Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

DECARBONYLATION AND DEHYDROHALOGENATION OF ALIPHATIC ACYL HALIDES BY IRIDIUM AND RHODIUM COMPLEXES*

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(Received May 20th, 1971)

SUMMARY

Chlorocarbonylbis(triphenylphosphine)iridium (I) catalyzes selectively, and under mild conditions, the transformation of aliphatic acid halides into mixtures of olefins. Aroyl halides are not affected. $[Rh(CO)_2Cl]_2$, $RhCl(PPh_3)_3$ and $RhCl_3(AsPh_3)_3$ catalyze the decarbonylation and dehydrohalogenation of acyl halides in the presence of PPh_3 to give terminal olefins selectively. A study of the iridium complexes isolated from the catalytic reaction mixtures, has led to a refined theory of the reaction mechanism.

INTRODUCTION

In previous publications[2-4], it was shown that above 200° aroyl halides are converted catalytically into aryl halides by several Rh^{I} and Rh^{III} complexes. The decarbonylation of aliphatic acid halides having at least one hydrogen atom at the β-position is accompanied by dehydrohalogenation and double bond migration to yield mixtures of olefins[5], and has thus been of little practical value. Efforts have been made[2-5] to elucidate the mechanism of the process by isolation of reaction intermediates. However, these are unstable under the conditions under which the catalytic reaction takes place, and so the rhodium–substrate complexes, which can be isolated at much lower temperatures, were used in arriving at tentative descriptions of the catalytic pathway.

We report now the decarbonylation of acyl halides by the iridium complex $IrCl(CO)(PPh_3)_2$ (I). At the temperature of the reaction, this catalyst forms iridium–substrate complexes which can be isolated, and the study of these has given a clearer insight into the reaction mechanism. We also describe selective inhibition of the double bond migration which occurs after the decarbonylation and dehydrohalo-

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* Paper presented in part at the 40th Conference of the Israel Chemical Society, October 18–20, 1970, Haifa (*Cf.* ref. 1).

genation of long chain aliphatic acyl halides; this inhibition leads to the formation of olefins with terminal double bonds only.

RESULTS AND DISCUSSION

Whilst $IrCl(CO)(PPh_3)_2$ (I) does not catalyze the conversion of aroyl halides (*vide infra*), at 78° it does catalyze, albeit slowly, the evolution of carbon monoxide and hydrogen halide from acyl halides carrying β-hydrogen atoms to give mixtures of olefins. The catalysis proceeds much more quickly and with high yields above 135°. Some representative results are summarized in Table 1.

The isomer distribution of the olefins formed is often erratic, but in decarbonylation/dehydrohalogenation reactions requiring prolonged periods (*e.g.*, expt. 7), equilibrium mixtures are obtained[6].

Phenylacetyl chloride (which has no hydrogen in the β position) cannot be decarbonylated by the iridium complex (I), though it is pyrolyzed gradually into toluene, benzyl chloride, *trans*-stilbene, bibenzyl and other minor products. No CO is set free from aroyl halides, regardless of the nature of substituents attached to the aromatic ring; even high boiling polycyclic compounds such as 9-phenanthroyl chloride (b.p. 370°), are not decarbonylated catalytically at their boiling points.

The great difference in reactivity between aliphatic and aromatic acid halides in the presence of $IrCl(CO)(PPh_3)_2$ (I), made it possible to eliminate selectively one carbonyl function from the dichloride of 4-(*p*-carboxyphenyl)butyric acid, *p*-$ClOC$-$C_6H_4CH_2CH_2CH_2COCl$. Exactly 0.5 mole of each HCl and CO were evolved from 1 mole of the diacyl chloride. The unstable *p*-allylbenzoyl chloride and its isomerization products were treated with methanol, but extensive polymerization occurred, so that only 10% of the expected monoesters could be isolated.

The inability of $IrCl(CO)(PPh_3)_2$ (I) to catalyze decarbonylation and dehydrohalogenation of aroyl chloride can be explained by the high stability of an aryl–iridium complex $ArIrCl_2(CO)(PPh_3)_2$ (III) formed from stoichiometric amounts of (I) and the aroyl chloride. These complexes do not decompose by heating above their melting points or in the presence of an excess of aroyl (or aliphatic acyl) halides. (They do, however, decompose in the presence of arenesulfonyl chlorides[7].) The fact that unlike $(C_6H_5CO)IrCl_2(CO)(AsPh_3)_2$[8], for example, the aroyl–iridium–triphenylphosphine complex $(ArCO)IrCl_2(CO)(PPh_3)_2$ (II) liberates carbon monoxide already at 45°, made it impossible to isolate these species. However, their existence has been proven by the observation of new transient carbonyl bands in the 1600–1680 cm^{-1} region a short time after (I) is treated with the aroyl chlorides in boiling benzene.

Aroyl bromides give pentacoordinated aryl complexes, $Ar'IrBrCl(CO)(PPh_3)$ (IV), which are as stable as the hexacoordinated analogs (III). Elimination of one triphenylphosphine ligand is facilitated also by the presence of bulky aryl groups; thus 1-naphthoyl chloride reacts with $IrCl(CO)(PPh_3)_2$ (I) to give mainly the pentacoordinated aryl complex $(1\text{-}C_{10}H_7)IrCl_2(CO)(PPh_3)$. The even more sterically hindered 2-methyl-1-naphthoyl chloride gives the pentacoordinated aroyl complex $(Ar''CO)IrCl_2(CO)(PPh_3)$ (V) [IR (Nujol) 1640 and 2080 cm^{-1}], which could not be converted into the corresponding aryl–iridium compound.

