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Chloro- and Bromo-(alkene)iridium(I) Complexes*

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Chloro- and bromo-(alkene)iridium(I) complexes were prepared by the reaction of monoenes, acyclic conjugated dienes, and cyclic polyenes with the cyclooctene complexes $IrX(C_8H_{14})_2$ with $X = Cl$ or Br.

$IrCl(C_2H_4)_4$ is an unstable penta-coordinated compound from which the planar chlorine-bridged dimer $[IrCl(C_2H_4)_2]_2$ is formed upon ethylene dissociation. From the absence of broadening of the ethylene PMR resonances in chloroform upon cooling to −60°C, low barriers to rotation of the ethylene ligands around the metal-alkene bond were concluded. In toluene the appearance at −60°C of the "frozen out"-situation for the equatorial ligands suggested a considerably higher barrier for these ligands in this solution. The equatorial ethylene ligands show slow exchange with free ethylene by an associative mechanism. No exchange with the axial ethylene ligand could be detected.

Acyclic conjugated dienes formed penta-coordinated complexes of the type $IrX(alk)_2$.

1,5-Cyclooctadiene formed the dimer complexes $[IrX(C_8H_{12})]_2$ and the monomer complexes $IrX(C_8H_{12})_2$.

The investigation of the bromo compounds was limited to their identification by elementary analysis and by their IR spectrum in the 4000-400 cm^{-1} region. Their far-IR spectra were used as an aid in the assignment of the ν(Ir-Cl) in the corresponding chloro compounds.

From the comparison of the far-IR spectra of corresponding chloro(alkene)-rhodium(I) and -iridium(I) complexes it was concluded that the metal-alkene as well as the metal-chlorine bonds are stronger in the iridium(I) compounds.

Introduction[1]

In contrast to rhodium(I), relatively few alkene complexes of iridium(I) without strongly π-accepting ligands such as carbon monoxide or chelating alkenes are known. This is mainly due to the ease with which iridium(I), being a member of the third transition metal series, is oxidized to its third oxidation state. By consequence most of the iridium(I) complexes tend to be oxidized during the synthesis by oxidative addition reactions[2,3] or, alternatively, are protected from oxidation by the addition of a π-accepting ligand as carbon monoxide[4] or a chelating alkene.[5]

The improved synthesis under non-oxidizing conditions of the halogenobis(cyclooctene)iridium(I) complexes, $[IrX(C_8H_{14})_2]_n$ with $X = Cl$ or Br, of which the chloro complex was first reported by Shaw and Singleton,[6] gave us the opportunity to prepare new iridium(I) complexes by replacing the cyclooctene ligands by other alkenes or by phosphine and arsine ligands.[7] Analogous methods were reported[8-10] to prepare rhodium(I) complexes from the corresponding chlorobis(cyclooctene)rhodium(I), $RhCl(C_8H_{14})_2$. In this paper the reactions with alkenes and the properties of the resulting complexes will be discussed.

Experimental Section

Materials. $(NH_4)_3IrCl_6$ and K_2IrBr_6 were purchased from Messrs. Drijfhout, Amsterdam; cyclooctene, 1,5-cyclooctadiene, isoprene and 1,3-trans-pentadiene from Fluka; and ethylene, propylene and butadiene from Air Liquide. All solvents were reagent-grade quality and degassed before use. All experiments were carried out under nitrogen or argon. The following complexes were prepared by literature methods: $[RhCl(C_2H_4)_2]_2$ (ref. 21), $[RhCl(C_3H_6)_2]_2$ (ref. 21), $RhCl(C_8H_{14})_2$ (ref. 25), $RhCl(C_4H_6)_2$ (ref. 25), $[RhCl(C_8H_8)]_2$ (ref. 9) and $[IrCl(C_8H_{12})]_2$ (ref. 5). The preparation and the analytical data of the other complexes prepared are given in Table I.

Measurements. IR-spectra were measured on Hitachi EPI-G2 (4000-400 cm cm^{-1}) and Hitachi EPI-L (700-200 cm^{-1}) spectrometers. PMR spectra were recorded on the Varian spectrometers A-60 and HA-100, equipped with a variable temperature probe. X-ray powder photographs were taken with a Debye-Scherrer camera, using Cu-Kα radiation. Microanalysis were carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany and TNO, Utrecht, Holland. Molecular weight measurements were carried out with a Hitachi-Perkin Elmer osmometer.

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Table I. Preparation and analysis of halogeno(alkene)iridium(I) complexes.

