2-Substituted Propyl-Iridium(III) Complexes of the Type $[IrCl_2(CH_2CHXCH_3)(CO)L_2]$

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σ-Allyl complexes of the type $[IrCl_2(CH_2CH{:}CH_2)(CO)L_2]$ react with HCl readily to give the 2-chloropropyliridium complexes $[IrCl_2(CH_2CHXCH_3)(CO)L_2]$ (X = Cl). These are readily converted into the 2-methoxy- or 2-ethoxy-derivatives (X = OMe or OEt) when treated with methanol or ethanol, to the 2-hydroxy-complex (L = PMe_2Ph, with sodium carbonate in aqueous acetone) or to the 2-acetoxy complex (with sodium acetate). *mer*-$[IrCl_3(PEt_2Ph)_3]$ when treated with potassium hydroxide in allyl alcohol and then with dilute hydrochloric acid and methanol gives a mixture of $[IrCl_2(CH_2CHXCH_3)(CO)(PEt_2Ph)_2]$ with X = $OCH_2CH{:}CH_2$ and OMe. I.r. and ^1H n.m.r. data are given. The ^1H n.m.r. spectrum of $[IrCl_2(CH_2CHOHCH_3)(CO)(PMe_2Ph)_2]$ was analysed in the presence of the 'shift reagent' $[Eu(fod)_3]$.

WHEN *mer*-$[IrCl_3(PEt_2Ph)_3]$ is heated with potassium hydroxide in boiling allyl alcohol and the resultant mixture treated with hydrochloric acid, colourless crystals are formed after isolation with methanol. This material was first reported in 1960 [1] but not identified. We now find it to be a mixture of two compounds, $[IrCl_2(CH_2CHXCH_3)(CO)(PEt_2Ph)_2]$ with X = $OCH_2CH{:}CH_2$ and X = OCH_3, both of configuration (I). These two complexes were synthesised independently as described below.

We have previously reported that the σ-allyl complex $[IrCl_2(CH_2CH{:}CH_2)(CO)(PMe_2Ph)_2]$ of configuration (II) when treated with dry hydrogen chloride gives the 2-chloropropyl complex $[IrCl_2(CH_2CHClCH_3)(CO)(PMe_2Ph)_2]$ of configuration (I).[2] We have now made the corresponding diethylphenylphosphine complex $[IrCl_2(CH_2CHClCH_3)(CO)(PEt_2Ph)_2]$ by treating the σ-allyl complex in dichloromethane solution with concentrated hydrochloric acid. This 2-chloropropyl complex solvolyses rapidly in methanol or allyl alcohol to give the

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[1] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

[2] A. J. Deeming, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 374.

corresponding 2-methoxypropyl- or 2-allyloxypropyl-complexes. Microanalytical and ^1H n.m.r. data suggest that these 2-methoxypropyl- and 2-allyloxypropyl-complexes are present in the approximate proportions of 3 : 1 in the mixture produced by treating *mer*-$[IrCl_3(PEt_2Ph)_3]$ with allyl alcohol, *etc.* (see above). The 2-allyloxypropyl-complex was very readily converted to the 2-methoxypropyl-complex by treatment with methanol and a trace of hydrochloric acid; the 2-allyloxypropyl–2-methoxypropyl mixture was similarly converted to the pure 2-methoxypropyl-complex. However, on heating the mixture (3 : 1) with allyl alcohol and a trace of hydrochloric acid only partial conversion of the methoxypropyl- to the allyloxypropyl-complex occurred (final proportions *ca.* 1 : 3 from the ^1H n.m.r. intensities).

We have studied other reactions of the 2-chloropropyl-iridium system but using the corresponding dimethylphenylphosphine complexes because of the usefulness and simplicity of their ^1H n.m.r. spectra. This chloro-complex was rapidly solvolysed in methanol to give $[IrCl_2(CH_2CHOMeCH_3)(CO)(PMe_2Ph)_2]$, configuration (I) or in ethanol to the corresponding ethoxy-complex (analytical and other data in Tables). Treatment of the chloro-complex $[IrCl_2(CH_2CHClCH_3)(CO)(PMe_2Ph)_2]$ with sodium acetate in acetic acid gave the acetoxy-complex $[IrCl_2(CH_2CHOAcCH_3)(CO)(PMe_2PH)_2]$. This product gave an analysis a little high in carbon and a little low in chlorine possibly because of a partial replacement of chloride ligand by acetate. The slightly impure product when treated with lithium chloride in acetone–water gave the required compound $[IrCl_2(CH_2CHOAcCH_3)(CO)(PMe_2Ph)_2]$ of acceptable purity. When treated with sodium carbonate in acetone–water the 2-chloropropyl-complex $[IrCl_2(CH_2CHClCH_3)(CO)(PMe_2Ph)_2]$ gave the 2-hydroxypropyl-complex $[IrCl_2(CH_2CHOHCH_3)(CO)(PMe_2Ph)_2]$ configuration (I).

