Some New Iridium Complexes Derived from Chlorotricarbonyliridium

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Reactions of $[Ir(CO)_3Cl]_n$ with chelating agents L–L (L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2AsCH_2CH_2AsPh_2$) to give $Ir(CO)_2(L–L)Cl$ complexes are reported. Complexes of the type $[Ir(CO)_2LCl]_n$ (L = SEt_2, $SeEt_2$, or $TeEt_2$) have also been isolated by making $[Ir(CO)_3Cl]_n$ react with ligands containing Group VIB donor atoms. Oxidative addition reactions on the cationic four-co-ordinated $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ are included and discussed according to the σ-donor ability of the co-ordinated ligands and the positive charge of the complex. The i.r. spectral properties of the complexes are discussed.

INTEREST in the preparation of new d^8 complexes is related to the ability of some of them to undergo oxidative additions[1] and to catalyse the homogeneous hydrogenation of olefins and acetylenes.[2] Compounds of the type $M(CO)L_2X$, ML_3X, and $[M(L–L)_2]^+$ (M = Rh or Ir; L = P, As, or Sb containing ligands; L–L = $Ph_2PCH_2CH_2PPh_2$; X = Cl, Br, or I) seem to have a particular versatility for these reactions.

In this paper we report on the preparation of new products obtained by reacting $[Ir(CO)_3Cl]_n$ with chelating agents L–L (L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2AsCH_2CH_2AsPh_2$) and with monodentate ligands SEt_2, $SeEt_2$, and $TeEt_2$. Oxidative addition reactions on the cationic four-co-ordinated complex $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ are also included.

RESULTS AND DISCUSSION

Reactions with Chelating Agents.—On refluxing, for several hours, a (1 : 1 molar) suspension of $[Ir(CO)_3Cl]_n$ and L–L in benzene, the colour of the reaction mixture turns to orange-red. After filtering, evaporating the solvent, and crystallization of the crude product from CH_2Cl_2–ether, a yellow compound is obtained. On the basis of the analytical data (Table) the complexes could be formulated as five-co-ordinated species $Ir(L–L)(CO)_2Cl$. Conductivity data for acetone solutions of the complexes and the molecular weight in acetone solution for the $Ir(CO)_2(Ph_2PC_2H_4PPh_2)Cl$ are given in the Table. No molecular weight measurement could be made for $Ir(CO)_2(Ph_2AsC_2H_4AsPh_2)Cl$ because of its limited solubility in acetone. The conductivity values are lower than those expected for a complete dissociation of the five-co-ordinated species as 1 : 1 electrolytes and an equilibrium of the type:

$$Ir(CO)_2(L–L)Cl \rightleftharpoons [Ir(CO)_2(L–L)]^+ + Cl^- \quad (1)$$

could be operating. Moreover, equilibrium (1) is shifted further to the right when L–L = $Ph_2AsCH_2CH_2AsPh_2$ than when L–L = $Ph_2PCH_2CH_2PPh_2$ and this may be due to steric as well as to electronic effects.

