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Some Addition Compounds of Chlorobis(Triphenylphosphine)Iridium(I)

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The synthesis and properties of chlorobis(triphenylphosphine)iridium(I), $IrCl(PPh_3)_2$*, and some of its addition products are reported.*

With ethylene, $IrCl(C_2H_4)(PPh_3)_2$ *is formed. Indications have been found pointing to the formation, at low temperature, of the unstable bis(ethylene) adduct* $IrCl(C_2H_4)_2(PPh_3)_2$*. With one equivalent of allene,* $IrCl(C_3H_4)(PPh_3)_2$ *is formed. The reaction product with excess of allene is* $IrCl(C_6H_8)(PPh_3)_2$*, in which the 2,2'-bi-σ,π-allyl ligand is present.*

In the presence of an excess of ethylene, $IrCl(C_2H_4)(PPh_3)_2$ *forms with molecular oxygen* $IrCl(C_2H_4)(O_2)(PPh_3)_2$*, in which ethylene can be replaced by other ligands. With sulfur dioxide,* $IrCl(C_2H_4)(PPh_3)_2$ *and* $IrCl(C_3H_4)(PPh_3)_2$ *form the adducts* $IrCl(C_2H_4)(SO_2)(PPh_3)_2$ *and* $IrCl(C_3H_4)(SO_2)(PPh_3)_2$*.*

The stability of five-coordinated compounds of the type $IrCl(PPh_3)_2XY$ *is discussed on the basis of the donor and acceptor properties of the ligands X and Y.*

Introduction

Chlorotris(triphenylphosphine)iridium(I), $IrCl(PPh_3)_3$, was recently reported to be inactive in the hydrogenation of alkenes[1] and in the polymerisation of allenes.[2] This inactivity might be due to the strong iridium-phosphine bond, which prevents the complex from becoming more unsaturated by dissociation of a phosphine ligand. As was shown in hydrogenation experiments using the corresponding rhodium(I) compound, $RhCl(PPh_3)_3$, such a process enables the metal to activate the substrate.[4]

In hydrogenation reactions, we tested the catalytic activity of benzene solutions of the iridium(I)-cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ to which different amounts of triphenylphosphine had been added.[3] It was found that the resulting systems were active with respect to the hydrogenation and isomerization of alkenes. The maximum hydrogenation rate at a phosphine/iridium ratio 2 suggested the active species to be chlorobis(triphenylphosphine)iridium(I) $IrCl(PPh_3)_2$.[**]

We report here the synthesis and properties of $IrCl(PPh_3)_2$ and its addition products obtained by reaction with ethylene, allene, butadiene, oxygen and sulfur dioxide. The method of alkene replacement used to prepare $IrCl(PPh_3)_2$ from $[IrCl(C_8H_{14})_2]_2$ is generally applied in the synthesis of rhodium(I) compounds.[4-6]

Experimental Section

Materials. Ethylene, butadiene (l'Air Liquide), allene, sulfur dioxide (Baker Chemicals) were used without purification. All solvents were reagent-grade quality and degassed before use. All experiments were carried out under nitrogen or argon. The preparation and the analytical data of the complexes prepared are given in Table I.

Measurements. IR-spectra were measured on Hitachi EPI-G2 (4000-400 cm^{-1}) and Hitachi EPI-L (700-200 cm^{-1}) spectrometers. PMR spectra were recorded on the Varian spectrometers A-60, HA-100 and HR 220 and partly on a Jeol 100. Microanalyses were carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Some of the oxygen adducts were analysed by the Analytical Department of the Imperial College of Science and Technology, London, England.

(a) *Chlorobis(triphenylphosphine)iridium(I),* $[IrCl(PPh_3)_2]_n$. A solution of $[IrCl(C_8H_{14})_2]_2$ in benzene, to which two equivalents of triphenylphosphine are added catalyses the hydrogenation and isomerization of alkenes.[3] From this solution, a fine powder of the light-yellow complex $[IrCl(PPh_3)_2]_n$ (*1*) can be isolated after addition of pentane. Once precipitated,

$$[IrCl(C_8H_{14})_2]_2+4PPh_3 \rightarrow [IrCl(PPh_3)_2]_n(1)+4C_8H_{14}$$

the compound is only slightly soluble in benzene and a solution of the redissolved complex does not show any catalytic activity.[7] From this we suppose that the complex is precipitated as an inactive dimer or polymer from the active solution in which it is, at least partly, present as an active monomer. This be-

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(**) The fourth coordination site is probably occupied by a solvent molecule.

(1) M.A. Bennett and D.L. Milner, *Chem. Commun.*, 581 (1967); *J. Amer. Chem. Soc.*, *91*, 6983 (1969).

(2) S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 191 (1969).

(3) H. van Gaal, H.G.A.M. Cuppers, and A. van der Ent, *Chem. Commun.*, 1694 (1970).