Compound		Starting from	Procedure	Yield (%)	Elem. analysis (calc./found) C	H	Cl	Br	Properties
1a	$[IrCl(C_8H_{14})_2]_2$	2g$(NH_4)_3IrCl_6 . H_2O$ and 4 ml cyclooctene in 10 ml 2-propanol + 30 ml water	reflux for 2 h, cool, decant, cryst. oil under ethanol at 0°C, wash 2x with ethanol, dry under vacuum over P_2O_5, store under argon	80	42.9 43.0	6.3 6.1	7.9 7.8		yellow crystals; mol. wt. 887 (40°C, benzene)(theor. 896); m.p. 168°C (dec.)
1b	$[IrBr(C_8H_{14})_2]_n$	1 g K_2IrBr_6 and 2 ml cyclooctene in 5 ml 2-propanol + 15 ml water	heat for 6 h at 55-60°C; etc. see *1a*	70	39.2 38.0	5.7 5.7		16.3 17.0	brown-yellow; dec. >120°C without melting
2	$IrCl(C_2H_4)_4$	0.5 g *1a* suspended in 5 ml heptane	bubble through C_2H_4 at 0°C until clear-red solution (suspension above sintered-glass filter with cooling device); cryst. by rapid cooling to —50°C; filter under C_2H_4 at —50°C; recryst. under C_2H_4 from heptane	65					white needles; stable under C_2H_4<0°C; stable in vacuo <—50°C
3	$[IrCl(C_2H_4)_2]_2$	2	decomposition at room temperature under argon; store under nitrogen at —20°C		16.9 18.5	2.8 2.8	12.5 12.1		red; dec. >90°C without melting
4	$[IrCl(C_3H_6)_2]_2$	soln. of *3* in iso-pentane, sat. with C_2H_4	bubble through propylene at room temp.; evaporate soln. to dark-red oil; store 2 days at —30°C until solidification	90	23.2 23.0	3.9 3.7	11.4 11.3		red oil
5a	$IrCl(C_4H_6)_2$	fresh soln of 0.1 g *1a* (or 3) in 10 ml benzene	bubble through butadiene at room temp.: immediate cryst.; recryst from CH_2Cl_2	75	28.6 28.6	3.6 3.7	10.6 10.3		white prisms; m.p. 178-181°C (dec.)
5b	$IrBr(C_4H_6)_2$	as *5a* from *1b*	see *5a*; wash with ethanol and dry under vacuum	74	25.3 25.9	3.2 3.4		21.1 23.2	light-brown; m.p. 114-118°C (dec.)
6a	IrCl(isoprene)$_2$	0.5 g *1a* (or 3) suspended in 5 ml isoprene	immediate cryst.; filter off, wash with hexane, dry under vacuum	74	33.0 33.1	4.4 4.6	9.8 9.8		off-white chystals; m.p. 91-95°C (dec.)
6b	IrBr(isoprene)$_2$	as *6a* from*1b*	see *6a*	50	29.4 29.2	3.9 4.0		19.6 20.1	light-brown; dec. >140°C without melting
7a	IrCl(1,3-tr-pentadiene)$_2$	0.5 g *1a* (or *3*) suspended in 10 ml hexane + 2 ml 1,3-trans-pentadiene	after 5 min filter off precipitate, wash with hexane, dry under vacuum	82	33.0 33.2	4.4 4.6	9.8 9.9		off-white; dec. >120°C without melting
8	$Rh_2Cl_2(C_4H_6)_3$	0.5 g $[RhCl(C_8H_{14})_2]_2$ suspended in 15 ml 100% ethanol	pass through at 40°C gaseous butadiene: after few minutes cryst.; filter off, dry in N_2 stream	78	32.8 32.8	4.1 4.2	16.2 16.0		yellow-greenish crystals; dec. 104-108°C
9b	$[IrBr(C_8H_{12})]_2$	0.2 g *10b* in 25 ml hexane	filter off after 30 min., evaporate red filtrate to dryness	58	25.3 26.8	3.2 3.5		21.1 20.0	dark-red; m.p. 196-199°C (dec.)
10a	$IrCl(C_8H_{12})_2$	0.2 g *1a* suspended in 4 ml *pure* 1,5-cyclooctadiene	after 10 min filter off; wash 2x with pentane, dry under vacuum	67	43.2 43.2	5.4 5.5	8.0 7.8		brown-yellow; transition point 70°C (*10a*→yellow isomer of *9a*)
10b	$IrBr(C_8H_{12})_2$	as *10a* from *1b*	see *10a*	60	39.4 40.7	4.9 5.3		16.4 15.8	brown; transition point 97°C; (*10b*→*9b*)
11	$[IrCl(C_8H_8)]_n$	0.5 g *1a* (or 3) suspended in 5 ml *pure* cyclooctatetraene	after 20 min filter off, wash with alcohol, dry under vacuum	63	29.0 29.1	2.4 2.6	10.7 10.7		cream
12	$IrCl(C_8H_8)(C_5H_5N)$	0.18 g *11* suspended in 10 ml benzene	treat with 50.6 mg pyridine; after 5 h evaporate solvent with N_2; recryst. from alcohol	41	38.0 38.0	3.2 3.7	8.7 8.6		yellow crystals; elementary N: calc. 3.4, found 3.5

