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XXX *. HOMOGENEOUS CATALYSIS BY IRIDIUM(I) COMPLEXES OF THE REACTION BETWEEN SILANES AND ALCOHOLS OR DIDEUTERIUM

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Summary

The complexes $IrX(CO)L_2$, $IrCl(N_2)(PPh_3)_2$, $[IrCl(C_8H_{14})_2]_2$, and $IrClL_2$ (X = halide, L = tertiary phosphine or arsine) are excellent catalysts for the reactions of $HSiR_3$ (R = Ph, Et, OEt) with R'OH (R' = Et, Me). With $IrX(CO)L_2$ the reaction is inhibited by an excess of $HSiR_3$ and by the product, H_2. The proposed mechanism involves intermediate formation of $ClSiR_3$ by elimination from the silyl complex $IrHX(SiR_3)(CO)L_2$. The iridium(I) complex $IrH(CO)L_2$, also formed in this step, reacts with HCl in the catalytic cycle or with H_2 or $HSiR_3$ in the inhibition reactions. The exchange reaction of $HSiR_3$ (R = OEt, Et) with D_2 is catalysed by $IrCl(CO)(PPh_3)_2$ or $IrH_3(CO)(PPh_3)_2$, and probably has a similar mechanism. Catalysis of the $HSiR_3$-R'OH reaction by the other iridium(I) complexes probably involves direct attack by the alcohol on the coordinated silyl group of the intermediate $IrHCl(SiR_3)L_2$.

Introduction

Homogeneous catalysis by transition-metal complexes of the O-silylation reaction (eq. 1) has been little studied, despite the utility of the reaction.

$$R_3SiH + HOR' \rightarrow R_3Si(OR') + H_2 \qquad (1)$$

Brief reports have appeared of the use of $Co_2(CO)_8$ [2], $RhCl(PPh_3)_3$ [3], $RuCl_2(PPh_3)_3$ [3], $CoH_3(PPh_3)_3$ or $CoH(N_2)(PPh_3)_3$ [4], and $FeH_2(PMePh_2)_4$ and $FeH_2(N_2)(PEtPh_2)_3$ [5]. We wish now to report the activity of some iridium(I) complexes.

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* Part XXIX is Ref. [1].

Results and discussion

Catalysis by IrX(CO)L$_2$

The addition of a benzene solution of Vaska's complex, $IrCl(CO)(PPh_3)_2$, to a mixture of $HSi(OEt)_3$ and EtOH gave immediate evolution of hydrogen and the formation of $Si(OEt)_4$ in high yield. The activity of a range of related complexes was estimated qualitatively with the results shown in Table 1. Attempts were made to establish the kinetics of the reaction using Vaska's complex by monitoring the evolution of hydrogen, but the reaction does not go to completion in closed systems. In constant-volume apparatus, initially evacuated, gas evolution stopped after 60—70% reaction, and a white solid separated from the reaction mixture. At constant pressure, initially under nitrogen, complete reaction could be achieved by use of relatively high concentrations of catalyst [10^{-2} mol per mol of $HSi(OEt)_3$], but with lower amounts the reaction tailed off rapidly and stopped at 20—50% (cf. Table 2). A reaction which had stopped could be restarted by the addition of a further quantity of catalyst. These results suggest inhibition by hydrogen or by the silane, or both. Under these conditions, meaningful kinetic data could not be obtained, but results suggested that the initial rate increased with increase in the concentration of the silane or of the catalyst and was almost independent of that of the alcohol. Similar results were obtained with $IrCl(CO)(AsPh_3)_2$ as catalyst.

The white precipitate obtained in the constant-volume experiments was identified by its IR spectrum as $IrH_2Cl(CO)(PPh_3)_2$ together with some $IrHCl_2(CO)(PPh_3)_2$ and *fac*-$IrH_3(CO)(PPh_3)_2$ (Table 3). With $IrCl(CO)(AsPh_3)_2$ as catalyst, approximately half of the iridium was recovered as $IrHCl_2(CO)(AsPh_3)_2$; the remainder was a very soluble species which contained no chlorine. The redistribution of chlorine in this manner suggests cleavage of the Ir—Cl bond at some stage in the reaction.

