Reactions of Allyl- and Propadienyl-rhodium(III) and -iridium(III) Complexes with Polyhalogenomethanes. Rhodium(II) and Iridium(II) Species as Reactive Intermediates

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Several allylcarbonyldihalogenobis(phosphine)-rhodium(III) and -iridium(III) complexes react with $CBrCl_3$ to give the carbonyltrihalogenobis(phosphine)metal(III) complex and 4,4,4-trichlorobut-1-ene. More highly substituted allyldihalogenobis(phosphine)-rhodium(III) and -iridium(III) complexes give mixtures of the corresponding trichlorobutene and allyl halide. Carbonyldihalogenobis(phosphine)propadienyl-rhodium(III) and -iridium(III) complexes give the 4,4,4-trichlorobut-1-yne either as the sole organic product or mixed with the corresponding organic halides. By analogy with reactions of allyl- and propadienyl-cobaloximes, it is suggested that the trichlorobutenes and trichlorobutynes are formed by a chain reaction involving two steps, the displacement of a five-co-ordinate rhodium(II) or iridium(II) complex by regiospecific attack of trichloromethyl radicals on the γ-carbon of the allyl or propadienyl group and the formation of trichloromethyl radicals by reaction of the rhodium(II) or iridium(II) complex with $CBrCl_3$. The organic halide is formed by a concurrent ionic reductive elimination supported by capture of the rhodium(I) or iridium(I) product by $CBrCl_3$.

We recently described a number of novel reactions in which allyl-, propadienyl-, and benzyl-cobaloximes react with polyhalogenomethanes, such as bromotrichloromethane, to give halogenocobaloxime(III) and polyhalogeno-organic products [equations (1)—(3); Hdmg = dimethylglyoximate(1−), py = pyridine, imH = imidazole].[1-3] Each of these processes is believed to be a chain reaction in which the propagation steps involve the reaction of the polyhalogenomethane with a low concentration of cobaloxime(II) [equation (4); M = $Co(Hdmg)_2L$] to give a polyhalogenomethyl radical which then reacts rapidly with the bulk organocobaloxime(III) reagent to regenerate cobaloxime(II) and give the observed organic product [equation (5); M = $Co(Hdmg)_2L$]. The particular novelty of the process lay in reaction (5) which, for various types of R (allyl, propadienyl, or benzyl) represented the first examples of $S_{H}2'$ displacement of a transition metal from carbon by attack at unsaturated carbon,* and the first example of $S_{H}2$ homolytic displacement at saturated carbon in solution.[2]

$$CCl_4 + [Co(CH_2CH{=}CH_2)(Hdmg)_2(py)] \xrightarrow{100\%} CCl_3CH_2CH{=}CH_2 + [CoCl(Hdmg)_2(py)] \quad (1)$$

$$CBrCl_3 + [Co(CH{=}C{=}CMe_2)(Hdmg)_2(imH)] \xrightarrow{>90\%} CCl_3CMe_2C{\equiv}CH + [CoBr(Hdmg)_2(py)] \quad (2)$$

$$CBrCl_3 + [Co(CH_2Ph)(Hdmg)_2] \xrightarrow{>70\%} PhCH_2CCl_3 + [CoBr(Hdmg)_2(imH)] \quad (3)$$

$$M^{\bullet} + CBrCl_3 \longrightarrow MBr + CCl_3^{\bullet} \quad (4)$$

$$CCl_3^{\bullet} + MR \longrightarrow RCCl_3 + M^{\bullet} \quad (5)$$

Such processes should not be confined to the organocobaloximes, but should be observable, in principle, for any n-co-ordinate organometallic complex (1) with the metal in the mth oxidation state, where that metal can exist, preferentially transiently, as the corresponding $(n-1)$-co-ordinate complex (2) with the metal in the $(m-1)$th oxidation state.

$$\begin{array}{cc} [M^{m}RL_{n-1}] & [M^{m-1}L_{n-1}] \\ (1) & (2) \end{array}$$

In view of suggestions[4,5] that rhodium(II) and iridium(II) complexes may be intermediates in some oxidative-addition reactions of iridium(I) and rhodium(I) complexes with organic halides, we started our investigation of other metal systems with the reaction of a series of allyl-rhodium(III) and -iridium(III) complexes with polyhalogenomethanes.