Aliphatic acid halides behave differently: their addition complexes with (I) are much less stable. Acetyl chloride readily forms $(CH_3CO)IrCl_2(CO)(PPh_3)_2$

[(VI), R=CH_3] which behaves analogously to $(CH_3CO)IrCl_2(CO)(PEt_2Ph)_2$[9] and evolves CO upon heating for 1 min at 150° to yield dichloro(methyl)carbonylbis(triphenylphosphine)iridium(III) [(VII), R=CH_3]. Higher aliphatic acyl halides [which add smoothly to $IrCl(CO)(PEt_2Ph)_2$[9]] do not give readily addition compounds (VI) or (VII), but instead give $HIrCl_2(CO)(PPh_3)_2$ (VIII)[10], generally in quantitative yield. Only the heavier acyl chlorides, such as those of n-undecanoic or 3-phenylpropionic acid, yield $(RCO)IrCl_2(CO)(PPh_3)_2$ (VI) when treated with the catalyst (I) at 135° for 5 min, or (in better yields and higher purity) for 4 h at 45°. Upon prolonged heating these acyl complexes (VI) suffer (*a*) evolution of CO and isomerization to $RIrCl_2(CO)(PPh_3)_2$ (VII), and (*b*) partial or complete elimination of one PPh_3 molecule. The alkyl–iridium compounds (VII) could be isolated in pure state when solid acyl complexes (VI) were heated for 1–5 min at 135–150°.

The formation of pentacoordinated acyl– and alkyl–iridium complexes is facilitated (as in the aromatic series) by the use of the acyl bromide, or by the use of a bulky group. At 45°, n-undecanoyl bromide, adds to the starting complex (I) to give pure $[CH_3(CH_2)_9]IrBrCl(CO)(PPh_3)$ only after 26 h. Shorter reaction periods give mixtures of this complex with the hexa- and penta-coordinated acyl complexes $[CH_3(CH_2)_9CO]IrBrCl(CO)(PPh_3)_2$ and $[CH_3(CH_2)_9CO]IrBrCl(CO)(PPh_3)$, respectively. At 135° the compounds $(RCO)IrBrCl(CO)(PPh_3)$ (X) are further transformed to $RIrBrCl(CO)(PPh_3)$ (XI). Finally, $[CH_3(CH_2)_9]IrBrCl(CO)(PPh_3)$ could be decomposed, at 150°, to decenes and an iridium–hydrido complex having a transient band at 2095 cm^{-1}.

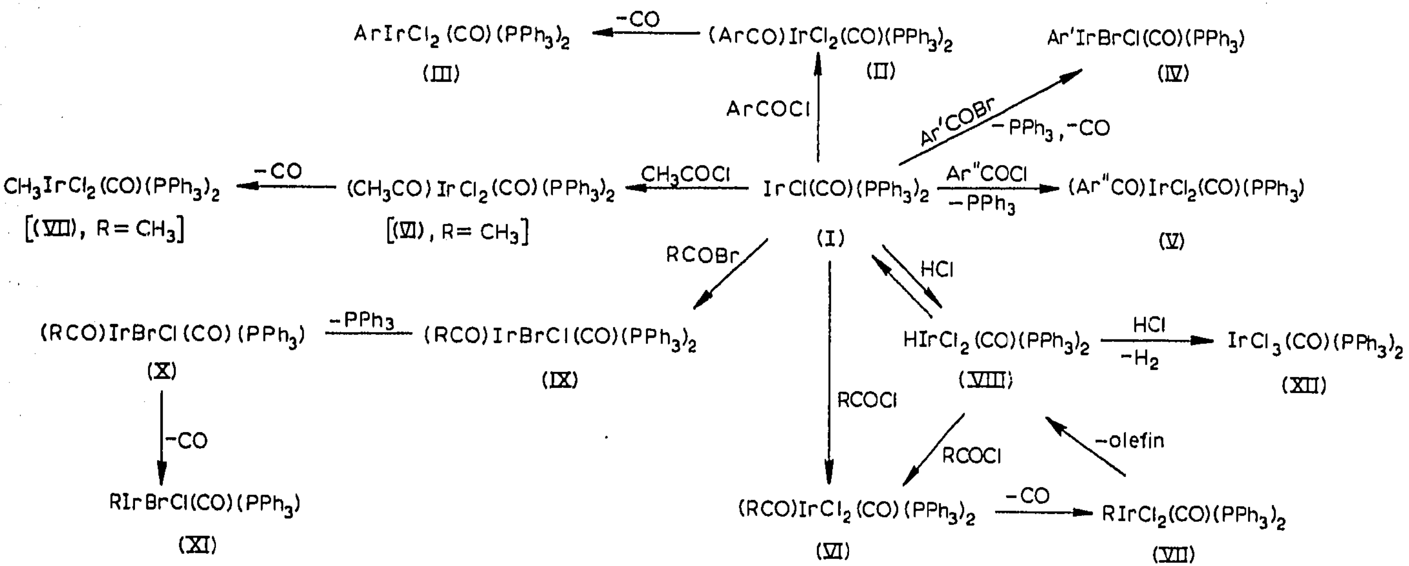
It should be noted that the elimination of PPh_3 allows halogen exchange between catalyst and acyl bromide, which has indeed been observed. The course of oxidative addition of the acyl halide to the catalyst (I)[8,11] is therefore unimportant to the mechanism of the catalytic process.