TABLE 1

Melting point, % yield, microanalytical (%) (calculated values in parentheses) and i.r. (cm^{-1}) data (Nujol mulls) for complexes of the type $[IrCl_2(CH_2CHXCH_3)(CO)L_2]$ configuration (I)

L	X	M.p.	Yield (%)	Analysis C	Analysis H	Analysis Cl	ν(C≡O)	ν(Ir–Cl)
PMe_2Ph	OMe	162—168° [a]	80	39·2 (39·35)	4·6 (4·9)	11·35 (11·1)	2030	302s, 258s
	OEt	128—133	94	40·6 (40·35)	5·25 (5·1)	10·7 (10·8)	2021	302s, 260s
	OAc [b]	160—163 [a]	92	40·05 (39·5)	4·9 (4·7)	10·4 (10·6)	2035	308s, 263s
	OH [c]	140—149 [a]	72	38·45 (38·35)	4·85 (4·65)	11·2 (11·3)	2038	307s, 250s
PEt_2Ph	Cl	160—165 [a]	95	41·4 (41·2)	5·3 (5·2)	15·75 (15·2)	2042	305s, 248s
	OAllyl	159—162 [a]	90	44·2, 44·1 (44·95)	5·5, 5·65 (5·7)	9·85 (9·8)	2038	305s, 248s
	OMe	158—160 [a]	70	43·3 (43·1)	5·75 (5·65)	10·4 (10·2)	2024	306s, 250s

[a] With decomposition. [b] ν(C=O) (acetate) 1732 cm^{-1}. [c] ν(O–H) 3420 cm^{-1}.

We have previously shown that the 2-bromoethyl complex $[IrBr_2(CH_2CH_2Br)(CO)(PMe_2Ph)_2]$ is solvolysed by methanol to the corresponding 2-methoxyethyl complex $[IrBr_2(CH_2CH_2OMe)(CO)(PMe_2Ph)_2]$[3] and there are many other examples of the labilisation of substituents on an alkyl ligand which is bonded to a transition metal, *e.g.* the interconversion reactions of $[W(CH_2Cl)(CO)_3(\pi\text{-}C_5H_5)]$ and $[W(CH_2OMe)(CO)_3(\pi\text{-}C_5H_5)]$.[4] Substituents on ferrocene rings can be similarly labilised and ferrocenyl carbonium ions are particularly stable.[5]

The i.r. data for our various new complexes are given in Table 1. Each complex shows a very intense absorption band due to ν(C≡O) and two strong bands due to ν(Ir–Cl). In addition the acetoxy-complex showed a band at 1732 cm^{-1} due to ν(C=O) and the hydroxy-complex a medium band due to ν(O–H). The ^1H n.m.r. data (Table 2) show some interesting features. Since the carbon attached to the ' X ' group, configuration (I), is asymmetric and there is no plane of symmetry along the P–Ir bonds the two *trans*-PMe_2Ph ligands are non-equivalent and all four phosphine methyls are non-equivalent. However, each methyl signal is a triplet showing that the two *trans*-phosphorus nuclei must have very nearly the same (or the same) ^{31}P chemical shifts and be strongly coupled.[6,7] In all cases the terminal methyl of the CH_2CHXCH_3 group forms a well-defined doublet at high τ-value (*ca.* 9·4) and the non-equivalent methylene protons and the methine proton form multiplets. The 2-hydroxypropyl-complex $[IrCl_2(CH_2CHOHCH_3)(CO)(PMe_2Ph)_2]$ gives a ^1H n.m.r. pattern in which most of the resonances are too close together and too complex to be assigned with certainty [see Figure (a), and Table 2 for probable assignments]. However, on adding the n.m.r. shift reagent $[Eu(fod)_3]$ (fod = $[Bu^tCOCHCOC_3F_7]$), large changes occurred in some of the chemical shifts and in 0·8M $[Eu(fod)_3]$ solution the spectrum is as shown in Figure (b) with the assignments as in Table 2. Presumably the shift reagent operates *via* the –OH group and the biggest shift (6·3 p.p.m.) occurs for the methine proton (–C*H*OH–). The methyl group ($-CH_2CHOHCH_3$) shifts to τ 5·09 and was shown to be coupled to the methine by double resonance. The phosphine methyls also become well separated and even the phenyl protons are shifted. We assume that the *o*-protons undergo the largest shift since they will be closest to the –O–Eu grouping. As can be seen from

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[3] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 376.