RESULTS AND DISCUSSION

The complexes listed in Table 1 were prepared by reaction of the appropriate organic halide with $[Ir^{I}Cl(CO)(PPh_3)_2]$ or $[M^{I}X(CO)(PMe_2Ph)_2]$ (M = Rh or Ir, X = Cl or Br) in benzene or chloroform.[6,7] Several of the organo-rhodium(III) and -iridium(III) complexes were isolated; the majority have been characterised elsewhere and were identified *in situ* from their ^1H n.m.r. spectra.[6,7] Each of the organo-rhodium(III) or -iridium(III) complexes was treated with bromotrichloromethane and, in some cases, other polyhalogeno-compounds, and the products (Table 2) were identified by ^1H n.m.r. spectra and g.l.c., and by comparison with authentic materials prepared in earlier studies.[3]

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* Displacement of tributyltin radicals from allyltributyltin complexes has also been observed (J. Grignon, C. Servens, and M. Pereyre, *J. Organometallic Chem.*, 1975, **96**, 225).

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[4] D. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

[5] J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 7908.

[6] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1562.

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

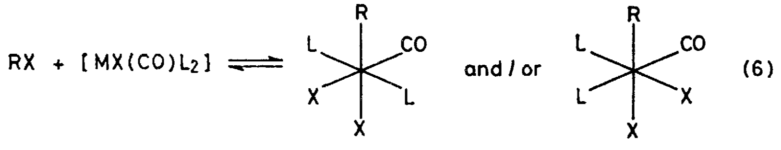
There are two main problems in studies of organo-iridium and -rhodium complexes of the type $[MRX_2(CO)L_2]$ (L = a tertiary phosphine, X = halide). First, there may be up to nine configurational isomers (six isomers where only one type of halogen is involved) and, secondly, they are likely to undergo reversible reductive-elimination–oxidative-addition processes [equation (6); L = PMe_2Ph or PPh_3], the latter being more common in the case of rhodium complexes. Fortunately, only two configurations, (I) and (II), seem to predominate and these have been well characterised by ^1H n.m.r. using phosphorus coupling and i.r. data.[6] Under our conditions we have used only the *trans* configurations (with respect to the two phosphine ligands), believed to be (I).

TABLE 1

Hydrogen-1 n.m.r. spectra of allyl- and propadienyl-metal complexes $[MR(X)Y(CO)L_2]$

						^1H N.m.r. (δ/p.p.m.)					
R	M	X	Y	L	Solvent	H^1	H^2	H^3	Other	Phosphine (CH_3)	$^2J(PH) + {}^3J(PH)$ [a]
$CH_2CH{=}CH_2$	Rh	Br	Br	PMe_2Ph	Benzene	2.60	*ca.* 5.4	4.40,		1.94, 1.99	
	Ir	Cl	Cl	PMe_2Ph	$CDCl_3$	2.6	5.48	4.25		2.06, 2.16	8, 8.8 [b]
$CH_2CMe{=}CH_2$	Rh	Cl	Cl	PMe_2Ph	Benzene	2.82		4.37, 4.25	1.31	1.90, 1.97	8.2, 8.2 [c]
	Ir	Cl	Cl	PMe_2Ph	$CDCl_3$	2.44		4.12, 4.00	1.23	2.07, 2.18	8.8, 8.2
$CH_2CH{=}CHMe$	Rh	Br	Br	PMe_2Ph	Benzene	2.61	*ca.* 5.0	*ca.* 4.9	1.19	1.95, 2.02	
$CH_2CH{=}CHPh$	Rh	Br	Br	PMe_2Ph	Benzene	2.80	obscured			2.00, 2.06	
	Rh	Cl	Cl	PMe_2Ph	Benzene	2.73	obscured			*ca.* 1.95	
$CH{=}C{=}CH_2$	Rh	Br	Br	PMe_2Ph	Benzene	4.06		5.90		1.73, 2.14	8, 8
	Ir	Br	Cl [d]	PPh_3	$CDCl_3$	3.64		5.40			
CH_2Ph	Rh	Br	Br	PMe_2Ph	Benzene	3.40				2.00, 2.07	
	Ir	Cl	Br	PMe_2Ph	Benzene	3.15				*ca.* 2.05	

[a] Sum of couplings in Hz to phosphine methyl protons. [b] Ref. 7. [c] Ref. 6. [d] The dichloro-derivative was prepared in ref. 11.


