

UNCLASSIFIED

AD 262 065

*Reproduced
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**



UNCLASSIFIED

DISCLAIMER NOTICE

**THIS DOCUMENT IS BEST QUALITY
PRACTICABLE. THE COPY FURNISHED
TO DTIC CONTAINED A SIGNIFICANT
NUMBER OF PAGES WHICH DO NOT
REPRODUCE LEGIBLY.**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

262065

AFOSR 1204

~~XXXXXXXXXX~~

MONITORING AGENCY DOCUMENT N°

ASTIA DOCUMENT N°

CATALOGED BY ASTIA
AS AD NO.

TITLE OF REPORT

PART I - STUDIES ON RHENIUM COORDINATION COMPOUNDS
HEXAISOCYANIDERHENIUM(I) SALTS

PART II - STUDIES ON IRIIDIUM COMPOUNDS
ISOCYANIDE DERIVATIVES OF IRIIDIUM
CARBONYL DERIVATIVES OF IRIIDIUM IODIDES

NAME OF AUTHOR

Lamberto MALATESTA

Professor of Chemistry

NAME OF ORGANIZATION

University of Milano (ITALY)

TECHNICAL FINAL REPORT

CONTRACT N° 61 (052) - 83

DATE OF REPORT

March 31st, 1961

61-1-3
XEROX

CREDIT LINE

The research reported in this document has been sponsored by: AIR FORCE OFFICE
OF SCIENTIFIC RESEARCH of the AIR RESEARCH AND DEVELOPMENT COMMAND,
UNITED STATES AIR FORCE, through its European Office.

~~ATOC 100000~~

MONITORING AGENCY DOCUMENT N°

ASTIA DOCUMENT N°

TITLE OF REPORT

PART I - STUDIES ON RHENIUM COORDINATION COMPOUNDS

HEXAISOCYANIDERHENIUM(I) SALTS

PART II - STUDIES ON IRIIDIUM COMPOUNDS

ISOCYANIDE DERIVATIVES OF IRIIDIUM

CARBONYL DERIVATIVES OF IRIIDIUM IODIDES

NAME OF AUTHOR

Lamberto MALATESTA

Professor of Chemistry

NAME OF ORGANIZATION

University of Milano (ITALY)

TECHNICAL FINAL REPORT

CONTRACT N° 61 (052) - 83

DATE OF REPORT

March 31st, 1961

CREDIT LINE

The research reported in this document has been sponsored by: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH of the AIR RESEARCH AND DEVELOPMENT COMMAND, UNITED STATES AIR FORCE, through its European Office.

SUMMARY.....	pag.	1
--------------	------	---

PART I

STUDIES ON RHENIUM COORDINATION COMPOUNDS

Summary of the Technical Notes n.2 and 4 "	2
Hexaisocyaniderhenium(I) salts..... "	3
Experimental..... "	7

PART II

STUDIES ON IRIDIUM COMPOUNDS

Summary of the Technical Notes n.1 - 3 and 5..... "	9
Section I - Isocyanide Derivatives of Iridium(I)..... "	10
Experimental..... "	14
Section II - Iodocarbonyliridium Derivatives..... "	18
a) Carbonylation of Iridium triiodide... "	19
b) Carbonylation of the mixture IrI ₃ +KI. "	21
c) Carbonylation of the mixture IrI ₄ -KI. "	23
Experimental..... "	25
Infrared spectra in the carbonyl region of the iodocarbonyliridium compounds.... "	32

SUMMARY

PART I - Hexaisocyaniderhenium(I) salt

The reaction of ReI_3 with p-tolylisocyanide at 150° and with ethylisocyanide at room temperature gives the triiodide of the hexaisocyaniderhenium(I) cations $[\text{Re}(\text{RNC})_6]^+$. Both the alifatic and aromatic derivatives are stable, diamagnetic substances, from which other salts as the iodide, the perchlorate, etc. have been prepared.

PART II - Isocyanide derivatives of Iridium(I)

From the reaction of $\text{Ir}(\text{CO})_2(\text{p-toluidine})(\text{Cl})$ with p-tolylisocyanide (RNC) the cations $[\text{Ir}(\text{CO})(\text{RNC})_3]^+$ and $[\text{Ir}(\text{RNC})_4]^+$ were obtained in solution and isolated as salts with bromide, perchlorate and iodide anions. These salts are stable crystalline, diamagnetic substance, of intense blue color, soluble in polar solvents.

Iodocarbonyliridium derivatives

The reaction of IrI_3 and IrI_4 alone, and in mixture with KI, with carbon monoxide at high pressure gave the following products:

1) $[\text{Ir}(\text{CO})_3\text{I}_3]$; 2) $[\text{Ir}(\text{CO})_2\text{I}_3]_2$; 3) $[\text{Ir}_2(\text{CO})_3\text{I}_6]$; 4) $[\text{Ir}(\text{CO})_2\text{I}_2]$;
5) $[\text{Ir}(\text{CO})_3\text{I}]$; 6) $\text{K}[\text{Ir}^{\text{III}}(\text{CO})_2\text{I}_3]$; 7) $\text{K}[\text{Ir}^{\text{III}}(\text{CO})\text{I}_4]$; 8) $\text{K}[\text{Ir}^{\text{III}}(\text{CO})_2\text{I}_4]$;
9) $\text{K}[\text{Ir}^{\text{III}}(\text{CO})\text{I}_5]$ and 10) K_2IrI_5 ; all except 4) and 5) previously unknown. The conditions of formation and the separation of these compounds are given and their possible structure is discussed.

PART I - STUDIES ON RHENIUM COORDINATION COMPOUNDS

Summary of the Technical Notes n. 2 and n. 4

In the first technical note concerning the study of the coordination compounds of rhenium, we described several coordination compounds of Re^{I} , Re^{II} , Re^{III} , with carbon monoxide and triphenylphosphine (PR_3). The reaction of ReCl_3 with PR_3 gave $\text{Re}(\text{PR}_3)\text{Cl}_3$, which on treating with carbon monoxide under pressure yielded $\text{Re}(\text{PR}_3)_2(\text{CO})_3\text{Cl}$. The reduction of HReO_4 in the presence of PR_3 and HBr or HI gave respectively $\text{Re}(\text{PR}_3)_2\text{Br}_2$ and $\text{Re}(\text{PR}_3)_2\text{I}_2$. Under carbonylation the former yielded $\text{Re}(\text{PR}_3)_2(\text{CO})_2\text{Br}$ and $\text{Re}(\text{PR}_3)_2(\text{CO})_3\text{Br}$, the latter $\text{Re}(\text{PR}_3)_2(\text{CO})\text{I}$. The reduction of HReO_4 and PR_3 with hydrazinium chloride gave $\text{Re}(\text{PR}_3)_2\text{Cl}_2$, while in the presence of an excess of hydrochloric acid gave $\text{Re}(\text{PR}_3)_2\text{Cl}_3$. The analogous $\text{Re}(\text{PR}_3)_2\text{X}_3$ ($\text{X}=\text{Br}, \text{I}$) were obtained from $\text{Re}(\text{PR}_3)_2\text{X}_2$ by oxidation with the corresponding halogen.