(4) S. Montelatici, A. van der Ent, J.A. Osborn and G. Wilkinson, *J. Chem. Soc. (A)*, 1051 (1968).

(5) K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, *90*, 99 (1968).

(6) J.T. Mague and G. Wilkinson, *J. Chem. Soc.* (A), 1736 (1966).

(7) H.G.A.M. Cuppers, personal communication.

haviour would then parallel the properties of the corresponding chloro(triphenylphosphine)rhodium(I) system in which the dimer $[RhCl(PPh_3)_2]_2$ was, in contrast with the monomer, likewise inactive.[8] The far IR-spectrum of *1* shows in the ν(Ir-Cl) region a strong absorption at 302 cm^{-1}. It is extremely sensitive to oxygen and in air it forms a grey-green reaction product, which, according to absorption bands at 1120 and 720 cm^{-1} in its IR-spectrum, contains triphenylphosphine oxide. This reaction product is probably identical to the unidentified product obtained by Collman *et al.*[9] from the decomposition in air of the molecular nitrogen complex $IrCl(N_2)(PPh_3)_2$. *1* slightly dissolves in chloroform, but by reaction with the solvent it is rather quickly partly oxidized to an iridium(III) complex. This was demonstrated by the reaction of a fresh and an one-hour-old chloroform solution with carbon monoxide. The reaction product of the former was identified on the basis of its IR-spectrum to be Vaska's compound, $IrClCO(PPh_3)_2$, whereas from the latter solution a mixture of compounds was isolated with ν(CO) at 1955 and 2060 cm^{-1}, being indicative of iridium(I) and (III) complexes respectively.[10]

Prepared *in situ* by the above-mentioned procedure in benzene, *1* undergoes readily addition reactions. Because of its extreme sensitivity towards oxygen and its presumed tendency to form polymers in solution, it sometimes appeared profitable to prepare the ethylene adduct $IrCl(C_2H_4)(PPh_3)_2$ (*2*) first and to use this complex *in situ* or after isolation as a starting compound for the preparation of the adducts of *1*.

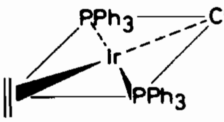
(b) *Reaction of* $IrCl(PPh_3)_2$ *with ethylene.* Chlorobis(triphenylphosphine)(ethylene)iridium(I), $IrCl(C_3H_4)(PPh_3)_2$ (2) can be prepared at room temperature by passing ethylene through a benzene solution of $[IrCl(C_8H_{14})_2]_2$ and two equivalents of triphenylphosphine.

$$[IrCl(C_8H_{14})_2]_2 + 4PPh_3 \xrightarrow[\text{benzene}]{C_2H_4} IrCl(C_2H_4)(PPh_3)_2 \ (2)$$

$$[IrCl(C_2H_4)_2]_2 \xrightarrow{PPh_3} [IrCl(C_2H_4)PPh_3]_2 \ (3) \xrightarrow{PPh_3} IrCl(C_2H_4)(PPh_3)_2 \ (2)$$

Orange crystals of *2* with about a half solvent molecule of benzene separated after addition of pentane. Alternatively, *2* may be prepared by the addition of two equivalents of triphenylphosphine to a benzene solution of the bis(ethylene) dimer[11] $[IrCl(C_2H_4)_2]_2$. In this reaction, one of the ethylene ligands in this dimer is first replaeed by a triphenylphosphine ligand, followed by splitting of the chlorine bridge by the second phosphine ligand. This may be concluded from the immediate precipitation of the dimeric complex $[IrCl(C_2H_4)(PPh_3)]_2$ (3) after addition of one equivalent phosphine.

2 is stable under vacuum, but in air it slowly forms phosphine oxide containing products. It is moderately soluble in $CHCl_3$ and CH_2Cl_2, but reacts slowly with these solvents. The far IR-spectrum shows an iridium chlorine stretching frequency at 301 cm^{-1} with a weak shoulder at 295 cm^{-1}. Apart from phenyl hydrogen resonances, the weak PMR-spectrum shows a resonance due to coordinated ethylene; in $CDCl_3$ a broad resonance at τ 8.95 and in CD_2Cl_2 an apparent triplet at τ 8.95 ($J_{P\text{-}H} \approx 4$ c/s). Unlike solutions of the corresponding rhodium compound,[8] the solution of *2* in $CHCl_3$ does not lose ethylene on sweeping with nitrogen, as may be concluded from the unchanged PMR-spectrum. This illustrates the stronger metal-alkene bond in iridium complexes. The spectroscopic data of *2* are in agreement with a square planar structure like the structure (I) of the corresponding tetrafluoroethylene complex $IrCl(C_2F_4)(PPh_3)_2$ with the chlorine ligand *trans* to the alkene.[3,12]



(I) (compound 2)

