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Oxidative-Addition and Reductive-Elimination Reactions of Carborane–Iridium Complexes

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The addition reactions of diatomic molecules, X–Y (X–Y = HCl, HBr, HI, Cl_2 and Br_2) to square-planar d^8 carborane–iridium(I) complexes of general formula trans-*[Ir(σ-carb)(CO)L_2], where L = PPh_3, $PMePh_2$ and carb = –2–R–1,2– and –7–R–1,7–B_{10}-C_2H_{10} (R = H, CH_3, C_6H_5) have been investigated in both the solid state and in solution of a variety of solvents. The stereochemistry of the obtained octahedral adducts was determined by i.r. and ^1H nmr spectroscopy. The stereochemical course of the addition reactions appears to be dependent on the reaction medium and on the type of the carborane anionic ligands. Evidence suggesting that these oxidative-addition reactions proceed through solvent-containing intermediates when they are carried out in coordinating solvents is reported.*

The HX adducts of general formula [Ir(H)(X)(σ-carb)(CO)L_2], (X = Cl, Br, I), reductively eliminate the carborane molecule, H-carb. Factors governing these elimination reactions are also described.

Introduction

Oxidative-addition and its reverse, reductive elimination, are very important reactions in transition metal chemistry and catalysis and in this connection the role of d^8 metal complexes of the type *trans*-[IrX(CO)L_2], where L = tertiary phosphines or arsines and X = halogen, has been widely investigated [1–7].

In a previous paper [8] we have reported the results of an investigation on the oxidative-addition reactions of molecular hydrogen to 1,2- and 1,7-dicarba-*closo*-dodecarborane(12)–Iridium(I) complexes, isoelectronic and isostructural with Vaska's complex, formed through carborane carbon–metal σ bonds. The stereochemical course of these reactions appears to be solvent dependent and three octahedral isomeric adducts have been obtained and characterized. On the other hand, it is a well-known fact that the stereochemical course of the addition of hydrogen to complexes of the type *trans*-[IrX(CO)L_2] is always stereospecifically *cis* and is unaffected by the nature of the solvent, a single isomer in which the phosphine ligands remain *trans* being formed [1]. The peculiar behaviour shown by the carborane–iridium(I) complexes toward hydrogen addition prompted us to extend our investigation on the oxidative-addition reactions to these complexes in an attempt to assess the role of the carborane ligand in determining the stereochemistry of the addition reactions. Thus, we report herein a study of the oxidative additions of diatomic molecules, X–Y (X–Y = HCl, HBr, HI, Cl_2, Br_2) to the complexes *trans*-[Ir(σ-carb)(CO)L_2], where L = PPh_3, $PMePh_2$ and carb = –2–R–1,2–, –7–R–1,7–$B_{10}C_2H_{10}$ (R = H, CH_3, C_6H_5), carried out in solution and in the solid state.

In addition we also present some qualitative data on the reductive elimination reaction of the carborane molecule, H-carb, from the complexes [Ir(H)(X)(σ-carb)(CO)L_2], X = Cl, Br, I, in dependence on the coordination sphere and on the configuration.

Results and Discussion

Oxidative Addition of Hydrogen Halides and Halogens

The complexes *trans*-[Ir(σ-carb)(CO)L_2], where L = PPh_3 and $PMePh_2$, carb = –2–R–1,2– and –7–R–1,7–$B_{10}C_2H_{10}$ (R = H, CH_3, C_6H_5), readily react with diatomic molecules, as HCl, HBr, HI, Cl_2 and Br_2, at room temperaure either in solution or in the solid state to give octahedral addition products.

TABLE I. Analytical Data for the Carborane–Iridium(III) Complexes, $[Ir(X)(Y)(\sigma\text{-carb})(CO)L_2]$.

