Four-co-ordinate Cationic Dicarbonyl(phosphine)iridium(I) Complexes obtained from Chlorotricarbonyliridium

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The chlorotricarbonyliridium, $[Ir(CO)_3Cl]_n$, reacts, in the presence of $AgBF_4$ or $NaBPh_4$, with tertiary phosphines L [L = PPh_3, $P(o\text{-tolyl})_3$, $P(isopropyl)_3$, $P(cyclohexyl)_3$, or PPh_2Bu^t] giving cationic four-co-ordinated products $[Ir(CO)_2L_2]^+$. Steric rather than electronic factors seem to be very important for the formation of the above reported compounds. The complexes $[Ir(CO)_2L_2]^+$ [L = PPr^i_3, $P(C_6H_{11})_3$, PPh_2Bu^t] absorb CO giving cationic five-co-ordinated compounds $[Ir(CO)_3L_2]^+$; the same reaction does not occur when L = PPh_3 or $P(o\text{-tolyl})_3$ and this confirms the importance of the phosphine basicity in promoting five-co-ordination. The chloride ion reacts with $[Ir(CO)_2L_2]^+$ complexes giving the neutral compounds *trans*-$Ir(CO)L_2Cl$. Some oxidative addition reactions on $[Ir(CO)_2L_2]^+$ complexes are described.

RECENTLY we reported that $[Ir(CO)_3Cl]_n$ reacts with chelating ligands such as bis(1,2-diphenylarsino)ethane (molar ratio 1 : 1) in alcoholic solution and in the presence of $NaBPh_4$ giving $[Ir(Ph_2AsCH_2CH_2AsPh_2)(CO)_2]BPh_4$ as the only product.[1]

We have extended this type of reaction, including other tertiary phosphines, and in some cases we succeeded in preparing $[Ir(CO)_2L_2]^+$ compounds. Other authors have described different routes to some of these salts.[2,3] However we have found that the methods reported here are most suitable for the preparation of a variety of four-co-ordinated dicarbonylphosphine salts of iridium(I). We also report the results of some oxidative addition reactions of $[Ir(CO)_2L_2]^+$ complexes.

RESULTS AND DISCUSSION

The complex $[Ir(CO)_3Cl]_n$ reacts with phosphines or arsines, in toluene heated under reflux, to produce the neutral complexes *trans*-$Ir(CO)L_2X$.[4] By reacting an ethanolic suspension of $[Ir(CO)_3Cl]_n$, heated under reflux, with a phosphine such as PPh_3, $P(o\text{-tolyl})_3$, PPr^i_3,

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P(cyclohexyl)$_3$, or PPh$_2$Bu^t in the presence of a slight excess of AgBF$_4$, the iridium compound dissolves and the solution becomes red. Cationic complexes [Ir(CO)$_2$L$_2$]$^+$ can be obtained as described in the Experimental section. When PEt$_2$Ph, PPh$_2$Me, or PEt$_3$ were used, intractable materials together with *trans*-Ir(CO)L$_2$Cl complexes were obtained.

The cationic complexes are red, air-stable crystals * and behave as 1 : 1 electrolytes in solution. The i.r. spectra (Table) show a very strong band *ca.* 2000 cm^{-1} in the CO stretching region and this supports a *trans*-configuration. The phosphines used as ligands in these reactions differ both in basicity and bulk. The results indicate that the bulk of the ligands is an essential factor for the formation of the cationic complexes [Ir(CO)$_2$L$_2$]$^+$. Bulky phosphines produce four-co-ordinated cationic compounds, but basic phosphines do not. When carbon monoxide is bubbled through a solution containing [Ir(CO)$_2$L$_2$]$^+$ complexes [L = PPr$^i_3$, PPh$_2$Bu^t, P(cyclohexyl)$_3$] the red colour disappears and five-co-ordinated [Ir(CO)$_3$L$_2$]$^+$ compounds can be isolated. Similar results [3] were reported for [Ir(CO)$_2$L$_2$]$^+$ complexes [L = PPr$^i_3$, P(cyclohexyl)$_3$]. The white compound [Ir(CO)$_3$(PPh$_2$Bu^t)$_2$]$^+$ easily loses CO to give the corresponding four-co-ordinated compound.