(6)

(I) (II)

TABLE 2

Organometallic products from allyl halides (RX) and metal(I) species $[MY(CO)L_2]$, and their products of reaction with polyhalogenomethane reagents

Solvent	RX	L	M	Y	Time (yield/%)	Organometallic product	Reagent	Conditions		Organic products (yield/%) [a]
								Time	θ_c/°C [b]	
Benzene	C_3H_5Br	PMe_2Ph	Rh	Br	30 min (90)	$[Rh(CH_2CH{=}CH_2)Br_2(CO)L_2]$	$CBrCl_3$	2 min	r.t.	$CCl_3CH_2CH{=}CH_2$ (sole) [c]
							CBr_4	<2 min	r.t.	$CBr_3CH_2CH{=}CH_2$ (sole) [c]
							Cl_3CCN	<20 min	r.t.	$NCCCl_2CH_2CH{=}CH_2$ (sole) [d]
							CCl_4 [e]	2 h	60	$CCl_3CH_2CH{=}CH_2$ (48), $CH_2ClCH{=}CH_2$ (52) [f]
							CCl_4 [g]	4 h	25	$CCl_3CH_2CH{=}CH_2$ (66), $CH_2ClCH{=}CH_2$ (34) [f,h]
							CCl_4 [i]	3 h	25	$CCl_3CH_2CH{=}CH_2$ (75), $CH_2ClCH{=}CH_2$ (25) [h]
Benzene	$MeCH{=}CHCH_2Br$	PMe_2Ph	Rh	Br	37 min (75)	$[Rh(CH_2CH{=}CHMe)Br_2(CO)L_2]$ [j]	$CBrCl_3$	2 min	25	$CCl_3CHMeCH{=}CH_2$ (sole) [c]
Benzene	$PhCH{=}CHCH_2Br$	PMe_2Ph	Rh	Br	12 min (95)	$[Rh(CH_2CH{=}CHPh)Br_2(CO)L_2]$ [j]	$CBrCl_3$	4 h	60	$CCl_3CHPhCH{=}CH_2$ (40), $CH_2ClCH{=}CHPh$ (60) [k]
Benzene	$PhCH{=}CHCH_2Cl$	PMe_2Ph	Rh	Cl	5 h (85)	$[Rh(CH_2CH{=}CHPh)Cl_2(CO)L_2]$ [j]	$CBrCl_3$	6 h	60	$CCl_3CHPhCH{=}CH_2$ (22), $CH_2ClCH{=}CHPh$ (78)
Benzene	$CH_2{=}CMeCH_2Cl$	PMe_2Ph	Rh	Cl	30 min (50)	$[Rh(CH_2CMe{=}CH_2)Cl_2(CO)L_2]_2$ [j]	$CBrCl_3$	5 min	25	$CCl_3CH_2CMe{=}CH_2$ (sole)
Benzene	$PhCH_2Br$	PMe_2Ph	Rh	Br	24 h (90)	$[Rh(CH_2Ph)Br_2(CO)L_2]$ [j]	$CBrCl_3$	24 h	60	$PhCH_2CCl_3$ (33), $PhCH_2Cl$ (33) [h,l] $PhCH_2Br$ (33)
Benzene	$HC{\equiv}CCH_2Br$	PMe_2Ph	Rh	Br	<3 h (95)	$[Rh(CH{=}C{=}CH_2)Br_2(CO)L_2]$ [j]	$CBrCl_3$	8 h	60	$CCl_3CH_2C{\equiv}CH$ (sole) [c]
$CDCl_3$	C_3H_5Br	PMe_2Ph	Ir	Cl	isolated	$[Ir(CH_2CH{=}CH_2)Cl_2(CO)L_2]$	$CBrCl_3$	2 h	53	$CCl_3CH_2CH{=}CH_2$ (sole)
$CDCl_3$	$CH_2{=}CMeCH_2Cl$	PMe_2Ph	Ir	Cl	isolated	$[Ir(CH_2CMe{=}CH_2)Cl_2(CO)L_2]$	$CBrCl_3$	5 h	53 [m]	$CCl_3CH_2CMe{=}CH_2$ (sole)
$CDCl_3$	C_3H_5Br	PPh_3	Ir	Cl	isolated	$[Ir(CH_2CH{=}CH_2)Br(Cl)(CO)L_2]$	$CBrCl_3$	5 h	50	$CCl_3CH_2CH{=}CH_2$ (78) $CH_2ClCH{=}CH_2$ (22) [h]
$CDCl_3$	C_3H_5Cl	PPh_3	Ir	Cl	isolated	$[Ir(CH_2CH{=}CH_2)Cl_2(CO)L_2]$	$CBrCl_3$	3 h	55	$CCl_3CH_2CH{=}CH_2$ (66), $CH_2ClCH{=}CH_2$ (34)
						$[Ir(CH_2CH{=}CH_2)Cl_2(CO)L_2]$	CCl_4	3 h	60	$CCl_3CH_2CH{=}CH_2$ (40) $CH_2ClCH{=}CH_2$ (60)
$CDCl_3$	$MeCH{=}CHCH_2Br$	PPh_3	Ir	Cl	isolated	$[Ir(CH_2CH{=}CHMe)Br(Cl)(CO)L_2]$	$CBrCl_3$	10 min	48	$CCl_3CHMeCH{=}CH_2$ (50), $CH(Me)ClCH{=}CH_2$ (50)
$CDCl_3$	$HC{\equiv}CCH_2Br$	PPh_3	Ir	Cl	isolated	$[Ir(CH{=}C{=}CH_2)Br(Cl)(CO)L_2]$	$CBrCl_3$	4 h	40	$CCl_3CH_2C{\equiv}CH$ (sole)
Benzene	$PhCH_2Br$	PMe_2Ph	Ir	Cl	10 h (20)	$[Ir(CH_2Ph)Br(Cl)(CO)L_2]$	none			$PhCH_2Cl$ (*ca.* 1 mol)
$CDCl_3$	$PhCH_2Br$	PMe_2Ph	Ir	Cl	10 h (0)	[n]	none			$PhCH_2Cl$ (>1 mol)