An orange, ethylene-saturated, chloroform solution of *2* becomes colourless on cooling to –50°C. Addition of pentane precipitates an unstable white compound

$$IrCl(C_2H_4)(PPh_3)_2(2) + C_2H_4 \xrightarrow{-50°C} IrCl(C_2H_4)_2(PPh_3)_2 \ (4)$$

which cannot be isolated completely free from solvent. At room temperature it decomposes with evolution of ethylene into *2*. The ethylene content of the gas sample obtained on pyrolysis at 180°C, as determined by the Wijs' method, was found to correspond to two molecules of ethylene per iridium atom. We suppose that the white compound is the five-coordinated bis(ethylene) adduct $IrCl(C_2H_4)_2(PPh_3)_2$ (*4*), which may be considered isostructural with the likewise unstable ethylene adduct of Vaska's compound, $IrCl(CO)(C_2H_4)(PPh_3)_2$.[13]

(c) *Oxygen adducts of* $IrCl(PPh_3)_2$. A suspension of *2* in benzene reacts with molecular oxygen, forming triphenylphosphine oxide containing products. In the presence of one or more equivalents of free ethylene, however, the diamagnetic oxygen complex $IrCl(C_2H_4)(O_2)(PPh_3)_2(C_6H_6)$ (5) is rapidly formed. This

$$IrCl(C_2H_4)(PPh_3)_2 \ (2) + O_2 \xrightarrow[\text{benzene}]{C_2H_4} IrCl(C_2H_4)(O_2)(PPh_3)_2(C_2H_6) \ (5)$$

suggests that this reaction proceeds via the unstable bis(ethylene) adduct *4*. A possible explanation may be that *4* produces upon dissociation of one ethylene ligand a reactive non-planar four-coordinated intermediate, which is then supposed to react fast with an oxygen molecule before it adopts the less reactive square planar form. Alternatively, *4* may undergo an associative substitution process in which a six-

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[8] J.A. Osborn, F.H. Jardine, J.F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1711 (1966).

[9] J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun, and J.W. Kang, *J. Amer. Chem. Soc.*, *90*, 5430 (1968).

[10] L. Vaska, *Acc. Chem. Res.*, *1*, 335 (1968).

[11] a) A. van der Ent and T.C. van Soest, *Chem. Commun.*, 225 (1970); b) A.L. Onderdelinden and A. van der Ent, *Inorg. Chim. Acta* *6*, 420 (1972).

[12] B. Clarke, M. Green, and F.G.A. Stone, *J. Chem. Soc. (A)*, 951 (1970).

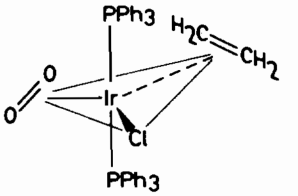
Table I. Preparation and analysis of chlorobis(triphenylphosphine)iridium(I) complexes