In the Technical Note n. 4, we described compounds of Re^{I} , Re^{II} , and Re^{III} with carbon monoxide, p-tolylisocyanide (RNC), triphenylphosphine (PR_3), and triarylphosphites $\text{P}(\text{OR})_3$. The reaction of $\text{Re}(\text{PR}_3)_2(\text{CO})_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$) with p-tolylisocyanide gave the compounds $\text{Re}(\text{PR}_3)_2(\text{RNC})(\text{CO})\text{X}$ and $\text{Re}(\text{PR}_3)_2(\text{RNC})_2(\text{CO})\text{X}$. The carbonylation of $\text{Re}(\text{PR}_3)_2\text{X}_2$ at low temperature gave $\text{Re}(\text{PR}_3)_2(\text{CO})\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$). On

treating with p-tolylisocyanide in the cold, ReX_3 gave $\text{Re}(\text{RNC})\text{X}_3$ ($\text{X}=\text{Cl}, \text{I}$), while $\text{Re}(\text{PR}_3)_2\text{I}_2$ gave $[\text{Re}(\text{PR}_3)_2(\text{RNC})\text{I}]\text{I}$. The ionic structure of this compound was proved by conductivity measurements as well as by various exchange reactions. Finally, the compounds $\text{Re}[\text{P}(\text{OR})_3]_3\text{I}_3$ were obtained from K_2ReI_6 and triarylphosphites. The above results were published in papers (1) (2) (3) (4).

HEXAISOCYANIDERHENIUM(I) SALTS

Organic isocyanides are among the very few stable compounds containing a "divalent carbon" atom. Their structural analogy with carbon monoxide is evident ($\text{R}-\text{N}=\text{C} \rightleftharpoons \text{R}-\text{N}\equiv\text{C}$) and explains why isocyanides form with many transition metals, such as for instance Cr, Mo, W and Ni, coordination compounds strictly analogous to the corresponding carbonyls.

It must be noted, however, that it is only when the metal has an even number of electrons, and forms a monomeric carbonyl, that this perfect analogy seems possible. In other cases, when the metal has an odd number of electrons and forms dimeric carbonyls, often with bridging carbonyl groups and always with metal to metal bonds, the corresponding isocyanide derivative cannot be obtained, and instead the polyisocyanide-metal(I) cations become exceedingly stable. This

is, for instance, the case of manganese, cobalt and rhodium, which form the following compounds with carbon monoxide and isocyanides: $(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5$; $(\text{CO})_3\text{Co}(\text{CO})_2\text{Co}(\text{CO})_3$; $(\text{Co})_3\text{Rh}(\text{CO})_2\text{Rh}(\text{CO})_3$; $[\text{Mn}(\text{RNC})_6]^+(^5)$; $[\text{Co}(\text{RNC})_5]^+(^6)$; $[\text{Rh}(\text{RNC})_4]^+(^7)$. This different behavior might be due to the larger size of organic isocyanides with respect to carbon monoxide, which would hinder the formation of metal to metal bonds, or to the fact that isocyanides are not able to act as bidentate ligands in bridge-formation. Besides, the tendency of isocyanides to form π bonds is lower than that of carbon monoxide and therefore isocyanides are less apt to stabilize the zero-valent oxidation states of the transition metals.

The stabilities of both the pure carbonyls and the isocyanide derivatives of the transition metals vary in an irregular and often unpredictable way. In the VI A subgroup, chromium, molybdenum and tungsten form hexacarbonyls the stability of which are not very different, while the ease of preparation decreases enormously from tungsten to chromium. A similar trend is observed in the Re-Mn subgroup. In the triad Ni, Pd, Pt, nickel is the only one to give a pure carbonyl. The stability of the hexaisocyanide derivatives decreases instead with increasing atomic weight along the VI A subgroup (⁸), while Mn does not form any zerovalent isocyanide derivative at all. In the Ni, Pd, Pt series, only Ni gives zero-

-valent isocyanide derivative.

It seemed therefore worthwhile to extend our previous research, on isocyanide-complexes, to the metals of the second and third transition series, still not investigated. On the basis of the above considerations it could be expected that rhenium would form reasonable stable derivatives in the oxidation state +1, similar to those of Mn^{I} previously prepared in our Institute⁽⁵⁾. Attempts to obtain isocyanide-complexes of rhenium(I) by reaction of stable phosphine-derivatives of the Re^{II} and isocyanide had in fact given some positive results (Technical Note N. 4, page 11), but the experimental conditions, were rather difficult and not easily reproducible. More satisfactory results were obtained when ReI_3 was used as starting material.

The first product of the reaction between ReI_3 and isocyanide in acetone solution is an addition compound of formula $\text{Re}(\text{RNC})\text{I}_3$. This, on further treatment with pure isocyanide at 150° , undergoes a hexothermal reaction, yielding $\text{Re}(\text{RNC})_6\text{I}_3$ together with a small amount of $\text{Re}(\text{RNC})_6\text{I}$, which can be separated by fractional crystallization. The compound $\text{Re}(\text{RNC})_6\text{I}_3$ has to be considered a triiodide of a Re^{I} complex cation, and not an iodide of a hexacoordinated Re^{III} . In fact its electrical conductivity indicates a uni-univalent electrolyte, and the compound is diamagnetic as

expected for a Rh^{I} hexacoordinated cation. All known Re^{III} hexacoordinated compounds have instead magnetic moment in agreement with the value predicted by the Kotani theory for a octahedral Re^{III} (generally $1.6-2.2 = \text{B.M.}$)(⁹).

Moreover, by exchange reaction with $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ the compound yields the salt $[\text{Re}(\text{RNC})_6][\text{B}(\text{C}_6\text{H}_5)_4]$, which is also obtained by exchange from the iodide $\text{Re}(\text{RNC})_6\text{I}$. The iodide $\text{Re}(\text{RNC})_6\text{I}$, which is formed in small yields in the reaction of ReI_3 and RNC , is best prepared by reduction of the triiodide with NaBH_4 in ethanol. From the iodide, a number of other salts, namely the nitrate, perchlorate and tetraphenylborate, were prepared by exchange reactions. All these salts are well crystallized substances, soluble in polar solvents (the aliphatic derivatives being more soluble than the aromatic), stable to air both in the solid state and in solution. In nitrobenzene they have molar conductivity of about $27 \text{ ohm}^{-1} \text{ cm}^2$ in 10^{-3} molar solution at 30° , as expected for uni-univalent complex salts. The cation $[\text{Re}(\text{RNC})_6]^+$ must be considered to have a perfect octahedral structure. In it, the central atom reaches its maximum coordination number and the E.A.N. of the next inert gas radon.

EXPERIMENTAL: RHENIUM COMPOUNDS

Hexakis(ethylisocyanide)rhenium(I) triiodide. One gramme of ReI_3 was treated with 0.75 g of ethyl^{iso}cyanide. A reaction took place, with evolution of heat. The solid mass thus obtained was extracted with hot benzene and filtered. On cooling, the solution separated a dark-brown crystalline product, m.p. 206° .

(Found: Re, 20.2; I, 41.0; N, 9.4; C, 24.6; H, 3.45%. $\text{C}_{18}\text{H}_{30}\text{N}_6\text{I}_3\text{Re}$ requires Re, 20.8; I, 42.4; N, 9.4; C, 24.1; H, 3.3%).

Hexakis(p-tolylisocyanide)rhenium(I) triiodide. One gramme of ReI_3 was treated with 1.5 g of p-tolylisocyanide (97-98%), and the mixture heated at 150° . The reacted mass was extracted with boiling ethanol and filtered. The ethanol solution gave on cooling brown needles, m.p. 170° . (Found: Re, 15.0; I, 29.0; N, 6.5; C, 45.2; H, 3.4%. $\text{C}_{48}\text{H}_{42}\text{N}_6\text{I}_3\text{Re}$ requires Re, 14.7; I, 30.0; N, 6.6, C, 45.4; H, 3.3%).