The data are best accommodated by the series of reactions 2—6. Reaction 2 is well known [1,6—8] and the products are labile to isomerisation in solution [1], allowing reductive elimination of $ClSiR_3$ (eq. 3). This latter reac-

TABLE 1

ACTIVITY OF $IrX(CO)L_2$ AS O-SILYLATION CATALYSTS

L	X	EtOH		MeOH	
		$HSiEt_3$	$HSi(OEt)_3$	$HSiEt_3$	$HSi(OEt)_3$
PPh_3	Cl	moderate	vigorous		vigorous
	Br		vigorous		vigorous
	I	slow	vigorous	slow	vigorous
	F		vigorous	moderate	vigorous
	N_3		moderate	slow	vigorous
	SCN		vigorous		vigorous
$PMePh_2$	Cl	vigorous	moderate	vigorous	vigorous
	Br	slow	vigorous	moderate	vigorous
$AsPh_3$	Cl [a]	vigorous	vigorous	vigorous	vigorous
	Br	vigorous	slow	vigorous	vigorous

[a] Vigourous for $HSiEt_3$ and ROH (R = n-Pr, i-Pr, n-Bu, n-Hex); $HSi(OEt)_3$ and ROH (R = n-Hex, n-Hept, n-Oct). Moderate for $HSiEt_3$ and ROH (R = n-Bu, t-Bu, n-Hept, n-Oct).

TABLE 2

CATALYSIS BY $IrCl(CO)(PPh_3)_2$ OF THE $HSi(OEt)_3$/EtOH REACTION

Conc. of catalyst ($mol\ dm^{-3}$)	Initial rate ($cm^3\ H_2\ min^{-1}$)	Final % Reaction
0.05	v. slow	7
0.5	0.87	26
1.12	0.96	29
2.5	1.3	70
5.0	1.8	100
7.5	2.0	91
1.12	0.97	59 [a]
1.12 [b]	1.2	10
1.12 [c]	0.75	70
1.12 [d]	v. slow	4
1.12 [e]	0	0
1.12 [f]	0	0
1.12 [g]	3.5	
1.12 [h]	0.5	

Initial concentrations, unless otherwise specified, $[HSi(OEt)_3] = [EtOH] = 0.5\ mol\ dm^{-3}$. [a] After addition of an extra aliquot of catalyst. [b] [EtOH] 1.0 mol dm^{-3}. [c] [EtOH] 0.25 mol dm^{-3}. [d] 0.5 mol dm^{-3} of PPh_3 also present. [e] catalyst was $IrH(CO)(PPh_3)_3$. [f] Catalyst was $IrH_2[Si(OEt)_3](CO)(PPh_3)_2$. [g] Alcohol was MeOH. [h] Alcohol was t-BuOH.

tion has been shown to occur in the formation of $IrH_2(MR_3)(CO)L_2$ from $IrCl(CO)L_2$ and HMR_3 (M = Si, Ge) [8—10]. The complex $IrH_3(CO)(PPh_3)_2$ is known to be in equilibrium with $IrH(CO)(PPh_3)_2$ in solution (eq. 7) [11]. and

$$IrCl(CO)L_2 + HSiR_3 \rightarrow IrHCl(SiR_3)(CO)L_2 \quad (2)$$

$$IrHCl(SiR_3)(CO)L_2 \rightarrow IrH(CO)L_2 + ClSiR_3 \quad (3)$$

$$ClSiR_3 + HOR' \rightarrow Si(OR')R_3 + HCl \quad (4)$$

$$IrH(CO)L_2 + HCl \rightarrow IrH_2Cl(CO)L_2 \quad (5)$$

$$IrH_2Cl(CO)L_2 \rightleftharpoons IrCl(CO)L_2 + H_2 \quad (6)$$

we have found it to react readily with HCl to give $IrH_2Cl(CO)(PPh_3)_2$ initially (eq. 8), and then $IrCl(CO)(PPh_3)_2$ and $IrHCl_2(CO)(PPh_3)_2$ [12]. Finally, reaction 6 is well known to be a labile equilibrium [13].