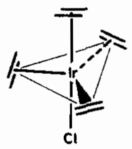
Table II. Absorption frequencies (cm^{-1}) of halogene(alkene)-rhodium(I) and -iridium(I) complexes in the far-IR region

Compound	ν(M-X)	Other bands
$[RhCl(C_2H_4)_2]_2$	274(s), 260(sh), 248(s)	502(w), 407(sh), 398(s)
$[IrCl(C_2H_4)_2]_2$	292(sh), 289(m), 260(m)	537(w), 448(s), 308(vw)
$IrCl(C_2H_4)_4$	308(sh,br), 280(s)	505(m), 397(m), 372(w)
$[RhCl(C_3H_6)_2]_2$	290(m,br), 250(br)	508(m), 419(m), 386(s)
$[IrCl(C_3H_6)_2]_2$	290(s,br), 255(s,br)	537(s), 455(s,br), 440(vs,br), 405(w)
$[RhCl(C_8H_{14})_2]_2$	318(s), 290(m), 254(s)	548(s), 520(s), 414(m)
$[IrCl(C_8H_{14})_2]_2$	318(s), 302(m), 273(s), 270(sh)	578(s), 555(s), 545(s), 463(w), 436(s), 352(w)
$[IrBr(C_8H_{14})_2]_n$		577(m), 550(sh), 544(s), 434(m)
$[RhCl(C_8H_{12})]_2$	274(s), 254(s)	382(m), 247(sh) Ref. 22
$[RhBr(C_8H_{12})]_2$		379(m), 250(w), 244(w)
$[IrCl(C_8H_{12})]_2$	291(s), 258(m)	530(s), 508(m), 497(s), 428(vw), 413(s), 333(w), 327(sh)
$[IrCl(C_8H_{12})]_2$ (yellow isomer)	295(sh), 283(s), 265(m)	533(s), 512(m), 498(s), 417(s), 333(w)
$[IrBr(C_8H_{12})]_2$		529(m), 505(m), 495(m), 410(s), 330(w,br)
$IrCl(C_8H_{12})_2$	210(br)	585(m), 515(m), 477(w), 460(m), 426(w), 397(w), 376(w), 320(s), 271(s), 244(s)
$IrBr(C_8H_{12})_2$		584(m), 514(m), 475(m), 458(m), 425(w), 397(w), 375(w), 318(s), 270(s), 240(s)
$RhCl(C_4H_6)_2$	265(s), 261(sh)	504(m), 463(w), 443(s)
$IrCl(C_4H_6)_2$	288(vs), 283(sh)	528(m), 480(w), 463(s), 410(w), 323(m), 315(sh)
$IrBr(C_4H_6)_2$		520(m), 479(w), 459(s), 411(w), 323(s), 315(sh)
IrCl(isoprene)$_2$	278(s)	597(m), 540(m), 523(m), 475(m), 453(s), 334(sh), 327(br), 317(sh), 243(s), 222(m)
IrBr(isoprene)$_2$		597(m), 537(m), 521(s), 473(m), 452(s), 443(sh), 410(w), 356(w), 327(s), 310(s), 277(w), 245(s), 217(br)
IrCl(1,3-*tr*-pentadiene)$_2$	290(s)	523(m), 505(m), 489(m), 443(s), 408(m), 317(m), 258(w), 254(w),, 210(m,br)