Compound	Starting from	Procedure	Yield in % (g)	Elementary analysis $\frac{\text{calculated}}{\text{found}}$						Properties
				C	H	Cl	P	other	Formula for calculated values	
1 $IrCl(PPh_3)_2$	$[IrCl(C_8H_{14})_2]_2$ (0.5 g, 0.56 mmole) in 40 ml benzene + PPh_3 (0.58 g, 2.2 mmole)	Stir mixture for a few minutes, add 80 ml pentane, collect crystals, wash with alcohol, dry under vacuum, store under nitrogen.	78 (0.65)	57.4 57.0	4.0 4.4	4.7 4.5	8.2 8.0		$C_{36}H_{30}ClP_2Ir$	Very O_2 sensitive, pale-yellow crystals
2 $IrCl(C_2H_4)(PPh_3)_2(C_6H_6)_{\sim\frac{1}{2}}$	See 1	Stir mixture for a few minutes, bubble through C_2H_4 (15 min), add 80 ml C_2H_4-satd. pentane. Filter off precipitate, wash with pentane, dry under vacuum, store under nitrogen.	80 (0.70)	60.0 59.4	4.5 4.7	4.3 4.3	7.6 7.6		$C_{41}H_{37}ClP_2Ir$	Yellow-orange M.p. 144°-148°C (dec.)
3 $[IrCl(C_2H_4)(PPh_3)]_2(C_6H_6)_2$	$[IrCl(C_2H_4)_2]_2$ (0.16 g, 0.29 mmole) in 10 ml benzene + PPh_3 (0.15 g, 0.57 mmole)	Leave 5 min, filter off precipitate, wash with pentane, dry under vacuum, store under argon.	60 (0.20)	51.1 51.4	4.5 4.5	5.9 5.9	5.3 5.3		$C_{52}H_{50}Cl_2P_2Ir_2$	Pale-yellow, ν(Ir-Cl) 250 cm^{-1} $\tau(C_2H_4)$ in $CDCl_3$ at -30°C 6.65 ppm
4 $IrCl(C_2H_4)_2(PPh_3)_2$	2 (0.12 g) in 8 ml C_2H_4-satd. chloroform	Cool the solution (orange) to -50°C (colourless), add pentane, decant solvent from precipitate formed, freeze-dry at -50°C for 30 min.								White, stable at -50°C
5 $IrCl(C_2H_4)(O_2)(PPh_3)_2(C_6H_6)$	2 (0.30 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Sweep carefully O_2 over slowly stirred soln. until light-red; concentrate by sweeping with C_2H_4, filter off precipitate, dry under vacuum, store under C_2H_4 at -30°C	67 (0.21)	59.4 60.3	4.5 4.8	4.0 3.9	7.0 7.2	$\left.\begin{matrix}3.6\\2.6\end{matrix}\right\}O$	$C_{44}H_{40}ClP_2O_2Ir$	Pale-yellow
6 $IrCl(O_2)(PPh_3)_3$	5 (0.15 g) in 15 ml C_2H_4-satd. C_6H_6 + PPh_3 (44.2 mg, 1 eq.)	Stir mixture for 5 min, concentrate solution under argon to 1/3 of orginal volume, add pentane, filter off precipitate, wash with pentane, dry under vacuum, store under nitrogen.	70 (0.11)	62.0 61.0	4.3 4.2	3.4 3.3	9.2 9.0		$C_{54}H_{45}ClP_3O_2Ir$	Yellow
7a $IrCl(O_2)(PPh_3)_2(C_3H_4)$	5 (0.125 g) suspended in 20 ml C_6H_6 + 1 eq. allene	Stir mixture for 15 min at room temp add pentane, filter off precipitate, wash with pentane, dry under vacuum	79 (0.09)	56.8 54.8	4.1 4.2	4.3 4.6	7.5 7.6		$C_{39}H_{34}ClP_2O_2Ir$	Yellow-brown M.p. 169°-171°C (dec.)
7b $IrCl(O_2)(PPh_3)_2(CH_3CN)$	5 (0.1 g) suspended in 5 ml CH_3CN	Leave 5 min to obtain soln., add pentane, filter off precipitate, wash with ether, dry under vacuum.	84 (0.07)	55.3 54.1	4.0 3.6	4.3 4.1	7.5 7.3	$\left.\begin{matrix}1.7\\2.0\end{matrix}\right\}N$	$C_{38}H_{33}ClP_2NO_2Ir$	Light-yellow
7c $IrCl(O_2)(PPh_3)_2(AsPh_3)$	See 6; 1 eq. $AsPh_3$	See 6	70	59.5 58.1	4.1 4.2	3.3 3.7	5.7 6.1	$\left.\begin{matrix}6.9\\7.2\end{matrix}\right\}As$	$C_{54}H_{45}ClP_2AsO_2Ir$	Yellow
7d $IrCl(O_2)(PPh_3)_2(C_5H_5N)$	5 (0.2 g) in 5 ml pyridine	Leave 10 min, add pentane, filter off precipitate, wash with ether, dry under vacuum, store under nitrogen.	83 (0.16)	57.0 55.4	4.1 4.3	4.1 5.2	7.2 7.0	$\left.\begin{matrix}1.6\\1.7\end{matrix}\right\}N$ $\left.\begin{matrix}3.7\\2.8\end{matrix}\right\}O$	$C_{41}H_{35}ClP_2NO_2Ir$	Yellow
8 $IrCl(C_3H_4)(PPh_3)_2$	2 (0.20 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Sweep carefully allene over slowly stirred suspension until yellow solution; concentrate by sweeping with argon, precipitate with pentane.	65 (0.12)	59.1 58.4	4.3 4.7	4.5 4.5	7.8 7.8		$C_{39}H_{34}ClP_2Ir$	Yellow M.p. 172°-175°C (dec.)
9 $IrCl(C_3H_4)(SO_2)(PPh_3)_2$	8 (0.20 g) in 20 ml C_6H_6	Bubble through SO_2 during 30 min, precipitate with pentane	77 (0.17)	54.7 54.9	4.0 4.5	4.2 4.1	7.3 7.0	$\left.\begin{matrix}3.7\\3.7\end{matrix}\right\}S$	$C_{39}H_{34}ClP_2SO_2Ir$	Yellow-green
10 $IrCl(C_6H_8)(PPh_3)_2$	2 (0.5 g) suspended in 15 ml alcohol or aceton	Bubble trough allene during 15 min at room temp.; filter off precipitate, wash with toluene, dry under vacuum	85 (0.41)	60.6 61.9	4.6 4.9	4.3 4.3	7.5 7.0		$C_{42}H_{38}ClP_2Ir$	White M.p. > 200°C
11 $IrCl(C_2H_4)(SO_2)(PPh_3)_2C_6H_6$	2 (0.5 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Bubble through SO_2 during 2 min until solution; concentrate by sweeping with C_2H_4, filter off complex, dry under vacuum.	72 (0.39)	57.3 57.4	4.3 4.6	3.9 4.1	6.7 6.9	$\left.\begin{matrix}3.5\\3.6\end{matrix}\right\}S$	$C_{44}H_{40}ClSO_2P_2Ir$	Yellow-green M.p. > 200°C
12 $IrCl(C_5H_5N)(SO_2)(PPh_3)_2$	11 (0.15 g) in 4 ml pyridine	Add pentane after 30 min, filter off precipitate, wash with pentane, dry under vacuum.	69 (0.10)	55.1 54.9	3.9 4.1	4.0 4.2	6.9 7.3	$\left.\begin{matrix}3.6\\3.6\end{matrix}\right\}S$ $\left.\begin{matrix}1.6\\1.6\end{matrix}\right\}N$	$C_{41}H_{35}ClSO_2NIr$	Yellow
13 $IrCl(C_4H_6)(PPh_3)_2$	2 (0.30 g) suspended in 20 ml C_2H_4-satd C_6H_6	Bubble through butadiene for 10 min until yellow-red soln., concentrate by sweeping with butadiene, add pentane, filter off precipitate wash with pentane. dry under vacuum.	75 (0.22)	60.7 60.7	4.3 4.7	4.3 4.3	7.5 7.3		$C_{40}H_{36}ClP_2Ir$	Pale yellow M.p. 164°-167°C (dec.)