The observed inhibition of the reaction at high ratios of silane : catalyst is due to the suppression of reaction 6 by the build-up of H_2 and to the removal of

TABLE 3

IR DATA FOR RECOVERED CATALYST AND RELATED MATERIALS (cm^{-1}, Nujol)

	ν(Si—H)	ν(CO)	ν(Ir—Cl)
Catalyst	2238w 2190m 2100m 2065m	2020m 1975s	310w 265m
$IrH_2Cl(CO)(PPh_3)_2$	2190m 2100m	1975s	270ms
$IrHCl_2(CO)(PPh_3)_2$	2237m	2020s	313m 265m
fac-$IrH_3(CO)(PPh_3)_2$	2112m 2060s	1950s	

$IrH(CO)(PPh_3)_2$ by reaction with H_2, HCl, or $HSiR_3$ (eqs. 5, 7, 9);

$$IrH(CO)L_2 + H_2 \rightleftharpoons IrH_3(CO)L_2 \quad (7)$$

$$IrH_3(CO)L_2 + HCl \rightarrow IrH_2Cl(CO)L_2 + H_2 \quad (8)$$

$$IrH(CO)L_2 + HSiR_3 \rightarrow IrH_2(SiR_3)(CO)L_2 \quad (9)$$

the complex $IrH_2(SiR_3)(CO)(PPh_3)_2$ showed no catalytic activity, demonstrating the importance of the Ir—Cl bond in the reaction. The reaction was also inhibited by the addition of PPh_3 which resulted in the precipitation of $IrHCl_2(CO)(PPh_3)_2$, suggesting that $IrH(CO)(PPh_3)_2$ was removed as the stable $IrH(CO)(PPh_3)_3$ and the HCl produced in reaction 4 then combined with $IrCl(CO)(PPh_3)_2$. Separate experiments showed that $IrH(CO)(PPh_3)_3$ was not a catalyst. In the qualitative tests reported in Table 1, it is noticeable that chloro-complexes are the best catalysts, with corresponding bromo- or iodo-complexes showing less activity; this trend is also consistent with cleavage of the iridium—halogen bond during the reaction.

Qualitative estimates were also made of the reactivity of other alcohols with $HSi(OEt)_3$, using $IrCl(CO)(PPh_3)_2$ as catalyst. The relative rates were MeOH (3.5) > EtOH (1.0) > t-BuOH (0.5); $HOSiPh_3$ reacted extremely slowly. Similar trends were found with other catalysts.

The polysilane $Me_3SiO[SiH(Me)O]_nSiMe_3$ ($n \sim 50$) reacted extremely rapidly and exothermically with EtOH with all the catalysts mentioned in Table 1 at concentrations equivalent to or lower than those used with $HSi(OEt)_3$, giving ca. 95% yield in about 20 seconds. The HCl-adducts of the catalysts were again formed. It is unlikely that this high reactivity is an electronic effect, since $HSiEt_3$ reacts more slowly than $HSi(OEt)_3$ and an $HSiMe(O\text{-})_2$ unit would be expected to have intermediate reactivity. It is possible that steric interactions with the polymer enhance the dissociation step (analogous to eq. 3) or that the close proximity of the Si—H bonds increases the probability of their reaction.

Catalysis by $[IrCl(C_8H_{14})_2]_2$

The complex $[IrCl(C_8H_{14})_2]_2$ has been observed to interact with $HSi(OEt)_3$ [1]. It is also an effective catalyst for the reaction of silanes with alcohols. With $SiH(OEt)_3$, reaction was rather faster, under comparable conditions, than with $IrCl(CO)(PPh_3)_2$ as catalyst, and went to ca. 80%. Reaction with $HSiEt_3$ was approximately ten times faster again, was considerably exothermic, and went effectively to completion. With $HSiPh_3$, an induction period (20—30 seconds) was followed by very rapid reaction. An extremely violent reaction was obtained with the polysilane. In each case the yellow reaction mixture became dark brown, and attempts to recover the catalyst gave only air-sensitive oils and a fine brown precipitate which may have been iridium metal.