When dichloro(n-decyl)carbonylbis(triphenylphosphine)iridium(III) [(VII), R=$CH_3(CH_2)_9$] was heated further 1-decene and $HIrCl(CO)(PPh_3)_2$ (VIII) were isolated. The latter hydride dissociates partly to (I) and HCl in boiling *p*-xylene or on heating above its melting point. The hydride (VIII) was also obtained during the catalytic process when HCl was not removed continuously (with the aid of nitrogen or argon). After several hours under these conditions, the hydride (VIII) reacts with the dissolved HCl to give $IrCl_3(CO)(PPh_3)_2$ (XII)[10]. The formation of this complex causes a slowing down of the catalytic reaction. Heating of the hydride (VIII) with degassed acyl halides leads to the formation of the same acyl– and alkyl–iridium complex as (I).

The various transformations observed with $IrCl(CO)(PPh_3)_2$ (I) and acid halides are outlined in Scheme 1.

It remains to be proven that only the hydrogen atoms located β to the carbonyl group are involved in the dehydrohalogenation. This proof has been provided by distilling the deuterated and non-deuterated 3-phenylpropionyl chlorides [(XIII)–(XVI)] over $IrCl(CO)(PPh_3)_2$ (I) for 10 min. Under these conditions, which do not cause significant internal hydrogen–deuterium exchange, the chlorides (XIII) and (XIV) evolve deuterium-free HCl while (XV) and (XVI) give only DCl. Thus neither aromatic hydrogen atoms nor those located α to the carbonyl group are incorporated in the formation of hydrogen halide. The olefins obtained from (XIII), (XIV) and (XV) are isotopically pure $C_6H_5CH{=}CH_2$, $C_6D_5CH{=}CH_2$ and $C_6H_5CD{=}CD_2$, respective-

SCHEME I[a]



[a] Ar = C_6H_5, 4-$H_5C_2OC_6H_4$, 4-$O_2NC_6H_4$, 3,4-$Cl_2C_6H_3$, 2-C_4H_3S; Ar' = C_6H_5, 3-BrC_6H_4; Ar'' = β-CH_3-α-$C_{10}H_7$; R = $CH_3(CH_2)_9$, $C_6H_5CD_2CD_2$

ly, while in the deuterated styrene from (XVI) part of the terminal ^{1}H exchanged with the benzylic deuterium atoms.

$C_6H_5CH_2CH_2COCl$ (XIII)	$C_6D_5CH_2CH_2COCl$ (XIV)
$C_6H_5CD_2CD_2COCl$ (XV)	$C_6D_5CD_2CH_2COCl$ (XVI)

It is noteworthy that alkyl halides (*e.g.*, 1-decyl, phenethyl and 3-phenylpropyl chloride) are not dehydrohalogenated upon refluxing with complexes (I), (VI) or (VIII) for several hours. The hydrogen halide must therefore be abstracted while the organic moiety is still bound to the iridium atom as a ligand.

These observations lead us to suggest that 2 related mechanisms are involved in the catalytic reaction (Scheme 2). In the first step the acyl halide adds oxidatively to the square-planar Ir^I compound (I). The acyl complex (XVII), so formed, evolves CO to give (XVIII) which, in turn, sets free the olefin molecule by a four-centered mechanism leaving the iridium hydride (VIII) behind. The occurrence of compound (XVII) makes it possible to explain the behaviour of the acyl bromides and of those chlorides that cause the elimination of triphenylphosphine: loss of PPh_3 from (XVII) gives the pentacoordinated acyl complex (XIX). The latter may also derive from (XVIII) by elimination of PPh_3. From (XX) the olefin is formed together with the highly reactive hydride (XXI), which by dehydrohalogenation and recombination with a molecule of the acyl halide brings us back to (XIX).

(*continued on p.* 234)

