H, 4.24; Cl, 3,76%).

Reaction of (I) with tributylstannane - a. Complex (I) (41 mg.) was placed in a ^1H n.m.r. tube fitted with a 10 ml. glass bulb. Tributylstannane (0.05 ml.) and deuterobenzene (0.6 ml.) were added, degassed and the tube sealed under vacum. On warming to room temperature the original yellow solution became colourless, some bubbling occurring. The ^1H n.m.r. spectrum was recorded immediately. (Figure 1). ***b.*** In a similar experiment in a break-seal tube, (I) (600 mg.), Bu_3SnH (1.5 ml.) and benzene (8 ml.) were heated at 50° for 8 weeks. The solution lightened in colour but work up gave a viscous yellow liquid which could not be crystallised.

Dihydrido (carbonyl) trimethylstannylbis (triphenylphosphine) iridium (III). Trimethylstannane (1 ml.) and benzene (5 ml.) were condensed onto $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ (496 mg.) in an evacuated tube equipped with a break-seal, and maintained at 30° for 4 weeks. Me_3GeH was identified in the volatiles. The residue was crystallised from cyclohexane to give the white crystalline complex. (378 mg., 72%) m.p. 146-147°. (Found: C, 52.41; H, 4.48. $C_{40}H_{41}IrOP_2Sn$ requires C, 52.75; H, 4.51%).

Reaction of $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ with trichlosilane. Pure $HSiCl_3$ (1 ml.) was condensed onto $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ (645 mg.) and benzene (5 ml.) as previously described. A white crystalline precipitate formed almost immediately; recrystallisation from benzene gave the complex, $(Ph_3P)_2(Cl_3Si)(CO)(H)_2Ir$ (420 mg., 64%), m.p. 284-286°. (Found: C, 49.58; H, 3.54; Cl, 12.14; $C_{37}H_{32}SiIrOP_2$ requires C, 50.41; H, 3.63; Cl, 12.09%).

Trimethylgermane was detected in the volatiles.

Reaction of $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ with trichlorogermane. Trichlorogermane (0.5 ml.) and benzene (5 ml.) were condensed onto $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ (230 mg.). On heating overnight at 50°C, white crystals formed. Recrystallisation from a large volume of benzene gave $(Ph_3P)_2(Cl_3Ge)(CO)(H)_2Ir$ (180 mg., 73%). Me_3GeH was identified in the volatiles.

Reaction of $(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$ with trichlorosilane. Trichlorosilane (0.5 ml.), benzene (3 ml.) and $(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$ (45 mg.) were kept at 30° for 4 hours when white crystals of $(Ph_3P)_2(Cl_3Si)(CO)(H)_2Ir$ formed (26 mg., 64%), identified by i.r. comparison. Me_3SnH was identified in the volatiles.

Reaction of $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ and tributylstannane. Tributylstannane (1 ml.) and benzene (5 ml.) were added to $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ (506 mg.) in an evacuated break-seal tube. After 6 days at 70° the volatiles were removed, Me_3GeH being identified, leaving a syrupy yellow liquid containg unreacted stannane, not all of which could be removed. It proved impossible to crystallise the product.

Reaction between $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ and trimethyldeuterostannane. Trimethyldeuterostannane (1 ml.) and benzene (3 ml.) were condensed onto $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ir$ (296 mg.) and maintained at 30° for 2 days. The volatiles were removed leaving a white crystalline solid identified by i.r. and ^1H n.m.r. spectroscopy as partially deuterated $(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$. (Found: C, 52.46; H, 4.54. $C_{40}H_{41}IrOP_2Sn$ requires C, 52.75; H, 4.51%). Proton integration corresponded to: Ph(30): Me(9): IrH(0.65 and examination of the high field resonances showed that both Ir-H protons had been equally deuterated. Trimethyl-germane and-deuterogermane were identified in the volatiles.

Reaction of bis (bis-1,2-diphenylphosphinoethane) iridium (I) chloride and trimethylgermane. Trimetylgermane (1 ml.) was condensed onto the chelate iridium complex (637 mg.) and ethanol (6 ml.) and left at room temperature for 6 weeks. The solution lightened from its original orange colour and removal of volatiles gave a light brown solid. This was dissolved in ethanol and an ethanolic solution of sodium tetraphenylborate added giving an immediate flocculent white precipitate of $[(diphos)_2(H)_2Ir(III)]BPh_4$, m.p. 218° identified by its i.r. spectrum.

(ν(Ir-H) 2088 and 2060 cm^{-1} (nujol); 2092, 2078 (sh) and 2063 (sh) cm^{-1} (CsI). (Found: C, 69.14; H, 5.60; $C_{76}H_{70}BIrP_4$ requires C, 69.67; H, 5.35%).

Reaction between $(Ph_3P)_2(Me_3Ge)(CO)(H)_2Ge$ and hex-2-yne. Hex-2-yne (1 ml.) was condensed onto the complex (182 mg.) in a break-seal tube. After 1 week at room temperature, an off-white solid had settled out. This was identified as $(Ph_3P)_2(Me_3Ge)(CO)Ir$ and hex-2-ene was detected in the liquid phase.

Acknowledgements. One of us (J.G.I.) thanks the Ministry of Education (N. Ireland) for a research award.