Tetra(isocyanide)iridium(I) Cations obtained from Poly(tricarbonylchloroiridium)

By **Felice Faraone,* Rosario Pietropaolo,** and **Enrico Rotondo,** Istituto di Chimica Generale ed Inorganica dell'Università, 98100 Messina, Italy

Poly(tricarbonylchloroiridium), $[\{Ir(CO)_3Cl\}_n]$, reacts with alkyl and aryl isocyanides to give tetra(isocyanide)-iridium(I) cations, $[Ir(CNR)_4]^+$ (I; R = C_6H_{11}, p-MeC_6H_4, or p-$MeOC_6H_4$). I.r. spectra support a square-planar structure for these complexes. No five-co-ordinate compound has been obtained by treating (I) with CO, $PPhMe_2$, or RNC and no neutral four-co-ordinate compounds were isolated in the reaction with Cl^-. A comparison between the reactivity of (I) and cationic dicarbonyl(phosphine)iridium(I) complexes is also made. Complexes (I) undergo oxidative addition to give cationic six-co-ordinate iridium(III) species through *trans*-addition. This process is easier for the alkyl than the aryl isocyanide derivatives. A comparison is made between the reactivity of (I) towards oxidative addition and that of other cationic and neutral iridium(I) complexes.

THERE is much interest in the chemistry of transition-metal complexes with isocyanide ligands[1] and recently reactions of nucleophiles with co-ordinated isocyanides have been extensively studied.[2] In previous papers[3-5] we showed that $[\{Ir(CO)_3Cl\}_n]$ is a useful starting material for the preparation of neutral and cationic iridium(I) derivatives and we thought of using it again for the preparation of new isocyanide complexes, with the aim of investigating the chemical behaviour of such potentially interesting compounds. Despite the recent attention given to the preparation of neutral and cationic four-co-ordinate alkyl and aryl isocyanide complexes of rhodium(I),[6-13] the analogous iridium(I) complexes have not been extensively studied since Malatesta[14] succeeded in preparing the first such complex. During the progress of this work we learned that $[Ir(CNR)_4]^+$ (I; R = Bu^t and p-ClC_6H_4) and other mixed isocyanidephosphine complexes have been isolated.[12,13,15] A preliminary account of this work has been presented.[16]

RESULTS AND DISCUSSION

By treating $[\{Ir(CO)_3Cl\}_n]$ with a small excess of the appropriate isocyanide, in benzene solution and at room temperature, complexes $[Ir(CNR)_4]Cl$ (I; R = p-MeC_6H_4, p-$MeOC_6H_4$, or C_6H_{11}) were obtained as described in the Experimental section. Tetraphenylborate salts were obtained by adding $NaBPh_4$ dissolved in methanol to a solution of the chloride salts in the same solvent. No five-co-ordinate species was obtained using an excess of ligand and following the reaction for a longer time. Complexes (I) are 1 : 1 electrolytes in methanol solution and their colour varies with the co-ordinated isocyanide; the cyclohexyl isocyanide complex is yellow-orange, whereas the aryl isocyanides give dark blue-green complexes. Analytical data and some physical properties, including characteristic i.r. bands, of the prepared complexes are given in the Table.

The i.r. spectra of complexes (I) showed a strong C–N stretching band, in accordance with the expected E_u mode of vibration for a D_{4h} square-planar configuration. However the ν(CN) value was higher than that observed in the free isocyanide, indicating a higher C–N bond order in the complex. This means that there is no significant electron flow from the metal d to antibonding π-orbitals of the ligand; *i.e.* CNR groups behave essentially as σ-donors. ν(CN) Differences between co-ordinated and free isocyanides were higher for the aryl than for the alkyl isocyanides. A similar trend was observed for other isocyanide complexes.[12]

The ^1H n.m.r. spectrum of the chloride salt (I; R = p-MeC_6H_4), in $CDCl_3$, showed a singlet at τ 7·82 due to a CH_3 resonance. The intensity ratio relative to proton absorptions of the C_6H_4 group was 3 : 4 as expected; the p-$MeOC_6H_4$ salt showed a singlet at τ 6·40, characteristic of the OCH_3 group.

The complex $[\{Ir(CO)_3Cl\}_n]$ gives different substitution products when it reacts with various neutral ligands;[3,4] however only isocyanide ligands give complete substitution of CO affording four-co-ordinate cations. Although it is hard to understand, at the moment, it is likely that electronic rather than steric factors are responsible for this behaviour.