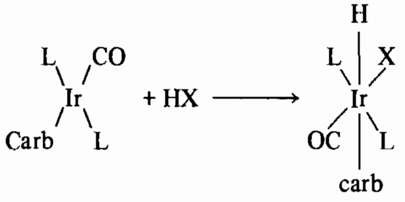
	Complex	Conf.	Mp. °C	Analysis, % (calcd.)		
				C	H	halogen
1)	$1\text{-}[Ir(H)(Cl)(CO)(PPh_3)_2]\text{-}$	A	130[a]	49.81	4.48	3.75
	$\text{-}2\text{-}H\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(50.67)	(4.58)	(3.83)
2)	$1\text{-}[Ir(H)(Cl)(CO)(PPh_3)_2]\text{-}$	A	153[a]	50.18	4.53	3.68
	$\text{-}7\text{-}H\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(50.67)	(4.58)	(3.83)
3)	$1\text{-}[Ir(H)(Cl)(CO)(PPh_3)_2]\text{-}$	B	120–121[a]	51.55	4.40	3.95
	$\text{-}2\text{-}CH_3\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(51.19)	(4.72)	(3.78)
4)	$1\text{-}[Ir(H)(Cl)(CO)(PPh_3)_2]\text{-}$	A	124–126[a]	50.49	4.60	4.02
	$\text{-}7\text{-}CH_3\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(51.19)	(4.72)	(3.78)
5)	$1\text{-}[Ir(H)(Cl)(CO)(PPh_3)_2]\text{-}$	A	113–115[a]	54.60	4.61	3.76
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(54.06)	(4.63)	(3.54)
6)	$1\text{-}[Ir(H)(Cl)(CO)(PMePh_2)_2]\text{-}$	A	118–120[a]	43.93	5.10	4.65
	$\text{-}7\text{-}CH_3\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(44.24)	(4.95)	(4.35)
7)	$1\text{-}[Ir(H)(Cl)(CO)(PMePh_2)_2]\text{-}$	A	131–133[a]	48.30	4.89	4.10
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(47.90)	(4.83)	(4.04)
8)	$1\text{-}[Ir(H)(Br)(CO)(PPh_3)_2]\text{-}$	A	92–93[a]	51.44	4.14	7.49
	$\text{-}7\text{-}C_6H_5\text{-}1,7(\sigma\text{-}B_{10}C_2H_{10})$			(51.72)	(4.43)	(7.65)
9)	$1\text{-}[Ir(H)(I)(CO)(PPh_3)_2]\text{-}$	A	103[a]	49.55	4.15	12.25
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(49.49)	(4.24)	(11.63)
10)	$1\text{-}[Ir(H)(Cl)(CO)(CH_3CN)(PPh_3)]\text{-}$	C + D	n.d[b]	44.53	4.34	4.61[d]
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(44.70)	(4.40)	(4.55)
11)	$1\text{-}[Ir(H)(Cl)(CO)(C_6H_5CN)(PPh_3)]\text{-}$	C + D	n.d[b]	49.05	4.25	4.18[d]
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(49.96)	(4.31)	(4.21)
		E	148–149[c]	41.87	4.59	8.15
				(42.45)	(4.63)	(8.35)
12)	$1\text{-}[Ir(Cl)_2(CO)(PMePh_2)_2]\text{-}$	F	193–194[c]	42.51	4.54	8.01
	$\text{-}7\text{-}CH_3\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(42.45)	(4.63)	(8.35)
13)	$1\text{-}[Ir(Cl)_2(CO)(PMePh_2)_2]\text{-}$	E	145–146[e]	45.82	4.66	7.73
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(46.15)	(4.53)	(7.78)
14)	$1\text{-}[Ir(Br)_2(CO)(PMePh_2)_2]\text{-}$	E + F	n.d.[b]	41.87	3.99	15.07
	$\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$			(42.05)	(4.13)	(15.98)

[a] Decomposes without melting on heating in a capillary tube sealed under vacuum. [b] Not determined: mixture of isomers. [c] Decomposes on melting in a capillary tube sealed under vacuum. [d] Complex *10*: N = 1.74(1.80%); complex *11*; N = 1.65(1.67%).

Table I lists the obtained carborane–iridium(III) adducts with the pertinent analytical data. The configuration of these iridium(III) derivatives follows from i.r. and ^{1}H nmr spectroscopic data which are reported in Table II.

Hydrogen halides

With the exception of the iridium(I) derivative containing the $-2-CH_3-1,2-B_{10}C_2H_{10}$ ligand being unreactive toward gaseous hydrogen halides in the solid state, the crystalline carborane–iridium(I) complexes add stereospecifically gaseous hydrogen chloride, bromide and iodide giving only octahedral *cis* addition products (complexes *1, 2, 4–9* of Table I) having the configuration *A* (eqn. 1).



A (1)

X = Cl, Br, I; carb = $-2-H-1,2-$, $-7-R-1,7-B_{10}C_2H_{10}$ (R = H, CH_3, C_6H_5)

The obtained complexes exhibit the hydride proton nmr resonance as a triplet centered at τ 21–22 (J_{PH} ca. 17–18 Hz), in agreement with a structure in which

TABLE II. Infrared and ^{1}H N.m.r. Data for the Carborane–Iridium(III) Adducts.