Catalysis by $IrCl(N_2)(PPh_3)_2$ *and* $IrClL_2$

The complex $IrCl(N_2)(PPh_3)_2$ was an effective catalyst for reaction of EtOH with $HSiEt_3$, $HSiPh_3$, $HSi(OEt)_3$ or $Me_3SiO[SiH(Me)O]_nSiMe_3$. On addition of the silane to a solution of the catalyst, a yellow colour developed which persisted throughout the reaction, until the silane was consumed, and could be regenerated by the addition of more of the silane. This colour suggests the presence of the complex $IrHCl(SiR_3)(PPh_3)_2$ which is known to be formed by reaction of the dinitrogen complex with silanes [1], and this complex was itself an effective catalyst. Since similar complexes could be obtained from silanes and "$IrClL_2$" (prepared in situ by treating $[IrCl(C_8H_{14})_2]_2$ with four molar equivalents of the ligand) [1], this system was also examined and was found to be effective for a range of ligands [Pcy_3, Pcy_2Ph, $PcyPh_2$, PPh_3, $P(n\text{-}Bu)_3$, $P(C_6H_4Me\text{-}p)_3$, PMe_2Ph, $PMePh_2$, PEt_3, $AsPh_3$, $AsMe_2Ph$, $SbPh_3$; cy = cyclo-hexyl; arranged in order of decreasing activity for $HSi(OEt)_3$ and increasing activity for the polysilane]. The system $[IrCl(C_8H_{14})_2]_2/4\ PPh_3$ showed precisely similar behaviour to an equivalent amount of $IrCl(N_2)(PPh_3)_2$.

When reaction was complete, the iridium-containing species were isolated, spectroscopic data for which are presented in Table 4. When EtOH was present in excess, IrH_2ClL_2 was isolated. The addition of an extra molar equivalent of ligand (PPh_3) gave extremely slow reactions and the precipitation of $IrH_2Cl(PPh_3)_3$. When the silane was in excess, silyl complexes $IrHCl(SiR_3)L_2$ were isolated, corresponding to those reported previously [1], except that the PPh_3-derivative appeared to contain about 30% of a second isomer. In no case were complexes containing more than one chloride ligand observed.

Preliminary kinetic data (for the $HSi(OEt)_3/EtOH$ system) do not seem to be susceptible to simple interpretation. The rate of evolution of hydrogen was constant over at least 90% of the reaction, regardless of the initial ratios of reactants, and was also independent of the initial concentration of EtOH (Fig. 1). Increase

