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DISPROPORTIONATION OF THE CYCLOOCTENE LIGAND IN THE REACTION OF $[IrCl(C_8H_{14})_2]_2$ WITH $AgOCOCF_3$: FORMATION OF $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ AND $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$ AND THEIR CONVERSION INTO CATIONIC ARENE COMPLEXES

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Summary

Reaction of $[IrCl(C_8H_{14})_2]_2$ with $AgOCOCF_3$ in CH_2Cl_2 affords a mixture of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ and $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$. These iridium trifluoroacetates, when treated with CF_3COOH and arenes are converted into cations of general formula $[Ir(arene)L_2]^+$ (L = cyclooctene, L_2 = 1,5-C_8H_{12}).

Introduction

In the course of our studies on Group VIII metal based catalysts for the polymerization via metathesis of cycloolefins, we have studied the polymerization of strained cycloolefins catalyzed by $[IrCl(C_8H_{14})_2]_2$ [1]. We have also reported that it is possible to prepare an efficient catalyst for the ring-opening polymerization of medium ring cycloolefins by treating $[IrCl(C_8H_{14})_2]_2$ with $AgOCOCF_3$, and bringing the resulting oily product into reaction with benzene and CF_3COOH [2]. The nature of the processes occurring during the preparation of this catalytic system remained obscure at the time. We have now investigated this preparation and observed some interesting reactions, leading eventually to cationic arene complexes of iridium(I).

Results and discussion

Reaction of $[IrCl(C_8H_{14})_2]_2$ with $AgOCOCF_3$

$[IrCl(C_8H_{14})_2]_2$ reacts rapidly in pentane with a molar equivalent of $AgOCOCF_3$. After removal of silver chloride by filtration and evaporation of the solvent an oily product is obtained, and after addition of a few drops of pentane this gives golden-yellow crystals of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$. This product can also be prepared by carrying out the reaction in acetone. On the other hand if CH_2Cl_2 is used as the solvent or, alternatively, if pure $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ is kept in a CH_2Cl_2 solution for some hours, $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$ is eventually obtained in addition to the starting iridium trifluoroacetaie (Scheme 1).

SCHEME 1

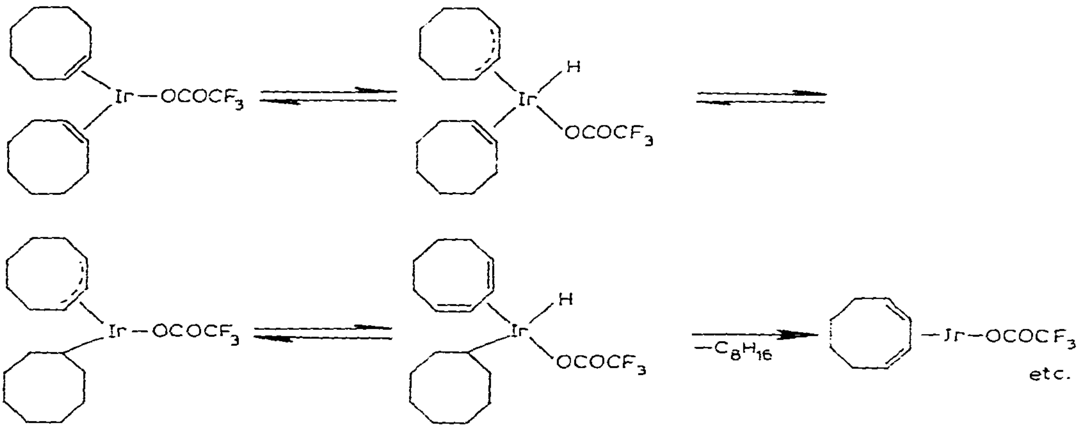
$$\begin{tikzcd}
{[IrCl(C_8H_{14})_2]_2} \arrow[r, "AgOCOCF_3", "n\text{-pentane}"'] \arrow[d, dash, "20h,\ 20^{\circ}C"'] & {[Ir(OCOCF_3)(C_8H_{14})_2]_2} \arrow[d, "20\ h,\ 20^{\circ}C"', "CH_2Cl_2"] \\
{} \arrow[r, "AgOCOCF_3", "CH_2Cl_2"'] & {[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})] + C_8H_{16}}
\end{tikzcd}$$

The GLC analysis of the products obtained by treating the reaction mixture with 1,2-bis(diphenylphosphino)ethane, shows the presence of cyclooctene, cyclooctane and cyclooctadienes (1,5, and traces of 1,3 and 1,4 isomers). Cyclooctane and cyclooctadienes appear to be present in roughly equimolar amounts.