Hexakis(p-tolylisocyanide)rhenium(I) iodide. One gramme of $[\text{Re}(\text{RNC})_6]\text{I}_3$ was treated with a solution of 0.07 g of NaBH_4 in 20 ml of ethanol. On standing the color of the solution turned pale yellow and after a few minutes yellow needles separated, m.p. 238° (Found: Re, 17.9; I, 12.7; N, 8.1% $\text{C}_{48}\text{H}_{42}\text{N}_6\text{IRe}$ requires Re, 18.3; I, 12.5; N, 8.3%).

Hexakis(p-tolylisocyanide)rhenium(I) perchlorate. One gramme of $[\text{Re}(\text{RNC})_6]\text{I}$ was warmed with a solution of NaClO_4 (0.1 g) in ethanol (10 ml). On cooling yellow crystals separated, m.p. 241° . (Found: Re, 18.3; N, 8.5; Cl, 3.7%. $\text{C}_{48}\text{H}_{42}\text{O}_4\text{ClRe}$ requires Re, 18.9; N, 8.5; Cl, 3.6%).

Hexakis(p-tolylisocyanide)rhenium(I) tetrphenylborate. One gramme of $[\text{Re}(\text{RNC})_6]\text{I}_3$ was treated with a solution of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ (0.25 g) in ethanol (10 ml), and the mixture warmed to boiling. On cooling, yellow needles separated, m.p. 215° . (Found: Re, 16.0; N, 6.9; C, 70.1; H, 4.9%. $\text{C}_{72}\text{H}_{62}\text{BN}_6\text{Re}$ requires Re, 15.4; N, 6.95; C, 71.6; H, 5.1%).

Hexakis(p-tolylisocyanide)rhenium(I) nitrate. One gramme of $[\text{Re}(\text{RNC})_6]\text{I}$ was treated with a solution of AgNO_3 (0.15 g) in ethanol (10 ml). After filtering off AgI , the solution was concentrated under reduced pressure and a crystalline precipitate was obtained; yellow needles, m.p. 206° . (Found: Re, 19.0; N, 10.2; C, 60.0; H, 4.3%. $\text{C}_{48}\text{H}_{42}\text{O}_3\text{N}_7\text{Re}$ requires Re, 19.6; N, 10.3; C, 60.7; H, 4.4%).

compound (1)	color	X_m (cm ² /mole) of the solid at 22°	solubility (2)	molar conductivity (ohm ⁻¹ cm ²) in 10 ⁻³ nitrobenzene at 20°
$[\text{Re}(\text{RNC})_6] \text{I}_3$	yellow- brown	$-560 \cdot 10^{-6}$	v.s. CH_2Cl_2 , CHCl_3 ;	18
$[\text{Re}(\text{RNC})_6] \text{ClO}_4$	yellow	$-460 \cdot 10^{-6}$	s. CH_3COCH_3 , $\text{C}_6\text{H}_5\text{NO}_2$;	27
$[\text{Re}(\text{RNC})_6] [\text{B}(\text{C}_6\text{H}_5)_4]$	pale- yellow	$-640 \cdot 10^{-6}$	sl. C_6H_6 , $\text{C}_2\text{H}_5\text{OH}$;	23
			i. $(\text{C}_2\text{H}_5)_2\text{O}$, C_6H_{12}	
$[\text{Re}(\text{C}_2\text{H}_5\text{NC})_6] \text{I}_3$	yellow- brown	$-380 \cdot 10^{-6}$	v.s. CH_2Cl_2 , CHCl_3 ,	31
$[\text{Re}(\text{RNC})_6] \text{NO}_3$	yellow	$-400 \cdot 10^{-6}$	CH_3COCH_3 , $\text{C}_2\text{H}_5\text{OH}$,	27
$[\text{Re}(\text{RNC})_6] \text{I}$	yellow	$-430 \cdot 10^{-6}$	C_6H_6 , $\text{C}_6\text{H}_5\text{NO}_2$;	27
			i. $(\text{C}_2\text{H}_5)_2\text{O}$, C_6H_{12}	

(1) R = p-tolyl

(2) v.s. = very soluble; s. = soluble; s.l. = slightly soluble; i. = insoluble

PART II - STUDIES ON IRIDIUM COMPOUNDS

Summary of Technical note n. 1, 3 and 5.

In the Technical Note n. 1, Section I, we described the reaction of K_2IrBr_6 with carbon monoxide at high pressure and temperature, which yielded as the main product $K_2[Ir_2(CO)_4Br_5]$. The mode of formation and the structure of the complex anion $[Ir_2(CO)_4Br_5]^{-2}$ were investigated by mean of various reactions. The cleavage of $K_2[Ir_2(CO)_4Br_5]$ with acids gave a number of other carbonylanions, namely $[Ir^I(CO)_2Br_2]^-$, $[Ir^{II}(CO)Br_3]^-$, $[Ir_2^I(CO)_4Br_3]^-$, all isolated as tetraphenylarsonium salts. In the Section II of the same technical note, we described the carbonylation of K_2IrCl_6 to give $K_2[Ir_2(CO)_4Cl_5]$, a salt strictly analogous to the bromo-derivative described in Section I, and in the Section III we reported the results obtained by treating with amines the salts $K_2[Ir_2(CO)_4X_5]$ ($X=Cl, Br$). This reaction gave, among others, the interesting compounds $Ir(CO)_2AmX$ (Am =isopropylamine and p-toluidine). The results of these researches were published in papers (¹⁰) and (¹¹).

In the Technical Note n. 3 we described the reaction of $K[Ir(CO)_2I_4]$ with triphenylphosphine PR_3 , triphenylphosphites $P(OR)_3$, triphenylarsines (AsR_3), p-toluidine (T) and α, α' -dipyridile (Dip). The following compounds were obtained, in which the oxidation

state of iridium depends on the π -bonding character of the ligands:
 $\text{Ir}^{\text{I}}(\text{CO})_2(\text{PR}_3)_2\text{I}$, $\text{Ir}^{\text{II}}(\text{CO})(\text{PR}_3)_2\text{I}_2$, $\text{Ir}^{\text{II}}(\text{CO})_2\text{T}_2\text{I}_2$, $\text{Ir}^{\text{II}}(\text{CO})_2(\text{Dip})\text{I}_2$,
 $\text{Ir}^{\text{III}}[\text{P}(\text{OR})_3]_2\text{I}_3$, $\text{Ir}^{\text{III}}(\text{CO})_2(\text{AsR}_3)_2\text{I}_3$ and $\text{Ir}^{\text{III}}(\text{CO})(\text{AsR}_3)_3\text{I}_3$.

In the Technical Note N. 5 we described the reaction of
 $\text{K}[\text{Ir}(\text{CO})\text{I}_5]$ with ammonia and primary amines, to give complex anions
of the type $[\text{Ir}(\text{CO})\text{LI}_4]^-$ ($\text{L}=\text{NH}_3, \text{RNH}_2$) and non-ionic compounds of
formula $\text{Ir}^{\text{III}}(\text{CO})\text{L}_2\text{I}_3$ and $\text{Ir}^{\text{II}}(\text{CO})\text{L}_3\text{I}_2$ respectively. This work
published in paper (¹²).