Analytical data, physical properties, and characteristic i.r. bands

	Analyses[a]					I.r. spectral data[b]		
Complex	C	H	Cl	Colour	M.p./°C	ν(CO)	ν(Ir–H)	ν(Ir–Cl)[c]
[Ir(CO)$_2$(PPh$_3$)$_2$]BPh$_4$	68·3 (68·2)	4·75 (4·6)		Red	91—95	2008vs		
[Ir(CO)$_2$(PPh$_2$Bu^t)$_2$]BF$_4$	49·7 (49·8)	4·75 (4·65)		Red	98—102	1998vs		
[Ir(CO)$_2${P(*o*-tolyl)$_3$}$_2$]BF$_4$	55·75 (56·0)	4·8 (4·5)		Red	105—108 dec.	2022vs		
[Ir(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$	36·5 (36·65)	6·4 (6·45)		Red	89—95	1985vs		
[Ir(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$]BF$_4$	50·7 (50·95)	7·3 (7·4)		Red	72—80 dec.	1988vs		
Ir(CO)(PPh$_2$Bu^t)$_2$Cl	53·4 (53·55)	5·2 (5·2)	4·6 (4·8)	Yellow		1948vs		312m
Ir(CO){P(*o*-tolyl)$_3$}$_2$Cl	59·5 (59·75)	5·0 (4·9)	4·3 (4·1)	Yellow	284—287 dec.	1955vs		315s
Ir(CO)(PPr$^i_3$)$_2$Cl	40·7 (40·6)	7·9 (7·85)	6·35 (6·65)	Yellow	222—225	1935vs		308m
[Ir(CO)$_3$(PPh$_2$Bu^t)$_2$]BF$_4$	49·75 (49·6)	4·7 (4·5)		White		1920s		
[Ir(CO)$_2$(PPh$_2$Bu^t)$_2$H$_2$]BF$_4$	49·45 (49·7)	4·75 (4·9)		White	149—152	2050vs 2082s	2160s 2180sh	
[Ir(CO)$_2$(PPh$_2$Bu^t)$_2$Cl$_2$]BF$_4$	46·0 (45·85)	4·6 (4·3)	8·65 (8·95)	Pale yellow		2060vs		
[Ir(CO)$_2${P(*o*-tolyl)$_3$}$_2$Cl$_2$]BF$_4$	52·2 (52·1)	2·4 (2·6)	7·1 (7·0)	Pale yellow		2033vs		
[Ir(CO)$_2$(PPr$^i_3$)$_2$Cl$_2$]BF$_4$	33·2 (33·05)	6·0 (5·8)	10·05 (9·75)	Pale yellow		2040vs		329s
[Ir(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$]BF$_4$	47·25 (47·2)	6·7 (6·9)	7·5 (7·35)	Yellow	248—251	2025vs		331s

[a] Calculated values in parentheses. [b] CH$_2$Cl$_2$ solution, value in cm^{-1}. [c] For Nujol mulls.

[Ir(CO)$_2$(PPh$_3$)$_2$]$^+$ and [Ir(CO)$_2$(P(*o*-tolyl)$_3$)$_2$]$^+$ show a different behaviour; they do not give five-co-ordinated complexes when carbon monoxide is bubbled through the solution or when PPh$_3$ is added. It is now generally accepted that the five-co-ordination is favoured by an increase in electron density on the metal. The triphenylphosphine and tris(*o*-tolyl)phosphine are the least basic ligands used to prepare [Ir(CO)$_2$L$_2$]$^+$ compounds and this could explain the observed behaviour.

[Ir(CO)$_2$L$_2$]$^+$ complexes react with Cl$^-$ affording *trans*-Ir(CO)L$_2$Cl. A similar reaction was reported [6] for the five-co-ordinated cationic complex [Ir(CO)$_3$L$_2$]$^+$. This observation supports the idea that when [Ir(CO)$_3$Cl]$_n$ reacts with phosphines or arsines to give Vaska-type complexes, the cationic complexes [Ir(CO)$_2$L$_2$]$^+$ could be involved as an intermediate.

The *trans*-Ir(CO)L$_2$Cl [L = PPr$^i_3$, PPh$_2$Bu^t, P(*o*-tolyl)$_3$, P(C$_6$H$_{11}$)$_3$] are all yellow solids and show ν(CO) stretching *ca.* 1950 cm^{-1} in their i.r. spectra.

Oxidative Addition Reactions.—Recently Shaw and Stainbank [7] observed that the presence of bulky tertiary phosphines co-ordinated to the metal in a d^8 complex can greatly reduce the basicity and the tendency of the complexes to undergo oxidative addition reactions.

We find that the reaction of [Ir(CO)$_2$L$_2$]$^+$ with a variety of molecules, such as hydrogen, oxygen, and chlorine, does not show any influence by steric factors.

All the four-co-ordinated complexes [Ir(CO)$_2$L$_2$]$^+$ reported here, with the exception of the P(*o*-tolyl)$_3$ derivative, readily react with hydrogen at room tem-

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* When [Ir(CO)$_2$(PPh$_3$)$_2$]BPh$_4$ is precipitated by hydrocarbons from CH$_2$Cl$_2$ or acetone solutions it appears as a yellow solid. However the elemental analysis and the i.r. spectrum in solution, are identical to those of the red analogue. It is possible that these variations are due to differences in crystal packing. Effects of crystal packing have recently been proposed [5] to account for the two crystalline forms of the complex [Ir(CO)$_2$(PMe$_2$Ph)$_3$]ClO$_4$.