Although we have not been able to separate the two trifluoroacetates in a pure form from this mixture the identities of the products are supported by spectroscopic data. The ^1H NMR spectrum is the sum of the spectra of the two pure trifluoroacetates.

Although several stoichiometric and catalytic disproportionation reactions have been already reported, there is a distinct paucity of reports concerning disproportionation of an olefin to diolefin and alkane [3,4] *. The above results may be satisfactorily explained by postulating a sequence of hydrogen atoms transfer reactions (Scheme 2).

SCHEME 2



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* While this paper was in preparation an additional report appeared on this topic by Crabtree et al. [5].

Thus transfer of hydrogen between two cycloolefin groups gives an η^3-allyl-σ-alkyl intermediate; a second transfer produces a coordinate 1,3-cyclooctadiene plus free cyclooctane. The 1,5-cyclooctadieneiridium complex can then be formed by further hydrogen transfer reactions.

There are two important points which must be considered namely the role of the trifluoroacetate anion in promoting the several oxidative addition steps necessary for the disproportionation of the cycloolefin and the influence of the solvent on the transformation. At the moment the available data do not allow us to reach any firm conclusions on these points.

Reaction of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ *and* $[Ir(OCOCF_3)(C_8H_{12})]_2$ *with* CF_3COOH *and arenes*

The reaction of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ with benzene and an excess of CF_3COOH for 2 h at room temperature followed by removal of volatile materials gave an oily product. This was dissolved in the minimum amount of CH_2Cl_2 and addition of ethyl ether gave a precipitate of white needles of $[Ir(C_8H_{14})_2(C_6H_6)]H(OCOCF_3)_2$. No isolable cationic compound with cyclooctene was found by using other aromatic molecules such as hexamethylbenzene and mesitylene, probably because of equilibrium 1, which is largely shifted

$$1/2[\mathrm{Ir(OCOCF_3)(C_8H_{14})_2}]_2 \underset{-\mathrm{CF_3COOH}}{\overset{\mathrm{arene/CF_3COOH}}{\rightleftharpoons}} [\mathrm{Ir(C_8H_{14})_2(arene)}]\mathrm{H(OCOCF_3)_2} \tag{1}$$

to the left when high boiling arenes are used: in these cases the excess of acid is removed first during the evaporation of the organic products.

The $H(OCOCF_3)_2^-$ salt, was converted into the hexafluorophosphate salt by treatment with KPF_6, and was found to be identical with an authentic sample prepared following an alternative route [6].

$$\begin{tikzcd}
\lbrack \mathrm{Ir(OCOCF_3)(C_8H_{14})_2} \rbrack_2 \arrow[r, "\mathrm{C_6H_6}", "\mathrm{CF_3COOH}"'] & \lbrack \mathrm{Ir(C_8H_{14})_2(C_6H_6)} \rbrack \mathrm{H(OCOCF_3)_2} \arrow[d, "\mathrm{KPF_6}"] \\
 & \lbrack \mathrm{Ir(C_8H_{14})_2(C_6H_6)} \rbrack \mathrm{PF_6}
\end{tikzcd}$$

The complex $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$ also reacts with arenes (benzene, mesitylene, hexamethylbenzene) in CF_3COOH to give the corresponding $[Ir(1,5\text{-}C_8H_{12})(arene)]PF_6$ in high yields. The corresponding $H(OCOCF_3)_2^-$ salt has been isolated only in the case of the $[Ir(1,5\text{-}C_8H_{12})(C_6H_6)]^+$ cation. However, even in the solid state this compound slowly loses benzene and CF_3COOH to give $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$. The reaction is easily monitored by ^1H NMR spectroscopy; the signal due to coordinated benzene decreases in intensity and, at the same time, the signal due to free benzene increases.