SCHEME 2

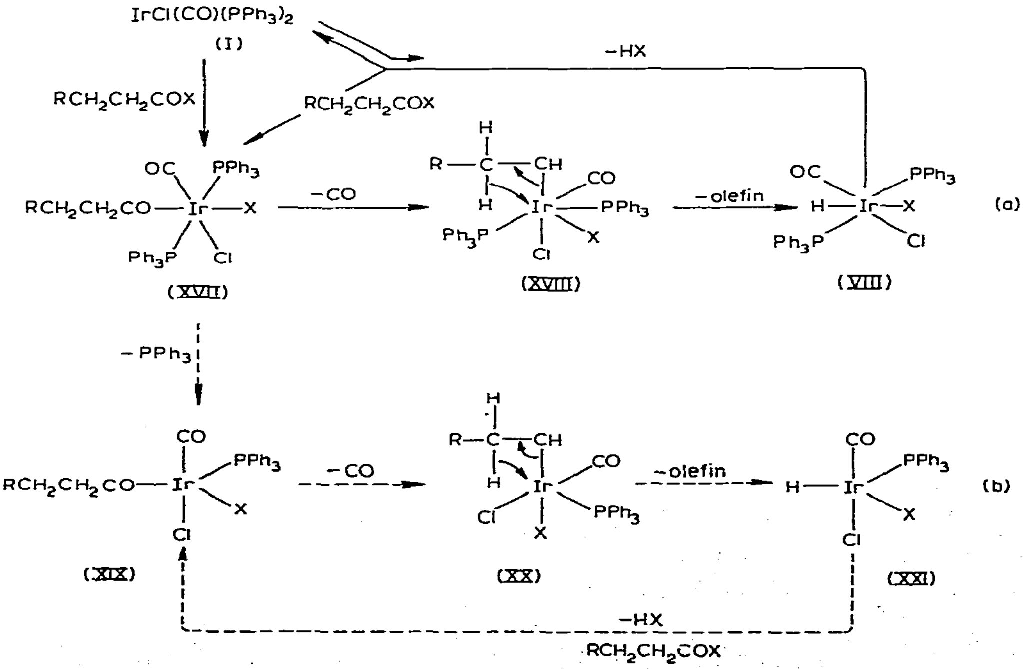


TABLE 1

DECARBONYLATION/DEHYDROHALOGENATION OF ACYL CHLORIDES BY $IrCl(CO)(PPh_3)_2$

No.	Acyl chloride (g/g catalyst)	Solvent (ml)	Reaction		Products (%)
			Temp. (°C)	Time (min)	
1	Undecanoyl (4.9/0.1)	Benzene (20)	78	1560	Decenes (18)
2	Undecanoyl (2.0/0.2)	*p*-Xylene (20)	135	900	Decenes (95)
3	Undecanoyl (61/0.6)		Reflux	20	1-Decene (41), isomerized decenes (49)
4	Lauroyl (10/0.1)		Reflux	15	1-Undecene (38), isomerized undecenes (46)
5	3-Phenylpropionyl (4.0/0.05)		Reflux	30	Styrene (100)[a]
6	4-Phenylbutyryl (4.0/0.05)		Reflux	15	Allylbenzene (75), *cis*-β-methylstyrene (3), *trans*-β-methylsyrene (20)
7	5-Phenylvaleryl (1.5/0.4)	*p*-Xylene (30)	135	330	4-Phenyl-1-butene (3.2), *cis*-1-phenyl-2-butene (2.6), *trans*-1-phenyl-2-butene (12.5), *trans*-1-phenyl-1-butene (40.8)
8	5-Phenylvaleryl (4.0/0.06)		Reflux	10	4-Phenyl-1-butene (40), *cis*- and *trans*-1-phenyl-2-butene (38), *trans*-1-phenyl-1-butene (12)

[a] Partially polymerized.

TABLE 2

EFFECT OF TRIPHENYLPHOSPHINE AND OTHER REAGENTS ON THE CATALYTIC DECARBONYLATION OF n-UNDECANOYL CHLORIDE

Catalyst	Additive (molar ratio catalyst/additive)																			
	None		PPh_3 (1/1)		PPh_3 (1/100)		$AsPh_3$ (1/1)		$AsPh_3$ (1/100)		$SbPh_3$ (1/1)		$SbPh_3$ (1/100)		$BiPh_3$ (1/1)		$BiPh_3$ (1/100)		I_2 (1/100)	
	A[a]	B[a]	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
$IrCl(CO)(PPh_3)_2$	73	55	43	46	43	36	71	46	73	43	79	46	81	30	62	25	3	67	3	81
$[Rh(CO)_2Cl]_2$	69	53	71	54	57	4	71	59	69	23	69	57	65	37	70	28	0		32	39
$RhCl(PPh_3)_3$	71	49	62	38	48	4	71	56	66	20	71	23	65	13	70	13	0		62	18
$RhCl_3(AsPh_3)_3$	78	63	76	63	33	4	83	55	57	13	75	57	67	19	20	12	17	19	38	14
$RhCl_3$	29	20	25	7	37	3	38	42	17	13	40	36	46	22	8	22	0		34	41
$RhCl_3 \cdot 3\,H_2O$	19	10	11	2	25	5	18	30	22	12	27	30	12	18	2	17	0		<1	90

[a] A: Yield (%) of decenes in standard experiments (0.46 g n-undecanoyl chloride and 2.2×10^{-5} mole catalyst, after 15 min; see Experimental); B: Percentage of non-terminal olefins in the mixture of decenes.

The second mechanism, which we believe to be the main pathway, accounts mainly for the relative long induction periods observed for the decarbonylation–dehydrohalogenation of several acyl halides (also "unhindered" ones). n-Undecanoyl chloride, *e.g.*, requires 40 min before the maximum rate of reaction (0.23% min^{-1}) is achieved in the decarbonylation by (I) or by (VIII) in boiling *p*-xylene. The induction period cannot be due to a slow step (I)→(XVII) as the rate of this step almost equals that of (VIII)→(XVII) at 135°; it is thus most probable that a slow step (XVII)→(XIX) is involved.

The transformation (XVIII)→(VIII) and (XX)→(XXI) may *a priori* proceed via the unstable π-olefin complexes $\pi\text{-(RCH=CH}_2\text{)IrHCl}_2\text{(CO)(PPh}_3\text{)}_2$ and $\pi\text{-(RCH=CH}_2\text{)IrHCl(CO)(PPh}_3\text{)}$, respectively, but there is no indication of their involvement in the catalytic process. These complexes may, of course, play a part in the double bond migration in the olefinic products, which is independent of the catalytic reaction discussed here.

When this paper was completed and ready for submission, Kubota and Blake[8] reported on similar experiments with acyl, alkyl and aryl complexes of iridium from acid chlorides. Whilst in may essential points the two studies have led to the same results, there are the following differences:

(*a*). We have observed that benzoyl chloride *does* react with $\text{IrCl(CO)(PPh}_3\text{)}_2$ (I); it does not give the benzoyl but the phenyl complex (as indicated by the spectrum), and this in excellent yield. However, this reaction takes place at a temperature of 135°, while Kubota and Blake limited their experiments to room temperature.

(*b*). When (I) was used the aroyl complexes, in general, did spontaneously liberate carbon monoxide, yielding aryl complexes. Kubota and Blake report that with the analog of (I) based on methyldiphenylphosphine, the acyl complexes are extremely stable. It may be that the two different phosphine compounds lead to aroyl complexes of different stability.