[5] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 2705.

[6] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6975.

[7] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716; *J.C.S. Dalton*, 1972, 223.

perature and pressure, in CH_2Cl_2 solution, giving six-co-ordinated $[Ir(CO)_2H_2L_2]^+$ complexes.

Under the same experimental conditions no reaction was observed when oxygen or sulphur dioxide were used. Some dihydride complexes reported here were previously prepared by different methods.[3] In the 2000 cm^{-1} region, the i.r. spectra of the dihydride complexes show four bands and are very similar to those reported for other complexes of the same type. We attribute to them a structure having two *cis*-carbonyl groups and the hydride ligands *cis* to the two phosphines.

The $[Ir(CO)_2L_2]^+$ complexes [$L = P(C_6H_{11})_3$, PPh_2Bu^t, $P(o\text{-tolyl})_3$, PPr^i_3] react with chlorine giving six-co-ordinated cationic $[Ir(CO)_2L_2Cl_2]BF_4$ compounds. The i.r. spectra of these complexes show a CO band *ca.* 2040 cm^{-1} and a ν(Ir–Cl) band at 330 cm^{-1} as expected for a *trans*-configuration.

$[Ir(CO)_2(PPh_3)_2]^+$ reacts differently with a CH_2Cl_2–chlorine solution producing $Ir(CO)(PPh_3)_2Cl_3$ previously obtained by oxidative addition of chlorine to the Vaska compound $Ir(CO)(PPh_3)_2Cl$.

Iodine reacts similarly giving $Ir(CO)(PPh_3)_2I_3$. When following this reaction with i.r. spectroscopy, we noted that $Ir(CO)(PPh_3)_2I_3$ is obtained in a two step reaction, the first step of which produces $Ir(CO)_2(PPh_3)_2I$ previously reported by Malatesta and co-workers.[6] $Ir(CO)(PPh_3)_2Cl_3$ is probably formed in a similar way.

EXPERIMENTAL

General experimental particulars as before.[1]

Dicarbonylbis(triphenylphosphine)iridium(I) *Tetraphenylborate.*—To a suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol) in ethanol, PPh_3 (molar ratio 1 : 3) and $NaBPh_4$ were added. The mixture was refluxed for *ca.* 2 h. A green-yellow precipitate was formed which was washed with benzene in order to remove traces of $IrCl(CO)(PPh_3)_2$ and then with ether. Extraction with CH_2Cl_2 gives, after evaporation of the solvent, red needles (yield 60%). The product is soluble in chlorinated solvents, acetone, slightly soluble in benzene. It is obtained as yellow crystals when it is precipitated with hydrocarbons.

Dicarbonylbis(diphenyl-t-butylphosphine)iridium(I) *Tetrafluoroborate.*—To a suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol) in ethanol, PPh_2Bu^t (molar ratio 1 : 2) and an excess of $AgBF_4$ were added. The mixture was refluxed for *ca.* 1 h. The solution became red. A dark compound was also formed. The solution was filtered and evaporated. The crude product was crystallized from CH_2Cl_2–ether to afford red plates (yield 65%). The complex is soluble in chlorinated solvents and acetone.

*Dicarbonylbis[tris(*o*-tolyl)phosphine]iridium*(I) *Tetrafluoroborate.*—To a suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol), $P(o\text{-tolyl})_3$ and an excess of $AgBF_4$ were added. The mixture was left at 50 °C for *ca.* 30 min (a further rise in temperature lowers the yield). The red solution was filtered, the solvent evaporated and the crude product was crystallized from CH_2Cl_2–ether (yield 50%) to give red crystals.

Dicarbonylbis(tri-isopropylphosphine)iridium(I) *Tetrafluoroborate.* A suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol) in ethanol reacts with PPr^i_3 and an excess of $AgBF_4$. The reaction mixture was refluxed for *ca.* 1 h and then nitrogen was bubbled through. The crude product obtained after filtration of the solution and evaporation of the solvent was crystallized from CH_2Cl_2–ether and a red solid was obtained soluble in chlorinated solvents, acetone, and methanol.