[4] M. L. H. Green, ' Organometallic Compounds,' Methuen, 1968, pp. 209—217.

[5] M. Rosenblum, ' Chemistry of the Iron Group Metallocenes,' Wiley, New York, 1965.

[6] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

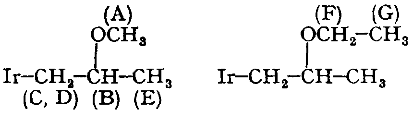
[7] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128, and references therein.

TABLE 2

^1H N.m.r. data for complexes of type $[IrCl_2(CH_2CHXCH_3)(CO)L_2]$ of configuration (I). Measured in deuteriochloroform solution at 34° and 60 MHz unless stated otherwise. τ-values ±0·02 p.p.m. *J*-values ±0·2 Hz; s = singlet, m = multiplet, b = broad, t = 1 : 2 : 1 triplet, q = quartet

		PMe_2Ph		Other resonances	
L	X	τ	$\lvert {}^2J(P–H) + {}^4J(P–H) \rvert$	τ	Assignments [a]
PMe_2Ph	OMe [b]	7·86t	7·8	7·14s	A
		7·91t	8·2	7·57m	B
		7·95t	8·6	8·25—8·74b	C, D
		8·13t	9·0	9·36d (*J* = 5·8)	E
PMe_2Ph	OEt	7·83t	7·8	6·4—7·65m	B, F
		7·87t	7·9	8·58q	C, D
		7·95t	8·2	9·08t	G
		8·02t	9·0	9·43d (*J* = 5·8)	E
PMe_2Ph	OAc	7·81t	7·9	6·21m	B
		7·89t	7·9	8·31s	$COCH_3$
		7·99t	8·0	8·2—8·52b	C, D
		8·07t	8·2	9·42d (*J* = 5·9)	E
PMe_2Ph	OH [b]	7·84t	8·0	*ca.* 2·40b	*o*-Phenyl H
		7·84t	8·0	*ca.* 2·57b	*m,p*-Phenyl H
		7·94t	8·4	6·88b	B
		7·99t	9·0	8·67m	C, D
				9·37d (*J* = 5·8)	E
PMe_2Ph in the presence of 0·8M $[Eu(fod)_3]$	OH [b]	7·53t		0·58b	B
		7·34t		1·16b 1·94b	*o*-Phenyl H
		6·97t			
		6·91t		2·42b	*m,p*-Phenyl H
				4·34b 5·91b	C, D
				5·09b	E
PEt_2Ph	Cl			6·62m	B
				9·35d (*J* = 6)	E
PEt_2Ph	OMe			7·01s	A
				9·50d(*J* = 6)	E
PEt_2Ph	$OCH_2CH=CH_2$			9·55d (*J* = 6)	E
				6·30m	$OCH_2CH{:}CH_2$
				3·8—5·0m	$OCH_2CH{:}CH_2$

[a] Labelling scheme:


$Ir–CH_2–CH(OCH_3)–CH_3$ (A) OCH₃; (C, D) CH₂; (B) CH; (E) CH₃
$Ir–CH_2–CH(OCH_2–CH_3)–CH_3$ (F) OCH₂; (G) CH₃

[b] At 90 MHz (see the Figure).