coordinated intermediate is involved. Such a process has been shown to occur in the penta-coordinated $IrCl(C_2H_4)_4$ during ethylene exchange.[11]

The oxygen addition is irreversible and the compound does neither lose oxygen nor ethylene under vacuum (5 h). It has a very low solubility in most solvents, but it is moderately soluble in chlorinated solvents in which it decomposes slowly.

The weak PMR-spectrum at –50°C of the benzene-solvated product in $CDCl_3$ shows resonances at τ 2.73 and 6.65 due to aromatic protons and ethylene protons respectively. The IR-spectrum is characterized by a sharp absorption band at 880 cm^{-1} indicative of a structure in which the two oxygen atoms coordinate to the metal forming an isosceles triangle: the O-Ir-O ring.[14] The iridium-chlorine stretching frequency is at 307 cm^{-1}. This value compares with the (Ir-Cl) frequency at 315 cm^{-1} in the oxygen adduct of Vaska's compound $IrCl(CO)(O_2)(PPh_3)_2$, which has been shown by X-ray investigation[15] to possess a trigonal bipyramidal structure II. So we tentatively suggest a similar structure for this compound.



(II) (compound 5)

The ethylene ligand in 5 can be substituted by other ligands to form

$$IrCl(C_2H_4)(O_2)(PPh_3)_2\ (5) + L \rightarrow IrCl(O_2)(PPh_3)_2L\ (6,7)$$

complexes of the type $IrCl(O_2)(PPh_3)_2L$ (5) with L = triphenylphosphine (*6*), allene (*7a*), acetonitrile (*7b*), triphenylarsine (*7c*) and pyridine (*7d*). The complexes *6* and *7a* can also be prepared directly from $IrCl(PPh_3)_3$ and $IrCl(C_3H_4)(PPh_3)_2$ (*8*), respectively, by reaction with molecular oxygen. Like the parent compound, the complexes *6* and *7a-d* are characterized by strong IR-absorption bands between 800 and 900 cm^{-1} (Table II). The allene compound *7a* exhibits two absorptions in the 800-900 cm^{-1} region, e.g. at 890 and 862 cm^{-1}. Isotopic substitution with $^{18}O_2$ shifts the former band to 840 cm^{-1}, leaving the position of the other band unchanged. The magnitude of the shift equals the mass effect calculated for a simple harmonic oscillator. The 862 cm^{-1} band is assigned to the $\delta(CH_2)$ vibration of the allene ligand. This assignment is also supported by the presence of a weak overtone of this fundamental at 1724 cm^{-1} (see Table III).

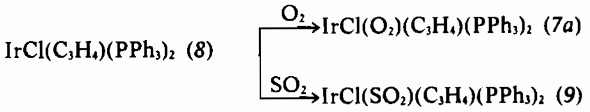
As is shown in Table II, the position of the characteristic absorption depends on L. In view of the insensitivity of this frequency to the O-O bond length, it was earlier suggested that this mode was not a pure O-O stretching vibration and that it might mix with the symmetrical metal-oxygen vibration.[14]

Table II. «ν(O-O) in $IrCl(O_2)(PPh_3)_2L$ (in KBr)

Complex	L	ν(O-O) in cm^{-1}
7a	C_3H_4	890 [a]
5	C_2H_4	880
7b	CH_3CN	862
Ref. 10	CO	857
7c	$AsPh_3$	854
6	PPh_3	848
7d	C_5H_5N	844

[a] 840 cm^{-1} in $^{18}O_2$-adduct.