Dicarbonylbis(tricyclohexylphosphine)iridium(I) *Tetrafluoroborate.*—Tricyclohexylphosphine (1·25 g, 4·82 mmol) and an excess of $AgBF_4$ were added to a suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol) in ethanol (150 ml). The reaction mixture was refluxed for *ca.* 40 min. During this time, from the red solution, a green-yellow precipitate, characterized as *trans*-$Ir(CO)\{P(C_6H_{11})_3\}_2Cl$, was formed. The residue was filtered off, the solvent evaporated and the crude product crystallized from CH_2Cl_2–ether to give a red coloured solid, soluble in chlorinated solvents, acetone, methanol, and slightly soluble in benzene.

Chlorocarbonylbis(diphenyl-t-butylphosphine)iridium(I).—*Method* (*a*). $[Ir(CO)_2(PPh_2Bu^t)_2]BF_4$ (0·50 g, 0·61 mmol) dissolved in CH_2Cl_2 (60 ml) reacts with an excess of NaCl. The colour changes from red to yellow. The solution was filtered, the solvent evaporated and the crude product crystallized from benzene–methanol to give a green-yellow solid.

Using this method were prepared other *trans*-$Ir(CO)L_2Cl$ complexes [L = tri-isopropylphosphine, tri(*o*-tolyl)phosphine, triphenylphosphine, tricyclohexylphosphine].

Method (*b*). A suspension of $[Ir(CO)_3Cl]_n$ (0·50 g, 1·60 mmol) in benzene reacts with PPh_2Bu^t (1 : 2). The mixture was refluxed for *ca.* 3 h. The yellow solution was filtered, the solvent evaporated to a small volume and then, by adding methanol, a yellow solid was obtained. Using this method were prepared *trans*-$Ir(CO)L_2Cl$ complexes [$L = PPr^i_3$, $P(o\text{-tolyl})_3$, $P(C_6H_{11})_3$].

Absorption of Carbon Monoxide.—When CO is bubbled through a chloroform solution containing $[Ir(CO)_2L_2]^+$ complexes [$L = PPh_2Bu^t$, PPr^i_3, $P(C_6H_{11})_3$] the solution becomes colourless and the i.r. spectrum, in the CO stretching region, shows bands which are close to those previously reported[3] for $[Ir(CO)_3L_2]^+$ complexes [$L = PPr^i_3$, $P(C_6H_{11})_3$]. By adding pentane to the concentrated solution, the cationic five-co-ordinated $[Ir(CO)_3L_2]BF_4$ compounds were obtained as white solids. $[Ir(CO)_3(PPh_2Bu^t)_2]BF_4$ is less stable than the analogous compounds and easily loses CO, under vacuum, giving $[Ir(CO)_2(PPh_2Bu^t)_2]BF_4$. However it is stable under carbon monoxide. Complexes such as $[Ir(CO)_2(PPh_3)_2]^+$ and $[Ir(CO)_2\{P(o\text{-tolyl})_3\}_2]^+$ do not absorb CO in the same experimental conditions.

Absorption of Hydrogen.—When hydrogen is bubbled through a chloroform solution containing $[Ir(CO)_2L_2]^+$ complexes [$L = PPh_3$, PPr^i_3, PPh_2Bu^t, $P(C_6H_{11})_3$] the solution rapidly becomes colourless. By adding pentane to the concentrated solution the white solids $[Ir(CO)_2L_2H_2]BF_4$ were obtained. The i.r. spectra agree with those, previously reported, for the compounds containing PPr^i_3 and $P(C_6H_{11})_3$ as ligands. The *trans*-$[Ir(CO)_2\{P(o\text{-tolyl})_3\}_2]^+$ does not absorb hydrogen.

Oxidative Additions of Chlorine. When chlorine was bubbled through a benzene solution of $[Ir(CO)_2L_2]^+$ complexes ($L = PPr^i_3$, $P(o\text{-tolyl})_3$, $P(cyclohexyl)_3$,PPh_2Bu^t], the colour changed from red to yellow. The solution was stirred for about 5 min at room temperature. The complexes *trans*-$[Ir(CO)_2L_2Cl_2]^+$ were isolated as white solids by addition of pentane. When a CH_2Cl_2 solution of chlorine is added dropwise to the $[Ir(CO)_2(PPh_3)_2]BPh_4$ dissolved in the same solvent the i.r. band at 2008 cm^{-1} disappears and a new one is formed at 2072 cm^{-1}. No more chlorine was added when all the compound had reacted. By adding pentane to the concentrated solution the white solid $Ir(CO)(PPh_3)_2Cl_3$ was obtained. By adding dropwise a CH_2Cl_2 solution of I_2 to $[Ir(CO)_2(PPh_3)_2]BPh_4$ dissolved in the same solvent the white solid $Ir(CO)(PPh_3)_2I_3$ was isolated. The reaction was followed by i.r. spectroscopy and $Ir(CO)_2(PPh_3)_2I$ was detected as an intermediate.

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