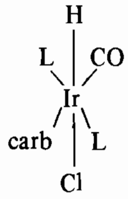
	Complex	Conf.	ν(Ir–H)^a, cm^{-1}		ν(CO)^a, cm^{-1}		ν(Ir–Cl)^a, cm^{-1}	Hydride Resonance^b		PCH$_3$ Resonance^b		Other Resonances^b	
			nujol	CH$_2$Cl$_2$	nujol	CH$_2$Cl$_2$	nujol	τ	J(P–H)	τ	J(P–H)	τ	Assignment
1)	1-[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]-	A	2170m	2174m	2044s	2047s	307w	21.44t	17.4			7.20s	carborane
	-2-H-1,2-(σ-B$_{10}$C$_2$H$_{10}$)	B	2238m	2256m	2051s	2048s	265w	26.14t	11.0			7.10s	CH proton
					2068sh								
					2040sh								
2)	1-[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]-	A	2170m	2162m	2044s	2040s	310w	21.15t	17.4			7.60s	carborane
	-7-H-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	B	2234m	2252m	2056s	2051s	250w	26.28t^c	11.0			7.71s	CH proton
3)	1-[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]-	B	2243m	2234m	2036s	2041s	263w	25.33t	11.9			7.87s	carborane
	-2-CH$_3$-1,2-(σ-B$_{10}$C$_2$H$_{10}$)												CH$_3$ protons
4)	1-[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]-	A	2179m	2165m	2039s	2042s	315w	21.06t	17.4			8.84s	carborane
	-7-CH$_3$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)				2049sh								CH$_3$ protons
5)	1-[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]-	A	2185m	2170m	2035s	2044s	310w	21.10t	18.3				
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	B	2243m	2236m	2043s	2050s	260w	25.53t	11.0				
6)	1-[Ir(H)(Cl)(CO)(PMePh$_2$)$_2$]-	A	2153m	2149m	2037s	2034s	310w	22.66t	17.4	7.60t	4.1	8.60s	carborane
	-7-CH$_3$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)				2031sh								CH$_3$ protons
7)	1-[Ir(H)(Cl)(CO)(PMePh$_2$)$_2$]-	A	2124m	2119m	2038s	2036s	310w	21.71t	18.3	7.65t	3.7		
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)												
8)	1-[Ir(H)(Br)(CO)(PPh$_3$)$_2$]-	A	2169m	2172m	2040s	2042s		21.67t	17.4				
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)												
9)	1-[Ir(H)(I)(CO)(PPh$_3$)$_2$]-	A	2180m	2170m	2040s	2042s		22.75t	17.4				
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)												
10)	1-[Ir(H)(Cl)(CO)(CH$_3$CN)(PPh$_3$)]-	C^c	2205m	–	2047s	–	310w	28.06d	12.8			8.05s	nitrile
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	D^c	2245m	–	2047s	–	265w	27.00d	10.1			8.17d^d	CH$_3$ protons
11)	1-[Ir(H)(Cl)(CO)(C$_6$H$_5$CN)(PPh$_3$)]-	C^c	2204m	–	2048s	–	310w	27.55d	13.2				
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	D^c	2244m	–	2048s	–	260w	26.79d	10.5				
12)	1-[Ir(Cl)$_2$(CO)(PMePh$_2$)$_2$]-	E			2054s	2057s	280; 315w			7.53t	4.4	7.72s	carborane
	-7-CH$_3$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	F			2045s	2058s	330w			7.84t	5.5	7.72s	CH$_3$ protons
13)	1-[Ir(Cl)$_2$(CO)(PMePh$_2$)$_2$]-	E			2060s	2062s	280; 315w			7.55t	4.6		
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	F			2075s	2082s	330w			7.68t	4.0		
14)	1-[Ir(Br)$_2$(CO)(PMePh$_2$)$_2$]-	E			2048s	2062s				7.35t	4.0		
	-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$)	F			2083s	2084s				7.52t	4.0		

[a] Key: s, strong; m, medium; w, weak; sh, shoulder. [b] Measured in CDCl$_3$ solution, at *ca.* 27 °C and 60 MHz with a Brucker WP-60 FT spectrometer. τ values (±0.02) in ppm relative to internal TMS (τ = 10.00); J(P–H) values ±0.1 Hz; t = triplet; d = doublet; s = singlet. [c] Complex *10*: ν(CN) = 2290 cm^{-1}, w(nujol). Complex *11*: ν(CN) = 2330 cm^{-1}, w(nujol). [d] J(P–H) = 1.8 Hz.

the two phosphine ligands are mutually *trans*. Moreover, the observed values for the hydrido chemical shift indicate that these adducts contain the hydride *trans* to the carboranyl group [8]. In addition, the far-infrared spectra of the hydrogen chloride adducts show the iridium–chlorine stretching absorptions around 310 cm^{-1} corresponding to chlorine *trans* to carbon monoxide [9].

The lack of reactivity toward gaseous hydrogen halides exhibited by the crystalline derivative of iridium(I) containing the $-2-CH_3-1,2-B_{10}C_2H_{10}$ ligand is possibly due to steric congestion in the coordination sphere caused by the presence around the metal atom of a bulky carboranyl group together with two triphenylphosphines having high cone angle rather than to electronic factors. On the other hand, this complex slowly adds hydrogen chloride when it is suspended in benzene yielding stereospecifically a *trans* addition product (complex *3*) having the structure B.

