INTERACTION OF $Ir(CO)Cl(PPh_3)_2$ WITH METAL IONS

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The interaction between $Ir(CO)Cl(PPh_3)_2$ (further abreviated as Irk) and $Hg(ClO_4)_2$ or Hg. .$(DMSO)_6(ClO_4)_2$ leads to a consecutive formation of complexes of the type $[(Irk)_nHg](ClO_4)_2$ ($n = 1, 2, 3$) and $[(Irk)_3Hg(ClO_4)_x](ClO_4)_{2-x}$ depending on the Irk : Hg^{2+} ratio. In presence of metallic mercury a further complex with the stoichiometry $[(Irk)_4Hg](ClO_4)_2$ was identified. The Vaska complex $Ir(CO)Cl(PPh_3)_2$ acts as a ligand also towards further metal ions, such as Cu^{2+} and Fe^{3+}, forming complexes with the stoichiometry $(Irk)CuCl_2$ and $(Irk)_2FeCl_3$, respectively. Spectroscopic and polarographic characterization of these complexes is given.

By electrolysis of $Ir(CO)Cl(PPh_3)_2$ (further Irk) at the anodically polarized mercury electrode in CH_2Cl_2 using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte a mixture of complexes with the stoichiometry $[(Irk)_3Hg]^{2+}$ and $[(Irk)_4.Hg]^{2+}$ (as perchlorate salts) is obtained[1]. It can be assumed that the electrode process consists in oxidizing the electrode to mercury ions which subsequently react with Irk. In an attempt to prove this and to prepare the iridium–mercury complexes chemically we studied in the present work the interaction between Irk and mercuric perchlorate. To compare the interaction of Irk with other metal ions the study was extended also to interactions with Cu^{2+} and Fe^{3+}.

EXPERIMENTAL

The electrochemical experiments were carried out with the Radelkis Model OH 102 polarograph. As supporting electrolyte 0·1M-TBAP in CH_2Cl_2 was used. All potentials were measured against the saturated aqueous calomel electrode. The mercury dropping electrode had the following characteristics: $t_1 = 2.85$ s, $m = 1.96$ mg s^{-1} at the mercury level 64 cm and the applied voltage 0·0 V in the supporting electrolyte. In all measurements a potentiostatically controlled three-electrode system was used. The large-area electrolyses were carried out with the potentiostat Jaissle 1 000 T. The charge transferred in the course of the electrolyses was measured by means of the Amel Integrator M 558. In the spectroscopic measurements the Unicam SP 800B instrument was used for the UV and visible region, and the Perkin–Elmer Model 257 for the IR region. The conductometric measurements were carried out with the Phillips PR 9501 instrument. The EPR spectra were recorded with the Varian E-4 model spectrometer.

The dichloromethane (Uvasol-Merck) was refluxed and distilled under inert atmosphere with P_2O_5 prior to use. The complex $Ir(CO)Cl(PPh_3)_2$ was prepared by a standard procedure[2].

$Hg(DMSO)_6(ClO_4)_2$ was obtained according to a described method[3]. All experiments were carried out under inert atmosphere of argon or nitrogen purified on the BTS catalyst (BASF) column and dried over P_2O_5.

Since the simple anhydrous mercuric perchlorate is insoluble in nonaqueous media the anodic dissolution of mercury was used in the first part of the experiments for the examination of the interaction of Irk with mercury ions. The large-area mercury electrode polarized potentiostatically to a potential +1·0 V yields in 0·1M-TBAP CH_2Cl_2 solution a white suspension of Hg $(ClO_4)_2$ the amount of which can be determined coulometrically and which, due to its fine dispersion, is able to react quantitatively with Irk. After completion of the electrolysis Irk was gradually added to the generated $Hg(ClO_4)_2$ directly in the electrolytic cell, *i.e.* in presence of the metallic mercury.

In the second part of the experiments $Hg(DMSO)_6(ClO_4)_2$ dissolved in acetone was reacted with dichloromethane solution of Irk in absence of metallic mercury. It was found that the presence of metallic mercury played an important role in formation of the products at higher Irk : Hg^{2+} ratios (see below) but otherwise in both cases essentially the same results were obtained. The present study was aimed at obtaining information concerning the formation and chemical behaviour of the species in solution. For this reason the different molar ratios Irk : Hg^{2+} were characterized by polarographic and spectroscopic patterns indicating the formation of the individual complexes and the microanalyses of the products were carried out only exceptionally in cases where other evidence was lacking. The components of the new species obtained were analyzed polarographically after the decomposition *in situ*.

