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XI*. THE STEREOCHEMISTRY OF $Ir(H)Cl(SiR_3)CO(PPh_3)_2$, AND THE *trans*-INFLUENCE OF SUBSTITUTED SILYL, GERMYL, AND STANNYL GROUPS

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SUMMARY

The infrared spectra of the complexes $Ir(X)Y(SiR_3)CO(PPh_3)_2$ (X=H, D; Y=Cl, Br: SiR_3=SiF_3, $SiCl_3$, $Si(OEt)_3$. $SiCl_2Me$, $SiClMe_2$) show that the structure involves the *trans*-pairs of ligands (Ph_3P, Ph_3P), (X, CO) and Y, SiR_3). From the variation in the metal–chlorine stretching frequencies in these complexes and in related platinum(II) complexes, the following *trans*-influence series are deduced: $SiF_3 \approx SiCl_3 < SiCl_2Me < Si(OEt)_3 \ll SiClMe_2$; $SiCl_3 < SiCl_2H < SiClH_2 < SiH_3 \ll SiMe_3$; $GeClH_2 \ll GeMe_3$; $SnMe_3 \ll GeMe_3 \approx SiMe_3$; $SnCl_3 \ll SnMe_3 \approx SiCl_3$.

INTRODUCTION

Tertiary silanes react with Vaska's complex (I) in two stages[2]. The first stage (eqn. 1) is direct oxidative addition, while the second (eqn. 2) is thought to involve reductive elimination of a chlorosilane, R_3SiCl, followed by oxidative addition of R_3SiH to the resulting iridium(I) complex $Ir(H)CO(PPh_3)_2$. The same product, (III), has been obtained from reaction of tertiary silanes with the complex $Ir(H)CO(PPh_3)_3$ or, better, with $IrH_3CO(PPh_3)_2$[4]. The mechanism of reactions (1) and (2) was first proposed for the corresponding reactions of (I) with an excess of teriary germanes, R_3GeH, in which only the final dihydrido species $IrH_2(GeR_3)CO(PPh_3)_2$ was detected[5], although it has recently been suggested that triphenylgermane gives the five-coordinate complex $Ir(H)Cl(GePh_3)CO(PPh_3)$[6]. The configuration of the dihydrido complexes has been established by infrared and NMR spectroscopy[3,5] and in one case by X-ray crystallography[5] as (IV, M=Si, Ge). This stereochemistry is unusual in that the phosphine ligands are mutually *cis* in contrast to the *trans* arrangement in (I) and its adducts.

$$\underset{\text{(I)}}{IrCl(CO)(PPh_3)_2} + R_3SiH \rightarrow \underset{\text{(II)}}{Ir(H)Cl(SiR_3)CO(PPh_3)_2} \qquad (1)$$

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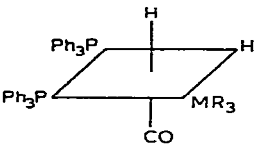
* For Part X see ref. 1.

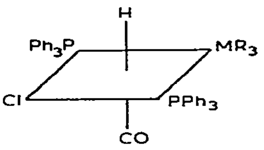
$$\text{(II)} + R_3SiH \rightarrow \underset{\text{(III)}}{IrH_2(SiR_3)CO(PPh_3)_2} \qquad (2)$$



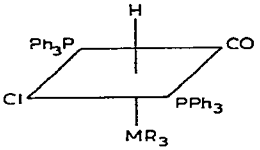
(IV)

The configuration of the intermediate (II) is not known, but two isomers of $Ir(H)Cl(SnR_3)CO(PPh_3)_2$ are formed in the reaction of (I) with tertiary stannanes[7]. With the assumption that the phosphine ligands were mutually *trans* these isomers were assigned configurations (V, M=Sn) and (VI, M=Sn) on the basis of their infrared spectra[7].

The high-field NMR signal found[2] for a solution presumed to contain the complex $IrCl(H)[Si(OEt)_3]CO(PPh_3)_2$ is consistent with either configuration (V) or (VI) $[MR_3=Si(OEt)_3]$. NMR spectra of other derivatives of this type could not be obtained because of their insolubility and ease of dissociation.



(V)



(VI)

We have therefore prepared a series of complexes of type (II) and examined their IR spectra in order to establish the stereochemistry. The results allow the *trans*-influence of different silyl groups to be assessed.