B

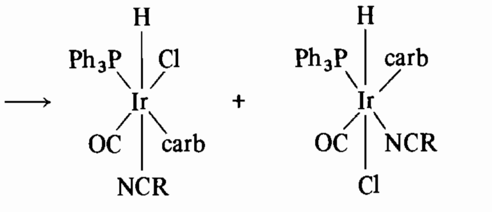


carb = $-2-CH_3-1,2-B_{10}C_2H_{10}$
L = PPh_3,

The ^1H (hydride) nmr spectrum of *3* exhibits the hydrido resonance as a triplet centered at τ 25.33 (J_{PH} = 10.9 Hz) in accordance with an hydrido ligand *trans* to Cl and *cis* to two equivalent phosphorus nuclei [10]. In addition, the far infrared spectrum of *3* exhibits the ν(Ir–Cl) absorption at 263 cm^{-1}, suggesting the chlorine to be *trans* to H [9], and then the structure *B* accommodates all these data. The other carborane-iridium(I) complexes react with hydrogen chloride, bromide or iodide in solution of dry non polar solvents, as benzene or dichloromethane, yielding only products of *cis* addition, structure *A*. On the other hand, mixures of *cis* and *trans* addition products (complexes *1, 2, 5* of Table II) are obtained by reacting the iridium(I)–carborane derivatives with gaseous hydrogen chloride in wet benzene or $CH_3OH–CH_2Cl_2$ solution. A similar solvent effect on the stereochemical course of oxidative addition reactions to iridium(I) complexes was also found by Blake and Kubota [4]. However, the origin of the mixtures of *cis* and *trans* addition products formed in wet benzene of $CH_3OH–CH_2Cl_2$ was not clarified. This observed effect of the polar solvents on the stereochemical course of oxidative additions could be due to several reasons, such as a thermodynamic solvent effect or the formation of solvent-containing intermediates.

In this connection we were able to obtain two isomeric carborane–iridum(III) adducts (complexes 10 and *11*, Table I) containing a coordinated nitrile molecule in place of a triphenylphosphine ligand, $[Ir(H)(Cl)(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$, R = CH_3, C_6H_5, by adding gaseous HCl to *trans*-$[Ir(\sigma\text{-carb})(CO)(PPh_3)_2]$ in acetonitrile/benzene or benzonitrile/benzene (1 to 1) solutions (eqn. *2*).

$$trans\text{-}[Ir(\sigma\text{-carb})(CO)(PPh_3)_2] \xrightarrow[\text{RCN/benzene}]{\text{+HCl}}$$



(2)

10 C, 11 C *10 D, 11 D*

The ^1H (hydride) nmr spectra (Table II) of the reaction mixtures exhibit two doublets [complex *10*: τ 27.00 (J_{PH} = 10.1 Hz) and τ 28.06 (J_{PH} = 12.8 Hz); complex *11*: τ 26.79 (J_{PH} = 10.5 Hz) and τ 27.55 (J_{PH} = 13.2 Hz)], which are consistent with the presence of two isomeric octahedral species having both the hydrido ligand *cis* to the triphenylphosphine. The doublets at lower field are in agreement with a structure in which the hydrido ligand is *trans* to Cl atom (structure *D*), whereas those at higher field can be assigned to H *trans* to RCN group (structure *C*) [11]. In addition, the ^1H nmr spectrum of the acetonitrile–iridium (III) adducts (complex *10*) exhibits the nitrile methyl proton resonance as a doublet centered at τ 8.17 (J_{PH} = 1.8 Hz), attributed to the isomer *D*, and a singlet at τ 8.05, assigned to the isomer *C*. The occurence of the observed doublet for the resonance of the nitrile methyl protons is the result of a long-range P–H coupling [11] and it is further evidence for a *trans* arrangement of CH_3CN and PPh_3 in structure *D*.

Finally, the far-infrared spectra of nitrile containing adducts show the ν(Ir–Cl) absorption at *ca.* 310 and 260 cm^{-1}, which are in agreement with Cl *trans* to CO and *trans* to H, respectively. The formation of two isomers having the structures *C* and *D*, respectively, is then in accordance with all these data. It is to be noted that mixtures of the isomers *C* and *D* are formed by treating with gaseous hydrogen chloride either the bis-phosphino-iridium(I) complex in benzene/nitrile solution or the nitrile–phosphino-iridium(I) complexes in benzene, as summarized in the reaction scheme 1. In both the cases the nmr evidence shows that the isomers *C* and *D* are formed in the ratio 1:2. On treating the isomer mixture of the HCl nitrile–iridium(III) adducts (*10* and *11*) with free triphenylphosphine ligand, a reversible displacement of the nitrile ligand occurs with formation of a mixture of both *cis* and *trans* HCl bis-

$$\begin{tikzcd}
trans\text{-}[\mathrm{Ir}(\sigma\text{-carb})(\mathrm{CO})(\mathrm{PPh_3})_2] \arrow[r, "\mathrm{HCl}"] \arrow[d, shift right, "+\mathrm{RCN}"'] & {[\mathrm{Ir}(\mathrm{H})(\mathrm{Cl})(\sigma\text{-carb})(\mathrm{CO})(\mathrm{PPh_3})_2]} \arrow[d, shift right, "+\mathrm{RCN}"'] \\
{[\mathrm{Ir}(\sigma\text{-carb})(\mathrm{CO})(\mathrm{RCN})(\mathrm{PPh_3})]} \arrow[r, "\mathrm{HCl}"] \arrow[u, shift right, "+\mathrm{PPh_3}"'] & {[\mathrm{Ir}(\mathrm{H})(\mathrm{Cl})(\sigma\text{-carb})(\mathrm{CO})(\mathrm{RCN})(\mathrm{PPh_3})]} \arrow[u, shift right, "+\mathrm{PPh_3}"']
\end{tikzcd}$$