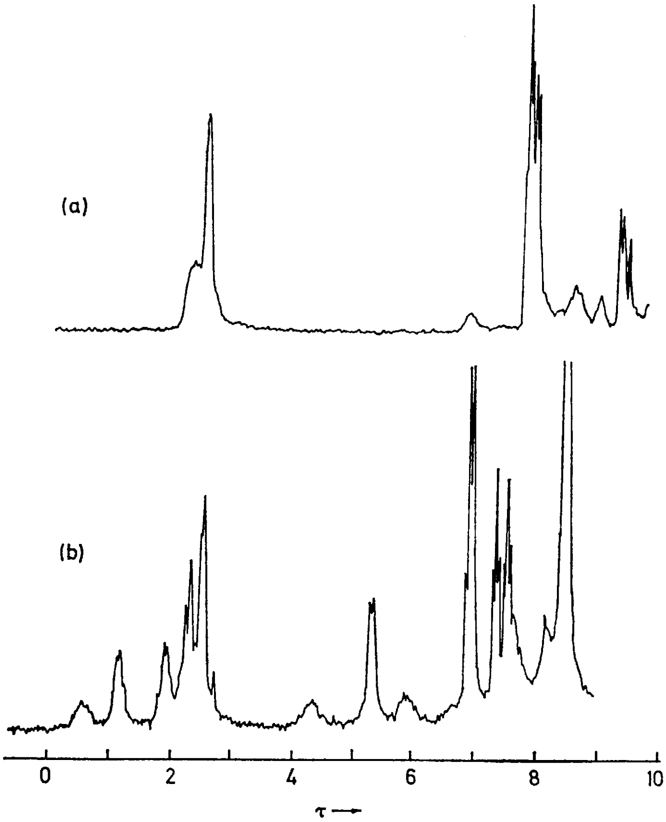
Figure (b) the phosphine methyls occur as triplets indicating that the two *trans*-phosphorus nuclei must have virtually the same chemical shift. Indeed for the complexes $[IrCl_2(CH_2CHOMeCH_3)(CO)(PMe_2Ph)_2]$ and $[IrCl_2(CH_2CHOHCH_3)(CO)(PMe_2Ph)_2]$ with and without $[Eu(fod)_3]$ we could only see one ^{31}P n.m.r. signal (a singlet using random noise decoupling of protons). This is surprising but presumably the centre of asymmetry is too far away to cause differences between the two ^{31}P shifts even though there are differences in the spin–spin couplings to the two phosphorus nuclei.

EXPERIMENTAL

Dichloro{1-(2-*chloro*)*propyl*}(*carbonyl*)*bis*(*diethylphenylphosphine*)*iridium*(III).—Concentrated hydrochloric acid (0·10 g) was added to a solution of dichloro(σ-allyl)(carbonyl-bis(diethylphenylphosphine)iridium(III) (0·10 g) in dichloromethane (0·5 ml). The resultant mixture was shaken for *ca.* 1 min and then diluted with light petroleum (b.p. 30—40°, 4 ml). The desired product separated as white *needles* (0·10 g).

Dichloro{1-(2-*methoxy*)*propyl*}(*carbonyl*)*bis*(*diethylphenylphosphine*)*iridium*(III).—Methanol (3 ml) was added to a solution of dichloro{1-(2-chloro)propyl}(carbonyl)bis(diethylphenylphosphine)iridium(III) (0·045 g) in dichloromethane (1 ml). The resultant solution was boiled for 1 min and then cooled to 0° when the required product separated as large *prisms* (0·042 g) containing one mole of methanol of crystallisation per iridium.

Treatment of mer-*Trichlorotris*(*diethylphenylphosphine*)-*iridium*(III) *with Potassium Hydroxide in Allyl Alcohol.*—A solution of the trichloro-complex (3·14 g, 3·94 mmol) in refluxing allyl alcohol (40 ml) was treated with aqueous potassium hydroxide (2·4 ml, 12·0 mmol). The solution turned red-brown. After 2 h at reflux the mixture was cooled to *ca.* 20° and just acidified with conc. hydrochloric acid (1·2 ml, 12·0 mmol). The solvent was removed by evaporation under reduced pressure and the residue taken up in benzene. The benzene solution was washed with water (thrice), dried ($MgSO_4$), and evaporated to dryness. The residue was taken up in the minimum of methanol and the solution cooled to $-20°$. After several days light yellow *prisms* (0·61 g) were obtained which gave white *prisms*, m.p. 130—150° (decomp.) from dichloromethane–methanol.