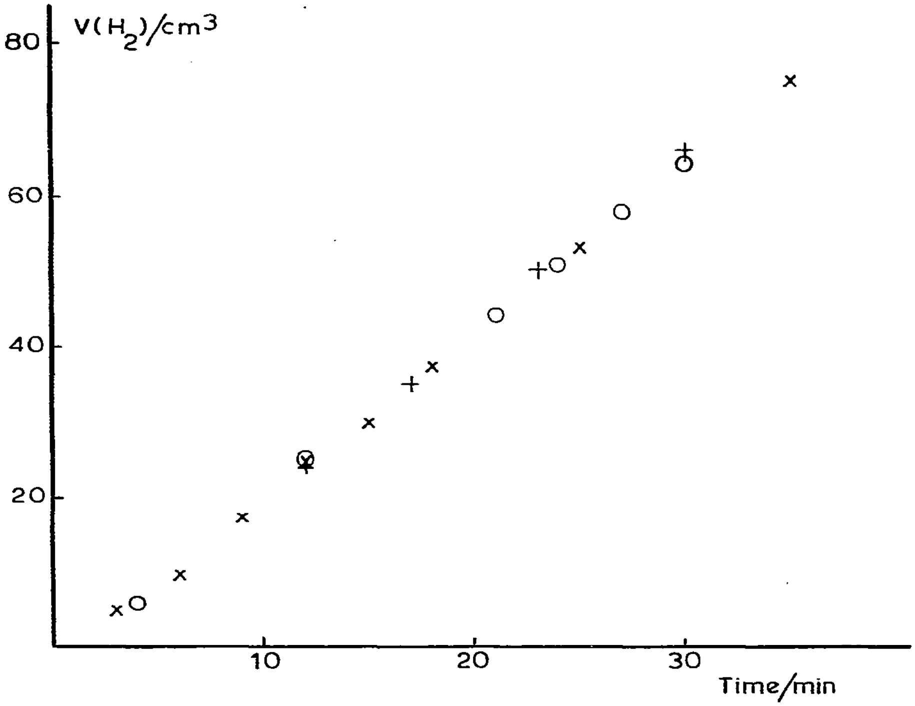

Fig. 1. Rate of evolution of H_2 in the $HSi(OEt)_3/EtOH$ reaction catalysed by $[IrCl(C_8H_{14})_2]_2/4\ PPh_3$. Concentrations are: catalyst, 0.0145 *M*; $HSi(OEt)_3$. 0.172 *M*; EtOH, × 0.344 *M*, ○ 0.860 *M*, + 1.72 *M*. Total volume of solution, 6.91 cm^3, solvent toluene. 100% reaction corresponds to 89.6 cm^3 H_2.

TABLE 4

IR, NMR AND ANALYTICAL DATA FOR IRIDIUM COMPLEXES ISOLATED AFTER CATALYSIS

	ν(Ir—H) (cm^{-1})	ν(Ir—Cl) (cm^{-1})	τ(Ir—H)	^2J(P—H) (Hz)	Analysis Found (Calcd.) (%)		
					C	H	Cl
$IrH_2Cl(PPh_3)_2$	2280	295	21.61	14	52.3(51.4)	4.3(4.2)	4.7(4.7)
$IrH_2Cl(PPh_3)_3$	1993	260	21.20 [a]	20	63.5(63.8)	4.8(4.6)	3.8(3.5)
	1979			130			
$IrH_2Cl(AsPh_3)_2$	2200	290	26.66		48.0(51.3)	4.1(3.8)	
	1980		31.31				
$IrH_2Cl(AsPh_3)_3$			complex		55.8(55.9)	4.3(4.1)	5.4(3.9)
$IrH_2Cl(SbPh_3)_2$	2140		32.65		45.6(46.2)	3.4(3.3)	4.0(3.8)
	1980						
$IrH_2Cl(SbPh_3)_3$	2130				48.3(49.9)	3.6(3.6)	2.6(2.7)
$IrH_2Cl(Ptol_3)_2$ [b]	2040	260	25.91	21	58.0(60.2)	4.5(5.3)	
	1958		26.80				
$IrHCl[Si(OEt)_3](PPh_3)_2$	2190	290	29.07	14	54.8(55.0)	5.0(5.0)	
	2180	278	28.57				
$IrHCl[Si(OEt)_3](AsPh_3)_2$	2170	285	30.52				

[a] Not scanned above τ30. [b] tol = p-C_6H_4Me.