RESULTS

The complexes were obtained by reaction of the complex (I) with an excess of the tertiary silane in the absence of solvent. Trifluorosilyl derivatives were obtained from n-hexane suspension. In the case of the triethoxysilyl derivative, an identical product is formed by the action of carbon monoxide on the complex $IrCl(H)[Si(OEt)_3](PPh_3)_2$[4]. The IR data are presented in Table 1. Bands were observed which are characteristic of the stretching of Ir–H (ca. 2100 cm^{-1}), C–O (ca. 2000 cm^{-1}), and Ir–Cl (ca. 260 cm^{-1}) bonds; the Ir–H deformation modes and bands due to the silyl and phosphine groups were also evident. These assignments were confirmed by the preparation of deuterio and bromo analogues. In the low-frequency region bands were found at about 330 cm^{-1}, which are not reported for the germyl and stannyl derivatives, and which may be assigned as Ir–Si stretching modes. Similar bands have been assigned to ν(Pt–Si) in platinum-silyl complexes[8,9]. The major C–O stretching band is often accompanied by a weak shoulder 5–10 cm^{-1} lower in frequency, and shoulders are occasionally observed on the Ir–H stretching bands. The additional

TABLE 1

INFRARED DATA FOR IRIDIUM SILYL COMPLEXES $Ir(Cl, Br)(H, D)(SiR_3)CO(PPh_3)_2$
Nujol or hexachlorobutadiene mulls, cm^{-1}, ±3.

H/D	*Cl/Br*	SiR_3	$\nu[Ir{-}H(D)]$	$\nu(CO)$	$\nu(SiR_3)$	$\delta[Ir{-}H(D)]$	$\nu(Ir{-}Si)$	$\nu(Ir{-}Cl)$
H	Cl	$SiMe_2Cl$	2110 m	2002 s 1995 sh	796 ms	827 m	332 m	228 mw
H	Br	$SiMe_2Cl$	2110 m	2001 s 1995 sh	793 ms	820 m	327 m	
H	Cl	$Si(OEt)_3$	2077 s 2085 sh	1972 s 1965 sh	1087 s	823 m 789 mw	not obs.	253 m
D	Cl	$Si(OEt)_3$	[a]	2000 s 1985 sh	1085 s	637 m 618 mw	not obs.	253 m
H	Br	$Si(OEt)_3$	2077 s	1970 s	1085 s	821 ms 780 w	not obs.	
H	Cl	$SiMeCl_2$	2118 sh 2100 s	1989 s 1981 sh	791 ms	840 mw 785 sh	331 w	260 m
H	Br	$SiMeCl_2$	2119 sh 2103 s	1989 s 1983 sh	787 ms	840 mw 791 sh	332 w	
H	Cl	$SiCl_3$	2105 s 2100 sh	1998 s 1988 sh	547 m	842 mw 789 w	330 w	269 m
H	Br	$SiCl_3$	2092 ms	1986 s	546 m	850 mw 788 w	330 w	
H	Cl	SiF_3	2103 sh 2085 s	1990 sh 1975 s	866 s 813 s	849 w 798 ms	335 sh 330 m	270 m
D	Cl	SiF_3	[a]	2003 s 1997 sh	867 s 814 s	623 m 635 m	337 sh 332 m	272 m
H	Br	SiF_3	2107 s	2002 s 1996 sh	871 s 818 s	846 mw 777 mw	333 m	

[a] Assumed $\nu(Ir{-}D)$ = ca. 1480 cm^{-1}, obscured by band due to Ph_3P.

bands could indicate the presence of more than one isomer. However, the frequency differences are small and no splitting is observed for the Ir–Cl and Ir–Si modes; it seems likely that the additional bands arise from "solid-state splitting".

Deuterio complexes were obtained from mixtures of R_3SiD and R_3SiH. The IR spectra of the products showed additional bands due to Ir–D deformation modes but no band corresponding to $\nu(Ir{-}D)$; this is presumably obscured by a band due to the phosphine at ca. 1480 cm^{-1}. An extra C–O stretching band was also observed ca. 30 cm^{-1} higher than in the corresponding hydrido complexes, which suggests that the Ir–H and C–O modes are coupled[7,10]. Both the main band and its shoulder are shifted, which is further evidence against the presence of isomers. The Ir–H and C–O stretching frequencies are unaffected by changing the halide ligand from chloride to bromide. The Ir–Si stretching frequencies cover a very narrow range (327–335 cm^{-1}), but the Ir–Cl stretching frequency is very dependent on the nature of the silyl group. The correctness of these two assingments is confirmed by the absence of the lower-frequency band from the spectra of the bromo complexes.

DISCUSSION

The deuteriation experiments demonstrate that the hydride and carbonyl

TABLE 2

APPROXIMATE RANGES FOR METAL–CHLORINE STRETCHING FREQUENCIES IN SIX-COORDINATE IRIDIUM(III) AND FOUR-COORDINATE PLATINUM(II) COMPLEXES

trans-Ligand	*ν(Ir–Cl) (cm^{-1})*	*ν(Pt–Cl) (cm^{-1})*
Halogen	315–330	325–340
CO	300–315	
R_3P, R_3As	260–290	275–300
Alkyl	255–275	245–280
H	245–265	270–280
Acyl	215–245	

ligands are mutually *trans*, and the sensitivity of the Ir–Cl stretching frequency to change in the silyl group suggests that these two ligands are also mutually *trans*.