The possibility of reaction of four-co-ordinate iridium(I) cations with neutral molecules to give five-co-ordinate cations depends on the basicity of the co-ordinated ligands.[3,4,17] The BPh_4 salts of (I) did not react with

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CO or PPh_2Me at room temperature, as inferred from i.r. spectra. It is generally accepted that five-co-ordination is favoured by an increase in electron density on the metal atom. As previously observed, isocyanides are stronger σ-donor ligands than carbonyl, but weaker than phosphines, so the electron density on the central metal atom is not sufficient to allow five-co-ordinate iridium(I) cations to be prepared. Furthermore, $[Ir(CO)_2L_2]^+$ (L = tertiary phosphine) complexes can be regarded as intermediate between (I) and four-co-ordinate iridium(I) complexes which do afford five-co-ordinate species. It has been observed that (I; R = Me) gave five-co-ordinate $[Ir(CNCH_3)_4L]^+$ (L = CO, MeNC, or solvent) complexes in low-energy photochemical reactions.[18] Complexes (I) did not react with Cl^- and this confirms that the Ir–CNR bond is very stable; $[Ir(CO)_2L_2]^+$ and $[Ir(CO)_3L_2]^+$ (L = tertiary phosphine) complexes, on the other hand, react very easily with Cl^- giving *trans*-$[Ir(CO)(L)_2Cl]$.[4,19]

Analytical data and characteristic i.r. bands (cm^{-1})

Complex	Colour	Analyses (%) [a]				ν(CN) [b]	ν(IrCl) [c]
		C	H	N	Halogen		
$[(C_6H_{11}NC)_4Ir]Cl$	Yellow-orange	50·8 (50·6)	6·8 (6·65)	8·6 (8·45)	5·6 (5·35)	2 185vs	
$[(C_6H_{11}NC)_4Ir]BPh_4$	Yellow-orange	65·6 (65·85)	7·01 (6·80)	6·3 (5·90)		2 190vs	
$[(p\text{-}MeC_6H_4NC)_4Ir]Cl$	Dark blue-green	55·4 (55·2)	4·2 (4·05)	8·1 (8·05)	4·9 (5·10)	2 145vs	
$[(p\text{-}MeC_6H_4NC)_4Ir]BPh_4$	Dark blue-green	68·4 (68·65)	4·8 (4·95)	5·8 (5·70)		2 150vs	
$[(p\text{-}MeOC_6H_4NC)_4Ir]Cl$	Dark blue-green	50·8 (50·55)	3·9 (3·70)	7·2 (7·35)	4·5 (4·65)	2 142vs	
$[(p\text{-}MeOC_6H_4NC)_4Ir]BPh_4$	Dark blue-green	64·3 (64·4)	4·4 (4·65)	5·1 (5·35)		2 148vs	
$[(p\text{-}MeC_6H_4NC)_4Cl_2Ir]BPh_4$	Yellow	63·8 (64·0)	4·3 (4·60)	5·5 (5·35)	6·9 (6·75)	2 190vs	325m
$[(p\text{-}MeOC_6H_4NC)_4Cl_2Ir]BPh_4$	Yellow	60·5 (60·3)	4·5 (4·35)	4·9 (5·00)	6·6 (6·35)	2 180vs	320m
$[(C_6H_{11}NC)_4Br_2Ir]BPh_4$	Yellow	56·5 (56·35)	6·0 (5·80)	4·9 (5·05)	14·6 (14·4)	2 218vs	
$[(p\text{-}MeC_6H_4NC)_4Br_2Ir]BPh_4$	Brown	59·2 (59·0)	4·4 (4·25)	5·1 (4·90)	14·2 (14·0)	2 175vs	
$[(p\text{-}MeOC_6H_4NC)_4Br_2Ir]BPh_4$	Brown	55·9 (55·85)	4·2 (4·00)	4·5 (4·65)	13·6 (13·25)	2 170vs	
$[(C_6H_{11}NC)_4I_2Ir]BPh_4$	Brown	51·7 (51·95)	5·4 (5·35)	4·8 (4·65)	20·9 (21·1)	2 235vs	
$[(p\text{-}MeC_6H_4NC)_4I_2Ir]BPh_4$	Brown	54·6 (54·5)	4·0 (3·90)	4·7 (4·55)	20·7 (20·55)	2 164vs	
$[(p\text{-}MeOC_6H_4NC)_4I_2Ir]BPh_4$	Brown	52·0 (51·8)	3·9 (3·75)	4·5 (4·30)	19·8 (19·55)	2 170vs	
$[(C_6H_{11}NC)_4I(Me)Ir]BPh_4$	White	58·1 (58·4)	6·3 (6·20)	5·3 (5·15)	11·9 (11·65)	2 230vs [c]	
$[(C_6H_{11}NC)_4(O_2)Ir]BPh_4$	Pale yellow	63·5 (63·7)	6·7 (6·60)	5·9 (5·70)		2 205vs	

[a] Calculated values in parentheses. [b] CH_2Cl_2 Solution. [c] Nujol mulls.