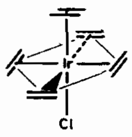
Results and Discussion

(a) *Monoene Complexes.* Bis[μ-chlorobis(cyclooctene)iridium(I), $[Ir(Cl(C_8H_{14})_2]_2$ (*1a*) was prepared in high yield by refluxing ammonium chloro-iridite, $(NH_4)_3IrCl_6.H_2O$, with cyclooctene in a 2-propanol/water mixture. The preparation of the corresponding bromo compound, $[IrBr(C_8H_{14})_2]_n$ (*1b*) proceeds analogously from K_2IrBr_6. The compounds are stable under vacuum and under nitrogen, but decompose slowly in air under the influence of moisture. In solutions *1a* is unstable, especially in halogen-containing solvents in which it is probably oxidized, as may be concluded from the isolation of a precipitate from old tetrachloride solutions, which gives a good analysis for $IrCl_3(C_8H_{14})$. Molecular weight measurements on the relatively stable benzene solution showed that *1a* was present in solution as a dimeric species. The far-IR spectrum shows absorptions at 318(ms), 302 (m), and 273(s) (Table II) which are assigned to iridium-chlorine stretching vibrations, ν(Ir–Cl), because of the absence of absorption bands in this region of the spectrum of (*1b*).

Chlorotetrakis(ethylene)iridium(I), $IrCl(C_2H_4)_4$ (*2*), is prepared by treating a suspension of *1a* in heptane with ethylene at 0°C and subsequently cooling to –50 °C. Up to 00°C it is stable under ethylene[*] under nitrogen it is only stable below about –50°C. At higher temperatures, it looses two molecules of ethylene and dimerizes to $[IrCl(C_2H_4)_2]_2$ (*3*). The bromo compound *1b* does not react with ethylene. An X-ray investigation[11] showed *2* to be monomeric and to have a trigonal bipyramidal structure (I) with one axial and three equatorial in-plane ethylene ligands. The iridium atom is situated slightly out of the equatorial plane toward the axial ethylene ligand. The far-IR spectrum (CsI-pellet) shows three absorptions of medium intensity in the $\nu(Ir–C_2H_4)$ region at 505, 397, and 372 cm^{-1}. The ν(Ir–Cl) band at 280 cm^{-1} has a broad shoulder centered at 308 cm^{-1} (Table II).



(I)



(II)

The PMR spectrum at –20°C of a chloroform solution of *2* (Figure 1a) shows two sharp resonances with an intensity ratio 1:3 at τ = 8.39 ppm (A) and at 6.49 ppm (B) due to the axial and equatorial ethylene ligands respectively.[**] No broadening of the resonances was observed on cooling to –50°C. These results show the absence of exchange processes between axial and equatorial ethylene on the NMR time scale.

Intramolecular exchange processes are quite common in penta-coordinated compounds as $Fe(CO)_5$, PF_5, RPF_4, and AsF_5 (ref. 12) and were recently also reported[13] to occur in the penta-coordinated cyclooctadiene (COD)iridium(I) complexes of the RIr(COD)-P_2 type with R = alkyl and P= phosphine. Intramolecular exchange processes in penta-coordinated compounds seem to play an important role in the catalysed isomerisation of tetragonal planar complexes.[14]

Although no broadening of the resonances was observed on cooling the chloroform solution, the PMR spectrum of a toluene solution at–60°C (Figure 2), ho-

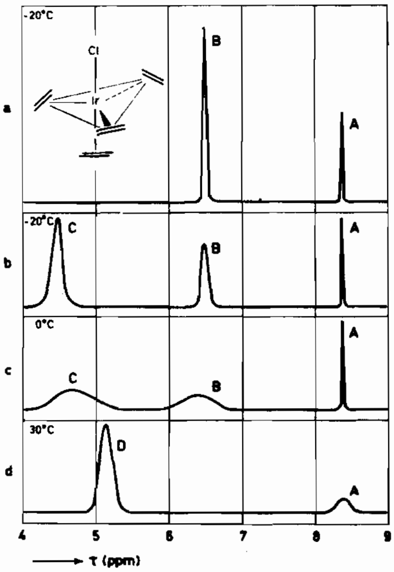


Figure 1. Diagrammatic 100 MHz PMR spectra of solutions of $IrCl(C_2H_4)_4$ in chloroform at different temperatures: (a) complex as such, (b-d) complex with free ethylene added. Resonances: (A) axial ethylene, (B) equatorial ethylene, (C) free ethylene. (D) merged resonance of free and equatorial ethylene.

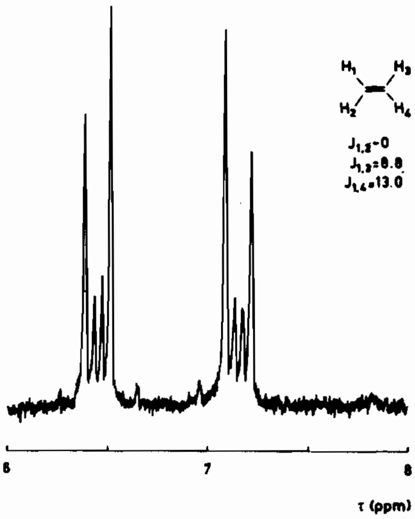


Figure 2. Equatorial ethylene resonances in the 100 MHz spectrum of $IrCl(C_2H_4)_4$ in toluene at –60°C. Coupling constants J in c/s.