The complexes therefore have configuration (V, M = Si) resulting from *cis* addition of the silane to (I). The same stereochemistry is found for the addition of other molecules to solid (I)[11].

The Ir–Si stretching frequencies cover a surprisingly narrow range. In five-coordinate iridium and rhodium silyl complexes the metal–silicon bond appears to grow weaker as chlorine is replaced by methyl in the silyl group, from Cl_3Si to Me_3Si[12,13], and a decrease in M–Si stretching frequency would be expected. This decrease would be offset by the decreasing mass of the silyl group. The Ir–Si band is too weak to be observed in the triethoxysilyl derivatives, an effect which is also found in other metal–silyl systems[4,14].

The variation in the Ir–Cl stretching frequency allows estimation of the *trans*-influence of the various silyl groups. The order of increasing *trans*-influence is $SiF_3 \approx SiCl_3 < SiCl_2Me < Si(OEt)_3 \ll SiClMe_2$. Reference to Table 2 shows that the Cl_3Si and F_3Si groups are comparable in *trans*-influence to tertiary phosphines and arsines, the $MeCl_2Si$ and $(EtO)_3Si$ groups to alkyl or hydride ligands; the Me_2ClSi group has a very high *trans* influence, being comparable to some acyl ligands. The trend to increasing *trans*-influence with decreasing electronegativity of the substituent is also seen in platinum(II) complexes where, for the complexes *trans*-$PtCl(SiR_3)(PEt_3)_2$, the Pt–Cl stretching frequency decreases in the order $SiR_3 = SiCl_3 > SiHCl_2 > SiH_2Cl > SiH_3 \gg SiMePh_2 \approx SiMe_3$ (see Table 3). In the complex $PtCl(SiMePh_2)(PMe_2Ph)_2$, the low Pt–Cl stretching frequency[15] is associated with a very long bond[16]. These trends are clearly related to the strong inductive effect of the silyl group which increases as the substituents become less electronegative and accords with the discussion given by Mason and Towl[16,17]. As the electronegativity of the substituents decreases the hybrid orbital used by the silicon atom will have more *p*-character and thus will be higher in energy and closer in energy to the metal *p*-orbital through which the *trans*-influence is transmitted.

Comparison with data for germyl and stannyl complexes (Table 3) shows similar trends in *trans*-influence: $GeClH_2 \ll GeMe_3$, $SnCl_3 \ll SnMe_3$. For corresponding complexes the order is $R_3Sn \ll R_3Ge \lesssim R_3Si$[18]; the $SnCl_3$ group has one of the lowest *trans*-influences known[19] while the $SiMe_3$, $GeMe_3$ and $SiMePh_2$ groups have the highest. Although the trends within any one series follow the expected order of

TABLE 3

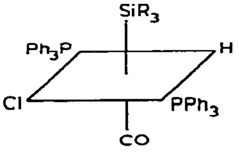
METAL–CHLORINE AND METAL–SILICON STRETCHING FREQUENCIES OF IRIDIUM AND PLATINUM SILYL, GERMYL, STANNYL AND PLUMBYL COMPLEXES

Complex	$\nu(M\text{–}Cl)$ (cm^{-1})	$\nu(M\text{–}Si)$ (cm^{-1})	*Phase*	*Ref.*
$IrCl(H)(SnMe_3)CO(PPh_3)_2{}^a$	290		Nujol	7
$IrCl(H)(SnEt_3)CO(PPh_3)_2{}^a$	280		Nujol	7
$IrCl_2(CCl_3)CO(PMe_2Ph)_2$	272^b, 320^c		Nujol	23
cis-$PtCl_2(SnCl_3)_2(NMe_4)_2$	352, 337		Nujol	19
trans-$PtCl(SnCl_3)(PPh_3)_2$	339		Nujol	19
trans-$PtCl(SnMe_3)(PPh_3)_2$	296		Nujol	24
trans-$PtCl(PbPh_3)(PEt_3)_2$	285		Nujol	25
trans-$PtCl(GeH_2Cl)(PEt_3)_2$	282		Benzene	9
trans-$PtCl(SnMe_3)(PEt_3)_2$	278			18
trans-$PtCl(SiCl_3)(PEt_3)_2$	275	330	Benzene	9
trans-$PtCl(SiHCl_2)(PEt_3)_2$	270	330	Benzene	9
trans-$PtCl(SiH_2Cl)(PEt_3)_2$	265	330	Benzene	9
trans-$PtCl(SiH_3)(PEt_3)_2$	260	330	Benzene	9
trans-$PtCl(GeH_3)(PEt_3)_2$	260		Benzene	9
trans-$PtCl(GeMePh_2)(PMe_2Ph)_2$	248		Polythene	15
trans-$PtCl(SiMePh_2)(PMePh_2)_2$	242		Nujol	15
trans-$PtCl(SiMe_3)(PEt_3)_2$	238	353^d	Nujol	8
trans-$PtCl(GeMe_3)(PEt_3)_2$	235		Nujol	8