In this final Report, Part II, we describe the isocyanide-
-iridium(I) salts (Section I) and a new series of iodocarbonyl
compounds of iridium (Section II).

SECTION I

ISOCYANIDE DERIVATIVES OF IRIDIUM(I)

In Part I of this final Report we mentioned that the elements
which form pure dimeric carbonyls do not seem able to give zero=
valent isocyanide derivatives, but form instead cationic complexes
corresponding to the oxidation state +1. Accordingly, rhenium
gives the hexaisocyaniderhenium(I) salts described in Part I,

Another element which gives polymeric pure carbonyls is iridium.
Of this element, no isocyanide-compounds had been reported so far,
while the above considerations let foresee at least the existence

of one stable isocyanideiridium(I) complex cation. It seemed therefore worthwhile to investigate the isocyanide-compounds of iridium, and here we report the results obtained.

We tried at first the reaction between iridium(III) halides IrX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) and isocyanide, with the idea of obtaining addition products of Ir^{III} to be reduced in a following stage to Ir^{I} compounds. This type of reaction, which had proved successful in the case of the lighter homologues of iridium, i.e. cobalt and rhodium, failed completely in the case of iridium. Actually Ir^{III} halides do not seem to form with isocyanides addition compounds of any reasonable stability, as shown by the fact that mild reducing agents are without effect on the reaction mixture, while strong reducing agents cause separation of metallic iridium. (If addition products of Ir^{III} and isocyanides were formed, they ought to be easily reduced to Ir^{I} compounds, owing to the high affinity of isocyanides with metals in low oxidation state).

It was therefore necessary to use as starting material one of the compounds of univalent iridium. Of those, $\text{Ir}(\text{CO})_3\text{Br}$ reacted only very slowly with isocyanides, while $\text{Ir}(\text{CO})_2\text{TCI}(\text{T}=\text{p-toluidine})$ reacted very easily and neatly. The fact that we found a new method for the preparation of the $\text{Ir}(\text{CO})_2\text{TCI}$, easier than that described in our Report N.1, pag. 33, made this compounds a very convenient

starting material.

On treating with isocyanide in the molar ratio 1.3, $\text{Ir}(\text{CO})_2\text{TCI}$ gives compounds of composition corresponding to $[\text{Ir}(\text{CO})(\text{RNC})_3]\text{Cl}$. These are dark-green substances, soluble in polar solvents, and have a salt-like structure as shown by their conductivity in nitrobenzene, and by the fact that chlorine is immediately replaced by the perchlorate ion. With an excess of isocyanide, $\text{Ir}(\text{CO})_2\text{TCI}$ gives instead the tetraisocyanideiridium(I) chloride $[\text{Ir}(\text{RNC})_4]\text{Cl}$. This is a substance with an extremely intense deep-blue colour, and so soluble that it cannot be isolated in a pure state. From it, the corresponding bromide, iodide and perchlorate, were prepared by exchange reactions. These are well crystallized diamagnetic substances, all very intensely coloured, the behavior of which corresponds to that of uni-univalent electrolytes.

The cation $[\text{Ir}(\text{RNC})_4]^+$ may be attributed the square planar configuration which, according to the valence-bond theory, corresponds to the dsp^2 hybrid orbitals. Iridium(I) is in fact isoelectronic with palladium(II), for which such a structure has been undoubtedly proved. Besides, the crystal field theory, considering the fact that isocyanides are among the ligands which create a "strong field" also leads independently to the same conclusion.

It is interesting to compare the isocyanide complex compounds

of the series Co^{I} , Rh^{I} , Ir^{I} . Cobalt(I) gives the extremely stable, coordinatively saturated $[\text{Co}(\text{RNC})_5]^+$. Rhodium(I) gives the tetracoordinated $[\text{Rh}(\text{RNC})_4]^+$ which, though unable to bind another molecule of isocyanide, shows its coordinative insaturation, due to the vacant $5p_z$ orbital, in its tendency to form stable addition products with polar solvents. Finally, the tetracoordinated $[\text{Ir}(\text{RNC})_4]^+$ does not show any unsaturated character. The fact that the tendency to reach coordinative saturation diminishes with the increasing atomic weight is quite general in series of isoelectronic complex cations, and has been related (¹³) to the increasing electronegativity of the metal ions, which as a consequence require a lower number of ligands to attain electroneutrality.

ESPERIMENTAL - IRIDIUM COMPOUNDS - SECTION I

Preparation of $\text{Ir}(\text{CO})_2(\text{p-toluidine})\text{Cl}$

In the Technical Note n. 1, Section II, we described the reaction of K_2IrCl_6 with carbon monoxide at high pressure. Under the same experimental conditions, Na_2IrCl_6 gave a salt-like substance containing carbon monoxide, chlorine, sodium and iridium in the oxidation state +1. This substance, which we did not isolate in the pure state; on treatment with p-toluidine at 60-70° gave with very good yield $\text{Ir}(\text{CO})_2\text{TCl}$ (T=p-toluidine). The experimental details are the following; 8 g of NaIrCl_6 were introduced into an open glass tube, drawn to a capillary size at both end, and the tube placed in an inoxidable steel pressure vessel containing copper filings to act as chlorine acceptor. The autoclave was filled with dry carbon monoxide at 200 atm., heated at 200° for three hours, and then allowed to cool very slowly while mantaining the carbon monoxide high pressure. A brick-red shiny mass was obtained, containing as the main product a not completely identified chlorocarbonyliridiate(I) (probably $\text{Na}[\text{Ir}(\text{CO})_2\text{Cl}_2]$ or $\text{Na}_2[\text{Ir}(\text{CO})_2\text{Cl}_3]$ or a mixture of both), together with Na_3IrCl_3 , $\text{Ir}(\text{CO})_3\text{Cl}$ and NaCl . The crude mixture was finely powdered and warmed for 30' at

60-70° with 1.5 g of p-toluidine (T) in benzene solution. The solution thus obtained was filtered; on cooling the crystalline $\text{Ir}(\text{CO})_2\text{TCI}$, m.p. 166°, separated in a pure state. Yields 2.5 g. (Found: Ir, 48.2; CO, 14.6; Cl, 8.8; N, 3.7%. Calculated for $\text{C}_9\text{H}_9\text{O}_2\text{NCI Ir}$: Ir, 49.2; CO, 14.3; Cl, 9.1; N, 3.6%).

Preparation of $[\text{Ir}(\text{CO})(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})]\text{Cl}$.

The compound $\text{Ir}(\text{CO})_2\text{TCI}$ was dissolved in methylene chloride and treated in the cold with pure (97%) p-tolylisocyanide (Ir/RNC ratio = 1/3). A brisk evolution of gas (CO) took place. The dark green solution thus obtained was carefully diluted with hexane: a dark green crystalline powder separated, which was filtered and washed with hexane. The compound could not be recrystallized. The compound has m.p. 250°, is diamagnetic and shows $\chi = 24 \text{ ohm}^{-1} \text{ cm}^2$ in 10^{-4} molar nitrobenzene solution at 20°.

(Found: Ir, 30.6; C, 48.1; H, 4.0; N, 17.1; Cl, 5.8%. $\text{C}_{25}\text{H}_{21}\text{ON}_3\text{Cl Ir}$ requires Ir, 31.8; C, 49.5; H, 3.5; N, 6.9, Cl, 6.1%).

