Interaction of Acyl Chlorides and Triethylsilane Catalysed by *cis*-Dichlorobis(triphenylphosphine)platinum(II) and Related Complexes

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The acyl halides XC_6H_4COCl (X = H, *p*-Me, *o*-MeO, *p*-MeO, *p*-Cl, *p*-Br, and *p*-NO_2) are converted into the aldehydes XC_6H_4CHO in 50—84% yield on treatment with triethylsilane at 120 °C in the presence of a 1×10^{-3} molar proportion of *cis*-$[PtCl_2(PPh_3)_2]$. Cinnamoyl and n-pentanoyl chloride give the corresponding aldehydes in 65 and 20% yield, respectively. A more detailed study using *p*-methoxybenzoyl chloride has shown that triethyl-*p*-methoxybenzyloxysilane is also formed, by further reaction of the aldehyde with the triethylsilane. The conversion of this chloride into aldehyde is also catalysed by *cis*-$[PdCl_2(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$, and *trans*-$[IrCl(CO)(PPh_3)_2]$, and, except for catalysis by the iridium complex, the benzyloxysilane is also formed.

WE recently discussed the reactions between acyl halides, RCOCl, and triorganosilanes catalysed by rhodium complexes, which give the corresponding ketone, R_2CO, or aldehyde, RCHO, or both, depending upon the nature of R.[1] We now describe the reaction catalysed by *cis*-$[PtCl_2(PR_3)_2]$ complexes [2] and by some complexes of palladium, iridium, and ruthenium.

Catalysis by Platinum Complexes.—Reactions between the acyl halides, RCOCl, and triethylsilane catalysed by *cis*-$[PtCl_2(PPh_3)_2]$ were carried out at 120 °C (bath temp.), with the results shown in the Table. For Et_3SiH : RCOCl ratios of up to 1.5 : 1, the reactions were carried on until the ν(SiH) band had disappeared, but the effective reaction could have been over well before this point, and so only large differences in reaction times between closely similar systems can be regarded as significant. In contrast to the systems catalysed by rhodium complexes, in which no apparent decomposition of catalyst occurred until all the acyl halide had been removed,[1] some separation of metallic platinum occurred in the later stages of the reaction while acyl halide still remained.

The reactions between acyl halides, RCOCl, and triethylsilane at 120 °C (bath temperature) catalysed by *cis*-$[PtCl_2(PPh_3)_2]$ in 1.0×10^{-3} mol ratio

R	RCOCl : Et_3SiH	*t*/h	RCHO, Yield (%) [a]
o-$MeOC_6H_4$	1 : 1.25	2.0	68
p-$MeOC_6H_4$	1 : 1.25	4.0	45
p-$MeOC_6H_4$	1 : 1.5	5.0	65
p-$MeOC_6H_4$	1 : 2.0	5.0	60
C_6H_5	1 : 1.25	8.0	78
p-ClC_6H_4	1 : 2.0	4.5	71
p-BrC_6H_4	1 : 1.5	4.0	84
p-$NO_2C_6H_4$	1 : 1.5	1.0	78
p-MeC_6H_4	1 : 1.25	4.0	51
$C_6H_5CH{=}CH$	1 : 1.25	6.0	65
CH_3CH_2	1 : 1.25	20.0	<2
n-C_5H_{11}	1 : 1.25	3.0	20

[a] Yield of 2,4-dinitrophenylhydrazone before recrystallization.

Good yields of aldehyde can be obtained, the best being the 84% of *p*-bromobenzaldehyde produced after 4 h by use of a *m*-BrC_6H_4COCl : Et_3SiH ratio of 1 : 1.5. Cinnamoyl chloride gave cinnamaldehyde in 65% yield. Propionyl chloride did not react, probably because its low boiling point kept down the temperature of the refluxing mixture, but a low yield of aldehyde was obtained from n-pentanoyl chloride. In no case was the possible ketone formed.