(*) At room temp. slow decomposition under formation of butenes.

(**) The width of resonance B is highly dependent on the purity of the compound.

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wever, exhibited an AA'BB' pattern with $\tau_A = 6.47$ and $\tau_B = 7.17$ ppm due to protons of the equatorial ethylene ligands. A sharp axial ethylene resonance was also observed at $\tau = 9.38$ ppm. According to the set of proton-proton coupling constants (Figure 2), which was obtained by spectrum simulation, the cis-protons of the equatorial ethylene ligands are equivalent in this 'frozen out' situation.[15] This corresponds with an in-plane orientation of the equatorial ethylene ligands in agreement with the structure found by X-ray methods.[11] Since the equatorial in-plane ethylene ligands use the metal orbitals $d_{x^2-y^2}$ and d_{xy} for π-back bonding, and the perpendicular ethylene ligands would compete with the axial ethylene ligand for the π-bonding metal orbitals d_{xz} and d_{yz}, the in-plane orientation is slightly more favourable from the point of view of π-backbonding possibilities. This alkene orientation has also been found in the trigonal bipyramidal complexes tetracarbonyl(fumaric acid)iron(0), $Fe(CO)_4(COOHCH{=}CHCOOH)$ (ref. 16), and chlorotri(3-butenyl)phosphinerhodium(I), $RhCl[P(CH_2CH_2\text{-}CH{=}CH_2)_3]$ (ref. 17).

The different dependency on temperature of the PMR spectra of *2* in chloroform and toluene demonstrates the solvent influence on the barrier of rotation of the equatorial ethylene ligands around the metal-alkene axes. From the coalescence temperature at about -30°C and the chemical shift difference $\tau_A - \tau_B = 70$ c/s toluene, it seems that this barrier in toluene is of the same magnitude as those reported for rhodium(I)—[15] and platinum(II)—alkene[18] complexes (about 10-15 kcal/mole). Although the low coalescence temperature below -60°C in chloroform may be due to a small chemical shift difference $\tau_A - \tau_B$ in cloroform, it may also suggest a barrier $\ll 10$ kcal/mole. The absence of any broadening of the axial ethylene resonances in chloroform as well as in toluene also indicates a very low barrier of rotation for this ligand.

In the solid state of *2* rotational barriers of 5.1 kcal/mole for the equatorial and 1.6 kcal/mole for the axial ethylene ligands were determined from the magnetic relaxation behaviour as a function of temperature.[19] Although the σ part of the metal-alkene bond remains more or less unperturbed during the rotation, the π part of this bond is ruptured after 90° rotation and may only be replaced by another bond of π symmetry if suitable metal orbitals are available. Apart from steric effects the barrier is therefore mainly determined by the difference in π-back bonding possibilities in the equilibrium and the rotational transition state. As mentioned before, the equatorial ethylene ligands in *2* have both in the "in-plane" and in the "perpendicular" orientation possibilities for π-back bonding. The low barriers in *2* probably reflect both the small change in π-back bonding during the rotation and the competition by the four ethylene ligands for the metal electron density.

The broadening of the equatorial ethylene resonance on admission of free ethylene to the chloroform solution at –20°C and 0°C (peak C in Figures 1b,c) indicates slow exchange with uncoordinated ethylene. No exchange between free ethylene and the axial ethylene ligand was detected. Only at 30°C (Figure 1d) is the axial ethylene resonance broadened due to partial decomposition of the complex.

The mechanism of exchange between free and equatorial ethylene may be associative (eq. 1) or dissociative (eq. 2):

$$IrCl(C_2H_4)_4 + C_2H_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} IrCl(C_2H_5)_5 \qquad (1)$$

$$\frac{1}{\tau_c} = k_1[C_2H_4] \quad \frac{1}{\tau_f} = k_1[IrCl(C_2H_4)_4]$$

$$IrCl(C_2H_4)_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} IrCl(C_2H_4)_3 + C_2H_4 \qquad (2)$$

$$\frac{1}{\tau_c} = k_1 \quad \frac{1}{\tau_f} = k_1\frac{[IrCl(C_2H_4)_4]}{[C_2H_4]}$$