(*c*). Kubota and Blake assume that the pentacoordinated aryl complexes, $\text{(RCO)IrCl}_2\text{(PPh}_3\text{)}_2$, can add carbon monoxide reversibly. Acceptance of this hypothesis, for which we have not found any evidence in our studies, would permit the formulation of an additional reaction scheme, in which loss of CO would occur instead of that of triphenylphosphine.

In an attempt to avoid the double bond migration following the Ir^{I}-catalyzed decarbonylation/dehydrohalogenation, we added to the reaction mixture triphenylphosphine, [which is known to inhibit isomerization by (I)[6,12]], and some other potential isomerization inhibitors (Table 2). However, those additives proved to be non-selective and lowered the rates of both isomerization and decarbonylation reactions. However, when PPh_3 was added to the Rh^{I}- and Rh^{III}-catalyzed decarbonylation/dehydrohalogenation reaction, 1-olefins were formed selectively. The phosphine, which is known also to inhibit rhodium catalyzed isomeriations[6,13] has only a limited inhibitory effect on the catalytic decarbonylation reaction by $[\text{Rh(CO)}_2\text{Cl}]_2$, $\text{RhCl(PPh}_3\text{)}_3$ and $\text{RhCl}_3\text{(AsPh}_3\text{)}_3$, and even acts as a promotor in the decarbonylation by rhodium trichloride. Triphenylarsine, -stibine and -bismuthine inhibit the isomerization to a smaller extent or not at all. Iodine has been reported[5] to prevent double bond migration during the decomposition of an acyl–rhodium complex $\text{(RCH}_2\text{CH}_2\text{CO)RhCl}_2\text{(PPh}_3\text{)}_2$ to HCl and olefin, but was found not to act as a selective inhibitor in the catalytic process.

The results obtained with n-undecanoyl chloride under standard conditions (see Experimental) are summarized in Table 2. Other long chain aliphatic acid chlorides (lauroyl, myristoyl and stearoyl chlorides behave analogously.

EXPERIMENTAL

The different methods used for the decarbonylation/dehydrohalogenation reactions listed in Table 1 are illustrated by the following examples.

Phenylbutenes from 5-phenylvaleryl chloride and $IrCl(CO)(PPh_3)_2$

To a hot solution of 395 mg $IrCl(CO)(PPh_3)_2$ (I) in 30 ml dry *p*-xylene, 1.50 g of 5-phenylvaleryl chloride was added. The resulting solution was refluxed under nitrogen for 5.5 h and analyzed on a 6.4 × 2000 mm GLC column packed with 10% Apiezon L on Chromosorb P at 150–200°. The olefinic fraction consisted of 40.8% *trans*-1-phenyl-1-butene, 15.1% *cis*- and *trans*-phenyl-2-butene (which were not separated) and 3.2% 4-phenyl-1-butene. The relative amounts of *cis*- and *trans*-1-phenyl-2-butene (2.6 and 12.5%, respectively) were determined by NMR (signals of vinylic hydrogen atoms at δ 7.53 and 6.52 ppm, respectively). The crude reaction mixture was treated with petroleum ether (b.p. 40–60°) to yield colorless microcrystals of (VIII) (90%) that were identical with $HIrCl_2(CO)(PPh_3)_2$ prepared from (I) and dry HCl[10]. IR (Nujol): (Ir–H) 2240, 848, 878; (CO) 2040 cm^{-1}. (Found: C, 54.6; H, 4.0; Cl, 8.8; P, 7.5%.)

A variation of this method was used for kinetic measurements of the decarbonylation/dehydrohalogenation of n-undecanoyl chloride by (I). Quantities of 2.5 μl of the mixture (that contained also *trans*-decalin as reference) were withdrawn every 15 min during 16 h and injected immediately into the GLC apparatus.

Allylbenzene and β-methylstyrene from 4-phenylbutyryl chloride and (I)

A mixture of 4.0 g of 4-phenylbutyryl chloride and 50 mg (I) was placed in a modified Claisen flask with a capillary gas inlet through which nitrogen was introduced, and a gas outlet that conducted the hydrogen chloride formed into 0.2 *N* aqueous sodium hydroxide. The reaction mixture, the color of which changed from red to yellow and back to red, was heated, so as to permit distillation of the olefins at 160–175° (15 min). The distillate (2.53 g) was analyzed by GLC (10% Apiezon L on Chromosorb P at 150°) and found to consist of 75% allylbenzene, 3% *cis*- and 20% *trans*-β-methylstyrene. The HCl evolved (in quantitative yield) was determined by back-titration of the excess sodium hydroxide.

1-*Decene from n-undecanoyl chloride,* $[Rh(CO)_2Cl]_2$ *and* PPh_3

A mixture of 61 g of n-undecanoyl chloride, 40 g triphenylphosphine and 0.6 g $[Rh(CO)_2Cl]_2$ was heated in a nitrogen atmosphere with a free flame, so as to permit distillation of the decenes formed between 160 and 173°. After 30 min no more olefin distilled over. The crude material was washed with 5% aqueous sodium hydroxide solution, neutralized, dried and fractionated twice to give 31.8 g (76%) of 1-decene (b.p. 167–168°) of 97% purity (determined by GLC as in the following procedure).