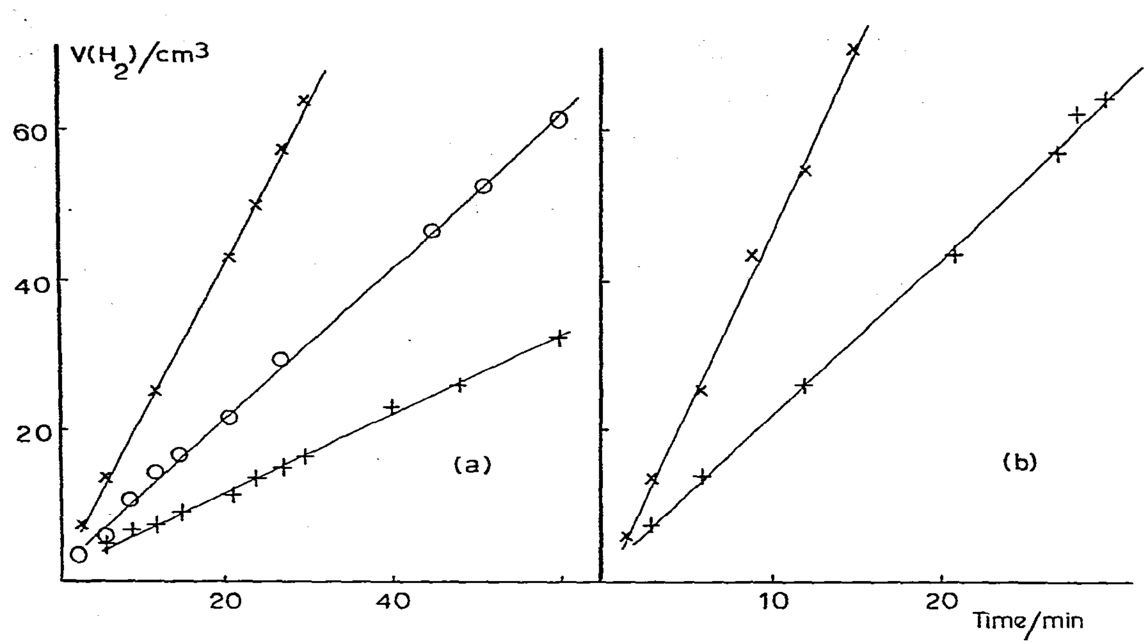

Fig. 2. Rate of evolution of H_2 in the $HSi(OEt)_3/EtOH$ reaction catalysed by $IrCl(N_2)(PPh_3)_2$. Concentrations are: (a) EtOH, 0.344 *M*; $HSi(OEt)_3$, 0.172 *M*; catalyst, X 0.0290 *M* ○ 0.0145 *M* + 0.00725 *M*. (b) EtOH, 0.344 *M*; catalyst, 0.0290 *M*; $HSi(OEt)_3$, X 0.344 *M* + 0.172 *M*. Note the difference in time scales. 100% reaction corresponds to 89.6 cm^3 H_2.

in the initial concentration of the silane or of the catalyst gave proportionate increases in rate (Fig. 2). Thus, the reaction appears to be zero order in ethanol, and first order in the silane and the catalyst but, during any one experiment, the constant rate suggests zero order in both ethanol and the silane. Further examination of this system is in hand.

The persistence of a yellow colouration during the reaction suggests that the iridium is present largely as $IrHCl[Si(OEt)_3]L_2$ which is presumably, therefore, involved in the rate-determining step. A chlorosilane-elimination mechanism analogous to that discussed above is possible but seems unlikely on two counts. Firstly, the elimination step (eq. 10) would be much less favoured than for the carbonyl complex (eq. 3), in that the product is formally a 14-electron complex (although it would presumably be solvated) and highly reactive. The carbonyl group stabilises the lower oxidation state and facilitates the reaction. Secondly, iridium is recovered at the end of the reaction either as IrH_2ClL_2 or as $IrHCl(SiR_3)L_2$, depending on which reagent was originally in excess. No evidence of chloride-redistribution was found, in contrast to catalysis by $IrCl(CO)L_2$.

$$IrHCl(SiR_3)L_2 \rightarrow IrHL_2 + ClSiR_3 \qquad (10)$$

An alternative mechanism would involve nucleophilic attack by the alcohol on the coordinated silyl group (eqs. 11—13), as we have previously suggested for catalysis by iron and cobalt complexes [4,5]. If reaction 12 is slow, as im-

$$IrHCl(SiR_3)L_2 + EtOR \rightleftharpoons IrHCl(SiR_3 \cdot EtOH)L_2 \qquad (11)$$