10, 11

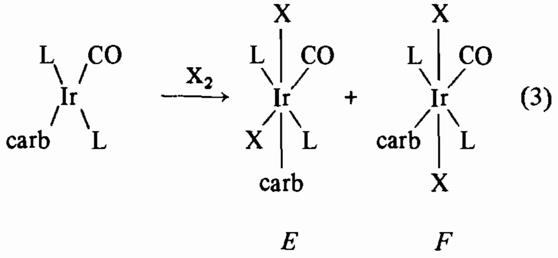
$R = CH_3, C_6H_5$. $\quad$ carb = $-7-C_6H_5-1,7-B_{10}C_2H_{10}$

Scheme 1

phosphino adducts having the structure *A* and *B*, respectively.

Halogens

The carborane–iridium(I) complexes, *trans*-[Ir(σ-carb)(CO)L_2] add irreversibly halogens either in the solid state or in solution. In order to obtain structural information from the ^1H nmr spectra, we decided to prepare iridium(I)–carborane complexes containing the diphenylmethylphosphine ligands, the methyl proton resonances of which permit determination of the relative position of the coordinated phosphines. All of the obtained products of halogen addition (complexes *12–14*) appear to contain the phosphines in mutual *trans* position, as shown by ^1H nmr spectra of the PCH_3 groups (triplet due to the virtual coupling between the phosphorus atoms, Table II). Once the phosphines are shown to be *trans*, only one adduct of *cis-addition (E)* and one adduct of *trans* addition (*F*) are possible (eqn. 3).



(3)

$X_2 = Cl_2, Br_2$; $L = PMePh_2$; carb = $-7-R-1,7-B_{10}C_2H_{10}$ $(R = CH_3, C_6H_5)$.

The mutual position of the halogen atoms on the metal can then be readily determined by far-infrared spectra [1,2].

The addition of gaseous chlorine to solid *trans*-[Ir(σ-carb)(CO)L_2] complexes gives rise stereospecifically to *cis*-addition products having the configuration *E* (complexes *12* and *13*). In fact the infrared spectra of *12* and *13* exhibit two ν(Ir–Cl) absorption bands at *ca.* 315 and 280 cm^{-1}. While the band at 315 cm^{-1} can be assigned to Cl *trans* to CO, that at 280 cm^{-1} is consistent with a chlorine *trans* to carboranyl group. On the other hand, the reaction with gaseous bromine carried out in the solid state affords a mixture of both *cis* (50%) and *trans* (50%) addition products (complexes *14 E* and *14 F*).

A dependence of the stereochemical course of the addition reaction on the type of carboranyl group bonded to the metal was found in the case of the reaction of gaseous chlorine with the carborane iridium(I) complexes carried out in solution. The complex containing $-7-C_6H_5-1,7-B_{10}C_2H_{10}$ as anionic ligand reacts with chlorine in dry benzene yielding a mixture of *cis* (60%) and *trans* (40%) adducts, structure *E* and *F* respectively. The formation of two addition isomers was proved by ^1H nmr and i.r. spectra (Table II). The far infrared spectrum of the product precipitated from the reaction mixture shows absorptions at 330, 315 and 280 cm^{-1} (nujol mull) attributed to iridium–chlorine stretching vibrations. The first one is characteristic of mutually *trans* chlorine atoms and is in accord with *trans* addition, configuration *F*. The absorptions at 315 and 280 cm^{-1} are assigned to two chlorines *trans* to CO and *trans* to the carboranyl group, respectively, and thus a product of *cis* addition (configuration *E*) accommodates these data. On the contrary, a *trans* addition product appears to be the unique product formed by adding chlorine to the iridium(I) complex containing the anionic ligand $-7-CH_3-1,7-B_{10}C_2H_{10}$ under the same conditions.

In order to exclude that isomerization of the hydrogen halide and halogen addition products occurred during work-up, we have carried out spectroscopic (^1H nmr and i.r.) measurements on the reaction mixture solutions and on the products separated by precipitation with methanol or hexane. The spectra obtained appear virtually identical, showing that isomerization is not significant under the experimental conditions. However, it is to be noted that the hydrogen halide adducts undergo reductive elimination reaction on standing in solution at room temperature (see below).