RESULTS AND DISCUSSION

Molar Ratio Irk : $Hg^{2+} = 1 : 1$

The brightly yellow solution of Irk in CH_2Cl_2 turns intensely deeply yellow on addition of the equimolar amount of $Hg(DMSO)_6(ClO_4)_2$ in acetone whereas no free Irk can be detected spectrophotometrically in the solution. After evaporation of the solution and benzene extraction the product is obtained in form of a deeply yellow oil which is readily soluble in dichloromethane, acetone and propylene carbonate, and insoluble in benzene. In alcohols it is immediately decomposed under liberation of metallic mercury.

The dichloromethane solution of the product shows an absorption band with $\lambda_{max} = 455$ nm ($\varepsilon_{max} = 10^3$ M^{-1} cm^{-1}) and the carbonyl stretching with $\nu_{CO} = 2035$ cm^{-1}. Another distinct IR band with $\nu = 1090$ cm^{-1} can be ascribed to the Cl—O vibration of the free perchlorate ion on the basis of its identity with the perchlorate band observed in the dichloromethane solution of TBAP. Conductometrically it is found that the product in CH_2Cl_2 behaves as an uni-bi electrolyte. On the basis of these results the product can be formulated as $[IrkHg](ClO_4)_2$.

A product with the same spectrophotometric characteristics results also from the reaction of Irk with electrolytically generated $Hg(ClO_4)_2$ in the molar ratio 1 : 1. Polarographically it shows a single cathodic irreversible wave with $E_{1/2} = +0{\cdot}710$ V the limiting current of which is diffusion controlled and corresponds to the uptake of 2 electrons (from comparison with the ferrocene wave).

The product reacts quantitatively with 2 moles of tetrabutylammonium halide (TBAX; X = Cl, Br, I) under formation of colourless or slightly yellow solutions with spectroscopic (visible and IR) and polarographic characteristics corresponding to the species $IrkHgX_2$. In excess of TBAX the product is decomposed to Irk and HgX_4^{2-} in the molar ratio 1 : 1. This behaviour corresponds to the known complexes $IrkHgX_2$ (ref.[1,4,5]). Hence it follows that the reactions at the ratio Irk : Hg^{2+} = 1 : 1 can be described by the following equations:

$$\mathrm{Irk} + \mathrm{Hg(ClO_4)_2} = [\mathrm{IrkHg}](\mathrm{ClO_4})_2 \quad (1)$$

$$[\mathrm{IrkHg}](\mathrm{ClO_4})_2 + 2\,\mathrm{TBAX} = \mathrm{IrkHgX_2} + 2\,\mathrm{TBAP} \quad (2)$$

$$\mathrm{IrkHgX_2} + 2\,\mathrm{TBAX} = \mathrm{Irk} + (\mathrm{TBA})_2\mathrm{HgX_4}\,. \quad (3)$$

The species $[IrkHg](ClO_4)_2$ differs from $IrkHgX_2$ (X = Cl, Br, I) not only in the ionic character of the former and the non-dissociative character of the latter molecule, but also in that the species $[IrkHg](ClO_4)_2$ can coordinate further molecules of Irk (see below) while the complex $IrkHgX_2$ does not react with Irk. This difference in behaviour points to the conclusion that in case of HgX_2, where X = Cl, Br, I the oxidative addition product X—Ir(III)(CO)(Cl($PPh_3)_2$—HgX is formed by the interaction with the Vaska complex (as postulated previously[5]), whilst in case of Hg.$(ClO_4)_2$ the adduct results from a simple donor-acceptor interaction and can be formulated as $[Irk.Hg](ClO_4)_2$.