Preparations of the $[\text{Ir}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4]\text{X}$ salts (X=Br, I, ClO_4)

The compound $\text{Ir}(\text{CO})_2\text{TCI}$ was dissolved in methanol and treated with pure p-tolylisocyanide (Ir/RNC ratio = 1/5). The mixture was refluxed for an hour and then taken to a small volume under reduced pressure. On treating with water, the residue gave a deep-blue solution mixed with oily drops (p-toluidine and the excess

of isocyanide). The aqueous layer was separated and repeatedly extracted with benzene; the dissolved benzene was then removed by bubbling nitrogen through the solution. Finally on addition of NaBr, NaI and NaClO₄, the solution separated the corresponding salts.

$[\text{Ir}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4 \text{ Br}]$ m.p. $> 260^\circ$ with decomposition.

(Found: Ir, 24.3; Br, 10.8; C, 49.7; H, 3.7; N, 7.7%. $\text{C}_{32}\text{H}_{28}\text{N}_4\text{BrIr}$ requires Ir, 26.1; Br, 9.8; C, 51.8; H, 3.7; N, 7.6%.)

$[\text{Ir}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4 \text{ I}]$ m.p. $> 260^\circ$ with decomposition

(Found: Ir, 24.2; I, 16.7; C, 48.9; H, 3.8; N, 7.0%. $\text{C}_{32}\text{H}_{28}\text{N}_4\text{I Ir}$ requires Ir, 24.5; I, 16.1; C, 48.8; H, 3.6; N, 7.1%).

$[\text{Ir}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4 \text{ ClO}_4]$ m.p. $> 260^\circ$ (with decomposition)

(Found: Ir, 24.5; Cl, 4.55; C, 50.9; H, 4.0; N, 7.6%.

$\text{C}_{32}\text{H}_{28}\text{O}_4\text{N}_4\text{Cl Ir}$ requires Ir, 25.4; Cl, 4.7; C, 50.6; H, 3.7; N, 7.4%).

Molar conductivity in nitrobenzene at 20° in $2 \cdot 10^{-4}$ molar solution

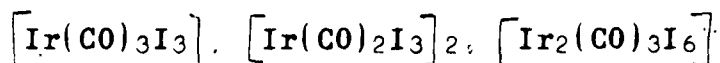
$$\Lambda = 27.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

SECTION II

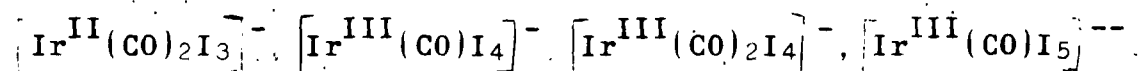
IODOCARBONYLIRIDIUM DERIVATIVES

by Luciana Naldini

In this Section we shall describe the carbonylation of iridium(III) and iridium(IV) iodides, both alone and as a mixture with alkali iodides, which led to the isolation of the new iodicarbonyliridium(III) compounds:



and of the iodicarbonyliridates:



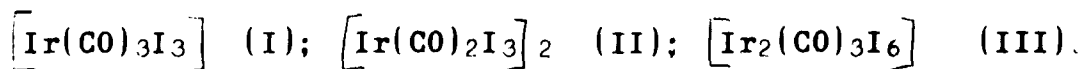
The only iodicarbonyliridium compounds previously known were $[\text{Ir}(\text{CO})_2\text{I}_2]$ and $[\text{Ir}(\text{CO})_3\text{I}]$, prepared in very small yields by Hieber (¹⁴) by treating $\text{IrI}_3 \cdot \text{H}_2\text{O}$ with carbon monoxide at room pressure and at 150° . In the course of the present research, we also obtained the salts of a new iodoiridate(III) anion of formula $[\text{IrI}_5]^{--}$.

These results show that the formation of low-valent carbonyl-derivatives of iridium is more difficult from IrI_3 than from IrCl_3 and IrBr_3 . These latter give in fact, under the above experimental conditions, $[\text{Ir}(\text{CO})_2\text{X}_2]$ and $[\text{Ir}(\text{CO})_3\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}$), and, with longer

reaction times, the pure carbonyl $\text{Ir}(\text{CO})_4$ and $\text{Ir}(\text{CO})_3$. According to Hieber (¹⁴) the reduction which usually accompanies the carbonylation reaction occurs because the formation of COCl_2 and COBr_2 makes the elimination of the alogens easy. In our opinion, the formation of COCl_2 and COBr_2 , though obviously favouring the removal of chlorine and - to a lesser extent - of bromine, has only a minor influence on the course of the reaction. The determing factor seems instead to be, as we already pointed out (¹⁵), the stabilization of the low valent states of iridium by coordination of the π bonding carbon monoxide molecules, or, conversely, the destabilization of the halogen of iridium bonds by effect of this coordination. The destabilization effect decreases from chlorine to iodine, probably because of the different electronegativities of the halogens. This view is supported by the fact that the salts $\text{K}_2[\text{Ir}_2(\text{CO})_4\text{Cl}_5]$ in which iridium has the average oxidation number 1.5 are remarkably resistant to oxidation while $\text{K}_2[\text{Ir}(\text{CO})_4\text{I}_5]$, which can be obtained in solution from the former by exchange with KI, is easily oxidized (¹⁵).

a Carbonylation of iridium triiodide

The carbonylation of IrI_3 with CO at high pressure at different temperature gives the compounds.

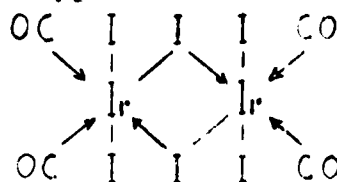


besides the previously known $[\text{Ir}(\text{CO})_2\text{I}_2]$ and $[\text{Ir}(\text{CO})_3\text{I}]$.

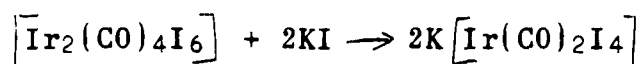
When IrI_3 is treated for 18 hours with dry carbon monoxide, at 100° and 250 atm. initial pressure, and the system is then allowed to cool slowly, the final product is I, which can be considered to be the primary product of the carbonylation process. I is rather instable and even in the solid state it loses carbon monoxide to give compound II. When the carbonylation is carried out as above, but with a rapid final cooling, a mixture of I, II and III is obtained. At higher temperature, Hieber's compounds $[\text{Ir}(\text{CO})_2\text{I}_2]$ and $[\text{Ir}(\text{CO})_3\text{I}]$ are formed, though in rather low yields, together with $[\text{Ir}(\text{CO})_3\text{I}_3]$. No formation of the pure carbonyl $\text{Ir}(\text{CO})_3$ is observed below 300° .

Compound II is extremely stable, both in the solid state and in solution of organic solvents, where it is dimeric. In ethanol solution containing hydroiodic acid, compound II splits up to give an iodocarbonyliridiate anion of formula $[\text{Ir}(\text{CO})_2\text{I}_4]^-$, which can be isolated as the tetraphenylarsonium (tpa) salt. The structure of I is very likely a distorted octahedron with the carbonyl groups in "cis" position. This assignment is based on the consideration that in the polycarbonyl-compounds the carbon monoxide groups tend to occupy "cis" position whenever possible. The I.R. spectrum of the compound in nujol ($2178, 2114, 2079 \text{ sh. cm}^{-1}$) does not disagree with the above formulation.