Reductive Elimination of the Carborane Molecule

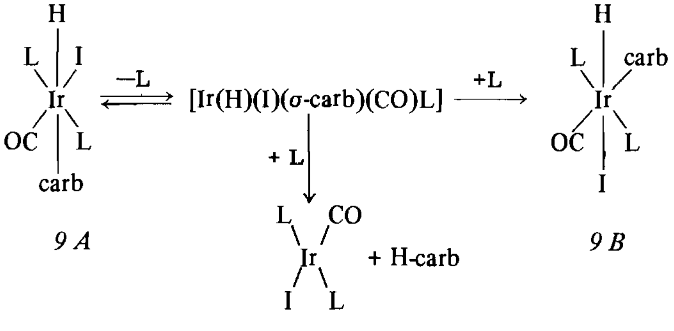
While the complexes of the type [Ir(X)$_2$(σ-carb)(CO)L_2], *12–14*, are stable toward reductive elimination, the hydrogen halide adducts, *1–9*, undergo reductive elimination of the carborane molecule H-carb giving Vaska's complex *trans*-[Ir(X)(CO)L_2], eqn. 4.

$$[\mathrm{Ir(H)(X)(\sigma\text{-}carb)(CO)L_2}] \rightarrow \textit{trans}[\mathrm{Ir(X)(CO)L_2}] + \text{H-carb} \qquad (4)$$

This elimination process, which occurs also in the solid state, takes place slowly on standing in benzene solution already at room temperature. The ease with which these iridium(III) adducts reductively eliminate the carborane molecule depends markedly on the phosphine and halogen ligands and on the type of carboranyl group bonded to the metal. Thus, we have investigated the influence of the ligand system on these reductive elimination processes.

Considering the iridium(III) adducts having the configuration *A*, for given phosphine, *e.g.* PPh_3, and halogen, *e.g.* Cl, the ease of carborane elimination increases in the order carb = –2–H–1,2– < –7–H–1,7– < –7–C_6H_5–1,7– < –7–CH_3–1,7–$B_{10}C_2H_{10}$. A combination of both steric and electronic factors, which are not readily separable, can be invoked to account for this trend. However, for the complexes *1* and *2* containing the unsubstituted 1,2- and 1,7-carboranyl ligands the observed different tendency to undergo reductive elimination must be related exclusively to electronic factors. In fact, these two carborane isomers show similar steric requirements, but the electron-withdrawing ability of the 1,2-derivative is greater than that of the 1,7-derivative [12]. The higher stability toward carborane elimination exhibited by the iridium(III) complex containing the –2–H–1,2–$B_{10}C_2H_{10}$ ligand, *1*, may be due to the higher carborane carbon–iridium bond strength. On the other hand, the greater tendency to lose the carborane molecule shown by the adducts containing the substituted carborane ligands may be determined by the considerable steric crowding effect of these ligands. For the complexes containing –7–C_6H_5–1,7–$B_{10}C_2H_{10}$ and chlorine as anionic ligands, the ease of carborane reductive elimination in dependence on the group 5 donor atom was found to increase on passing from $PMePH_2$ to PPh_3. This trend is in accordance with the order of increasing size of the phosphine ligands ($PMePh_2$ < PPh_3). However, considering that the reductive elimination is enhanced by the factors able to decrease the electron density on the metal atom, it could be also related to the decreasing ligand basicity order: $PMePh_2$ > PPh_3. Finally, for given carboranyl (–7–C_6H_5–1,7–$B_{10}C_2H_{10}$) and phosphine (PPh_3) ligands, the ease of carborane elimination decreases on passing from chlorine to iodine ($Cl \geqslant Br > I$). In fact, the chlorine and bromine derivatives show practically the same ability to undergo reductive elimination, while the iodine derivative is much more stable toward elimination. Electronic factors are invoked to account this observed order. In going from the chlorine to iodine the electron density on the iridium atom increases and consequently the ease of carborane elimination decreases.

As regards the influence of the molecular structure on promoting the elimination reaction, we have found that in the case of the HCl adducts, *e.g.* complexes *5A and 5B*, either the isomers of *cis* (structure *A*) or *trans* (structure *B*) addition appear to be able to eliminate the carborane molecule. But ^1H nmr evidence shows that the *trans* addition isomer, in which the carboranyl and hydrido ligands are mutually *cis*, eliminate H-carb faster than the *cis* addition one, in which the carboranyl and hydrido ligands are mutually *trans*. On the other hand, the HI adduct, complex *9*, exhibits a different reaction pattern. While the *trans* addition product appears to be stable for several days in solution at room temperature, the *cis* addition product undergoes either reductive elimination or isomerization reactions, as shown in *Scheme 2*.



L = PPh_3; carb = –7–C_6H_5–1,7–$B_{10}C_2H_{10}$

Scheme 2

In $CHCl_3$ or CH_2Cl_2 solution at room temperature isomer *9A* finally gives isomer *9B* together with the