	Analytical data										I.r. (Nujol mull, cm^{-1})	
	Found %			Required %								
Complex	C	H	Halogen	C	H	Halogen	*M* [a]	Colour	M.p. °C	Λ_M [b]	ν(CO)	νIr–Cl
$[Ir(CO)_2(Ph_2PCH_2CH_2PPh_2)Cl]$	49·25	3·65	5·0	49·2	3·55	5·2	699 [g] (683)	Pale yellow	>170 dec.	16	2048vs, 1962vs	328m
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl]$	43·7	3·3	4·8	43·65	3·15	4·60		Yellow-orange	120—140 dec.	60	2050vs, 1965vs, 1932sh,m	325m
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$	59·2	4·45	0·0	58·9	4·25	0·0		Pale yellow	215—219 dec.	96	2018w, 1932vs	
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl_2]BPh_4$	55·25	4·15	6·15	55·5	3·95	6·3		Yellow	102—105	89	2132vs, 2038vs	330s
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)I_2]BPh_4$	47·65	3·65	19·6	47·75	3·4	19·4		Yellow-orange	128—132	94	2064vs	
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(MeCO)Cl]BPh_4$								Yellow			2130vs, 2040vs, 1710s	
$[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(PhSO_2)Cl]BPh_4$ [c]	56·25	4·25	2·95	56·6	4·0	2·9		Yellow	138—142	98	2060vs	299m
$[Ir(CO)_2(SEt_2)Cl]_n$ [d]	19·15	2·85	9·4	19·3	2·7	9·5	1825	Dark violet	125—131 dec.		2060vs, 2021s	
$[Ir(CO)_2(SeEt_2)Cl]_n$ [e]	17·35	2·55	8·4	17·1	2·45	8·4	2418	Brown	>175 dec.		2050vs, 2018s	
$[Ir(CO)_2(TeEt_2)Cl]_n$ [f]	15·1	2·3	7·3	15·4	2·15	7·55	2215	Brown	184—198 dec.		2018vs, 1969m	

[a] In $CHCl_3$. [b] Molar conductivities for *ca.* 5×10^{-4}M-solutions in acetone at 25°; in $\Omega^{-1} mol^{-1} cm^2$. [c] S found 2·39%, required 2·60%. [d] O found 8·75%, required 8·56%. [e] O found 7·43%, required 7·61%. [f] O found 6·54%, required 6·83%. [g] In acetone solution; calculated value in parentheses.

The i.r. spectrum (Nujol mull) in the CO stretching region of the compound formulated as $Ir(CO)_2(Ph_2PCH_2CH_2PPh_2)Cl$ is slightly different from that of $Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl$. In the latter case there is a shoulder at 1934 cm^{-1} which appears as a sharp band in the spectrum of $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ (see below). The far-i.r. spectrum of $Ir(CO)_2(Ph_2PC_2H_4PPh_2)Cl$ shows a medium-weak band at 328 cm^{-1} which can be assigned to the Ir–Cl stretching frequency; the assignment of this stretching frequency at 325 cm^{-1} for the analogous $Ir(CO)_2(Ph_2AsC_2H_4AsPh_2)Cl$ is only tentative because there are other absorptions, due to the chelating ligand, in this region of the spectrum. In conclusion, conductivity, i.r., and molecular weight data suggest that the phosphine chelated compound is mainly a five-co-ordinated neutral species $Ir(CO)_2(Ph_2PC_2H_4PPh_2)Cl$ whereas the arsine chelated compound is a mixture of $Ir(CO)_2(Ph_2AsC_2H_4AsPh_2)Cl$ and $[Ir(CO)_2(Ph_2AsC_2H_4AsPh_2)]Cl$. By adding $NaBPh_4$ in methanol to a methanolic solution of $Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl$, a pale yellow precipitate is obtained which can be formulated as $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$ on the basis of elemental analysis, i.r. spectrum, and conductivity measurements.

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[2] 'Aspects of Homogeneous Catalysis,' ed. R. Ugo, vol. 1, Manfredi, Ed., Milan, 1970.

A similar precipitate is formed, as the only product, when a methanolic suspension of $[Ir(CO)_3Cl]_n$ reacts with $Ph_2AsCH_2CH_2AsPh_2$ in the presence of $NaBPh_4$.

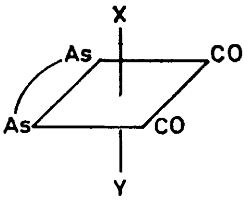
Iridium(I) complexes of the type $[Ir(CO)_xL_{5-x}]^+$, where $x = 1$—3, $[Ir(L-L)_2CO]^+$ [L = phosphine or arsine; L–L = bis(1,2-diphenylphosphine)ethane] have been reported.[3-7] Four-co-ordinated complexes such as $[Ir(L-L]_2]^+$ have also been prepared,[4,10] and complexes of the type $[Ir(CO)_2L_2]^+$ were postulated as intermediates in the reductive elimination of hydrogen from $[Ir(CO)_2H_2L_2]^+$ and isolated when $L = P(C_6H_{11})_3$ or $P(Pr^i)_3$.[6,8] Very recently, cationic complexes of the type $[Ir(CO)L_3]^+$ have been isolated.[7,9] Therefore, the complex $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ can be considered the first example of four-co-ordinated cationic iridium(I) complex containing CO and bidentate ligands.