It is interesting to note that when the treatment with arene/CF_3COOH is carried out on the mixture of trifluoroacetates derived from the reaction of $[IrCl(C_8H_{14})_2]_2$ with $AgOCOCF_3$ in CH_2Cl_2, the compound $[Ir(1,5\text{-}C_8H_{12})(arene)]PF_6$ is obtained directly in yields ranging from 30 to 50%, depending on the arene. The reaction proceeds under mild conditions and appears to be

TABLE 1

ANALYTICAL AND ^1H NMR SPECTROSCOPIC DATA FOR CATIONIC ARENE COMPLEXES

Compound	Analysis (found (calcd.) (%))			^1H NMR (δ(ppm)) [a]
	C	H	F	
$[Ir(C_8H_{14})_2(C_6H_6)]H(OCOCF_3)_2$	43.94	4.72	14.33	12.92(bs, H), 6.7(s, CH), 2.43—2.33(m, CH=CH), 1.65, 1.38(m, CH_2)
	(43.51)	(4.91)	(15.88)	
$[Ir(C_8H_{14})_2(C_6H_6)]PF_6$	40.9	5.5	18.1	6.66(s, CH), 2.41(m, CH=CH), 1.63, 1.37(m, CH_2)
	(41.57)	(5.39)	(17.93)	
$[Ir(C_8H_{12})(C_6H_6)]H(OCOCF_3)_2$	[c]	[c]	[c]	12.92(bs, H), 6.76(s, CH), 4.72(m, CH=CH), 2.16(m, CH_2)
	(35.70)	(3.16)	(18.82)	
$[Ir(C_8H_{12})(C_6H_6)]PF_6$	32.2	3.61		6.76(s, CH), 4.76(m, CH=CH), 2.16(m, CH_2)
	(32.12)	(3.46)	(21.78)	
$[Ir(C_8H_{12})(C_6H_3Me_3)]PF_6$	36.51	4.48	20.04	6.43(s, CH), 4.2(m, CH=CH), 2.40(s, CH_3), 2.15(m, CH_2)
	(36.10)	(4.25)	(20.17)	
$[Ir(C_8H_{12})(C_6Me_6)]PF_6$	39.39	4.80	18.14	3.56(m, CH=CH), 2.26(s, CH_3), 2.11(m, CH_2)
	(39.54)	(4.94)	(18.78)	
$[Rh(C_2H_4)_2(C_6H_3Me_3)]PF_6$ [b]	36.84	4.98		6.83(s, CH), 3.23—2.60(bm, C_2H_4), 2.4(s, CH_3)
	(36.81)	(4.75)		
$[Rh(C_2H_4)_2(C_6Me_6)]PF_6$ [b]	40.78	5.88		2.75—2.33(bm, C_2H_4), 2.35(s, CH_3)
	(41.21)	(5.62)		

[a] In CD_2Cl_2, TMS internal standard unless otherwise stated. [b] In Me_2CO-d_6. [c] Analysis results were unsatisfactory owing to fast decomposition of the complex.

fairly general. Indeed preliminary investigation showed that also the complexes $[Rh(OCOCF_3)(C_2H_4)_2]_2$ can be easily converted into the cationic $[Rh(C_2H_4)_2(arene)]^+$ complexes (arene = $C_6H_3Me_3$, C_6Me_6). No reaction occurs in the absence of CF_3COOH. Although many of these compounds have already been reported in the literature, this method represents a useful alternative route.

Trifluoroacetic acid has been used by Maitlis in converting iridium(III) trifluoroacetates into cationic derivatives [7]. The role of the acid in all these reactions is presumably to form a proton bridged anion CF_3COO--H--$OOCCH_3$ and consequently to leave a coordinatively unsaturated species of iridium which can easily coordinate an aromatic molecule. Salts of rhodium cationic compounds with hydrogen bis(trifluoroacetate) anion have been reported in the literature [8].