A significant dependence of the catalytic activity on the nature of the phosphine ligands was revealed by variation of *x* progressively from 0 to 3 in the complexes *cis*-$[PtCl_2(PEt_xPh_{3-x})_2]$. With *p*-methoxybenzoyl chloride, triethylsilane, and *cis*-$[PtCl_2(PEt_xPh_{3-x})_2]$ in $1 : 1.25 : 1 \times 10^{-3}$ mole ratio at 120 °C, the times for disappearance of the ν(SiH) band were (*x* =) 0, 4 h; 1, 9 h; 2, 29 h; 3, 72 h.

In the reaction between the acyl chlorides and triethylsilane in 1 : 1.25 mole ratio the i.r. spectrum showed that unchanged chloride often remained after all the triethylsilane had disappeared, indicating that the hydride was being consumed in some side reaction. Fractional distillation of the product from such a reaction (2 h at 120 °C) involving *p*-methoxybenzoyl chloride in larger amounts than usual gave the expected aldehyde in 66% yield and triethyl-*p*-methoxybenzyloxysilane, *p*-$MeOC_6H_4CH_2OSiMe_3$, in 27% yield. This latter product is formed by hydrosilylation of the initially produced aldehyde. This type of reaction catalysed by rhodium and ruthenium complexes is now well established,[3-5] and while *cis*-$[PtCl_2(PPh_3)_2]$ is not an effective catalyst for the interaction of aldehydes and triethylsilane, because it is rapidly decomposed by the hydride, conversion of *p*-methoxybenzaldehyde into triethyl-*p*-methoxybenzyloxysilane did occur in the presence of benzoyl chloride, which kept the catalyst in solution.

The catalytic cycle shown in the Scheme is analogous to that suggested for the formation of aldehydes under catalysis by *trans*-$[RhCl(CO)(PEtPh_2)_2]$.[1] In keeping with proposed steps in the cycle, *trans*-$[Pt(H)Cl(PPh_3)_2]$ was shown to react with a large excess of *p*-methoxybenzoyl chloride during 5 h at 120 °C to give *cis*-$[PtCl_2(PPh_3)_2]$ in 79% yield; g.l.c. showed that a little *p*-methoxybenzaldehyde was produced, but rather more anisole, showing that decarbonylation, as observed with

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[1] B. Courtis, S. P. Dent, C. Eaborn, and A. Pidcock, *J.C.S. Dalton*, 1975, 2460.

[2] S. P. Dent, C. Eaborn, and A. Pidcock, *Chem. Comm.*, 1970, 1703.

[3] C. Eaborn, K. Odell, and A. Pidcock, *J. Organometallic Chem.*, 1973, **63**, 93.

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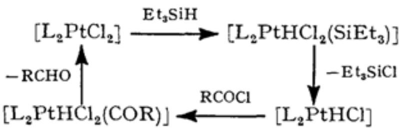
rhodium catalysts,[1] can occur under these conditions. The complex *trans*-[$PtCl(COC_6H_4OMe$-*p*)$(PPh_3)_2$] did not react with triethylsilane at room temperature, but decomposition was rapid at 120 °C.

The fall in the rate of reaction on passing from PPh_3 to PEt_3 as ligand phosphine is possibly associated with the increased stabilization (and thus reduced tendency to reductive elimination) of the Pt^{IV} species as the basicity of the phosphine is increased. The non-formation of ketones from acyl halides, which in some cases give such products predominantly in the rhodium-catalysed reactions, can be attributed to the reduced ease of the migration $RCOM \longrightarrow RM(CO)$ for M = Pt.

Catalysis by Complexes of other Group VIII Metals.—The palladium complex *cis*-[$PdCl_2(PEt_2Ph)_2$] was found to be more active than the corresponding platinum analogue, presumably because of the greater lability of the M^{IV} species. With a halide : silane : catalyst ratio of $1 : 1.25 : 2 \times 10^{-3}$, the ν(SiH) band disappeared in 3 h at 120 °C, compared with 29 h for the platinum analogue at half the concentration. The aldehyde was obtained in 86% yield, and some triethyl-*p*-methoxybenzyloxysilane was also formed. The complex decomposed to metal on treatment with triethylsilane alone, even at room temperature.