A "cis" structure of the type:



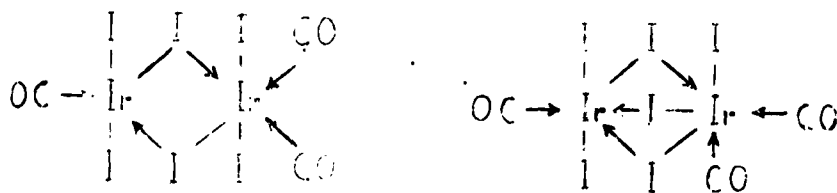
may be assigned to compound II, on the basis of its I.R. spectrum (2123 and 2087 cm^{-1} in nujol). Moreover the cleavage reactions with iodide ions give a mononuclear compound in which the carbonyl groups occupy "cis" position:



(I.R. of $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$: 2118 and 2066 cm^{-1} in nujol)

However it is not possible to decide which of the possible "cis" structures has to be assigned to the compound.

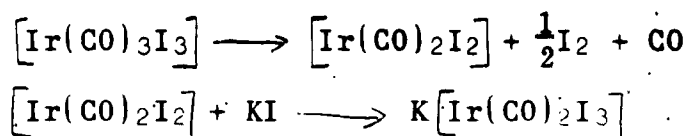
Compound III a very stable substance soluble without decomposition in organic solvents, is also dimeric and its formula may be either of the following:



b) Carbonylation of the mixture $\text{IrI}_3 + \text{KI}$

The potassium chloro and bromo-iridates(III) K_2IrX_6 ($\text{X} = \text{Cl}, \text{Br}$), when treated with carbon monoxide at 180-280° and 100-200 atm., form as the main product the salts $\text{K}_2[\text{Ir}_2(\text{CO})_2\text{X}_5]$ which represent an intermediate step in the reduction of K_2IrX_6 to $\text{Ir}(\text{CO})_3$. In fact on

prolonging the reaction times, the yields of $K_2[Ir_2(CO)_2X_5]$ decrease, while that of $Ir(CO)_3$ increase. The carbonylation of a mixture of IrI_3 and KI at 200 atm. and 250° , gives instead two products, namely $K[Ir(CO)_2I_3]$ (IV) and $K[Ir(CO)I_4]$ (V), which remain unaltered even on very prolonged treatment with carbon monoxide. The salt IV is the only iodocarbonyliridates so far isolated, in which the oxidation state of iridium is lower than +3. It is probably formed by the action of KI on the rather labile divalent iodocarbonyl $[Ir(CO)_2I_2]$, which in turn is formed by thermal dissociation of I at 200° . The reaction sequence leading to IV may therefore be written:



The salt IV is a crystalline substance, soluble in diethylether, acetone, alcohol, nitrobenzene and insoluble in benzene.

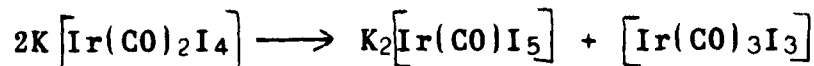
In nitrobenzene it behaves as a uni-univalent electrolyte. On exchange with tetraphenylarsonium iodide, the analogous tpa-salt is obtained. The I.R. spectrum of the anion $[Ir(CO)_2I_3]^{-1}$, shows two intense absorption bands (2136 and 2092 cm^{-1} in nujol mull), thus indicating that the carbon monoxide molecules are in "cis" position to each other. The above experimental evidence is compatible either with a mononuclear formula containing a five-covalent iridium(II) atom; or with a dimeric formula containing six-covalent

iridium atoms, and it does not seem possible at the present stage of the research, to make a definitive assignment. When the carbonylation of the mixture IrI_3 and KI is carried out at somewhat higher temperature, the salt V is obtained. V is a very stable crystalline substance, soluble in acetone and alcohol, insoluble in benzene and diethylether. In acetone it behaves as a uni-univalent electrolyte. On exchange with tetraphenylarsonium iodide it give the corresponding tpa-salt. The I.R. spectra of the $[\text{Ir}(\text{CO})\text{I}_4]^-$ anion shows one sharp band at 2051 cm^{-1} (in nujol). Again, it is not possible to decide, from the experimental data, the actual structure of the anion.

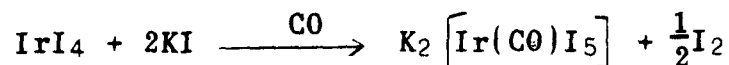
c) Carbonylation of the mixture $\text{IrI}_4 - \text{KI}$

The carbonylation under high pressure of the mixture $\text{IrI}_4\text{-KI}$ gives, depending on the experimental conditions (temperature and IrI_4/KI ratio) either or both the salts $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (VI) and $\text{K}_2[\text{Ir}(\text{CO})\text{I}_5]$ (VII). At about 200° and with a 1/1 iridium to potassium ratio the salt VI is formed in almost quantitative yields. It is a crystalline substance, soluble in water containing hydroiodic acid, in diethylether, acetone alcohol and easily recrystallizable from these solvents. The corresponding tpa-salt can be prepared by exchange with tpaI. Above 250° , under pressure of carbon monoxide, VI decomposed into a mixture of VII and $[\text{Ir}(\text{CO})_3\text{I}_3]$, according to

the reaction.



so that the carbonylation of $\text{IrI}_4 + \text{KI}$, when carried out at about 250° , gives:



The best yields of VII are obtained at 250° ; when the reaction mixture corresponds to a Ir/K ratio of 1/2.

Finally, in the temperature range $300-350^\circ$, the stable product of the carbonylation is a previously unknown pure iodoiridiate(III) of formula $K_2[\text{IrI}_5]$ (VIII), soluble in water, insoluble in organic solvents. This cannot be obtained from IrI_3 and KI in aqueous solution, nor is it formed by heating a solid mixture of the two reagents, unless carbon monoxide is present. It is instead easily formed by refluxing for a long time VII in diluted hydriodic acid. It seems therefore likely that VIII is formed from VII through loss of carbon monoxide. For the anion IrI_5^{-2} either a pentacoordinated mononuclear or a hexacoordinated dinuclear structure is possible, the dinuclear being the more likely on account of the fact that the haloiridates tend to reach coordinative saturation through polymeration.

EXPERIMENTAL

Preparation of iridium tetraiodide

An aqueous solution of KI (0.04 moles) was added to a concentrate hot solution of K_2IrCl_6 (0.01 moles) and refluxed for one hour. The solid product was filtered off and washed with water containing a few drops of HNO_3 , and then dried for two hours in vacuo at 100° .

Anal. Found: Ir, 27.15; I 71.9%; IrI_4 requires: Ir, 27.44; I, 72.55%.

Preparation of iridium triiodide

On treating IrI_4 at 210° in hydrogen stream, for two hours, IrI_3 was obtained in quantitative yields.

Anal: Found: Ir, 33.0; I, 66.9%; IrI_3 requires Ir, 33.52; I, 66.47%.

Carbonylation reactions

In the following experiments a stainless steel pressure vessel with a capacity of about 100 ml was used. The reactants were placed into a test tube having diameter of 10 mm and the length of 150 mm. and introduced in a copper tube

Preparation of triiodotricarbonyliridium(III)

IrI_3 finely ground was placed into the pressure vessel pumping carbon monoxide up to a pressure of 250 atm. The pressure vessel was then kept at 100° for 18 hours and then the temperature was slowly lowered. When opening the pressure vessel a dark-red crystalline sublimate (A) was observed at the top of the test tube and a brown red product (B) at the bottom. Both (A) and (B) were analysed and resulted corresponding to $[\text{Ir}(\text{CO})_3\text{I}_3]$.