Conclusions

The present investigation has clarified some of the reactions occurring in the preparation of an iridium based catalyst for the polymerization via metathesis of cycloolefins [2]. Surprisingly, the pure salts $[IrL_2(arene)]H(OCOCF_3)_2$ and the corresponding hexafluorophosphates are found not to be catalysts for the polymerization of cycloolefins. Because of the strict similarity between the preparation of the catalytic system and that of these complexes, this lack of catalytic activity appears rather intriguing. One can imagine that some other cationic species (or alternatively an hydride or alkyl species) is generated and is responsable for the catalytic activity. Preliminary results show that $[Ir(C_8H_{14})_2(C_6H_6)]H(OCOCF_3)_2$, when heated in benzene, is able to polymerize cyclopentene; this behaviour would be consistent with a rearrangement of this compound to give an iridium hydride or alkyliridium intermediate.

We are planning further work in order to clarify this point.

Experimental

$[IrCl(C_8H_{14})_2]_2$ [9], $[IrCl(1,5\text{-}C_8H_{12})]_2$ [10] and $[RhCl(C_2H_4)_2]_2$ [11] were prepared as described in the references cited. Solvents were used after dehydration and distillation. All operations were carried out under dry dinitrogen. Elemental analyses were carried out by the Laboratorio di Microanalisi of Istituto di Chimica Organica (Facoltà di Farmacia), Università di Pisa and by Dr. A. Bernhardt, Germany. ^1H NMR spectra were obtained with a Varian Model HA 100 spectrometer, IR spectra with a 125 Perkin—Elmer instrument. Melting or decomposition points were determined with a Kofler hot-stage apparatus and are uncorrected. GLC analyses were carried out with a HP 5750 instrument using a 12 ft × 1/8 in stainless steel column packed with Polyethylene glycol 400 20% on chromosorb W-AW-DMCS.

Reaction of $[IrCl(C_8H_{14})_2]_2$ with $AgOCOCF_3$

(a) In pentane: preparation of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$. To a suspension of $[IrCl(C_8H_{14})_2]_2$ (0.182 g, 0.2 mmol) in n-pentane (50 ml) was added $AgOCOCF_3$ (90 mg, 0.4 mmol) and the mixture was stirred vigorously at room temperature for 2 h. Silver chloride was filtered off and the solution was evaporated to

dryness under reduced pressure. The oily residue was treated with a few drops of cold heptane to give golden yellow crystals of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ (0.16 g, yield 75%), m.p. 131°C. Anal. Found: C, 41,03; H, 5.20; F, 10.30; Ir, 35.85. $C_{18}H_{28}F_3O_2Ir$ calcd.: C, 41.13; H, 5.37; F, 10.80; Ir, 36.37%. IR (cm^{-1}, KBr): 1665 $\nu(C{=}O)$, 1150, 1200 $\nu(C{-}O)$. ^1H NMR ($CDCl_3$): δ 1.53m, 2.12m (unsaturated protons are not separated from allylic and aliphatic protons). $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ may also be obtained using acetone as solvent (0.18 g of $[IrCl(C_8H_{14})_2]_2$, 0.090 g of $AgOCOCF_3$, 30 ml of acetone, stirring 0.5 h, yield 75%).

(b) In methylene chloride. Following the above procedure $[IrCl(C_8H_{14})_2]_2$ was stirred in CH_2Cl_2 with $AgOCOCF_3$ for 12 h. Work-up as above gave an oily red-orange residue (90% yield) of a mixture of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ and $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$. The same mixture was obtained by dissolving $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ (0.36 mmol) in CH_2Cl_2 (10 ml) and stirring for 12 h.

Preparation of $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$

A suspension of $[IrCl(1,5\text{-}C_8H_{12})]_2$ (292 mg, 0.435 mmol) in acetone (50 ml) was treated with $AgOCOCF_3$ (193 mg, 0.88 mmol) and the mixture was stirred at room temperature for 1 h. Work-up as above gave red crystals of $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$ (269 mg, yield 75%). Anal. Found: C, 29.17; H, 2.91. $C_{10}H_{12}F_3O_2Ir$ calcd.: C, 29.06; H, 2.9; F, 13.79; Ir, 46.51%. IR (cm^{-1}, KBr) 1665 $\nu(C{=}O)$, 1150, 1200 $\nu(C{-}O)$. ^1H NMR ($CDCl_3$): δ 1.57 (d, 4 H); 2.52 (bs, 4 H); 4.03 and 4.33 (bs, 4 H).