The ruthenium complex [$RuCl_2(PPh_3)_3$] had a comparable activity; with a chloride : silane : catalyst ratio of $1 : 1.25 : 2 \times 10^{-3}$, the ν(SiH) band disappeared in 5 h at 120 °C, and g.l.c. showed that the aldehyde was the predominant product, but that triethyl-*p*-methoxybenzyloxysilane and unchanged acyl chloride were also present. This complex catalysed the reduction of the aldehyde on its own to the benzyloxysilane, and, indeed, it was later shown to be a general catalyst for this type of reaction.[3] This catalyst is not decomposed to metal by triethylsilane alone, and, in keeping with the reactions in the Scheme, it was found to be converted into [$Ru(H)Cl(PPh_3)_3$] in good yield on treatment with triethyl- or triphenyl-silane in hot benzene.

Used with a chloride : silane : catalyst ratio of $1 : 1.25 : 2 \times 10^{-3}$, the iridium complex *trans*-[$IrCl(CO)(PPh_3)_2$] was rather less active, as judged by the time of 45 h at 120 °C needed for disappearance of the triethylsilane, but a good yield (69%) of the aldehyde was obtained. No significant amount of the benzyloxysilane was formed, and it is possible that the relatively long time needed for removal of all the silane, used in 25% excess, is deceptive in this case, and that the main reaction to give the aldehyde is complete in a substantially shorter time. In contrast to the results obtained with the rhodium analogue as catalyst, no ketone was formed, which is in keeping with the known lower tendency of iridium complexes to undergo decarbonylation.



SCHEME

Catalytic cycles analogous to that in the Scheme can be written in all cases. Since several types of complex show catalytic activity in this reaction, but with some variations in behaviour, it seems likely that a more thorough search would reveal rather more active catalysts, which would possibly give higher yields of aldehyde and also be effective at lower temperatures. However, the complexes [$CoCl_2(PPh_3)_2$], [$NiCl_2(PPh_3)_2$], [$NiCl_2(Me_2PCH_2CH_2PMe_2)$], and [$NiBr_2(Ph_2PCH_2CH_2PPh_2)$] showed no catalytic activity in the *p*-methoxybenzoyl chloride–triethylsilane reaction.

EXPERIMENTAL

All reactions were carried out under dry nitrogen. The temperature of 120 °C in all cases refers to the temperature of the bath, the mixtures being heated under a reflux condenser.

Interactions of Acyl Halides and Triethylsilane Catalysed by cis-[$PtCl_2(PPh_3)_2$].—In a typical case, *p*-bromobenzoyl chloride (2.195 g, 0.010 mol) and triethylsilane (1.45 g, 0.0125 mol) were added successively to *cis*-[$PtCl_2(PPh_3)_2$] (7.9 mg, 0.010 mmol). The mixture was heated under nitrogen beneath a reflux condenser in a bath at 120 °C, and the white platinum complex dissolved slowly during 0.5 h to give a pale yellow solution. After 3 h the i.r. spectrum no longer showed a ν(SiH) band at 2 095 cm^{-1} and the mixture was allowed to cool. It was then washed with methanol into excess of 0.01M-methanolic 2,4-dinitrophenylhydrazine (containing a little sulphuric acid). The precipitate was filtered off, washed with methanol, and dried under vacuum to give crystals (2.60 g, 71%) which were recrystallized from glacial acetic acid and shown to be *p*-bromobenzaldehyde 2,4-dinitrophenylhydrazone (2.28 g, 62%), m.p. 261–262 °C.

Similar procedures gave the results shown in the Table. Under similar conditions, but with the complexes *cis*-[$PtCl_2(PEt_xPh_{3-x})_2$], the disappearance of the ν(SiH) band required 4, 9, 29, and 72 h, respectively, for $x = 0$, 1, 2, and 3.