Oxidative-addition Reactions of Complexes (I).—Oxidative-addition reactions of d^8 transition-metal complexes have been extensively studied[20] in order to elucidate both the stereochemistry of the six-co-ordinate products and factors affecting the ability of the central metal atom to undergo oxidative addition. σ-Donor ligands favour the oxidative process, whereas π-acceptors lower the ability of the metal atom to such addition. Furthermore, bulky co-ordinated ligands can also reduce the reactivity of complexes towards oxidative addition.[21] Despite the large number of papers published on oxidative additions of phosphine and carbonyl-phosphine iridium(I) complexes, few reactions have been carried out with metal–isocyanide complexes; some results appeared when this paper was in progress.[12,13]

Reactions of the BPh_4^- salts of (I) with halogens in dichloromethane solution at room temperature gave $[Ir(CNR)_4X_2]BPh_4$ (X = halogen). When R = C_6H_{11} and $X_2 = Cl_2$, only intractable materials were obtained; the i.r. spectrum, however, suggested that oxidative addition occurs. I.r. spectra of the product cations were consistent with a *trans*-geometry; they showed, in fact, only one ν(CN) band and, in the case of the $[Ir(CNR)_4Cl_2]BPh_4$ complexes, a ν(Ir–Cl) stretching frequency at *ca.* 320 cm^{-1}. Oxidation of complexes (I) always caused an increase in ν(CN). Such behaviour, similar to that observed for the corresponding carbonyl complexes, can be attributed to a decrease in electron density on the metal atom; the strengthening of the CN bond is probably due to an increase in σ-donation from the isocyanide ligand to the metal atom rather than to further reduced back donation $d_\pi \longrightarrow \pi^*$ from the metal to the isocyanide. When halogens added to the

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same substrate (I), the ν(CN) value followed the same trend as that found in carbonyl complexes, increasing in the order $I < Br < Cl$; this variation was more marked for the alkyl than for the aryl isocyanides.

Reaction of MeI with (I; R = C_6H_{11}), at room temperature, gave $[Ir(CNC_6H_{11})_4(Me)I]BPh_4$ as a white solid. The ν(CN) band at 2 225 cm^{-1} confirmed, for this complex, *trans*-addition. The complex is slightly soluble in common organic solvents and allowed an n.m.r. spectrum to be recorded. The BPh_4^- salts (I; R = p-MeC$_6$H$_4$ or p-MeOC$_6$H$_4$) did not react with MeI under the same conditions. Dioxygen reacted only with (I; R = C_6H_{11}) giving the ion $[Ir(CNC_6H_{11})_4(O_2)]^+$; it is interesting to note that the reactivity of the former towards dioxygen is less than that of (I; R = Bu^t) which takes up dioxygen when it is exposed to air.[12] No reaction was observed between $NOPF_6$ and complexes (I).

In conclusion, the results reported indicate that the reactivity of (alkyl isocyanide)metal complexes towards oxidative addition is higher than for aryl isocyanide complexes. However, this tendency is lower for (I) than for neutral carbonylphosphineiridium(I) or cationic $[IrL_2]^+$ (L = $Ph_2PCH_2CH_2PPh_2$) complexes, but is comparable to that of four-co-ordinate cations containing carbonyl and tertiary phosphines.

EXPERIMENTAL

Poly(tricarbonylchloroiridium), $[\{Ir(CO)_3Cl\}_n]$, was a commercial product. Other reagents and solvents were used without purification. Isocyanide ligands were prepared, as reported,[22] using $COCl_2$. I.r. and ^{1}H n.m.r. spectra were recorded using Perkin-Elmer 457 and Hitachi–Perkin-Elmer R20/A 60 MHz spectrometers respectively. A conductivity meter W.T.W. LBR was used for conductivity measurements. Elemental analyses were by Bernhardt, Mülheim, Germany. All reactions were carried out under a dinitrogen atmosphere at room temperature.

Preparations.— *Tetra(cyclohexyl isocyanide)iridium*(I) *chloride*, (I; R = C_6H_{11}). To a suspension of the complex $[\{Ir(CO)_3Cl\}_n]$ (0·40 g, 1·28 mmol) in anhydrous benzene (250 cm^3), $C_6H_{11}NC$ (0·56 g, 5·15 mmol) was added. The reaction mixture was stirred for *ca.* 4 h until gas evolution ceased. The solvent was then removed leaving an orange residue. This was extracted using a small volume of dichloromethane, filtered, and, on addition of pentane, an orange solid was obtained. This was filtered off, washed with diethyl ether, and dried giving the *product* (yield 85%).