Decarbonylation/dehydrohalogenation of n-undecanoyl chloride under standard conditions (expts. listed in Table 2)

A mixture of 0.46 g n-undecanoyl chloride, 2.2×10^{-5} mole of the catalyst and the additve (as indicated in Table 2) was heated in an electric furnace in a microdistillation apparatus at 200°. The temperature was raised to 300° within exactly 15 min. The olefins which distilled over were dissolved in light petroleum ether (b.p. 40–60°) and filtered through a short column of alumina. Identification and analysis of the products were accomplished by comparison (GLC) with authentic samples of the various decenes. Using two 6.4×4000 mm columns packed with (a) 10% Apiezon M on Chromosorb W and (b) 10% β,β-oxydipropionitrile on Chromosorb W, operated at 85°, 1-, 2-, 3-, 4- and 5-decene could be separated. However, the separation of the *cis*- and *trans*-isomers was incomplete.

The results are reproducible within ±5% inspite of the unavoidable small variations in the rate of heating of the reaction mixtures.

4-(*p-Carboxyphenyl*)*butyric acid*

A mixture of 50 g 4-(*p*-bromophenyl)butyric acid[14], 40 g cuprous cyanide and 200 ml freshly distilled *N*-methylpyrrolidone was heated with agitation at 200° for 40 h. The reaction mixture was digested with 1.5 l of water and excess ferric chloride, and acidified with conc. hydrochloric acid. The nitrile was extracted with benzene and the organic layer washed with aqueous sodium carbonate solution and water, dried and concentrated. The resulting oil was refluxed with 10% aqueous potassium hydroxide for 24 h. Upon acidification 33 g (74%) of the crude diacid precipitated as colorless crystals; m.p. 185–187° (from water). (Found: C, 63.4; H, 6.0. $C_{11}H_{12}O_4$ calcd.: C, 63.5; H, 5.8%.)

2,2,3,3-*Tetradeuterio-3-phenylpropionic acid*

A solution of 25 ml methyl phenylpropiolate in 200 ml cyclohexane was treated with deuterium at room temperature and 3 atm pressure in the presence of 200 mg palladium on carbon (10%). Distillation of the resulting oil afforded 23.5 g (89%) of colorless methyl 2,2,3,3-tetradeuterio-3-phenylpropionate; b.p. 132° (16 mm); NMR (CCl_4): δ 7.17 (m, 5), 3.60 ppm (s, 3). The ester was saponified by refluxing with 27 g sodium methoxide in 100 ml D_2O for 7 h. Acidification with hydrochloric acid below 0°, yielded an oil. It was extracted with benzene and worked up in the usual manner to give 18 g (84%) of the colorless acid; m.p., 46.5°; NMR ($CDCl_3$): δ 7.38 (m, 5), 11.70 ppm (s, 1). (Found: C, 70.2; H, 6.5. $C_9H_6D_4O_2$ calcd*: C, 70.1; H, 6.5%.)

3-(*Pentadeuteriophenyl*)*propionic acid*

To a Grignard solution, prepared from 24 g bromobenzene-d_5[15], 3.6 g magnesium and 150 ml ether, there was added under nitrogen at −10°, 6.7 g ethylene oxide in 25 ml ether. The mixture was allowed to warm up to room temperature within 1 h. One hundred ml of ether was removed by distillation and replaced by dry benzene. The mixture was refluxed for 6 h and then left to stand overnight. The yellow paste obtained was decomposed with saturated ammonium chloride solution at 0°. After the usual work-up, the residue was fractionated at 25 mm, and the colorless

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* The total hydrogen content is calculated as ^1H in accordance with the analytical methods.

oil of boiling point 116–120° collected to give 10 g (53%) 2-(pentadeuteriophenyl)-ethanol. The carbinol was dissolved in 50 ml dry pyridine and treated at $-10°$ with 15 g *p*-toluenesulfonyl chloride in 50 ml of the same solvent. Upon dilution with 100 g ice cold water 13.6 g (62%) of the tosylate was obtained. M.p. 39° (from water). (Found: C, 63.8; H, 5.8; S, 11.3. $C_{15}H_{11}D_5O_3S$ calcd.*: C, 64.1; H, 5.7; S, 11.4%.)

A stirred mixture of 12.7 g of the tosylate, 5.8 g of sodium bromide and 30 ml of freshly distilled ethylene glycol was heated at 135° for 1 h. Then cooled and poured on 150 ml cold water. The organic material was extracted with methylene chloride, washed with water, dried and the solvent removed. The residue was distilled at 69–70° (1 mm) to yield 5.0 g (60%) of colorless 2-(pentadeuteriophenyl)ethyl bromide. (Found: C, 50.2; H, 5.1. $C_8H_4BrD_5$ calcd.*: C, 50.5; H, 4.7%.)

A Grignard reagent, prepared under argon from 2.4 g of the foregoing bromide and 0.5 g magnesium in 50 ml dry ether, was poured onto excess dry ice in ether. The mixture was allowed to warm up to room temperature, acidified and worked up to give 1.7 g (87%) of the required carboxylic acid. B.p. 110° (0.4 mm). The acid solidifies as long colorless needles of m.p. 46.5°; NMR (CCl_4): δ 2.51–3.11 (m, 4), 11.96 ppm (s, 1). (Found: C, 69.9; H, 6.7. $C_9H_5D_5O_2$ calcd.*: C, 69.7; H, 6.5%.)

3,3-*Dideuterio-3-(pentadeuteriophenyl)propionic acid*

A mixture of 18.8 g toluene-d_8, 33.2 g *N*-bromosuccinimide, 170 mg benzoyl peroxide and 200 ml CCl_4 was refluxed until all the reagent decomposed (2 h). The resulting benzyl bromide-d_7 (24 g, 72%) distilled over at 98° (25 mm) as a colorless liquid.