[a] 'Sole' implies only one organic product detected. [b] r.t. = Room temperature. [c] Inorganic product is $[RhBr_3(CO)L_2]$; allyl bromide is present from the start. [d] Several inorganic products $[RhX_3(CO)L_2]$ (X = halide). [e] Rh : CCl_4 = 1 : 3. [f] Allyl bromide formed first, then converted into allyl chloride. [g] Rh : CCl_4 = 1 : 20. [h] No C_2Cl_6 detectable by g.l.c. [i] Rh : CCl_4 = 1 : 100. [j] Not isolated. [k] Cinnamyl bromide formed first, then converted into cinnamyl chloride. [l] Benzyl chloride formed from benzyl bromide. [m] Similar result in 16 h at 25 °C. [n] No organometallic product detected.

Fortunately, the use of different halide ligands does not appear to influence the course of reaction and hence positional changes of non-identical halide ligands have been ignored.

$$CBrCl_3 + [M^{III}(CH_2CH{=}CHR)X_2(CO)(PMe_2Ph)_2] \longrightarrow \underset{(4)}{CCl_3CHRCH{=}CH_2} + [M^{III}BrX_2(CO)(PMe_2Ph)_2] \quad (7)$$

	M	R	X	
(3)	Rh	H	Br	(5)
(6)	Ir	H	Cl	(7)
(10)	Rh	Me	Br	(5)
(11)	Ir	Me	Cl	(7)

The extent of formation of the organorhodium(III) product from 1 : 1 mixtures of organic halide and rhodium(I) complex is shown in Table 2. Since the addition of allyl halide to the rhodium(I) complex is reversible, the further reactions of the organorhodium(III) complexes were usually carried out in the presence of detectable quantities of organic halides and rhodium(I) species.

The reaction of $[Rh(CH_2CH{=}CH_2)Br_2(CO)(PMe_2Ph)_2]$ (3) with $CBrCl_3$ in benzenes parallels exactly the corresponding reactions of allylcobaloxime(III) complexes;[3] at room temperature within a few minutes the reaction is complete and 4,4,4-trichlorobut-1-ene (4, R = H) is the organic product and $[Rh^{III}Br_3(CO)(PMe_2Ph)_2]$ (5) is the main inorganic product [equation (7)]. Allylcarbonyldichlorobis(dimethylphenylphosphine)iridium(III) (6) reacts similarly in $CDCl_3$ solution [equation (7)]. We therefore postulate a chain reaction [equations (8) and (9)] in which trichloromethyl radicals and the rhodium(II) or iridium(II) complexes (8) and (9) are the propagating species. Radical initiators may be provided by homolysis of either (3), (6), or $CBrCl_3$, or by an external radical [*e.g.* Q in equation (10)].