The linewidth of the resonances of the equatorial and the free ethylene ligands is proportional to the inverse lifetime of the corresponding species *e.g.* $1/\tau_c$ and $1/\tau_f$ respectively. The broadening of the equatorial ethylene resonance on admission of free ethylene (Figures 1a,b) shows that the associative process is operative. This mechanism involves a six-coordinated intermediate, like (II), in which the axial ethylene ligand has to preserve its distinct character. The existence of an intermediate containing a six-coordinated d^8 metal ion has recently also been suggested in the by $RhH(CO)_2(PPh_3)_2$ selectively catalysed hydroformylation of 1-alkenes to aldehydes.[20]

The dimeric complex $[IrCl(C_2H_4)_2]_2$ (*3*) decomposes slowly in air at room temperature and should therefore be stored under nitrogen at –20°C. In contrast to its rhodium analogue[21] *3* is moderately soluble in solvents such as benzene, chloroform and dichloromethane, but the resulting solutions are unstable at room temperature. Both compounds, which are shown by X-ray powder diagrams to be non-isomorphous, have similar IR spectra except in the far-IR region, where the iridium complex shows two and the rhodium complex three ν(metal-Cl) bands (Table II). On symmetry grounds one expects that the occurrence of two or three bands is consistent with a planar or a bent chlorine-bridge structure respectively.[22,23] So the IR spectrum suggests *3* to have a planar structure (III) in contrast to its rhodium analogue, which has been shown in agreement with its IR spectrum to possess a bent structure.[24] Also the PMR spectrum at –55°C in chloroform, which is of the AA'BB' type with $\tau_A = 6.40$ and $\tau_B = 7.70$ ppm, is consistent with the planar structure (III). The proton-proton coupling constants found by spectrum simulation

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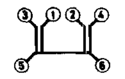
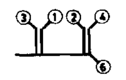
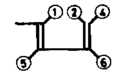
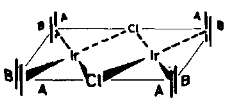
Table III. PMR data (τ in ppm, J in c/s) for chloro(alkene)iridium(I) complexes in $CDCl_3$.

Compound		τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_{CH_3}
$IrCl(butadiene)_2$ 		8.33 $J_{1,3}=2.0$ $J_{1,5}=8.0$		6.57 $J_{3,5}=5.4$		4.75		
$IrCl(isoprene)_2$ 	A	8.45 $J_{1,3}=2.2$	8.42 $J_{2,4}=2.2$ $J_{2,6}=9.0$	6.65	6.58 [a] $J_{4,6}\approx 7$		5.31	7.95
	B	— [b]	— [b]	— [b]	— [b]		4.83	8.24
$IrCl(1,3\text{-tr-pentadiene})_2$ 		7.73 [c] $J_{1,CH_3}\approx 6$	8.44 [a]		7.20 [d]	4.6-5.0 [e]		8.42

[a] Obscured by partial overlap with CH_3 resonance. [b] Not located. [c] Partly resolved quartet. [d] Unsymmetrical doublet. [e] Partly resolved multiplet.

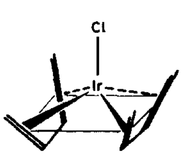


(III)

($J_{AA'}$ = 8.4; J_{AB} = 0; $J_{AB'}$ = 12.5) are not much different from those of the equatorial ethylene ligands in 2 and those of earlier reported rhodium-ethylene complexes.[15] At higher temperatures, the resonances are broadened and at about 10°C they converge into one absorption, corresponding with rapid proton equilibration caused by ethylene rotation around the metal-alkene bond, and/or metal-alkene bond dissociation.

The propene complex $[IrCl(C_3H_5)_2]_2$ (*4*), obtained as an oil by alkene substitution in 3, shows in its IR spectrum two ν(Ir–Cl) bands centered at 290 and 255 cm^{-1} (Table II). The broadness of these bands precludes any conclusions with regard to the planar or bent nature of the metal-chlorine bridge in this dimer.

(b) *Acyclic Conjugated Diene Complexes.* The penta-coordinated monomeric complexes *5a/b, 6a/b,* and *7a* of the type $IrX(alk)_2$ (X = Cl, Br; alk = butadiene, isoprene and 1,3-transpentadiene) show structure IV.

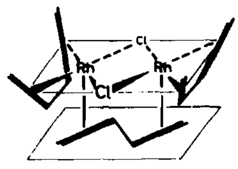


(IV)

All the far-IR spectra (Table II) of the chloro complexes show an absorption band in the 278-290 cm^{-1} region, which, being absent in the spectra of the bromo compounds is assigned to ν(Ir–Cl).