Tetra(p-*methoxyphenyl isocyanide*)*iridium*(I) *chloride*, (I; R = p-MeOC$_6$H$_4$). When a suspension of the complex $[\{Ir(CO)_3Cl\}_n]$ (0·35 g, 1·12 mmol) was treated with p-MeOC$_6$H$_4$NC (0·52 g, 4·5 mmol), gas was evolved and the solution became dark green. After *ca.* 6 h, a dark green solid was precipitated, filtered off, washed with diethyl ether, and dried. This was extracted using small volumes of dichloromethane and, on addition of pentane, a dark blue-green *solid* was obtained (yield 82%). *Tetra*(p-*tolyl isocyanide*)*iridium*(I) *chloride*, (I; R = p-MeC$_6$H$_4$), was prepared similarly and isolated as a dark blue-green *solid* (yield 80%). Tetraphenylborate salts of complexes (I) were prepared by adding $NaBPh_4$ dissolved in methanol to a solution of the chloride salt in the same solvent. They closely resemble the corresponding chloride salts except for lower solubility in organic solvents.

Dichlorotetra(p-*methoxyphenyl isocyanide*)*iridium*(III) *tetraphenylborate*. A dichloromethane solution of Cl_2 was added dropwise to a solution of the BPh_4^- salt of (I; R = p-MeO$_6$H$_4$) in the same solvent. The progress of the reaction was followed by i.r. spectroscopy. The colour of the solution become yellow. Partial evaporation of the solvent *in vacuo*, followed by addition of pentane, afforded a yellow solid. This was crystallized several times from dichloromethane–diethyl ether to give a yellow *powder*. *Dichlorotetra*(p-*tolyl isocyanide*)*iridium*(III) *tetraphenylborate and dichlorotetra*(*cyclohexyl isocyanide*)*iridium*(III) *tetraphenylborate* were prepared similarly. Only the p-tolyl isocyanide derivative was obtained as yellow solid; intractable materials were obtained with cyclohexyl isocyanide.

Dibromotetra(p-*methoxyphenyl isocyanide*)*iridium*(III) *tetraphenylborate*. A dichloromethane solution of Br_2 was added dropwise to a stirred solution of the BPh_4^- salt of (I; R = p-MeOC$_6$H$_4$) in the same solvent until the ν(CN) band at 2 148 cm^{-1} disappeared. The colour of the solution changed from dark blue-green to brown. After filtration and evaporation of the solvent, an oil was obtained. On addition of diethyl ether a brown *solid* was formed. This was crystallized from chloroform–pentane. *Dibromotetra*(p-*tolyl isocyanide*)*iridium*(III) *tetraphenylborate and dibromotetra*(*cyclohexyl isocyanide*)*iridium*(III) *tetraphenylborate* were prepared similarly.

Di-iodotetra(p-*methoxyphenyl isocyanide*)*iridium*(III) *tetraphenylborate*. A dichloromethane solution of I_2 was added, in slight excess, to the BPh_4^- salt of (I; R = p-MeOC$_6$H$_4$) dissolved in the same solvent. The colour of the solution passed from dark green to brown. When the i.r. spectrum indicated that the reaction was complete the solvent was evaporated. The product was obtained as a brown *solid* from dichloromethane–pentane. *Di-iodotetra*(p-*tolyl isocyanide*)*iridium*(III) *tetraphenylborate and tetra*(*cyclohexyl isocyanide*)*di-iodoiridium*(III) *tetraphenylborate* were obtained similarly.

Tetra(*cyclohexyl isocyanide*)*iodo*(*methyl*)*iridium*(III) *tetraphenylborate*. A mixture of the BPh_4^- salt of (I; R = C_6H_{11}) (0·12 g, 1·26 mmol) and methyl iodide (2 cm^3) was allowed to stand for *ca.* 5 h. During this time a white *solid* formed. This was filtered off, washed with diethyl ether, and dried. The complex is insoluble in common organic solvents and slightly soluble in chlorinated organic solvents.

Tetra(*cyclohexyl isocyanide*)(*dioxygen*)*iridium*(III) *tetraphenylborate*. Dioxygen was bubbled through a dichloromethane solution of the BPh_4^- salt of (I; R = C_6H_{11}) for *ca.* 4 h. During this time the colour changed from yellow to pale yellow. After partial evaporation of the solvent and addition of pentane, a pale yellow *solid* was obtained.

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