$$IrHCl(SiR_3 \cdot EtOH)L_2 \rightarrow IrH_2ClL_2 + SiR_3(OEt) \qquad (12)$$

$$IrH_2ClL_2 + HSiR_3 \rightarrow IrHCl(SiR_3)L_2 + H_2 \qquad (13)$$

plied by the colour of the reaction mixture, the rate is given by

$$d[H_2]/dt = d[SiR_3(OEt)]/dt = k_{12}[IrHCl(SiR_3 \cdot EtOH)L_2] = \frac{k_{12}K_{11}[Ir][EtOH]}{1 + K_{11}[EtOH]}$$

where [Ir] is the total concentration of iridium (the assumption is made that reaction 13 is sufficiently fast to keep $[IrH_2ClL_2]$ negligibly small). Provided $K_{11}[EtOH] >> 1$, this would give a constant rate of gas evolution during the reaction and first-order dependence on the catalyst. The same expression is derived from steady-state treatment if reaction 13 is rate-determining. However, these mechanisms are not compatible with the silane-dependence shown between different runs.

All the iridium catalysts are considerably more effective than the conventional tin—containing catalysts. For example, with $EtOH : HSi(OEt)_3 = 5 : 1$. 50 or 100% reaction is achieved in ca. 25 or 50 minutes (respectively) with 0.05 mol equivalents of $IrCl(N_2)(PPh_3)_2$ at 23°C, but requires 70 or 500 minutes with 0.1 mol of $Bu_2Sn(OAc)_2$ at 60°C [14].

When $HSiEt_3$ or $HSiPh_3$ were used, there was a small induction period (10—20 seconds) followed by extremely rapid rapid reaction [ca. 10 times faster than for $HSi(OEt)_3$]. In these cases it was necessary to allow long contact (several hours) between $IrCl(N_2)(PPh_3)_2$ and the silane before addition of the alcohol. Premature addition of ethanol gave a precipitate of $IrHCl(SiEt)_3(PPh_3)_2$, implying that this complex is not an active catalyst for O-silylation of $HSiEt_3$. Possibly conversion to other silyl complexes, such as $IrH_2(SiEt_3)(PPh_3)_2$, is required. These systems are under further investigation.

Catalysis of $D_2/HSiR_3$ exchange

Vaska's complex is known to catalyse exchange between ROH and D_2 (R = Me, Et, OAc) [15], and between $HSiR_3$ and $DSiR_3$ [16]. It was of interest to examine the utility of iridium complexes in $D_2/HSiR_3$ exchange as a route to deuteriosilanes. We have previously shown that $CoH(N_2)(PPh_3)_3$ is a useful catalyst [4].

A benzene solution of $HSi(OEt)_3$ and $IrCl(CO)(PPh_3)_2$ was sealed under D_2 for 36 hours. The solution rapidly became colourless and a white solid was slowly formed. The IR spectrum of the solid showed it to be $Ir(H, D)_2Cl(CO)(PPh_3)_2$ (see Experimental), while that of the recovered silane showed that statistical H/D exchange had occurred. The mass spectrum of the residual gas showed a large increase in the H-content. Similar results were obtained with $HSiEt_3$. The complexes $IrH_3(CO)(PPh_3)_2$ and $IrH_2[Si(OEt)_3](CO)(PPh_3)_2$ were also effective catalysts and in both cases the iridium was left in the form of $Ir(H, D)_2[Si(OEt)_3](CO)(PPh_3)_2$. However, $IrH(CO)(PPh_3)_3$ did not catalyse the exchange and the activity of $IrCl(CO)(PPh_3)_2$ was supressed by the addition of PPh_3.