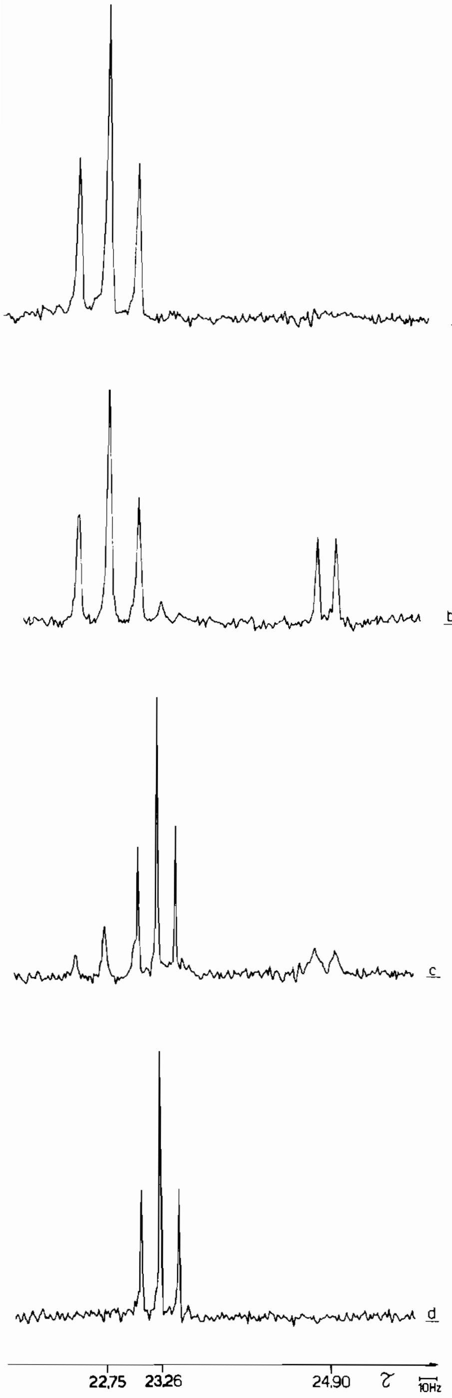


Fig. 1. ^{1}H (hydride) nmr spectrum ($CDCl_3$) of complex *9* as a function of time: a) t = 0 (isomer *9A*); b) t = 15 min; c) t = 300 min; d) t = 600 min (isomer *9B*).

elimination reaction products, *i.e.* carborane and *trans*-[Ir(I)(CO)(PPh_3)$_2$]. This reaction pattern has been investigated by ^{1}H nmr spectroscopy in $CDCl_3$ and CD_2Cl_2 solutions.

The proton (hydride) nmr spectrum (Fig. 1a) of a freshly prepared sample of the isomer *9A* exhibits, as expected, a triplet centered at τ 22.75 (J_{PH} = 17.4 Hz). After a few minutes, a doublet centered at τ 24.90 begins to appear (Fig. *1b*), at the expense of the initial triplet. Finally, a new triplet centered at τ 23.26 (J_{PH} = 11.0 Hz) appears, whereas the triplet at τ 22.75 due to species *9A* and the doublet at τ 24.90 progressively disappear (Fig. *1c* and *1d*). The appearance of the final triplet at τ 23.26 is in agreement with the formation of the isomer *9B* having the hydride *cis* to two mutually *trans* phosphines and *trans* to an iodine atom. The doublet resonance can be assigned to an intermediate five-coordinate species containing one phosphine ligand. The ^{1}H nmr spectra exhibit also a singlet centered at τ 7.04 due to the C–H resonance of the incoming carborane molecule [8] whose intensity increases in the time, as expected on the basis of the reaction *Scheme 2.*

The suggested intermediate five-coordinate species can then explain the observed formation of the isomer *9B* together with the elimination products, namely *trans*-[Ir(I)(CO)(PPh_3)$_2$] and H-carb [13].

Obviously, the suggested reaction scheme must be confirmed by kinetic investigations which are now in progress.

Experimental

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. The complexes *trans*[Ir(σ-carb)(CO)L_2], L = PPh_3, $PMePh_2$ and [Ir(σ-carb)(CO)(RCN)(PPh_3)], R = CH_3, C_6H_5, were prepared as previously reported [8, 11]. All of the reactions involving iridium(I) complexes were carried out under argon atmosphere. The ^{1}H nmr spectra were recorded at *ca.* 27 °C and at 60 MHz in $CDCl_3$ with a WP-60 FTNMR Bruker spectrometer. Infrared spectra were obtained with a Perkin-Elmer model 457 instrument and calibrated against polystyrene film. Melting points were determined by a conventional hot-stage microscope and are uncorrected.

Oxidative-addition Reactions to Trans-*[Ir(σ-carb)(CO)L$_2$] Complexes*

Hydrogen halides (1–9).