Molar Ratio Irk : Hg^{2+} = 2 : 1

The reaction between Irk and $Hg(ClO_4)_2$ or $Hg(DMSO_6(ClO_4)_2$ in the ratio 2 : 1, or the addition of the equimolar amount of Irk to $[IrkHg](ClO_4)_2$ leads to the formation of a greenish yellow solution characterized by a single distinct absorption with $\lambda_{max} = 462$ nm ($\varepsilon_{max} = 10^4 \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). In the IR region a single carbonyl stretching frequency $\nu_{CO} = 2030\,\mathrm{cm}^{-1}$ and a Cl—O vibration frequency $\nu_{ClO} = 1090\,\mathrm{cm}^{-1}$ corresponding to the free perchlorate ions is found. Polarographically the solution yields a single cathodic irreversible wave with $E_{1/2} = +0{\cdot}36$ V. The limiting current is diffusion controlled and corresponds to the uptake of 2-electrons per one Hg atom in the complex. Attempts to isolate this product failed due to a rapid decomposition of the substance during the separation procedure. On the basis of the experimental results the product can be formulated as the outer-sphere complex $[(Irk)_2Hg](ClO_4)_2$. Similar complexes with two metal–mercury bonds are known and have been studied thoroughly, as *e.g.* $Ru(Cp)_2Hg(ClO_4)_2$ (ref.[6]) or $(Irk)_2Hg.(NO_3)_2$ (ref.[1]).

The reaction of the outer-sphere complex $[(Irk)_2Hg](ClO_4)_2$ with NO_3^- ions leads to the formation of the neutral inner-sphere complex $(Irk)_2Hg(NO_3)_2$. It is noteworthy that in the transition from the mentioned outer-sphere to the inner-sphere complex the carbonyl stretching frequency remains essentially the same ($\nu_{CO} = 2030\ cm^{-1}$) while the electron spectra are dramatically changed (the complex $Irk_2Hg(NO_3)_2$ exhibits no absorption bands in the visible region). Also the polarographic behaviour of both complexes differs, the complex $Irk_2Hg(NO_3)_2$ being reduced more negatively ($E_{1/2} = +0{\cdot}23$ V) (ref.[1]).

With halide ions in form of TBAX the complex $[(Irk)_2Hg](ClO_4)_2$ reacts under splitting off one Irk molecule and formation of the above mentioned complex $IrkHgX_2$ which in excess of TBAX reacts further according to the equation (*3*).

Molar Ratio Irk : Hg^{2+} = 3 : 1

By the reaction between Irk and $Hg(DMSO)_6(ClO_4)_2$ in the ratio 3 : 1, or on mixing equimolar amounts of Irk and $[(Irk)_2Hg](ClO_4)_2$ an orange-yellow solution is formed which is characterized by the carbonyl stretching frequency $\nu_{CO} = 2020\ cm^{-1}$ and Cl—O frequency $\nu_{ClO} = 1090\ cm^{-1}$ in the IR region and by a distinct CT absorption band with $\lambda_{max} = 492$ ($\varepsilon_{max} = 10^4 M^{-1}\ cm^{-1}$) in the visible region. After evaporation of the solution *in vacuo* and addition of benzene the product can be isolated in form of red-brown crystals, which are soluble in CH_2Cl_2 and THF, and insoluble in benzene and hexane. In protic solvents it is rapidly decomposed.

The stoichiometric composition of the product was proved on the basis of the known decomposition reaction of the mercury–Irk complexes by means of halide ions[4]. In presence of an excess of TBAI in CH_2Cl_2 solution the product is quantitatively decomposed to Irk and HgI_4^{2-}. Using the known extinction coefficients[1] of the absorption bands of Irk and HgI_4^{2-} the molar ratio Irk : HgI_4^{2-} equal to 3 : 1 was found. Taking into account the presence of the absorption band with $\nu = 1090\ cm^{-1}$ corresponding to the free perchlorate in the dichloromethane solution of the product and the conductivity data indicating the electrolyte character of the product it can be assumed that the product has the composition $[(Irk)_3Hg](ClO_4)_2$.