Anal Found: A - CO 13.05, Ir 28.9; I 58.03%; B - CO 12.77; Ir 29.3; I 57.48%; $[\text{Ir}(\text{CO})_3\text{I}_3]$ requires: CO 12.78, Ir 29.23, I 57.96%

Preparation of hexaiodotetracarbonyliridium(III)

IrI_3 was reacted in the pressure vessel with carbon monoxide under the same conditions of the previous experiment. After 18 hours heating the pressure vessel was rapidly cooled with cold water. When opening a dark-red crystalline sublimate identified as

$\text{Ir}(\text{CO})_3\text{I}_3$ was observed at the top of the test tube while in the bottom was collected a product (C). This on treating with hexane and benzene gave an insoluble product (D) and a solution from which brown-red crystals (E) separated on evaporation. E was analysed and resulted to be $[\text{Ir}(\text{CO})_2\text{I}_3]_2$.

Anal Found: CO 8.72, Ir 30.85; I 60.3% $[\text{Ir}(\text{CO})_2\text{I}_3]_2$ requires: CO 8.90; Ir 30.56; I 60.52%. Molecular weight cryoscopic in 1% dibromoethane solution 1197 (calcd. 1258.6).

Preparation of hexaiodotricarbonyliridium(III)

The insoluble product D of the previous experiment was recrystallized from dry ethyl ether + chloroform and obtained as dark-red crystals corresponding to the formula $[\text{Ir}_2(\text{CO})_3\text{I}_6]$.
Anal. Found: C, 6.79; Ir, 30.87; I, 62.6%; $[\text{Ir}_2(\text{CO})_3\text{I}_6]$ requires: C, 6.83; Ir, 31.26; I, 61.90%.

Preparation of potassium triiododicarbonyliridiate(II)

IrI_3 (0.01 moles) and KI (0.01 moles) were placed into the pressure vessel with carbon monoxide at 200 atm. The temperature was maintained at 250° for 24 hours. The crude product was washed first with benzene in order to separate the non ionic iodicarbonyl-iridium derivatives, and then treated with dry ethyl ether. The solid product (F) was filtered off. The solution after evaporation yielded orange crystals which resulted to be $\text{K}[\text{Ir}(\text{CO})_2\text{I}_3]$.
Anal. Found: C, 7.97; Ir, 28.35; I, 55.75%. $\text{K}[\text{Ir}(\text{CO})_2\text{I}_3]$ requires: C, 8.38; Ir, 28.78; I, 56.98%.

Molar conductivity in nitrobenzene at 30° $\Lambda_m = 32.1$; $\Lambda_{500} = 29.42$,

$$\Lambda_{200} = 27.81 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}.$$

Molar conductivity in acetone at 30° $\Lambda_m = 154.2$; $\Lambda_{500} = 131.6$;

$$\Lambda_{200} = 119.8 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}.$$

Preparation of tetraphenylarsonium triiodocarbonyliridiate(II)

A solution of tetraphenylarsonium iodide in absolute ethanol was added to a solution of $\text{K}[\text{Ir}(\text{CO})_2\text{I}_3]$ also in ethanol. Light red crystals m.p. 284° , separated immediately, corresponding to $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ir}(\text{CO})_2\text{I}_3]$.

Anal. Found: C, 5.46; C, 30.81; H, 1.83; Ir, 18.27; I, 36.92%;

$\text{C}_{24}\text{H}_{20}\text{AsIrI}_3(\text{CO})_2$ requires: C, 5.53; C, 30.84; H, 1.99; Ir, 18.99; I 37.6%.

Molar conductivity in nitrobenzene at 30° : $\Lambda_\infty = 26.5$; $\Lambda_{500} = 23.75$;

$\Lambda_{200} = 22 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$.

Preparation of potassium tetraiodocarbonyliridiate(III)

The solid product (F) was dissolved in acetone and filtered. The solution by evaporation in vacuo, yielded dark-red crystals corresponding to $\text{K}[\text{Ir}(\text{CO})\text{I}_4]$.

Anal Found: C, 3.61; Ir, 24.92; I, 66.1%. $\text{K}[\text{Ir}(\text{CO})\text{I}_4]$ requires: C, 3.65; Ir, 25.06; I, 66.18%.

Molar conductivity in acetone at 30° : $\Lambda_\infty = 197$; $\Lambda_{500} = 161.2$;

$\Lambda_{200} = 140.3 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$.

Preparation of tetraphenylarsonium tetraiodocarbonyliridiate(III)

A solution of tetraphenylarsonium iodide in absolute ethanol was added to an ethanol solution of $\text{K}[\text{Ir}(\text{CO})\text{I}_4]$. The red crystals which separated were identified as $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ir}(\text{CO})\text{I}_4]$ m.p. 273° .

Anal. Found: C, 2.5; I, 44.8; Ir, 16.98; C, 26.91; H, 1.86%.

$C_{24}H_{20}AsIrI_4CO$ requires: C, 2.52; I, 45.68; Ir, 17.3; C, 27.01; H, 1.81%.

Molar conductivity in nitrobenzene at 30° : $\Lambda_\infty = 26.35$; $\Lambda_{500} = 23.6$;

$\Lambda_{200} = 22.0 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

Preparation of potassium tetraiododicarbonyliridiate(III)

IrI_4 (0.01 moles) and KI (0.01 moles) were placed into the pressure vessel with carbon monoxide at the initial pressure of 200 atm. The temperature was maintained at 120° for 12 hours. The crude product was washed first with benzene in order to separate the non ionic iodicarbonyliridium derivatives and then dissolved in dry ethyl ether. The filtered solution was evaporated in vacuo and yielded red crystals very soluble in ether, acetone alcohol and in dilute hydroiodic acid solution. The product resulted to be $K[Ir(CO)_2I_4]$.

Anal. Found: C, 7.4; Ir, 24.3; K, 4.92; I, 63.7%. $K[Ir(CO)_2I_4]$ requires C, 7.05; Ir, 24.18; K, 4.91; I, 63.8%.

Molar conductivity in acetone at 30° . $\Lambda_\infty = 148$; $\Lambda_{500} = 130$;

$\Lambda_{200} = 119.5 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

Preparation of tetraphenylarsonium tetraiododicarbonyliridiate(III)

A solution of tetraphenylarsonium iodide in methanol was added to a solution of $K[Ir(CO)_2I_4]$. The red crystals which separated m.p. 210° , resulted to be $[As(C_6H_5)_4][Ir(CO)_2I_4]$.

Anal. Found: CO, 3.73; I, 35.0; As, 4.96%. $C_{24}H_{20}AsIr(CO)_2I_4$ requires:
CO, 3.81; I, 34.58; As, 5.10%.

Molar conductivity in nitrobenzene at 30°: $\Lambda_{\infty}=32.65$; $\Lambda_{500}=28.7$;
 $\Lambda_{200}=25.4 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

Preparation of potassium pentaiodocarbonyliridiate(III)

IrI_4 (0.01 moles) and KI (0.02 moles) was placed into the pressure vessel with carbon monoxide at the initial pressure of 200 atm. The temperature was maintained at 240° for 12 hours. The crude product, washed with benzene as above, then with ethyl ether in order to separate a very small quantity of $K[Ir(CO)_2I_4]$, was finally dissolved in acetone. The filtered acetone solution, evaporated in vacuo, yielded dark-red crystals that resulted to be $K_2[Ir(CO)I_5]$.