In the CO stretching region, the four-co-ordinate complex $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ shows a weak band at 2018 cm^{-1} and a strong one at 1932 cm^{-1}, as would be expected.

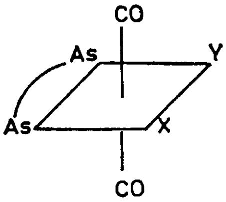
Oxidative Addition Reactions of $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$.—The ability of the complexes to undergo oxidative addition reactions is related to the electron density on the metal, which in turn depends on the nature of the co-ordinated ligands. In consequence, cationic four co-ordinated iridium(I) complexes should be less effective in the oxidative additions than the neutral ones. The only four-co-ordinated cationic complex which displays an aptitude for activating small molecules by oxidative addition, reminiscent of the Vaska complex, is $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$.[4] Complexes of the types $[Ir(CO)L_3]^+$ and $[IrL_4]^+$ ($L = PPh_3$, PPh_2Me, and PPh_2Et) react with hydrogen but only the compound containing more basic phosphines adds oxygen.[9]

The complex $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ does not react with H_2, O_2, and CH_3I in solution, but reacts with Cl_2, I_2, and $PhSO_2Cl$ very easily giving cationic six-co-ordinated adducts of iridium(III). In addition MeCOCl reacts with $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ to give $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(MeCO)Cl]^+$ as is confirmed by the i.r. spectrum, which shows two strong bands in the carbonyl stretching region at 2130 and 2040 cm^{-1} and a band at 1710 cm^{-1} due to the acyl CO stretching. However, the addition is reversible and we could not obtain the complex in a pure form.

A different stereochemistry has been observed for the six-co-ordinated cationic adducts of irridium(III) here reported. In the i.r. spectrum the compound $[Ir(CO)_2(Ph_2AsC_2H_4AsPh_2)Cl_2]BPh_4$ shows two strong ν(CO) bands at 2132 and 2038 cm^{-1} and a ν(Ir–Cl) band at 330 cm^{-1} due to two chlorine atoms in *trans*-positions. This suggests the structure (Ia) reported in the Figure.



(I)



(II)

(Ia; X = Cl, Y = Cl) (IIa; X = I, Y = I)
(Ib; X = Cl, Y = CH_3CO) (IIb; X = Cl, Y = $PhSO_2$)

A similar structure (Ib) can be formulated for the acyl compound. The complexes $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)I_2]^+$ and $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(PhSO_2)Cl]^+$ in the i.r. region give only a band ν(CO) at 2064 and 2060 cm^{-1} respectively. For the latter compound a band ν(Ir–Cl) at 299 cm^{-1} is indicative of a chlorine atom in *trans*-position to a bidentate ligand, as indicated in the structure (IIb). A different stereochemistry in the halogen addition was recently observed in the reaction of $[RhL_4]^+$ with Cl_2, Br_2, and I_2.[11] However the different configuration of the adducts could be due to a possible isomerization in solution or to a different pathway in the addition. In conclusion, the complex $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ is less effective in the oxidative additions than the neutral complexes or other chelated compounds such as $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$. Certainly the presence of two weak σ donor CO groups co-ordinated to the metal is a contributory factor in determining the observed behaviour.