The orange-yellow solutions of the complex $[(Irk)_3Hg](ClO_4)_2$ turn greenish with time and after 12 hours they become intensely green. At the same time the intensity of the absorption band with $\lambda_{max} = 492$ nm decreases and new absorption bands with $\lambda_{max} = 619, 634$ nm appear. In the IR region the intensity of the carbonyl band with $\nu_{CO} = 2020\ cm^{-1}$ decreases under the simultaneous increase of a new band with $\nu_{CO} = 2\,010\ cm^{-1}$ and splitting off the Cl—O band with $\nu_{ClO} = 1090\ cm^{-1}$ into two bands with $\nu = 1110\ cm^{-1}$ and $1040\ cm^{-1}$ which are assigned as corresponding to the coordinated perchlorate[7] (Fig. 1). This process reaches an equilibrium in which both the original and new bands are observed so that in the equilibrium state the solution is characterized by three absorption bands with $\lambda_{max} = 492, 619$ and 634 nm ($\varepsilon_{max} = 10^3 - 10^4 M^{-1}\ cm^{-1}$), two carbonyl stretching bands with $\nu_{CO} = 2020$ and $2010\ cm^{-1}$, and three Cl—O bands corresponding to the free perchlorate with $\nu_{Cl-O} = 1090\,cm^{-1}$ and to the coordinated perchlorate with $\nu_{Cl-O} = 1110$ and $1040\,cm^{-1}$, respectively. This equilibrium mixture of products is decomposed by the excess of TBAI to Irk and HgI_4^{2-} in the molar ratio Irk : Hg^{2+} = 3 : 1. Since a disproportionation reaction of $[(Irk)_3Hg](ClO_4)_2$ leading to products with lower and higher ratio Irk : Hg^{2+} can be excluded (the green colouration of the solution is not accompanied by the formation of spectral bands corresponding to complexes with a lower Irk : Hg^{2+} ratio) and since in the IR spectrum of the newly formed complex the bands corresponding to the coordinated perchlorate are observed it can be concluded that in the described slow reaction a transition from the outer-sphere to inner-sphere complex of the same over-all stoichiometry proceeds. This conclusion is corroborated also by the marked decrease of the conductivity of the solution during this reaction. In view of the fact that the new complex occurs always in an equilibrium mixture with the original complex it is difficult to determine the number of the coordinated perchlorate ions and thus the newly formed complex can be formulated as $[(Irk)_3Hg(ClO_4)_{2-x}$ $(x = 1$ or $2)$.

If the reaction between Irk and Hg^{2+} is carried out under stirring in presence of metallic mercury then after surpassing the ratio Irk : Hg = 2 : 1 the complex with the ratio 4 : 1 is formed in addition to the complexes with the ratio 3 : 1 as is described in the following paragraph. The polarography using the mercury dropping electrode shows a drawn-out cathodic wave with $E_{1/2} = +0{\cdot}15$ V.

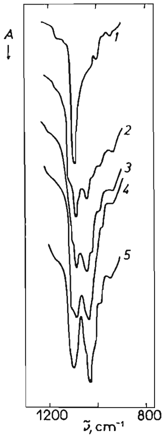

Fig. 1

Time Dependence of the IR Spectrum of the Complex $[(Irk)_3Hg].(ClO_4)_2$ in the Cl—O Stretching Frequency Region

1 Start; after: *2* 0·5; *3* 1; *4* 5; *5* 10 hours.

Molar Ratio Irk : Hg^{2+} > 3 : 1

When increasing the ratio Irk : Hg^{2+} above 3 : 1 in the Irk–$Hg(DMSO)_6(ClO)_4$ system no further change of the solution is observed except for the bands characteristic for the free Irk (λ_{max} = 340, 386, 438 nm, ν_{CO} = 1965 cm^{-1}) which appear in addition to the above described bands corresponding to the system with the ratio 3 : 1. However, further consumption of Irk up to the ratio Irk : Hg = 3·6 : 1 is observed when metallic mercury is present in the system. The solution turns blue-green after a short shaking and in the visible region a new absorption band appears with λ_{max} 508 nm which merges with the band with λ_{max} = 492 nm (vide supra at the ratio Irk : Hg = 3 : 1) forming a broad band with the apparent maximum at λ_{max} = = 500 nm. In the infrared region of the CO stretching frequencies a new very intense band with ν_{CO} = 2005 cm^{-1} appears. In addition to these newly formed bands both in the visible and IR region the bands described at the ratio Irk : Hg = 3 : 1 remain in the spectra so that it is evident that at the ratio Irk : Hg = 3·6 : 1 a mixture of substances is involved. Identical results are obtained when Irk is added to the electrolytically generated $Hg(ClO_4)_2$ in the electrolytic cell containing bottom mercury electrode.