$$CCl_3^{\bullet} + [M^{III}(CH_2CH{=}CHR)X_2(CO)(PMe_2Ph)_2] \longrightarrow CCl_3CHRCH{=}CH_2 + [M^{II}X_2(CO)(PMe_2Ph)_2] \quad (8)$$

(8) M = Rh, X = Br
(9) M = Ir, X = Cl

$$\underset{(8)\text{ or }(9)}{[M^{II}X_2(CO)(PMe_2Ph)_2]} + CBrCl_3 \longrightarrow \underset{(5)\text{ or }(7)}{[M^{III}BrX_2(CO)(PMe_2Ph)_2]} + CCl_3^{\bullet} \quad (9)$$

The chain character of these reactions is evident from the variable rates and erratic induction periods. In the case of slower reactions the induction period may be reduced by the addition of radical initiators such as benzoyl peroxide; *e.g.* in those cases where carbon tetrachloride is the reagent. The role of the propagating species is particularly interesting: whereas trichloromethyl radicals have been postulated as intermediates in many chain reactions, iridium(II) species of the above type [*e.g.* (9)] have only been suggested as possible intermediates in radical-chain oxidative-addition reactions of some organic halides with iridium(I) species [equations (10)—(13)], although recently some iridium(II) and rhodium(II) complexes containing bulky bidentate phosphine ligands have been isolated.[8]

The reactions of 2- and 3-methylallyl-iridium and -rhodium complexes, (10) and (11), with $CBrCl_3$ in benzene and in $CDCl_3$ are also rapid and near quantitative. The formation of 4,4,4-trichloro-3-methylbut-1-ene from the 3-methylallyl complexes gives further support to equation (5), illustrating the regiospecificity of the homolytic displacement, attack being solely at the γ-carbon of each allylic group. Similarly, $[Ir(CH{=}C{=}CH_2)Br(Cl)(CO)L_2]$ and the slower reacting cinnamyl metal complexes also give regiospecific products of the displacement reaction, but that from the cinnamyl complex is accompanied by appreciable formation of the reductive-elimination product, *i.e.* the cinnamyl halide. Indeed, as outlined below, the formation of the reductive-elimination products gives further information on the nature of that process, and hence of the reverse oxidative-addition process.

$$[IrX(CO)L_2] + Q^{\bullet} \rightleftharpoons [Ir^{II}Q(X)(CO)L_2] \quad (10)$$

$$RX + [Ir^{II}Q(X)(CO)L_2] \rightleftharpoons R^{\bullet} + [Ir^{III}QX_2(CO)L_2] \quad (11)$$

$$R^{\bullet} + [Ir^{I}X(CO)L_2] \rightleftharpoons [Ir^{II}R(X)(CO)L_2] \quad (12)$$

$$RX + [Ir^{II}R(X)(CO)L_2] \rightleftharpoons [Ir^{III}RX_2(CO)L_2] + R^{\bullet} \quad (13)$$

Studies of the corresponding bis(triphenylphosphine)-iridium complexes were hampered by their much lower solubility. However, in all respects the reactions of the allylbis(triphenylphosphine)iridium(III) complexes with $CBrCl_3$ are comparable with those for the bis(dimethylphenylphosphine) complexes, although the yields of reductive-elimination products are correspondingly higher at the expense of the displacement products. In the case of $[Ir^{III}(CH{=}C{=}CH_2)Br(Cl)(CO)(PPh_3)_2]$ [9] the induction period for the reaction in $CDCl_3$ was as much as 4 h, although the regiospecific and quantitative reaction [equation (14)] was complete in <5 h at 50 °C despite the low solubility of the reagent.

$$CBrCl_3 + \underset{(12)}{[Ir^{III}(CH{=}C{=}CH_2)Br(Cl)(CO)(PPh_3)_2]} \longrightarrow CCl_3CH_2C{\equiv}CH + [Ir^{III}Br_2Cl(CO)(PPh_3)_2] \quad (14)$$

The formation of the reductive-elimination products during the radical-chain displacement reactions, especially when CCl_4 is the reagent, provides further inform-

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[8] R. Mason, K. M. Thomas, H. D. Empsall, S. R. Fletcher, P. N. Heys, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1974, 612.