A larger scale reaction was carried out with *p*-methoxybenzoyl chloride (17.05 g, 0.10 mol), triethylsilane (17.4 g, 0.150 mol), and *cis*-[$PtCl_2(PPh_3)_2$] (0.079 g, 0.10 mmol). The ν(SiH) band had disappeared after 5 h, and fractionation gave *p*-methoxybenzaldehyde (9.1 g, 66%), b.p. 74—76 °C at 0.8 mmHg (authentic 2,4-dinitrophenylhydrazone) and triethyl-*p*-methoxybenzyloxysilane (7.1 g, 27%), b.p. 107—109 °C at 0.8 mmHg (Found: C, 66.9; H, 9.4. Calc. for $C_{14}H_{24}O_2Si$; C, 66.6, H, 9.6%).

Interaction of p-*Methoxybenzoyl Chloride and Triethylsilane catalysed by Complexes of Other Metals.*—(i) *p*-Methoxybenzoyl chloride (1.70 g, 0.010 mol) then triethylsilane (1.45 g, 0.0125 mol) were added to *cis*-[$PdCl_2(PEt_2Ph)_2$] (10 mg, 0.020 mmol). The mixture was kept in a bath at 120 °C for 3 h and then allowed to cool. G.l.c. analysis showed the presence of triethyl-*p*-methoxybenzyloxysilane. Treatment with methanolic 2,4-dinitrophenylhydrazine gave a precipitate, which was recrystallized from glacial acetic acid and shown to be *p*-methoxybenzaldehyde 2,4-dinitrophenylhydrazone (1.78 g, 56%), m.p. 253—254 °C.

(ii) In a similar procedure involving *trans*-[$IrCl(CO)(PPh_3)_2$] the ν(SiH) band disappeared in 45 h, and *p*-methoxybenzaldehyde 2,4-dinitrophenylhydrazone (2.18 g, 69%) was isolated.

(iii) In the reaction under similar conditions but with [$RuCl_2(PPh_3)_3$] as catalyst, the ν(SiH) band disappeared in 5 h. G.l.c. analysis showed that a substantial amount of *p*-methoxybenzaldehyde was produced, but that some acyl chloride still remained.

Interaction of p-*Methoxybenzoyl Chloride and* trans-[$Pt(H)Cl(PPh_3)_2$].—A mixture of *p*-methoxybenzoyl chloride (2 ml) and *trans*-[$Pt(H)Cl(PPh_3)_2$] (0.38 g, 0.50 mmol) was heated at 120 °C. A slow gas evolution took place, and after 0.5 h crystals began to separate. After 5 h the mixture was cooled, and the white crystals filtered off, washed with cold benzene, and shown to be *cis*-[$PtCl_2(PPh_3)_2$] (0.375 g, 95%), m.p. 309—310 °C (decomp.) (authentic i.r. spectrum). The yellow filtrate was shown by g.l.c. to contain *p*-methoxybenzoyl chloride, anisole, and a small amount of *p*-methoxybenzaldehyde.

Interaction of [$RuCl_2(PPh_3)_3$] *and Triethyl- or Triphenylsilane.*—Triethylsilane (2 ml) was added to a suspension of [$RuCl_2(PPh_3)_3$] (150 mg, 0.16 mmol) in benzene (1 ml). The mixture was warmed to reflux point and after 15 min was cooled and filtered to give red-violet [$Ru(H)Cl(PPh_3)_3$] (0.122 g, 84%), m.p. 114—125 °C (decomp.), ν(RuH) (Nujol) 2 020 cm^{-1} (lit.,[6] 2 020 cm^{-1}).

A similar procedure involving [$RuCl_2(PPh_3)_3$] (0.16 mmol) and triphenylsilane (2.0 mmol) gave [$Ru(H)Cl(PPh_3)_3$] (76%).

Interaction of p-*Methoxybenzaldehyde with Triethylsilane catalysed by* [$RuCl_2(PPh_3)_3$] (Cf. *Ref.* 3).—A mixture of *p*-methoxybenzaldehyde (13.6 g, 0.10 mol), triethylsilane (14.5 g, 0.125 mol), and [$RuCl_2(PPh_3)_3$] was heated under reflux at 120 °C for 40 h. The residual triethylsilane was distilled off, and the residue fractionated to give triethyl-*p*-methoxybenzyloxysilane (22.1 g,88%), b.p. 118—120 °C at 1.6 mmHg (authentic i.r. spectrum).

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