The same ratio Irk : Hg = 3·6 : 1 and the same spectroscopic and polarographic

TABLE I

Polarographic and Spectroscopic Characterization of Substances Resulting from the Interaction of Irk with $Hg(ClO_4)_2$

Complex	Wave $E_{1/2}$, V	λ_{max} nm	ν_{CO} cm^{-1}	ν_{Cl-O} cm^{-1}
$[(Irk)Hg](ClO_4)_2$	cathodic +0·71	455	2 035	1 090
$[(Irk)_2Hg](ClO_4)_2$	cathodic +0·36	462	2 030	1 090
$[(Irk)_3Hg](ClO_4)_2$	cathodic +0·15	492	2 020	1 090
$[(Irk)_3Hg(ClO_4)_x](ClO_4)_{2-x}$	cathodic +0·15	619, 634	2 010	1 110, 1 040
$[(Irk)_4Hg](ClO_4)_2$	cathodic +0·15	508	2 005	1 090
Irk	anodic +0·69	340, 386 438	1 965	—

pattern was observed in the product of the electrolysis of Irk at mercury electrodes which was identified[1] as a mixture of complexes with the stoichiometric ratio Irk : : Hg = 3 : 1 and 4 : 1. Therefore the species characterized by $\lambda_{max} = 508$ nm and $\nu_{CO} = 2005\ cm^{-1}$ can be ascribed to the complex $[(Irk)_4Hg](ClO_4)_2$. Chemical analysis of the mixture of complexes obtained in presence of metallic mercury has shown that they contain mercury in the amount corresponding to the original amount of the mercury salt used for the reaction with Irk. Hence it can be concluded that metallic mercury, the presence of which is a necessary condition of the formation of the complex with the ratio Irk : Hg = 4 : 1, acts as a "catalyst" in the sense that it enables the formation of the 4 : 1 complex and maintains the over-all stoichiometry 3·6 : 1 without being incorporated into the reaction products. This "catalytic" reaction is rapid enough to influence even the reaction products of the polarographic anodic electrode reaction of Irk at the mercury dropping electrode where the time of electrolysis is about 3 s. In this case the electrode process involves the complex formation of Irk with mercuric ions generated by the anodic dissolution of mercury. From the corresponding limiting current it has been inferred[1] that the products of this reaction which proceeds at the surface of the mercury electrode have the same stoichiometric composition with the ratio Irk : Hg = 3·6 : 1 as described above.

The mentioned complexes with the over-all stoichiometry 3·6 : 1 are reduced polarographically in a drawn-out irreversible wave with $E_{1/2} = +0{\cdot}15$ V. The limiting current is diffusion controlled and corresponds to the uptake of 2 electrons per one Hg atom in the complex.

The spectroscopic and polarographic characterization of the mercury–iridium complexes obtained at different ratios Irk : Hg is summarized in Table I. From this Table it follows that the carbonyl stretching frequency in the series $[(Irk)_nHg](ClO_4)_2$ ($n = 1-4$) depends on the number "n" similarly as the CN stretching frequency[7] in the series of complexes $[Hg(CN)_{2+n}]^{n-}$. With increasing n ν_{CO} decreases from $\nu_{CO} = 2035\ cm^{-1}$ in $[(Irk)Hg](ClO_4)_2$ up to $\nu_{CO} = 2005\ cm^{-1}$ in $[(Irk)_4Hg]$ . . $(ClO_4)_2$. With decreasing ν_{CO} the CT absorption bands are shifted to higher wave lengths from 455 nm up to 508 nm. These shifts show that the interaction between Irk and mercury ions is combined with the lowering of the electron density on the iridium atom this effect being less pronounced with increasing number of the coordinated Irk groups. Hence it follows that the Vaska complex behaves in the interaction as an electron donating ligand.