Anal. Found: CO, 3.2; Ir, 20.2; I, 68.0; K, 8.6%. $K_2[Ir(CO)I_5]$ requires:
CO, 3.0; Ir, 20.6; I, 68.0; K, 8.37%

Molar conductivity in acetone at 30°: $\Lambda_{\infty}=276$; $\Lambda_{500}=228$;
 $\Lambda_{200}=200 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

Preparation of tetraphenylarsonium pentaiodocarbonyliridiate(III)

A methanol solution of tetraphenylarsonium iodide, added to a methanol solution of $K_2[Ir(CO)I_5]$, gave after a few minutes brown-red crystals m.p. 308°(dec.), which resulted to be $[As(C_6H_5)_4]_2[Ir(CO)I_5]$.

Anal. Found: C, 1.78; I, 40.0; As, 9.3%. $C_{48}H_{40}As_2IrCOI_5$ requires:
C, 1.72; I, 39.13; As, 9.23%.

Molar conductivity in nitrobenzene at 30°: $\Lambda_{\infty}=64$; $\Lambda_{500}=53.4$;
 $\Lambda_{200}=47.3 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

Preparation of potassium pentaiodoiridate(III)

When the reaction of $IrI_4 + KI$ and carbon monoxide was carried out above 300° a new red crystals product was obtained which resulted to be K_2IrI_5 . The same compound could also be obtained by refluxing $K[Ir(CO)_2I_4]$ and $K_2[Ir(CO)I_5]$ with a solution of HI for many hours. K_2IrI_5 , insoluble in organic solvents, could be recrystallized from water.

Anal. Found: K, 8.4; Ir 22.0, I, 69.2%. K_2IrI_5 requires: K, 8.63; Ir, 21.24; I, 70.1%.

INFRARED SPECTRA IN THE CARBONYL REGION OF THE
 IODOCARBONYLIRIDIUM COMPOUNDS

COMPOUND	C-O stretches cm^{-1}		
$[\text{Ir}(\text{CO})_3\text{I}_3]$	2178 w	2114	2079 sh
$[\text{Ir}(\text{CO})_2\text{I}_3]$	2123	2087	
$[\text{Ir}_2(\text{CO})_3\text{I}_6]$	2118	2074	
$\text{K}[\text{Ir}(\text{CO})_2\text{I}_3]$	2136	2092	
$[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ir}(\text{CO})_2\text{I}_3]$	2100	2070	
$\text{K}[\text{Ir}(\text{CO})\text{I}_4]$	2051		
$[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ir}(\text{CO})\text{I}_4]$	2041		
$\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$	2118	2066	
$[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ir}(\text{CO})_2\text{I}_4]$	2109	2074	
$\text{K}_2[\text{Ir}(\text{CO})\text{I}_5]$	2032		
$[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Ir}(\text{CO})\text{I}_5]$	2008		

ASTIA NO:

Contract No. AF 61(052)-83

United States Air Force, Air Research and Development Command, European Office, Brussels, Belgium.

Final Report: TITLE - STUDIES ON IRIIDIUM AND RHENIUM COMPOUNDS by L.Malatesta

date: 31/3/1961 - 32 pages -

Organization: University of Milano - Italy
Abstract: HEXAISO CYANIDERHENIUM(I) SALTS -
The new salts $[\text{Re}(\text{RNC})_6]^+ \text{X}^-$ (R=p-tolyl, ethyl),
which are stable, diamagnetic, crystalline
substances are described.

ISOCYANIDE DERIVATIVES OF IRIIDIUM(I) - The

ASTIA NO:

Contract No. AF 61(052)-83

United States Air Force, Air Research and Development Command, European Office, Brussels, Belgium.

Final Report: TITLE - STUDIES ON IRIIDIUM AND RHENIUM COMPOUNDS - by L.Malatesta

date: 31/3/1961 - 32 pages -

Organization: University of Milano - Italy
Abstract: HEXAISO CYANIDERHENIUM(I) SALTS -
The new salts $[\text{Re}(\text{RNC})_6]^+ \text{X}^-$ (R=p-tolyl, ethyl),
which are stable, diamagnetic, crystalline
substances are described.

ISOCYANIDE DERIVATIVES OF IRIIDIUM(I) - The

ASTIA NO:

Contract No: AF 61(052)-83

United States Air Force; Air Research and Development Command, European Office, Brussels Belgium.

Final Report: TITLE - STUDIES ON IRIIDIUM AND RHENIUM COMPOUNDS - by L.Malatesta

Date: 31/3/1961 - 32 pages -

Organization University of Milano - Italy
Abstract: HEXAISO CYANIDERHENIUM(I) SALTS -
The new salts $[\text{Re}(\text{RNC})_6]^+ \text{X}^-$ (R=p-tolyl, ethyl),
which are stable, diamagnetic, crystalline
substances are described.

ISOCYANIDE DERIVATIVES OF IRIIDIUM(I) - The

ASTIA NO:

Contract No: AF 61(052)-83

United States Air Force; Air Research and Development Command, European Office, Brussels, Belgium.

Final Report: TITLE - STUDIES ON IRIIDIUM AND RHENIUM COMPOUNDS - by L.Malatesta

Date: 31/3/1961 - 32 pages

Organization: University of Milano - Italy
Abstract: HEXAISO CYANIDERHENIUM(I) SALTS -
The new salts $[\text{Re}(\text{RNC})_6]^+ \text{X}^-$ (R=p-tolyl, ethyl),
which are stable, diamagnetic, crystalline
substances are described.

ISOCYANIDE DERIVATIVES OF IRIIDIUM(I) - The

REFERENCES

- (¹) M.Freni e V.Valenti - Gazz.Chim.It. 90,1436,(1960)
- (²) M.Freni e V.Valenti - J.Inorg.Nucl.Chem. 16,1445,(1960)
- (³) M.Freni e V.Valenti - J.Inorg.Nucl.Chem. 16,240,(1961)
- (⁴) L.Malatesta,M.Freni,V.Valenti ed E.Bossi - Angew.Chem. 72,
323,(1960)
- (⁵) A.Sacco - Gazz.Chim.It. 86,201,(1956)
- (⁶) L.Malatesta ed A.Sacco - Atti Acc.Naz.Lincei.Rend.classe
Scienze Fisiche Matematiche e Naturali(VIII) 15,94,(1953)
- (⁷) L.Malatesta e L.Vallarino - Journ.Chem.Soc.London - 1867,(1956)
- (⁸) L.Malatesta - Progress in Inorganic Chemistry - vol.I^o pag.305
Interscience Publishers Inc.New York
- (⁹) Curtis, Fergusson and Nyholm - Chem.Ind. (1958),625.
- (¹⁰) L.Malatesta e M.Angoletta - International Symposium on the
chemistry of the coordination compounds - suppl.to "La Ricer=
ca Scientifica" 28^o,(1958)
- (¹¹) M.Angoletta - Gazz.Chim.It. 89,2359,(1959)
- (¹²) L.Naldini - Gazz.Chim.It. 90,1516,(1960)
- (¹³) Gillespie and Nyholm - Quarterly Reviews - 11,361,(1957)
- (¹⁴) W.Hieber,H.Lagally, and M.Mayr - Z.anorg Ch.246,138,(1941)
- (¹⁵) L.Malatesta - Report AFOSR TN 60-460 - note n.3