A quantity of 19 g of this bromide was added dropwise to a stirred mixture of diethyl sodiomalonate (prepared from 17.1 g diethyl malonate, 2.46 g sodium) and 50 ml absolute alcohol. The mixture was refluxed for 1 h and diluted with cold water. The organic material was extracted with ether and dried, and the solvent was removed *in vacuo* to yield 24.5 g (90%) of the crude diethyl ester. NMR (CCl_4): δ 1.00 (t, 6), 3.00 (s, 1), 3.97 ppm (q, 6). Upon saponification of the diester with 40% aqueous potassium hydroxide solution followed by acidification, the waxy deuterated benzylmalonic acid was obtained in almost quantitative yield. When 12 g of the dicarboxylic acid was heated at 180° until evolution of CO_2 ceased (30 min) and the residue distilled at 106° (0.2 mm), 5.4 g (60%) of the required acid was obtained; m.p. 48°; NMR ($CDCl_3$): δ 2.66 (s, 2), 10.33 ppm (s, 1). (Found: C, 69.0; H, 6.2. $C_9H_3D_7O_2$ calcd.*: C, 68.8; H, 6.4%.)

Decarbonylation and dehydrohalogenation of deuterated 3-*phenylpropionyl chlorides by* $IrCl(CO)(PPh_3)_2$

A quantity of 2.00 g of the acyl chloride and 50 mg of the catalyst (I) were heated with a free flame, while a stream of argon was bubbled through the mixture. The styrene formed within 10 min was collected in a receiver, analyzed by NMR and mass spectra, and compared with authentic samples of styrene and $\alpha,\alpha,\beta,\beta$-tetradeuteriostyrene. The gas evolved was taken up in triethylamine, and the solid hydrochloride, so formed, was filtered in a dry box, washed with light petroleum ether (b.p. 40–60°), and dried *in vacuo*; its solution in $CDCl_3$ was then analyzed by NMR.

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* The total hydrogen content is calculated as ^1H in accordance with the analytical methods.

The spectrum of the hydrochloride from (XIV) was identical with that of an authentic sample of Et_3NHCl; δ 1.40 (t, 9), 3.15 (q, 6), 10.42 ppm (s, 1-br). In the salts obtained from (XV) and (XVI) the peak at 10.42 ppm was absent.

The reaction with 3,3-dideuterio-3-(pentadeuteriophenyl)propionyl chloride (XVI), which gave mixtures of styrenes, was repeated and the gas collected in a trap at $-120°$. The condensed DCl was evaporated into an IR gas cell. In the spectrum appeared only bands of D–Cl at 2088 and 2165 cm^{-1}, but not of H–Cl 2860 and 2970 cm^{-1}. The spectra of HCl and DCl were recorded separately under the same conditions (*cf.* ref. 16).

Dichloro(aryl)carbonylbis(triphenylphosphine)iridium(III) (III)

A stirred solution of 200 mg of (I) in 25 ml purified *p*-xylene was brought to reflux in an atmosphere of nitrogen. An aroyl chloride (4.0 g) was added at once and the mixture refluxed for 6 h with agitation. The separation of pale yellow or white microcrystals was completed by addition of hexane. Repeated washing of the solid with hot methanol gave analytical pure (III) in 87–95% yield.

TABLE 3

ANALYTICAL DATA AND PHYSICAL PROPERTIES FOR ARYL–, ACYL– AND ALKYL–IRIDIUM COMPLEXES[a]

Compound	M.p. (°C)	ν(CO) (cm^{-1})		Analysis found (calcd.) (%)			
		Nujol mull	In KBr	C	H	Halogen	P
$C_{41}H_{33}Cl_2IrOP_2S$ [(III), Ar=2-C_4H_3S][b]	271	2060	2065	54.7 (54.8)	3.7 (3.7)	7.9 (7.9)	6.5 (6.9)
$C_{43}H_{33}Cl_4IrOP_2$ [(III), Ar=3,4-$Cl_2C_6H_3$]	269	2050	2052	53.4 (53.7)	3.6 (3.4)	14.8 (14.8)	
$C_{43}H_{34}Cl_2IrNO_3P_2$ [(III), Ar=4-$O_2NC_6H_4$][c,d]	278	2065	2070	54.8 (55.0)	3.6 (3.6)	7.7 (7.6)	
$C_{43}H_{35}Cl_2IrOP_2$ [(III), Ar=C_6H_5][d]	292	2048	2052	57.9 (57.8)	4.0 (3.9)	8.0 (8.0)	6.8 (6.9)
$C_{45}H_{39}Cl_2IrO_2P_2$ [(III), Ar=$C_2H_5OC_6H_4$]	260	2055	2052	57.9 (57.7)	4.3 (4.2)	7.6 (7.6)	
$C_{25}H_{20}BrClIrOP$ [(IV), Ar=C_6H_5]	279	2090	2080	44.6 (44.5)	3.2 (3.0)	24.2[e] (23.7)[e]	
$C_{39}H_{33}Cl_2IrO_2P_2$ [(VI), R=CH_3][d]	Dec.	1640, 2075	1630, 2070	54.9 (54.5)	3.8 (3.8)	8.6 (8.3)	6.8 (7.2)
$C_{46}H_{35}Cl_2D_4IrO_2P_2$ [(VI), R=$C_6H_5CD_2CD_2$]	Dec.	1610, 2010		57.7 (58.0)	4.2 (4.1)[f]	7.8 (7.5)	
$C_{48}H_{51}Cl_2IrO_2P_2$ [(VI), R=$CH_3(CH_2)_9$]	Dec.	1648, 2040		58.8 (58.5)	5.2 (5.2)	7.0 (7.2)	6.0 (6.3)
$C_{38}H_{33}Cl_2IrOP_2$ [(VII), R=CH_3][d]	208 dec.	2080		54.9 (54.9)	3.9 (4.0)	8.7 (8.6)	
$C_{47}H_{51}Cl_2IrOP_2$ [(VII), R=$CH_3(CH_2)_9$]	Dec.	2085		58.9 (58.9)	5.1 (5.3)		
$C_{29}H_{36}BrClIrOP$ [(XI), R=$CH_3(CH_2)_9$]	Dec.	2070	2080	46.9 (47.1)	4.8 (4.9)	20.5[e] (20.6)[e]	