Interaction of Irk *with* Cu^{2+} *and* Fe^{3+}

The Vaska complex has been described to react[8] in excess of $CuCl_2$ or $FeCl_3$ in the benzene–ethanol medium under formation of the complex $IrkCl_2$ (ν_{CO} = = $2078\ cm^{-1}$; Nujol) according to the equation (*4*):

$$Irk + 2\,CuCl_2\ (2\,FeCl_3) \rightarrow IrkCl_2 + 2\,CuCl\ (2\,FeCl_2)\,. \qquad (4)$$

However, in a spectrophotometric titration of the benzene solution of Irk with ethanolic solutions of $CuCl_2$ and $FeCl_3$ followed at $\lambda = 386$ nm we found that the equivalence point was reached (*i.e.*, Irk was completely consumed) with 0·5 mol $FeCl_3$ or 1 mol $CuCl_2$ per 1 mol Irk (Fig. 2). This result does not correspond to the stoichiometry of the reaction (*4*) and shows that the reaction proceeds with formation of intermediate products.

The product of the reaction between Irk and $CuCl_2$ in equimolar ratio was isolated by evaporating the benzene–ethanolic solution *in vacuo* in form of blue-green crystals which are soluble in dichloromethane, acetone and benzene. The IR spectra show a strong carbonyl stretching band with $\nu_{CO} = 2030\ cm^{-1}$ (main substance) and weak bands with $\nu_{CO} = 2078$ and $1995\ cm^{-1}$ evidently due to a small amount of by-products. In the course of the titration the EPR spectra exhibit a signal reaching its maximum intensity in the equivalence point. The signal which is obtained also with the isolated product differs in shape and splitting from that belonging to $CuCl_2$ (see comparison of the signals of both crystalline species in Fig. 3) but by analogy with other Cu(II) complexes it still can be ascribed to the Cu–d system[9]. Further

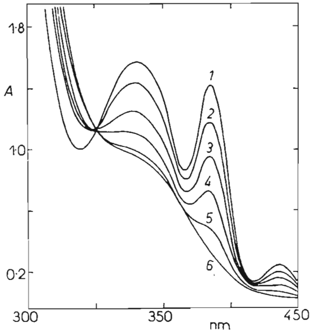

FIG. 2

Spectrophotometric Titration of Ir(CO). $.Cl(PPh_3)_2$ with $CuCl_2$

1 5 . 10^{-4}M-$Ir(CO)Cl(PPh_3)_2$ in benzene--ethanol mixture; [$CuCl_2$]: *2* 0·75 . 10^{-4}M *3* 1·5 . 10^{-4}M; *4* 2·25 . 10^{-4}M; *5* 3 . 10^{-4}M; *6* 5 . 10^{-4}M-$CuCl_2$.

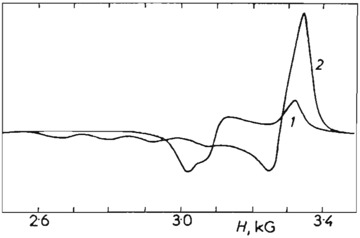

FIG. 3

The EPR Spectrum of the *1* Crystalline $CuCl_2 . 2\,H_2O$ and of the *2* Crystalline Product of the Reaction between Equimolar Amounts of $Ir(CO)Cl(PPh_3)_2$ and $CuCl_2$

it was previously found[9] that the product of the one-electron oxidation of Irk was a diamagnetic dimer with the carbonyl stretching frequency $\nu_{CO} = 2060 \text{ cm}^{-1}$ so that in case of the studied reaction between Irk and $CuCl_2$ a simple electron transfer can be excluded. This evidence leeds to the conclusion that the product of this reaction in the equivalent point is a complex with the stoichiometric composition Irk. $.CuCl_2$, and by analogy, in the reaction with $FeCl_3$ the compound has the composition $(Irk)_2FeCl_3$. It is evident that these addition compounds represent intermediates in the reaction (*4*) and are converted to the final products of this reaction only by the excess of the metal salts.

CONCLUSION

In the present paper evidence is given that the Vaska complex $Ir(CO)Cl(PPh_3)_2$ behaves towards the oxidizing ions, such as Hg^{2+}, Cu^{2+}, Fe^{3+}, as a Lewis base forming with them primarily more or less stable addition compounds. The stoichiometry of the corresponding interactions indicates that these reactions cannot be generally considered as redox additions. However, on the basis of the finding[9] that the Vaska complexes are very difficult to be oxidized by electron transfer reactions it can be concluded that the mentioned donor–acceptor interactions leading to the addition compounds represent an important partial step in the oxidative additions.

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