The PMR spectra of *5a-7a* (Table III) show complex resonances corresponding with the three types of olefinic protons and the methyl protons in the substituted butadiene compounds. The spectrum of the isoprene compound *6a* indicates the presence of two isomeric forms (ratio ≈4:1) which differ in the relative position of the methyl groups. From the point of view of steric hindrance it is probable that the predominant form (A) has the methyl groups trans to each other. The butadiene complex *5a* is far more stable in air and in solution than the earlier reported corresponding isomorphous rhodium(I) compound.[25,26] This is probably due to the stronger iridium-butadiene bond which prevents alkene dissociation and formation of a reactive coordinatively unsaturated species.

This view is supported by the isolation of the dimeric complex dichlorotris(butadiene)dirhodium(I), $Rh_2Cl_2(C_4H_6)_3$ (*8*) and the unsuccessful attempts to prepare the corresponding iridium(I) complex.



(V)

The treatment of a suspension of $RhCl(C_4H_6)_2$ with butadiene in absolute alcohol at 40°C gives the new complex *8*. Spectroscopic data are consistent with the dimeric structure (V) which shows one bridging and two chelating butadiene ligands:

— the PMR spectrum in chloroform at ambient temperatures shows broadened resonances at τ 4.11 (2); 4.54 (4); 4.96 (4); 7.83 (4); 9.27 (4) ppm;

— the IR spectrum in the 1600-1300 cm^{-1} region shows four absorption bands at 1470(sh), 1460(m), 1428(vs), and 1362(s), corresponding with a chelating butadiene ligand as in $RhCl(C_4H_6)_2$, and also absorption bands of medium intensity at 1542 and 1488 cm^{-1} due to a bridging butadiene ligand;

— the ν(Rh–Cl) bands at 232 and 218 cm^{-1} support by their low position the occurrence of a combined chlorine and butadiene bridging structure.[27]

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(25) L. Porri, A. Lionetti, G. Allegra and A. Immirzi, *Chem. Commun.*, 336 (1965).

(26) A. Immirzi and G. Allegra, *Acta Cryst.*, *B25*, 120 (1969).

The formation of *8* may be considered to proceed via butadiene dissociation followed by dimerisation and reaction of the formed dimer with a butadiene molecule.

(c) *Cyclic Polyene Complexes.* In solution *1a* and *1b* form with a slight excess of 1,5-cyclooctadiene (COD) dimers of the type $[IrX(COD)]_2$ with X = Cl (*9a*) or Br (*9b*). The former has been described earlier by Winkhaus and Singer.[5] In pure COD the complexes of the type $IrX(COD)_2$ with X = Cl (*10a*) or Br (*10b*) are formed. The IR spectra of *9* and *10* do not show absorption bands in the 1600 cm^{-1} region from which the absence of uncoordinated double bonds may be concluded. In solution *10a* and *10b* dissociate and dimerise forming *9a* and *9b*, respectively. Their IR spectra in the fingerprint region closely resemble the spectrum of the earlier reported[28] bis-(COD)compound $IrCl(SnCl_3)(COD)_2$, which has been shown to contain five-coordinated iridium in a distorted trigonal bipyramidal environment with four double bonds and one tin atom. The far-IR spectrum of *10a* shows four strong bands below 330 cm^{-1}. The lowest at 210 cm^{-1} has no corresponding absorption in the spectrum of the bromo compound *10b* and is therefore assigned to ν(Ir-Cl). On heating, *10a* and *10b* loose one COD ligand at 70°C and 97°C respectively. *10b* forms *9b* on this occasion, and *10a* forms a yellow isomer of *9a* which has an almost identical IR spectrum.

Pure cyclooctatetraene forms with *1a* or *3* the light brown coloured $[IrCl(C_8H_8)]_n$ (*11*). Its IR spectrum shows an absorption band at 1635 cm^{-1} indicating the presence of uncoordinated olefinic bonds as in the corresponding rhodium complex $[RhCl(C_8H_8)]_2$ (ref. 9). The spectra of both compounds differ in several other aspects, the most important being the splitting of the characteristic cyclooctatetraene bands in he range 1300-1400 cm^{-1} and near 800 cm^{-1} and the complex pattern consisting of four bands at 333, 307, 280-270 (broad, asymmetric) and 227 cm^{-1} (broad) in the ν(Ir-Cl) range. The spectrum of the rhodium compound has only two strong absorption bands in this range at 282 (s) and 257 (s) indicative of a planar bridged structure. Because of its insolubility and its complicated far-IR spectrum we conclude that *11* has a polymeric structure.