[9] J. P. Collman, C. J. Sears, and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.

ation about the mechanism of reductive elimination. In particular, the formation, in the *initial* stages of reaction, of allyl *bromide* from $[Rh^{III}(CH_2CH{=}CH_2)Br_2(CO)(PMe_2Ph)_2]$ and CCl_4, of cinnamyl *chloride* from $[Ir^{III}(CH_2CH{=}CHPh)Cl_2(CO)(PMe_2Ph)_2]$ and $CBrCl_3$, and of allyl *chloride* from $[Ir^{III}(CH_2CH{=}CH_2)Cl_2(CO)(PPh_3)_2]$ and $CBrCl_3$ [equation (15)] is not consistent with a free-radical process involving the reverse of equations (12) and (13). Had free allyl or substituted allyl radicals been formed they would both have reacted with the excess of polyhalogenomethane to give a different allyl halide from that observed in the initial stages [equations (16) and (17)]. Thus a concerted or ionic reductive elimination can take place even at the same time as a radical-chain process in the presence of a variety of radicals of different character.

$$CYCl_3 + [M^{III}RX_2(CO)L_2] \longrightarrow RX + [M^{III}(CCl_3)X(Y)(CO)L_2] \quad (15)$$

$$R^{\bullet} + CYCl_3 \longrightarrow RY + CCl_3^{\bullet} \quad (16)$$

$$CYCl_3 + [M^{II}X_2(CO)L_2] \longrightarrow CCl_3^{\bullet} + [M^{III}X_2Y(CO)L_2] \quad (17)$$

The further conversion of the allyl bromides into allyl chlorides is more difficult to rationalise. However, a non-radical process seems likely because allyl chloride is formed nearly quantitatively in the *final* stages of the reaction of $[Rh^{III}(CH_2CH{=}CH_2)Br_2(CO)(PMe_2Ph)_2]$ and CCl_4. A similar slow formation of up to 1 mol of benzyl chloride from $[Ir^{III}(CH_2Ph)Br(Cl)(CO)(PMe_2Ph)_2]$ and an excess of benzyl bromide occurs in benzene, whereas the corresponding reaction in $CDCl_3$ leads to significantly more than 1 mol of benzyl chloride, indicating incorporation of chloride from the solvent. Clearly, not only is the reductive elimination of benzyl chloride favoured over that of benzyl bromide, but the rhodium(III) and iridium(III) products must be unstable and react further with the polyhalogenomethyl solvents.

Polyhalogenobutenes are also formed when $[Rh^{III}(CH_2CH{=}CH_2)Br_2(CO)(PMe_2Ph)_2]$ reacts with other polyhalogenomethanes such as trichloroacetonitrile and carbon tetrabromide [equation (18)]. However, whilst these reactions illustrate the possible variety in the proposed chain reaction they are of much less preparative value than in the case of the cheaper allylcobaloximes.[3]

$$\begin{tikzcd}
 & CBr_3CH_2CH{=}CH_2 \\
{[Rh^{III}(CH_2CH{=}CH_2)Br_2(CO)(PMe_2Ph)_2]} \arrow[ur, "CBr_4"] \arrow[dr, "Cl_3CCN"'] & & (18) \\
 & CCl_2(CN)CH_2CH{=}CH_2
\end{tikzcd}$$

EXPERIMENTAL

Materials.—Rhodium trichloride (on loan) and chloroiridic acid were supplied by Johnson, Matthey. The allyl halides were commercial products whose purity was ascertained by ^1H n.m.r. spectroscopy. They were distilled prior to use where necessary. Polyhalogenomethanes were commercial products used without further purification.