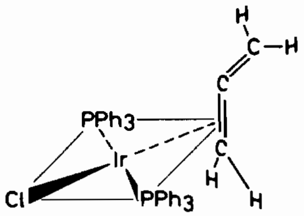
(d) *Reactions of $IrCl(PPh_3)_2$ with allene.* A solution of *1* or a suspension of *2* in benzene immediately reacts with one equivalent of allene forming the yellow complex $IrCl(C_3H_4)(PPh_3)_2$ (*8*).



$$IrCl(C_3H_4)(PPh_3)_2\ (8)\ \begin{cases} \xrightarrow{O_2} IrCl(O_2)(C_3H_4)(PPh_3)_2\ (7a) \\ \xrightarrow{SO_2} IrCl(SO_2)(C_3H_4)(PPh_3)_2\ (9) \end{cases}$$

On exposure to air, *8* forms the oxygen adduct *7a*. As mentioned under (c), this complex can also be obtained by treatment of a benzene suspension of the oxygen-ethylene adduct 5 with one equivalent of allene. The reaction product of *8* with sulfur dioxide is $IrCl(C_3H_4)(SO_2)(PPh_3)_2$ (*9*). Treatment of Vaska's compound, $IrCl(CO)(PPh_3)_2$, with allene in benzene yelds the unstable $IrCl(CO)(C_3H_4)(PPh_3)_2$. This compound loses allene on exposure to air within 10 minutes, but is stable in an allene atmosphere.

The IR-spectra (Table III) of these mono-allene complexes are, with the exception of *9* (see next section), characterised by a $\nu(C=C)$ absorption band of medium intensity in the 1700 cm^{-1} region and a strong $\delta(CH_2)$ band in the 800-900 cm^{-1} region with its weak overtone band at twice the fundamental frequency. These absorption bands are also found[17] in the spectrum of the rhodium complexes $RhX(C_3H_4)(PPh_3)_2$ (X = Cl, Br, or I) and are indicative of the presence of allene coordination using only one double bond. The far IR-spectrum of *8* reveals a band at 309 cm^{-1} with a shoulder at 303 cm^{-1}, which we assign to the ν(Ir-Cl) mode. The instability of *8* in chloroform and its low solubility in other solvents prevents PMR investigations. The structure of *8* is thought to be similar to the structure of $RhI(C_3H_4)(PPh_3)_2$, which can be described as square planar with the phosphine ligands in *trans*-position and the bent C=C=C system of the allene ligand approximately perpendicular to the molecular plane and coordinated to the metal through one C=C bond, the other C=C bond being bent away from the metal[18] (Structure III).



(III) (compound 8)

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(13) L. Vaska and R.E. Rhodes, *J. Amer. Soc.*, *87*, 4970 (1965).

(14) J.A. McGinnety, R.J. Doedens, and J.A. Ibers, *Inorg. Chem.*, 6, 2243 (1967).

(15) S.J. La Placa and J.A. Ibers, *J. Amer. Chem. Soc.* *87*, 2581 (1965).

Table III. IR- and PMR-spectra of allene complexes ($\delta(CH_2)$ data refer to the fundamental and the overtone frequency).

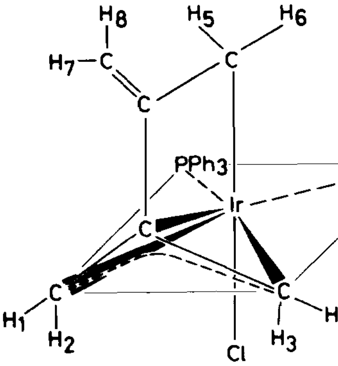
Compound	$MCl(C_3H_4)(PPh_3)_2L$		IR-data in cm^{-1}		τ-values in $CDCl_3$ (ppm)	
Complex no.	M	L	$\nu(C=C)$	$\delta(CH_2)$	uncoordinated CH_2	coordinated CH_2
8	Ir	—	1719	816, 1634	5.65(1), 5.92(1)	9.47(2)
Refs. 16, 17	Rh	—	1730	835	5.65(1), 5.92(1)	9.47(2)
7a	Ir	O_2	1760	862, 1724	3.97(1), 5.32(1)	7.34(2)
—	Ir	CO	1708	831, 1662		
9	Ir	SO_2			4.36(1). 5.33(1)	8.77(2) [a]

[a] Apparent triplet, $J_{P-H} \approx 3$ c/s.

Treatment of $IrCl(PPh_3)_3$ or complex *8* with excess of allene resulted in the formation of the white coloured complex $IrCl(C_6H_8)(PPh_3)_2$ (*10*), which showed characteristic IR-absorption bands at 2881, 1654, 944, 916 and 878 cm^{-1}. X-ray investigation[19] showed that the iridium atom was six-coordinated with two *cis*-phosphine ligands and a tridentate 2,2'-bi-σ,π-allyl ligand formed by allene dimerization (Structure IV). The position of Cl *trans* to the σ-bonded CH_2-group accounts for the low position of ν(Ir-Cl) at 253 cm^{-1}.