[a] Configuration (V). [b] *Trans* to CCl_3. [c] *Trans* to CO. [d] Another, unassigned band is at 332 cm^{-1}.

electron release, the difference between the silyl, germyl and stannyl groups is unexpected, since a high *trans*-influence is normally associated with ligands which form strong covalent bonds with the metal atom. The relative stabilities of several complexes suggest that stannyl groups are more strongly bound than germyl or silyl groups[9]. It is also noticeable that within the silyl series the *trans*-influence increases while the stability to dissociation of adducts such as $Rh(H)Cl(SiR_3)(PPh_3)_2$ decreases[13]. Mason's treatment suggests that the *trans*-influence is transmitted through a metal p_σ-orbital[17]; the differences between the various groups may therefore lie in the composition of the σ-bonding molecular orbital of the metal–metal bond. The variation in *trans*-influence with change in substituent rules out any major contribution from π bonding effects.

If the complexes $Ir(H)Cl(SiR_3)CO(PPh_3)_2$ obtained here by reaction of silanes with solid (I) have the same configuration as the adducts obtained by reaction in solution, an isomerisation to configuration (VI, M = Si) or (VII) would be needed to allow *cis*-elimination of $ClSiR_3$ and formation of the dihydrido complexes (II). Such an isomerisation could be assisted by labilisation of the chloride (V, M = Si) by the strong *trans*-influence of the silyl group.



(VII)

EXPERIMENTAL

Infrared spectra were recorded on Perkin–Elmer 621 and 257 spectrometers. Tertiary silanes were prepared by standard methods[20]. Triethoxysilane was distilled under dry nitrogen. Chlorosilanes were redistilled several times *in vacuo* but it proved impossible to remove all traces of hydrogen chloride; the IR spectra of the chlorosilyl complexes always showed bands due to traces of the hydrogen chloride adducts $IrXCl(H)CO(PPh_3)_2$ (X=Cl, Br)[11]. Deuteriosilanes were obtained as mixtures with the parent silane by equilibrating the silane and deuterium over $CoH(N_2)(PPh_3)_3$[14]. Iridium(I) complexes were obtained and purified by literature methods[21,22].

The complexes were prepared by reaction of the silane with (I) at room temperature. n-Hexane was used as reaction medium for the trifluorosilyl complexes. Manipulations at atmospheric pressure were carried out under nitrogen. The details given below are typical of the methods used for all the complexes.

Hydridochloro(trichlorosilyl)carbonylbis(triphenylphosphine)iridium(III)

Finely divided *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.1 g, 0.13 mmole) was dried at ca. 60° *in vacuo* for 15 min, trichlorosilane (ca. 1 ml, 10 mmole) was distilled on to it and the mixture sealed under vacuum and shaken for 18 h. The suspended yellow solid slowly changed from yellow to white. The excess silane was removed under reduced pressure and the white product washed with n-hexane.

The chlorosilyl and trifluorosilyl complexes prepared in this way are insoluble in organic solvents and dissociate when heated with a solvent. The triethoxysilyl complexes dissociate instantly on contact with benzene or dichloromethane at room temperature, giving the silane and (I).

Analytical data are given in Table 4.

TABLE 4

ANALYTICAL DATA FOR IRIDIUM–SILYL COMPLEXES $IrX(H)(SiR_3)CO(PPh_3)_2$

X	*SiR₃*	*Found (%)*			*Calcd. (%)*		
		C	*H*	*Other*	*C*	*H*	*Other*
Cl	SiF_3	51.2	3.6	6.3 (F)	51.3	3.6	6.6 (F)
Br	SiF_3	49.1	3.4	5.8 (F)	48.8	3.4	6.3 (F)
Cl	$SiCl_3$	48.7	3.4		48.5	3.4	
Br	$SiCl_3$	46.5	3.4		46.3	3.2	
Cl	$SiMeCl_2$	51.3	3.9	11.5 (Cl)	51.0	3.8	11.9 (Cl)
Br	$SiMeCl_2$	49.0	3.7		48.6	3.6	
Cl	$SiMe_2Cl$	53.8	4.2	8.3 (Cl)	53.6	4.2	8.1 (Cl)
Br	$SiMe_2Cl$	51.3	4.0		51.0	4.0	
Cl	$Si(OEt)_3$	54.7	5.1		54.7	4.9	
Br	$Si(OEt)_3$	52.2	4.9		52.2	4.6	

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