Preparations.—$[RhX(CO)(PMe_2Ph)_2]$ (X = Cl *or* Br). Carbon monoxide was passed for 4 h through a refluxing solution of $RhCl_3{\cdot}nH_2O$ (1.47 g) in absolute ethanol under nitrogen. After cooling, dimethylphenylphosphine (1.55 cm^3, 10.8 mmol) in absolute ethanol (15 cm^3) was added dropwise. The reaction mixture was stirred for 15 min and the solvent was removed *in vacuo*. Crystallisation from hot methanol (30 cm^3) gave yellow needles of carbonylchlorobis(dimethylphenylphosphine)rhodium(I), yield 1.24 g (Found: C, 46.2; H, 5.0; Cl, 8.1. $C_{17}H_{22}ClOP_2Rh$ requires C, 46.0; H, 5.0; Cl, 8.0%). Bromocarbonylbis(dimethylphenylphosphine)rhodium(I) was prepared by the literature method[10] (Found: C, 41.85; H, 4.6; Br, 16.4. $C_{17}H_{22}BrOP_2Rh$ requires C, 41.9; H, 4.5; Br, 16.2%).

$[RhRX_2(CO)(PMe_2Ph)_2]$ (X = Br, R = $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$, $CH{=}C{=}CH_2$, CH_2Ph, *or* $CH_2CH{=}CHPh$; X = Cl, R = $CH_2CMe{=}CH_2$, CH_2Ph, or $CH_2CH{=}CHPh$). All the rhodium(III) oxidative-addition products were prepared *in situ* in an n.m.r. tube under nitrogen by addition of a stoicheiometric quantity of the organic halide to a solution of the rhodium(I) reagent in benzene. Formation of the organorhodium(III) adduct was monitored by ^1H n.m.r. spectroscopy (Tables 1 and 2). Allyldibromocarbonylbis(dimethylphenylphosphine)rhodium(III), which crystallised from such a solution, was isolated (Found: C, 39.8; H, 4.6; Br, 26.5. $C_{20}H_{27}Br_2OP_2Rh$ requires C, 39.5; H, 4.5; Br, 26.3%).

$[IrCl(CO)(PMe_2Ph)_2]$ *and* $[IrRCl_2(CO)(PMe_2Ph)_2]$. Carbonylchlorobis(dimethylphenylphosphine)iridium(I) was prepared from $[Ir^{III}Cl_2H(CO)(PMe_2Ph)_2]$ by the literature method[9] and characterised by i.r. and ^1H n.m.r. spectroscopy. Allyl-, 2-methylallyl-, and 3-methylallyl-carbonyldichlorobis(dimethylphenylphosphine)iridium(III) were prepared as follows. The allyl halide (2—5 mmol) was added to $[Ir^{I}Cl(CO)(PMe_2Ph)_2]$ (0.30 g, 0.56 mmol) in benzene (6 cm^3). After 20 min at room temperature, light petroleum (b.p. 60—80 °C) was added and the white precipitate was filtered off. Since the ^1H n.m.r. spectra showed no impurities the complexes were used without further purification.

$[IrCl(CO)(PPh_3)_2]$ *and* $[IrR(Cl)X(CO)(PPh_3)_2]$. Carbonylchlorobis(triphenylphosphine)iridium(I) was prepared by the literature method.[8] The complexes $[IrR(Cl)X(CO)(PPh_3)_2]$ (X = Br, R = $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$, or $CH{=}C{=}CH_2$; X = Cl, R = $CH_2CH{=}CH_2$) were prepared by the literature method[11] and isolated before use. The complexes $[Ir(CH_2Ph)Cl(X)(CO)(PPh_3)_2]$ (X = Cl or Br) were prepared *in situ* in an n.m.r. tube under nitrogen as described above for the organorhodium(III) complexes.

Reaction of Organo-rhodium(III) *and -iridium*(III) *Complexes with Polyhalogenomethanes* (CBr_4, $CBrCl_3$, CCl_4, *or* CCl_3CN).—The polyhalogenomethane (*ca.* 0.3 mmol) was added to a solution (or suspension in the case of triphenylphosphine complexes) of the organo-rhodium(III) or

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[10] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.

[11] J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574.

-iridium(III) complex (*ca.* 0.1 mmol) in benzene or chloroform at room temperature. The solution was heated to start the reaction where necessary and the reaction was followed by ^1H n.m.r. spectroscopy. Products were identified by comparison of ^1H n.m.r. spectra and g.l.c. with authentic materials.[3] Tribromocarbonylbis(dimethylphenylphosphine)rhodium(III) was isolated from appropriate reaction mixtures (Found: C, 32.3; H, 3.6; Br, 37.4. $C_{17}H_{22}Br_3OP_2Rh$ requires C, 31.6; H, 3.4; Br, 37.1%).

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