These observations are consistent with a mechanism analogous to that proposed above for O-silylation catalysed by Vaska's complex. Chlorosilane-elimination (eq. 3) would generate the active intermediate $IrH(CO)(PPh_3)_2$ which undergoes reversible oxidative addition with D_2 and $HSiR_3$, leading to complete exchange (eqs. 14, 15). Reaction 15 has been demonstrated independently [12]. Exchange between $IrHD[Si(OEt)_3](CO)(PPh_3)_2$ and $HSi(OEt)_3$ and between $IrH_2(GeMe_3)(CO)(PPh_3)_2$ and $DSnMe_3$ have been reported [10,17], and a similar mechanism was proposed for the latter. The inhibition by PPh_3 is due to the trapping of $IrH(CO)(PPh_3)_2$ as the stable, catalytically inactive $IrH(CO)(PPh_3)_3$.

$$IrHCl(SiR_3)(CO)L_2 \rightarrow IrH(CO)L_2 + ClSiR_3 \qquad (3)$$

$$IrH(CO)L_2 + D_2 \rightleftharpoons IrHD_2(CO)L_2 \rightleftharpoons IrD(CO)L_2 + HD \qquad (14)$$

$$IrD(CO)L_2 + HSiR_3 \rightleftharpoons IrHD(SiR_3)(CO)L_2 \rightleftharpoons IrH(CO)L_2 + DSiR_3 \qquad (15)$$

Experimental

The complexes $IrX(CO)L_2$, $IrCl(N_2)(PPh_3)_2$, and $[IrCl(C_8H_{14})_2]_2$ were prepared by literature methods [18—22]. Analytical data were determined in the Microanalytical Laboratory of this Deparment.

O-Silylation Reactions

A typical reaction sequence was as follows. Ethanol (0.46 cm^3, 8.0 mmol) and the silane were mixed together and placed in a flask equipped with a tipping side-arm, and connected to a gas burette. The catalyst (0.05 mmol), dissolved in benzene, was placed in the side-arm and the apparatus flushed with nitrogen. The nitrogen flow was stopped and the apparatus allowed to stand for 10 minutes to allow equilibration of vapour. The catalyst solution was added to the reactants and the volume changes noted. The reaction was repeated with other ratios of reactants, the volume of the solvent being adjusted to keep the total volume always 20 cm^3. When the catalyst was $IrCl(N_2)(PPh_3)_2$ or $IrClL_2$, the complex was placed in the reaction vessel and the solvent (toluene, total volume 7 cm^3) and the silane were added by syringe through a serum cap. After equilibration, the alcohol was added. The products $Si(OEt)_4$ and $Si(OMe)(OEt)_3$ were identified by boiling points (obs. 155—166, 159°C; lit. [23] 166, 160°C respectively), and NMR spectra [$Si(OEt)_4$: τ6.15 q(2), 8.8 t(3), $^3J(H—H) = 7.0$ Hz. $Si(OMe)(OEt)_3$: τ6.05 q, 6.37 s (total integration, 1), 8.6 t(1)]. The product of reaction of $Me_3SiO[SiH(Me)O]_nSiMe_3$ with EtOH was identified by NMR: before reaction, τ5.08(5), 9.84(15), 9.94(3); after reaction, τ4.96(0.75), 6.10 q(7), 8.70 t(12), 9.72(14), 9.83(4). These figures indicate ca. 80% formation of $Me_3SiO[Si(OEt)(Me)O]_nSiMe_3$.

Exchange reactions

A benzene solution (5 cm^3) of Vaska's complex (0.078 g, 0.1 mmol) and $HSi(OEt)_3$ (1.1 g, 6.7 mmol), in a tube equipped with a 'Rotaflo' tap, was degassed and the tube filled to atmospheric pressure with D_2 (75 cm^3, 3.2 mmol). After 18 hours the solution was filtered and the IR spectra of the solid residue and of the solution were measured. Solid: ν(Ir—H) 2190, 2100; ν(C—O) 1975, 2000; ν(Ir—D) 1568; ν(Ir—Cl) 270 cm^{-1}; (H, D) $Si(OEt_3)$: ν(Si—H) 2097; ν(Si—D) 1520 cm^{-1}. The intensities indicated ca. 55% deuteriation of the silane when $IrCl(CO)(PPh_3)_2$ or $IrH_3(CO)(PPh_3)_2$ (0.08 mmol) was the catalyst, 20% with $IrH_2[Si(OEt)_3](CO)(PPh_3)_2$ (0.06 mmol), and 0% with $IrH(CO)(PPh_3)_3$.

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