Reaction of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ *with benzene and* CF_3COOH*: preparation of* $[Ir(C_8H_{14})_2(C_6H_6)]^+$ *salts*

A mixture of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ (0.3 g, 0.285 mmol), trifluoroacetic acid (4 ml) and benzene (0.2 ml) was kept at room temperature for 2 h. The resulting pale yellow solution was evaporated to dryness and the residue was dissolved in the minimum amount of CH_2Cl_2. Careful addition of ether gave white needles of $[Ir(C_8H_{14})_2(C_6H_6)]H(OCOCF_3)_2$ (0.24 g, 60% yield). This was dissolved in acetone and aqueous KPF_6 was slowly added to give white crystals of $[Ir(C_8H_{14})_2(C_6H_6)]PF_6$ (0.19 g, 90% yield). IR (cm^{-1}, KBr) 1780 $\nu(C{=}O)$, 1140, 1200 $\nu(C{-}O)$.

Preparation of $[Ir(1,5\text{-}C_8H_{12})(arene)]^+$ *salts*

Starting from $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})_2]_2$ and following the above procedure were obtained $[Ir(1,5\text{-}C_8H_{12})(C_6H_6)]H(OCOCF_3)_2$ (60% yield) and $[Ir(1,5\text{-}C_8H_{12})(C_6H_6)]PF_6$ (70% yield), m.p. 178°C (decomp.); $[Ir(1,5\text{-}C_8H_{12})(C_6H_3Me_3)]PF_6$ (78% yield), m.p. 175°C (decomp.) and $[Ir(1,5\text{-}C_8H_{12})(C_6Me_6O]PF_6$ (85% yield).

Reaction of the mixture of $[Ir(OCOCF_3)(C_8H_{14})_2]_2$ *and* $[Ir(OCOCF_3)(1,5\text{-}C_8H_{12})]_2$ *with* CF_3COOH *and arenes*

Following the above procedure were prepared $[Ir(1,5\text{-}C_8H_{12})(C_6H_6)]PF_6$ (34%), $[Ir(1,5\text{-}C_8H_{12})(C_6H_3Me_3)]PF_6$ (43%) and $[Ir(1,5\text{-}C_8H_{12})C_6Me_6)]PF_6$ (56%).

Preparation of $[Rh(OCOCF_3)(C_2H_4)_2]_2$

A suspension of $[RhCl(C_2H_4)_2]_2$ (0.95 g, 2.44 mmol) in n-pentane (50 ml) was treated with $TlOCOCF_3$ (1.55 g, 4.89 mmol) and the mixture was stirred at room temperature for 3 h. The TlCl was filtered off and the yellow filtrate was evaporated to dryness under reduced pressure to give dark red crystals of $[Rh(OCOCF_3)(C_2H_4)_2]_2$ (1.03 g, 78%). Anal. Found: C, 27.16; H, 3.04%. $C_6H_8F_3O_2Rh$ calcd.: C, 26.49; H, 2.95%. ^1H NMR (*o*-dichlorobenzene): δ 2.85 (s).

Preparation of $[Rh(C_2H_4)_2(C_6Me_6)]PF_6$

Following the procedure used for the preparation of iridium cationic compounds, $[Rh(OCOCF_3)(C_2H_4)_2]_2$ (0.462 g, 0.85 mmol) was treated with CF_3-COOH (5 ml) and hexamethylbenzene (0.380 g, 2.34 mmol) at 50°C for 3 h, and successively with aqueous saturated NH_4PF_6 (2.5 ml). The usual work-up gave cream microcrystals of $[Rh(C_2H_4)_2(C_6Me_6)]PF_6$ (0.348 g, 88%), m.p. 180°C (decomp.).

Preparation of $[Rh(C_2H_4)_2(C_6H_3Me_3)]PF_6$

A mixture of $[Rh(OCOCF_3)(C_2H_4)_2]_2$ (0.459 g, 0.845 mmol), CF_3COOH (5 ml) and mesitylene (0.433 ml, 3.12 mmol) was heated at 50°C for 3 h. Work-up as above gave $[Rh(C_2H_4)_2(C_6H_3Me_3)]PF_6$ (0.280 g, 78%), m.p. 135°C (decomp.).

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