Reactions with Ligands Containing Group VIB *Donor Atoms.*—In previous papers[12,13] we reported on the preparation of new complexes of the type *trans*-$[Rh(CO)L_2Cl]$ ($L = SEt_2$, $SeEt_2$, $TeEt_2$). Our aim has been, in part, the preparation of similar iridium(I) complexes. We recall, in this respect, that, *inter alia*, the compounds *trans*-$[Ir(CO)L_2Br]$ ($L = PPh_3$, $AsPh_3$) can be prepared by refluxing $[Ir(CO)_3Br]_n$ with the appropriate ligand in toluene.[14]

When a suspension of $[Ir(CO)_3Cl]_n$ is refluxed in benzene with SEt_2, $SeEt_2$, or $TeEt_2$, the compounds obtained can be formulated, on the basis of elemental analysis and molecular weight measurements, as $[Ir(CO)_2LCl]_n$. Metathetical reactions of these with LiBr or LiI, in acetone, give the corresponding bromo- and iodo-derivatives.

The chlorocarbonyliridium $[Ir(CO)_3Cl]_n$ is a compound

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[14] F. Canziani, U. Sartorelli, and F. Zingales, *Chim. e. Ind.* (*Milan*), 1967, **49**, 469.

with linear chains of metal atoms.[15] We think that there are similar metal–metal linkages in the case of the complexes $[Ir(CO)_2LCl]_n$. By making $[Ir(CO)_2LCl]_n$ react with PPh_3, using a 1 : 2 molar ratio, the Vaska compound is obtained, while the reaction with $Ph_2PCH_2CH_2PPh_2$ in benzene gives $Ir(CO)_2(Ph_2PCH_2CH_2PPh_2)Cl$. As shown in the Table, two i.r. bands in the CO stretching region are observed for $[Ir(CO)_2LCl]_n$ and their high values could be due to an increase of the formal charge in the iridium atoms as a consequence of iridium–iridium bonds.

When $[Ir(CO)_3Br]_n$ reacts with PPh_3 or $AsPh_3$, complexes analogous to the Vaska compounds are obtained.[14] The different behaviour of the ligands containing phosphorous or arsenic and SEt_2, $SeEt_2$, or $TeEt_2$ can be attributed to their different *trans*-activating ability.

EXPERIMENTAL

Chlorocarbonyliridium was a Strem product. Other reagents were used without purification. I.r. spectra were recorded with a Perkin-Elmer 457 spectrometer. Molecular weights were determined with a Knauer vapour pressure osmometer. M.p.s were determined on a Fisher-Jones hot-stage apparatus. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt, Mulheim, Germany.

All reactions were carried out under a nitrogen atmosphere.

Chlorodicarbonyl[bis(1,2-diphenylphosphino)ethane]iridium(I), $[Ir(CO)_2(Ph_2PCH_2CH_2PPh_2)Cl]$.—A suspension of $[Ir(CO)_3Cl]_n$ (0·400 g; 1·28 mmol) and $Ph_2PCH_2CH_2PPh_2$ (0·51 g, 1·28 mmol) in anhydrous benzene (150 ml) was refluxed for *ca.* 3 h. The red solution was filtered and evaporated *in vacuo*. The crude product obtained was crystallized from $CHCl_3$–ether to give a yellow solid soluble in CH_2Cl_2, $CHCl_3$, or acetone, but insoluble in ether and hydrocarbons (yield 65%).

Chlorodicarbonyl[bis(1,2-diphenylarsino)ethane]iridium(I), $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl]$.—A suspension of $[Ir(CO)_3Cl]_n$ (0·40 g, 1·28 mmol) and $Ph_2AsCH_2CH_2AsPh_2$ (0·62 g, 1·28 mmol) in benzene was refluxed for *ca.* 4 h. The orange solution was then filtered and concentrated to a small volume (2 ml). By adding ether an orange solid was obtained (yield 75%) soluble in chlorinated solvents or benzene.

Dicarbonyl[bis(1,2-diphenylarsino)ethane]iridium(I) *Tetraphenylborate*, $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$.—*Method* (*a*). $NaBPh_4$ was added to a solution of $Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl$ in methanol. The pale yellow precipitate, immediately formed, was washed with methanol and dried.