The structure of *11* is broken down in the reaction with pyridine which results in the formation of the complex $IrCl(C_8H_8)(pyr)$ (12) to which we assign a square planar structure. The PMR spectrum shows, together with the resonances due to pyridine, two equally intense resonances due to the protons of the eight-membered ring: a sharp singlet at $\tau = 4.33$ ppm and a broadened resonance at $\tau = 5.84$ ppm, correlating with the protons of the uncoordinated and coordinated olefinic bonds respectively. The IR spectrum shows, in agreement with the proposed structure, a band at 1626 cm^{-1} assignable to a free C=C stretching frequency.

(d) *Bond Strengths. Metal-chlorine.* From the comparison of the far-IR spectra of the chloro and bromo compounds given in Table II, the iridium-chloro stretching vibrations could be assigned. Some ν(M-Cl) bands have a shoulder on the low-frequency side which is due to the occurrence of the ^{37}Cl isotope. As noted before the number of ν(M-Cl) bands in the spectra of chlorine-bridged complexes is indicative of a planar or bent structure[22,23]. For instance, from the occurrence of two ν(Ir-Cl) absorption bands, at about 290 and at about 260 cm^{-1}, we may conclude that the bridged ethylene (*3*), propylene (*4*) and COD (*9a*) complexes posses a planar chlorine bridge. Comparison of the data for the chloro-rhodium and chloro-iridium complexes, and especially those of the isomorphous bis(butadiene) compounds, demonstrates the stronger iridium-chlorine bond.

Metal-alkene. The relative strength of the metal-alkene bond in rhodium(I) and iridium(I) compounds is a controversial subject. Winkhaus and Singer[5] found the iridium-alkene compounds less stable than the rhodium analogues. They explained this by the more diffuse character of the atomic orbitals in the valence shell of iridium, and the consequently smaller overlap in the metal-alkene bond in the iridium compounds. This argument is in conflict with the values of overlap integrals calculated by Brown and Fitzpatrick[29] using the analytical functions of Basch and Gray for the metal orbitals.

In the far-IR spectra of COD complexes of the formula $[MCl(COD)]_2$ (M = Rh or Ir), evidence for stronger metal-alkene and metal-chlorine bonds in the iridium compound was found.[22] Since free cyclocta-diene itself absorbs in the far-IR region, possible interference between internal ligand and metal-ligand vibrations renders the conclusion tentative. Since the frequency of the lowest vibration in free ethylene[30] at 800 cm^{-1} is well above the region of the metal-ligand vibration frequencies at < 550 cm^{-1}, the effect of this kind of interference may be supposed to be negligible in transition metal-ethylene complexes.

Analogous to Hiraishi 's interpretation[31] of the IR spectrum of Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$, we assign the 537 cm^{-1} and 448 cm^{-1} bands in the spectrum of *3* and the 502 cm^{-1} and 398 (407 sh) cm^{-1} bands in the spectrum of the corresponding dimeric rhodium-ethylene compound to the assymetric and symmetric metal-alkene stretching frequencies.

In spite of the difference in bridge structure in both compounds, the above data allow the conclusion that the iridium-alkene bond is stronger than the rhodium-alkene bond. Also the data of the complexes of the higher alkenes indicate, despite the possibility of interference, a stronger iridium-alkene bond.

In view of the stronger iridium-chlorine bond, having mainly σ-character, it is probable that the stronger iridium-alkene bond is caused by increased σ-donation as well as by increased π-backbonding. The far-IR spectra of corresponding chloro and bromo compounds

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(27) J. Powell and B.L. Shaw, *J. Chem. Soc.* (*A*), 597 (1968).
(28) P. Porta, H.M. Powell, R.J. Mawby and L.M. Venanzi, *J. Chem. Soc.* (*A*), 455 (1967).
(29) D.A. Brown and N.J. Fitzpatrick, *J. Chem. Soc.* (*A*), 315 (1967).
(30) T. Shimanouchi, *J. Chem. Phys.*, 26, 594 (1957).
(31) J. Hiraishi, *Spectrochim. Acta*, 25A, 749 (1969).

show absorption bands at slightly lower frequencies in the latter and suggest therefore equal or slightly weaker metal-alkene bon strenghts in the bromo compounds. However, the higher dissociation temperature of the bromobis(COD) compound *10b* as compared with that of the corresponding chloro compound *10a* is in favour of a stronger metal-alkene bond in the bromo compound. This behaviour is also in agreement with the greater tendency of bromo compounds to form pentacoordinated complexes[32] and with the consequently greater trans-influence of the bromo ligand.

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(32) L. Cattal.ni, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, *90*, 4800 (1968).