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Synthesis of New Cationic Rhodium(I) Complexes with Diolefins and Isoquinoline *N*-oxide as Ligands

ARISTIDES CHRISTOFIDES, DEMETRIUS DRIGAS and EUGENIA TOURKA

Dept. of General and Inorganic Chemistry, University of Thessaloniki, Gr-54006 Salonica, Greece

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Abstract

The preparation of cationic rhodium complexes of the types $[RhL(IQNO)_2]ClO_4$ (L = COD, COT and NBD) and $[Rh(COD)(IQNO)L']ClO_4$ (L′ = 4-NH_2py, 4-NMe_2py and PPh_3) and the reactions of $[Rh(COD)(IQNO)_2]ClO_4$ with N- and P-donor ligands are described.

Introduction

A survey of the literature reveals that rhodium complexes of isoquinoline 2-oxide have not been prepared up to now, although some coordination compounds of this ligand with nickel(II) and cobalt(II) have been known for many years [1, 2]. Other isoquinoline *N*-oxide complexes with different metals have also been described, e.g., with Mn [3], Cu [4], VO_2^{2+} [5, 6] and Sn [7] as well as its adducts with organotin halides [8]. Most of these complexes are monomeric and only the copper(II) ones are dimeric.

Following our earlier studies on rhodium(I) complexes with quinoline *N*-oxides [9] as ligands and having in mind that these compounds can possibly act as catalysts in hydrogen-transfer reactions [10], we tried to prepare the corresponding isoquinoline *N*-oxide complexes.

Our attempt also aimed at the investigation of the coordination capacity of this ligand towards rhodium in comparison with that of substituted quinoline-1-oxides. In order to find out the behaviour of complexes incorporating other olefins apart from COD (1,5-cyclooctadiene), isoquinoline *N*-oxide compounds with COT (cyclooctatetraene) and NBD (norbornadiene) have been prepared. The preparation of related mixed-ligand complexes $[Rh(COD)(IQNO)L']ClO_4$ (L′ = P- or N-donor ligand), and the interpretation of some spectral data are also reported and discussed.

Results and Discussion

The complexes **I**, **V** and **VI** were prepared in a similar manner to that used in our previous work [9], which was a modification of the procedure employed by Uson *et al.* [11] for the preparation of the corresponding pyridine *N*-oxide complexes. The new compounds (complexes **I**, **V** and **VI**) were formed (eqn. (1)) as yellow or brown air-stable solids.

$$[RhL(Me_2CO)_x]ClO_4 + 2IQNO \longrightarrow [Rh(IQNO)_2]ClO_4 + XMe_2CO \qquad (1)$$

The mixed complexes **II**, **III** and **IV** were formed by adding the stoichiometric amount of ligand L′ to the complex **I**. In the case of complex **IV** it is not necessary to isolate the complex **I**, since the PPh_3 and IQNO (1/1) can be added directly to an acetone solution of $[Rh(COD)(Me_2CO)_x]ClO_4$, the latter being prepared as was described elsewhere [11, 12]. This method is more generally applicable as it gives purer products, higher yields, and it even allows the preparation of complexes $[Rh(COD)(2\text{-}PhQNO)(PPh_3)]ClO_4$ and $[Rh(COD)(4\text{-}ClQNO)(PPh_3)]ClO_4$ [13].

$$[Rh(COD)(Me_2CO)_x]ClO_4 + PPh_3 + IQNO \longrightarrow [Rh(COD)(IQNO)(PPh_3)]ClO_4 + XMe_2CO \qquad (2)$$

The ^{31}P NMR spectrum of **IV** taken in deuterated chloroform shows double resonances at 27.9 ppm with rhodium–phosphorous coupling of 156 Hz. The observed chemical shift as well as the coupling constant are close to those reported for similar compounds [9, 10, 13]. It should be noted that this compound appears to be more stable in solution than its analogues prepared previously in this laboratory, since their ^{31}P NMR spectra taken in the same solvent show peaks assignable to decomposition products [9, 13]. In general, we may say that the complexes of isoquinoline *N*-oxide are more easily isolable as well as more stable than their substituted quinoline *N*-oxide counterparts.

The reaction of an excess of py, bipy, phen or of two moles of PPh_3, 4-aminopyridine(4-NH_2py) and 4-dimethylaminopyridine (4-NMe_2py) with complex **I** leads to the displacement of IQNO and formation of the corresponding previously prepared complexes [14–17]. The interaction of 1 mol of imidazole (Im)

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TABLE I. Analytical Results, Molar Conductivities, Yields and IR Data for Complexes $[RhL(IQNO)_2]ClO_4$ and $[Rh(COD)(IQNO)L']ClO_4$