Procedure A: Crystals of *trans*-[Ir(σ-carb)(CO)L_2] were placed in a flask which was purged with argon and then kept under anhydrous gaseous hydrogen halides (1 atm) at room temperature. While the complex containing carb = $-2-CH_3-1,2-B_{10}C_2H_{10}$ appeared to be unreactive and was quantitatively recovered unaffected, the other iridium(I)-carborane complexes reacted rapidly and the initiallly orange solid turned white in the course of 3–5 minutes The resulting white iridium(III) adducts were further purified by recrystallization from 1,2-dichloroethane/methanol or benzene/n-hexane (yields >95%)

Procedure B To 0 2–0 3 mmol of iridium(I)–carborane complexes placed in a flask previously purged with argon were added 5–8 ml of the appropriate solvent (dry benzene, wet-benzene, 1,2-dichloroethane, $CH_3OH–CH_2Cl_2$) Solutions of the anhydrous hydrogen halides (*ca* 0 25 *N*) in the respective solvents were added dropwise with stirring The initially orange solutious rapidly turned colorless After stirring for 1 hr, argon was bubbled into the solutions and then white solids were precipitated by addition of n-hexane The crude products were recrystallized from benzene/n-hexane (yields *ca* 80%)

Halogens (12–14)

Procedure A Crystals of *trans*-[Ir(σ-carb)(CO)L_2] placed in a flask previously purged with argon were kept under dry gaseous halogens at room temperature As the initially orange crystals became colorless and no further color change was observed, argon was let into the flask The resulting iridium(III) adducts were then purified by recrystallization from dichloromethane/methanol (yields >90%)

Procedure B To 0 2–0 3 mmol of the iridium(I)–carborane complexes dissolved in 5–8 ml of dry benzene, were added dropwise benzene solutions of the anhydrous halogens at room temperature The obtained solutions were stirred until the initially orange solutions turned colorless or yellow At this point, argon was bubbled into the solutions and then addition of n-hexane caused separation of the white or pale yellow adducts of iridium(III) The crude products were further purified by recrystallization from dichloromethane methanol (yields >80%)

Addition of HCl to 1-[Ir(CO)(PPh$_3$)$_2$]-2-CH$_3$-1,2-(σ-B$_{10}$C$_2$H$_{10}$) in Benzene Suspension (3)

This iridium(I)–carborane complex exhibits poor solubility and thus the addition reaction was carried out in a benzene suspension according to general procedure B The reaction is very slow at room temperature and only after stirring for 8 hr complete dissolution of the starting complex was attained and the initially orange solution turned pale yellow n-Hexane was then added to precipitate the white adduct *3* which was further purified by recrystallization from benzene–methanol As the complex *3* underwent extensive reductive elimination in the course of purification, the yield of the iridium (III) adduct was only *ca* 45%

Addition of HCl to [Ir(σ-carb)(CO)(PPh$_3$)$_2$] in RCN/C$_6$H$_5$ Solutions (10 and 11)

Dry hydrogen chloride was bubbled into a solution of 0 3 g (0 31 mmol) of 1–[Ir(CO)(PPh_3)$_2$]–7–C_6H_5–1,7–(σ-$B_{10}C_2H_{10}$) in 10 ml of acetonitrile/benzene or benzonitrile/benzene (1 to 1) The initially yellow solutions turned colorless in a few seconds The resulting mixtures were evaporated under vacuum and the solids were purified by recrystallization from benzene/n-hexane White crystals of *10* (yield, 85%) or *11* (yield, 91%) where obtained which proved to be mixtures of both *cis* (isomer *C*) and *trans* (isomer *D*) addition products (see text)

Reductive-elimination Reactions of the Carborane Molecule from the Complexes [Ir(H)(X)(σ-carb)(CO)L$_2$' General Procedure

The complexes [Ir(H)(X)(σ-carb)(CO)L_2], X = Cl, Br, I (*1–9*), lose the carborane molecule either on standing in solution (benzene or 1,2-dichloroethane) or on heating the solutions at the reflux temperatures yielding Vaska's analogues The reductive elimination reactions were followed by ir and ^{1}H nmr spectroscopies on the reaction mixtures

References

1 L Vaska, *Accounts Chem Res*, *1*, 335 (1968) and references therein

2 J P Collman and C T Sears Jr, *Inorg Chem*, *7*, 27 (1968)

3 A J Deeming and B L Shaw, *Chem Commun*, 751 (1968)

4 D M Blake and M Kubota, *Inorg Chem*, *9*, 989 (1970)

5 J Halpern, *Accounts Chem Res*, *3*, 386 (1970)

6 P S Braterman and R J Cross, *Chem Soc Rev*, *2*, 271 (1973)

7 J K Stille and K S H Lau, *Accounts, Chem Res*, *10*, 434 (1977)

8 B Longato, F Morandini and S Bresadola, *Inorg Chem*, *15*, 650 (1976), and references therein

9 J M Jenkins and B L Shaw, *J Chem Soc*, 6789 (1965)

10 T G Appleton, H C Clark and L E Manzer, *Coord Chem Rev*, *10*, 335 (1973)

11 B Longato and S Bresadola, *Inorg Chim Acta*, *33*, 189 (1979)

12 M F Hawthorne, T E Berry and P A Wegner, *J Am Chem Soc*, *87*, 4746 (1965)

13 Isomerization of octahedral complexes of the type [Ir(CO)L_2Cl_2(COEt)], L = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$ and $P(OMe)Ph_2$, was found in solution and a mechanism in which a five-co-ordinate intermediate is formed by loss of L was proposed on the basis of kinetic data See G Wright, R W Glyde and R J Mawby, *J Chem Soc Dalton*, 220 (1973)