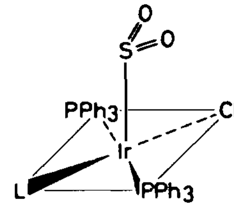
The PMR resonances of the CH_2-groups *trans* to the phosphine ligand at τ 9.37 (2, broad) and τ 7.33 (2, doublet $J_{P-H} = 8$ c/s) indicated coupling with P^{31}-nuclei. On account of the τ- and the J_{P-H}-value, we assign the former resonance to $H_{2,3}$ and the latter to $H_{1,4}$. The resonance of the protons $H_{5,6}$ was a sharp singlet at τ 6.85, whereas the uncoordinated protons $H_{7,8}$ located in the plane of symmetry of the molecule gave rise to two singlets at τ 5.71 and 5.86.

Unlike its rhodium analogue, $IrCl(PPh_3)_3$ is not a good catalyst for the oligomerisation of allene.[2] This is certainly due to the strong iridium-phosphorus bond which prevents further phosphine dissociation in complex *10* by which this complex can become coordinatively unsaturated and activate another allene molecule.*



(IV) (compound 10)

(e) *Sulfur dioxide adducts.* Treatment of *2* and *8* with SO_2 in benzene resulted in the formation of the adducts $IrCl(C_2H_4)(SO_2)(PPh_3)_2$ (*11*) and $IrCl(C_3H_4)(SO_2)(PPh_3)_2$ (*9*) respectively (Structure V). Both compounds are stable under vacuum and in air. They are only slightly soluble in benzene and chloroform.



(V) (compound 9 . 11)

The PMR spectrum in $CDCl_3$ of *11* shows resonances at τ 2.73 and 7.68 due to aromatic and ethylene protons respectively. Although the IR-spectrum of *9* did not show the characteristic ν(C=C) absorption in the 1600-1800 cm^{-1} region, its PMR spectrum proved the presence of allene (Table III).

The coordination geometry around the metal in *9* and *11* is probably similar to that in $MCl(CO)(SO_2)(PPh_3)_2$ with M = Rh[20] or Ir,[21] which is described as tetragonal pyramidal with CO, Cl and the trans-P-atoms in the base and the S of the SO_2 group at the apex.

The IR-spectra (Table IV) show strong absorption bands indicative of a SO_2-ligand, sulfur-bonded to the metal and acting as σ-Lewis acid.[20,22] With this type bonding, the metal-SO_2 moiety has a pyramidal structure with the S at the apex. This structure contrasts with the planar structure of the metal-SO_2 moiety found[23] in the complex $[RuCl(NH_3)_4SO_2]Cl$. Here the SO_2-ligand is acting as a Lewis base, and the metal-sulfur bond is shortenend by multiple π-bonding.

(f) *Butadiene adduct of* $IrCl(PPh_3)_2$. Treatment of a benzene suspension of *2* with butadiene for about ten minutes followed by addition of pentane gave the pale-yellow compound $IrCl(C_4H_6)(PPh_3)_2$ (*13*). The same complex can also be isolated by treatment of $IrCl(C_4H_6)_2$ (Ref. 11b) with two equivalents of triphenylphosphine. The PMR-spectrum at 60 and 100 MHz in $CDCl_3$ show broadened resonances at τ 4.44(1), 4.96(1), 6.92(1), 9.10(1), 10.18(1) and 10.78(1). The iridium-chlorine stretching frequency is at 276 cm^{-1} with a shoulder at 282 cm^{-1}. For rhodium the four-

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(*)This view is supported by the catalytic activity at 70°C in alcoholdichloromethane of the corresponding complex $IrCl(C_6H_8)(AsPh_3)_2$ containing the weaker iridium-arsine bonds. The IR-spectrum of the resulting poly-allene (m.p. 114-117°C)shows absorption bands due to unconjugated vinylidene groups.

(16) J.A. Osborn, *Chem. Commun.*, 1231 (1968).

(17) S. Otsuka, K. Tani, and A. Nakamura, *J. Chem. Soc.* (*A*). 1404 (1969).

(18) T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kukuko, *Chem. Commun.*, 317 (1969).

(19) T.C. van Soest, to be published.

(20) K.W. Muir and J.A. Ibers, *Inorg. Chem.*, *8*, 1921 (1969).

(21) S.J. La Placa and J.A. Ibers, *Inorg. Chem.*, 5, 405 (1966).

(22) L. Vaska and S.S. Bath, *J. Amer. Chem. Soc.*, *88*, 1333 (1966).

(23) L.H. Vogt, J.L. Katz, and S.E. Wiberley, *Inorg. Chem.*, 4, 1157 (1965).

(24) D.M. Roundhill, D.N. Lawson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 845 (1968).

Table IV. IR-spectra of SO_2-complexes.