[a] All compounds determined for mol.wt. proved to be monomeric. [b] Found: S, 3.8; calcd.: S, 3.6%. [c] Found: N, 1.5; calcd.: N, 1.5%. [d] The compound that has been reported by Kubota and Blake[8] has possibly a different configuration as evidenced by the different physical properties. [e] Calculated and determined as Br. [f] The total hydrogen content is calculated as ^1H in accordance with the analytical methods.

In the same manner the various bromochloro(aryl)carbonyl(triphenylphosphine)iridium(III) (IV) were obtained from (I) and aroyl bromides.

Acetyldichlorocarbonylbis(triphenylphosphine)iridium(III) [(*VI*), $R=CH_3$]

A solution of 200 mg of (I) in 10 ml of degassed dry benzene was cooled to 0°. Freshly distilled and degassed acetyl chloride (2.0 g) was added and the mixture allowed to warm up to room temperature. When the mixture became colorless, hexane was added and the ppt. washed with cold methanol to yield 200 mg (93%) of the acetyl complex; IR (Nujol): (CO) 1640, 2075 cm^{-1}. The analysis of the complex fits the theoretical values (see Table 3) though the presence of a minor contamination of the methyl–iridium compound reported by Kubota and Blake[8] was indicated by the weak carbonyl bands at 2025 and 2050 cm^{-1}.

Dichloro(methyl)carbonylbis(triphenylphosphine)iridium(III) [(*VII*), $R=CH_3$]

This compound was obtained when the foregoing acetyl complex was heated under nitrogen at 150° for 1 min. The colorless crystals of m.p. 208° showed no carbonyl band at 1640 cm^{-1}.

Dichloro(n-undecanoyl)carbonylbis(triphenylphosphine)iridium(III) [(*VI*), $R=CH_3(CH_2)_9$]

A mixture of 200 mg of (I) and 2.0 g of freshly distilled and degassed undecanoyl chloride, through which a slow stream of nitrogen was passed, was stirred and heated at 45° for 4 h. A white ppt. was formed. Hexane was added and the crystals were washed with methanol to yield 230 mg (95%) of the acyl complex; IR (Nujol): (CO) 1648, 2040 cm^{-1}.

When the reaction was carried out in the absence of nitrogen, either at 45° or at 135°, only $HIrCl_2(CO)(PPh_3)_2$ (VIII) could be isolated. Continuous heating of the reaction mixture for 24 h (without nitrogen) afforded trichlorocarbonylbis(triphenylphosphine)iridium(III) (XII)[10]. (Found: C, 51.8; H, 3.4; Cl, 12.4; P. 7.4. $C_{37}H_{30}Cl_3IrOP_2$ calcd.: C, 52.1; H, 3.5; Cl, 12.5; P, 7.3%.)

Decarbonylation of $[CH_3(CH_2)_9CO]IrCl_2(CO)(PPh_3)_2$ was accomplished by the procedure described for the acetyl complex. Dichloro(n-decyl)carbonylbis(triphenylphosphine)iridium(III) [(VII), $R=CH_3(CH_2)_9$] was obtained in quantitative yield.

The complexes $(C_6H_5CD_2CD_2CO)IrCl_2(CO)(PPh_3)_2$ and $(C_6H_5CD_2CD_2)IrCl_2(CO)(PPh_3)_2$ were prepared in the same manner.

Bromochloro(n-undecanoyl)carbonyl(triphenylphosphine)iridium(III) [(*X*), $R=CH_3(CH_2)_9$]

A mixture of 2.0 g of n-undecanoyl bromide (prepared from n-undecanoic acid and oxalyl bromide) and 200 mg of (I) was stirred and heated in a sealed tube for 10 h at 45°. The yellowish crystals were filtered and washed with light petroleum ether (b.p. 40–60°) and methanol. IR (Nujol): (CO) 1650, 2040 cm^{-1}.

When the reaction was carried out for 26 h at this temperature bromochloro(n-decyl)carbonyl(triphenylphosphine)iridium(III) [(XI), $R=CH_3(CH_2)_9$] was isolated; IR (Nujol): (CO) 2070 cm^{-1}.

When the reaction was stopped after 90 min and hexane was added, bromochloro(n-undecanoyl)carbonylbis(triphenylphosphine)iridium(III) [(IX), R=CH_3-$(CH_2)_9$] mixed with some of the pentacoordinated acyl complex was obtained.

Decarbonylation of [(X), R=$CH_3(CH_2)_9$] to [(XI), R=$CH_3(CH_2)_9$] could be effected also by heating of the solid acyl compound as described above.

ACKNOWLEDGEMENT

The authors wish to thank Professor Ernst D. Bergmann for his advice.

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