^{1}H N.m.r. resonance patterns of $[IrCl_2(CH_2CHOHCH_3)(CO)(PMe_2Ph)_2]$ at 90 MHz (a) in $CDCl_3$ (b) in $CDCl_3$ containing 0·8M $[Eu(fod)_3]$

The product was adjudged to be a mixture of $[IrCl_2(CH_2CHXCH_3)(CO)(PEt_2Ph)_2]$ with $X = OCH_2CH{=}CH_2$ and $X = OCH_3$ in the approximate proportions of 1 : 3, respectively, on the basis of microanalytical data and the ^{1}H n.m.r. spectrum (see Table 2). The mixture was converted into the methoxy-complex, *i.e.* X = OMe, in the following manner. A solution of the mixture (0·1 g) in methanol–benzene (5 ml, 1/1 v/v) was treated with conc. hydrochloric acid (0·1 ml). The resultant solution was boiled down to *ca.* 2 ml and cooled to $-20°$ when the required methoxy-complex (0·087 g) separated and was shown to be identical with an authentic sample, prepared as above, by its i.r. and ^{1}H n.m.r. spectra.

Dichloro{1-(2-*methoxy*)*propyl*(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III).—*Method* 1. *Acid-catalysed Addition of Methanol to Dichloro*(σ-*allyl*)(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III). A solution of hydrogen chloride (1 mmol) in ether (0·3 ml) was added to a solution of dichloro(σ-allyl)(carbonyl)bis(dimethylphenylphosphine)iridium(III) (0·575 g, 0·945 mmol) in dichloromethane (0·1 ml)–methanol (2 ml). The resultant solution was heated to boiling for 2 min and cooled to 0°. Addition of light petroleum (b.p. 30—40°) then gave the required product as white *microcrystals* (0·483 g, 0·758 mmol).

Method 2. *Methanolysis of Dichloro*{1-(2-*chloro*)*propyl*}(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III). A solution of dichloro{1-(2-chloro)propyl}(carbonyl)bis(dimethylphenylphosphine)iridium(III) (0·445 g, 0·692 mmol) in methanol (4 ml) was heated to boiling for 2 min. The required product formed as white *needles* (0·374 g, 0·584 mmol) on cooling to *ca.* −8 °C.

Dichloro{1-(2-*ethoxy*)*propyl*}(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III).—A solution of dichloro{1-(2-chloro)propyl}(carbonyl)bis(dimethylphenylphosphine)iridium(III) (0·439 g, 0·68 mmol) in ethanol (5 ml) was heated to boiling for 5 min. The required compound formed as white *microcrystals* (0·415 g, 0·635 mmol) on cooling the resultant solution to *ca.* −8 °C.

Dichloro{1-(2-*hydroxy*)*propyl*}(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III).—A solution of sodium carbonate (0·016 g, 0·155 mmol) in water (1 ml) was added to a solution of dichloro{1-(2-chloro)propyl}(carbonyl)bis(dimethylphenylphosphine)iridium(III) (0·1 g, 0·155 mmol) in acetone (1 ml). The resultant solution was cooled to *ca.* −8 °C, when sodium carbonate was precipitated and filtered off. The mother-liquor was evaporated to dryness, the residue washed with water and recrystallised from acetone to give the required product as white *microcrystals* (0·068 g, 0·109 mmol).

Action of Sodium Acetate–Acetic Acid on Dichloro{1-(2-*chloro*)*propyl*}(*carbonyl*)*bis*(*dimethylphenylphosphine*)*iridium*(III).—A solution of dichloro{1-(2-chloro)propyl}(carbonyl)bis(dimethylphenylphosphine)iridium(III) (0·2 g, 0·31 mmol) in dichloromethane (2 ml) was added to a solution of sodium acetate (0·082 g, 1 mmol) in acetic acid (1 ml). The resultant solution was heated for 1 min and evaporated to dryness. The residue was washed with water and recrystallised from light petroleum (b.p. 60—80 °C) to give white *microcrystals* (0·18 g), m.p. 160—163° (decomp.). Microanalysis showed the compound to be high in carbon (Found: C, 40·95; H, 4·8; Cl, 9·85. Calc. for $C_{22}H_{31}Cl_2O_3IrP_2$: C, 39·5; H, 4·7; Cl, 10·6%); this is considered to be due to partial substitution of chlorine attached to iridium by the acetoxy-group. A solution of the compound in acetone (2 ml) was added to a solution of lithium chloride (0·21 g, 5 mmol) in water (1 ml). The resultant solution was heated to boiling for 2 min. A white precipitate formed on addition of water; this was filtered off, washed with water, and recrystallised from light petroleum (b.p. 60—80°) to give white microcrystals of the required *complex*.

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