Compound Complex no.	$MCl(SO_2)(PPh_3)_2L$ M	L	SO_2 absorption bands (cm^{-1}) γ_{sim}	γ_{asim}
11	Ir	C_2H_4	1063	1215, 1190
9	Ir	C_3H_4	1040	1215, 1190
Ref. 22	Ir	CO	1048	1198, 1185
Ref. 22	Rh	CO	1057	1214, 1188
Ref. 23	$[RuCl(NH_3)_4(SO)_2)]Cl$		1100	1301, 1278

Table V. Occurrence and stability of pentacoordinated complexes of the type $IrCl(PPh_3)_2XY$.
(?) Occurence unknown, (+) isolated under normal conditions, (—) unstable under normal conditions

			I			II		III	
	Y X	C_2F_4	O_2	SO_2	CO	C_3H_4	C_2H_4	PPh_3	C_5H_5N
	C_2F_4	?							
I	O_2	?	?						
	SO_2	?	?	?					
	CO	$+^a$	$+^a$	$+^a$	$—^a$				
II	C_3H_4	?	+(*7a*)	+(*9*)	—	^{b}			
	C_2H_4	?	+(*5*)	+(*11*)	$—^a$	?	—(*4*)		
III	PPh_3	$+^c$	+(*6*)	?	?	?	?	?	
	C_5H_5N	?	+(*7d*)	+(*12*)	?	?	?	?	?

[a] Ref. 10. [b]-Occurrence concluded from formation of $IrCl(C_6H_8)(PPh_3)_2$ (*10*). [c] Ref. 12.

coordinated species $RhCl(C_4H_6)(PPh_3)$ has been reported.[24] *

Five-coordination. The tendency of transition metals to from penta-coordinated complexes depends on the metal, its oxidation state and on the ligands surrounding it. Shriver[25] discussed the stability of low-oxidation-state metal complexes with Lewis acid ligands, such as BF_3, BH_3, O_2, SO_2 and tetracyanoethylene, on the basis of the transition-metal basicity concept. So the increased stability of five-coordinated complexes going from rhodium(I) to iridium(I) parallels the increased basicity going down from the second to the third row in the transition metal group.

The influence of the nature of the X and Y ligands on the stability of the five-coordinated complexes of the type $IrCl(PPh_3)_2XY$ is very pronounced. In Table V the occurrence and stability of these complexes are summarized; the ligands are divided into three groups:

(I) ligands possessing primarily accepting properties (sulfur dioxide, oxygen, tetrafluoroethylene);

(II) "Biphilic" ligands with donor and acceptor abilities (ethylene, allene, carbon monoxide);

(III) primarily donating ligands (pyridine and triphenylphosphine).

Molecular orbital calculations on Pt^{II}-complexes with σ-donating ligands showed that the original metal-ligand bonds all weaken upon expansion of the coordination number from four to five.[26] This opposes the gain of the bond energy of the fifth metal to ligand bond. The same is likely to be true of complexes with primarily π-accepting ligands because of the competition for the metal-electron density. From this point of view, the absence of known complexes of the type $IrCl(PPh_3)_2XY$ with X and Y belonging both to group I or both to group III may be understood.*

Our results indicate that five-coordination is especially favoured by the presence of X and Y ligands which are strongly complementary in their donor and acceptor properties. The nature of metal may be described as "daulistic" in the sense that it acts as a base towards ligands with acid properties and vice versa. Noteworthy is the non-existence of complexes in which the biphilic group II ligands combine with the donating group III ligands, whereas with the acidic group I ligands stable complexes are formed. This seems to confirm Vaska's suggestion[27] that σ-basicity of these ligands appears to be an even more important feature than their acid function in these complexes. The instability of the complexes with X and Y being both amphoteric may be considered as the result of this weak σ-basicity of these ligands and the weakening of the other metal ← ligand σ-bonds on expansion of the coordination number from four to five.

Acknowledgement.. We thank Professors A. van der Avoird and D.A. van Dorp for their stimulating interest and Mr H. van Gaal for fruitful discussions. We are grateful to Dr M. van Gorkom, Messrs J. Barzilay and R.W. Schaier for measurements of the NMR-spectra.

(*) Misprints in this reference may lead to the erroneous conclusion that the five-coordinated complex $RhCl(C_4H_6)(PPh_3)_2$ was reported.

(25) D.F. Shriver, *Acc. Chem. Res.*, 3, 231 (1970).

(26) S.A. Zumdahl and R.S. Drago, *J. Amer. Chem. Soc.*, 90, 6669 (1968).

(*) It is known from thermochemical studies[10] that the entropy of formation of five-coordinated adducts of $IrCl(PPh_3)_2(CO)$ amounts -20 to -40 eu, corresponding to a free-energy contribution of about 10 kcal/mole at room temperature. So, in order to be stable at room temperature, the enthalpy of formation of five-coordinated complexes has to be larger than about -10 kcal/mole.

(27) L. Vaska, *Inorg. Chim. Acta*, 5, 295 (1971).