Method (*b*). To a suspension of $[Ir(CO)_3Cl]_n$ (0·40 g, 1·28 mmol) in ethanol, $Ph_2AsCH_2CH_2AsPh_2$ (0·62 g, 1·28 mmol) and $NaBPh_4$ (0·51 g, 1·5 mmol) were added and the mixture was refluxed for *ca.* 2 h. A mixture of yellow and dark compounds was formed; the yellow solid was dissolved in CH_2Cl_2 and, after evaporation of the solvent, crystallized from CH_2Cl_2–ether (yield 55%).

Bis[bis(1,2-diphenylphosphino)ethane]iridium(I) *Tetraphenylborate*, $[Ir(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$.—To a suspension of $[Ir(CO)_3Cl]_n$ (0·40 g, 1·28 mmol) in ethanol, $Ph_2PCH_2CH_2PPh_2$ (1·20 g, 2·56 mmol) and $NaBPh_4$ (0·52 g, 1·5 mmol) were added and the mixture was refluxed for 2 h. The red-orange precipitate formed was filtered off, then dissolved in CH_2Cl_2 to separate it from the starting material. By adding pentane $[Ir(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$ was formed.

Dichlorodicarbonyl[bis(1,2-diphenylarsino)ethane]iridium(III) *Tetraphenylborate*, $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl_2]BPh_4$.—A dichloromethane solution of Cl_2 was added to $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$ dissolved in CH_2Cl_2. The progress of the reaction was followed by i.r. spectroscopy. The solution was concentrated and by adding pentane a pale yellow solid was obtained. The compound is soluble in chlorinated solvents but less soluble in methanol and acetone.

Di-iododicarbonyl[bis(1,2-diphenylarsino)ethane]iridium(III) *Tetraphenylborate*, $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)I_2]BPh_4$.—A dichloromethane solution of I_2 (0·12 g, 0·5 mmol) was added to $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$ (0·40 g, 0·38 mmol) dissolved in the same solvent. After *ca.* 10 min the reaction was complete and by adding pentane a yellow-orange compound was obtained. The compound is soluble in chlorinated solvents and acetone.

Chlorodicarbonyl[bis(1,2-diphenylarsino)ethane](S-benzenesulphinate)iridium(III) *Tetraphenylborate*, $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(PhSO_2)Cl]BPh_4$.—$PhSO_2Cl$ in CH_2Cl_2 was added dropwise to a solution of $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$ in the same solvent. The reaction was followed by i.r. spectroscopy until the band $\nu(CO)$ at 1952 cm^{-1} disappeared. By adding light petroleum a yellow solid was obtained.

Chloro(acetyl)dicarbonyl[bis(1,2-diphenylarsino)ethane]iridium(III) *Tetraphenylborate*, $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)(CH_3CO)Cl]BPh_4$.—MeCOCl in dichloromethane was added dropwise to a solution of $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]BPh_4$ in the same solvent. The i.r. spectrum showed that the reaction was not complete. By concentrating the solution and adding pentane a yellow precipitate was formed, which still contained starting material. Attempts to separate the mixture have been unsuccessful.

Chlorodicarbonyl(diethyl sulphide)iridium, $[Ir(CO)_2(SEt_2)Cl]_n$.—To $[Ir(CO)_3Cl]_n$ dissolved in benzene (150 ml) an excess of SEt_2 was added and the solution was refluxed for 8 h. After filtration and evaporation an oil was obtained. By adding pentane a dark violet precipitate was formed which was crystallized from chloroform–light petroleum. Similarly *chlorodicarbonyl(diethyl selenide)iridium*, $[Ir(CO)_2(SeEt_2)Cl]_n$ and *chlorodicarbonyl(diethyl telluride)iridium*, $[Ir(CO)_2(TeEt_2)Cl]_n$ have been prepared.

The compounds of the type $[Ir(CO)_2LX]_n$ ($L = SEt_2$, $SeEt_2$, or $TeEt_2$; $X = Br$ or I) have been prepared by metathetical reactions of the chloro-derivatives with a slight excess of the corresponding halides in acetone. After *ca.* 12 h the solvent was evaporated and the residue washed with water and dried. The compounds have been crystallized from chloroform–light petroleum.

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