Complex	Found (calc.) (%)			ΛM (ohm^{-1} cm^2 mol^{-1})	Yield (%)	IR bands (cm^{-1})	
	C	H	N			ν(NO)	δ(NO)
I $[Rh(COD)(IQNO)_2]ClO_4$	51.58 (51.97)	4.22 (4.36)	4.49 (4.66)	144	79	1179	817
II $[Rh(COD)(IQNO)(4\text{-}NH_2py)]ClO_4$	48.16 (48.06)	4.44 (4.58)	7.44 (7.64)	156	60	1170	818
III $[Rh(COD)(IQNO)(4\text{-}NMe_2py)]ClO_4$	48.05 (49.88)	4.93 (5.06)	7.41 (7.27)	155	78	1182	820
IV $[Rh(COD)(IQNO)(PPh_3)]ClO_4$	58.67 (58.55)	4.75 (4.77)	2.14 (1.95)	179	94	1178	818
V $[Rh(NBD)(IQNO)_2]ClO_4$	50.03 (51.34)	3.78 (3.79)	4.31 (4.79)	113	85	1153	818
VI $[Rh(COT)(IQNO)_2]ClO_4$	51.62 (52.32)	3.54 (3.72)	4.70 (4.69)	160	74	1178	814

with complex **I** results in the formation of the novel mixed complex $[Rh(COD)(IQNO)(Im)]ClO_4$ whereas the poorer N-donors 2-CNpy or 4-CNPy do not react. Finally, addition of t-BuNC or dpe to solutions of **I** leads to the complete displacement of all ligands and formation of $[Rh(t\text{-}BuNC)_4]ClO_4$ [11, 18] or $[Rh(dpe)_2]ClO_4$, respectively [19]. The study of the reactions of $[Rh(COD)(IQNO)_2]ClO_4$ towards various ligands proved that its behaviour is analogous to that of $[Rh(COD)(4\text{-}MepyNO)_2]ClO_4$ [11].

The conductance data of the complexes **I–VI** suggest the presence of 1:1 electrolytes in acetone, indicating non-coordinated anions in this solvent [9, 20].

IR Spectra

All the complexes **I–VI** show the bands characteristic of the uncoordinated anion ClO_4^- (Td) [21] at 1090 (ν_3) and 630 (ν_4) cm^{-1}, along with the absorptions of all the coordinated ligands.

The values of ν(N–O) for all complexes are listed in Table I. Isoquinoline 2-oxide has a relatively strong peak at 1180 cm^{-1} which usually shifts to lower wavenumbers upon coordination, suggesting that this frequency has a significant N–O stretching component [1, 2]. In our compounds ν(N–O) is either found at the same almost frequency as in the free ligand, complexes **I**, **III**, **IV** and **VI** or shifted to lower energy by 10 or 27 cm^{-1} for complexes **II** or **V**, respectively. This shifting to lower frequencies for the complexes of the latter case is not unexpected since it was observed previously [2, 22]. The absence of shifting for the complexes of the former case is a new feature in their IR spectra, according to the above argument. Moreover, it may mean that the nitrogen–oxygen bond order remains essentially the same, indicating metal-to-ligand back donation of electron density. Another band of special interest is δ(N–O) occurring at 818 cm^{-1} for the free ligand, which is found almost unchanged in the spectra of the new complexes. This is in contrast with the up to now available IR data of isoquinoline *N*-oxide complexes showing that this band exhibits characteristic shifts upon complexation [2, 22]. However, in the analogous complexes of rhodium(I) with substituted quinoline and pyridine *N*-oxides the absorptions due to δ(N–O) do not exhibit appreciable shifting [9, 11]. In addition to peaks due to other ligands the IR spectrum of complex **II** shows weak absorptions at 3462, 3368 and 3190 cm^{-1}, indicating the presence of 4-aminopyridine [17].

Experimental

C, H and N analyses were done in our microanalytical laboratory with a Perkin-Elmer 240 analyzer. Infrared spectra were recorded on a Perkin-Elmer 1430 ration recording spectrophotometer (over the range 4000–200 cm^{-1}) and samples prepared as Nujol mulls or KBr discs.

The conductance measurements were run on an Industrial conductance bridge, model RC 216 B2, in *ca.* 5×10^{-4} M acetone solutions; these data appear in Table I. The ^{31}P NMR spectrum was recorded on JEOL FX-90Q FT spectrometer using $CDCl_3$ solution. $[RhCl(COD)]_2$ [23], $[RhCl(COT)]_2$ [24] and $[RhCl(NBD)]_2$ [24] and isoquinoline *N*-oxide [25] were prepared by literature methods. All reactions were conducted at room temperature in air.

Preparation of Complexes of the Type [RhL-(IQNO)$_2$]ClO$_4$ (I, V, VI)

(i) To a solution of [Rh(COD)(Me$_2$CO)$_x$]ClO$_4$, obtained by treating [RhCl(COD)]$_2$ (0.097 g, 0.2 mmol) with AgClO$_4$ (0.083 g, 0.4 mmol) in 80 ml of acetone and after the removal of the precipitated AgCl, isoquinoline *N*-oxide hydrate (0.145 g, 0.8 mmol) was added portionwise under constant stirring. The colour of the solution became intense yellow. It was then concentrated under vacuum to a small volume (*ca.* 10 ml) and diethylether (10 ml) was added. The resulting yellow solid was washed with diethylether (2 × 5 ml) affording yellow microcrystals of [Rh(COD)(IQNO)$_2$]ClO$_4$ (**I**) (0.19 g) which were dried in air.

For complex **VI** after the addition of diethylether all the volatile material was removed *in vacuo* and the solid left was dissolved in the minimum amount of acetone. The solution was concentrated to half to its original volume and diethylether added. The formation of the crystals was helped by prolonged stirring and scratching with a spatula.

Preparation of Complexes of the Type [Rh(COD)-(IQNO)L′]ClO$_4$ (II–IV)

To a solution of [Rh(COD)(IQNO)$_2$]ClO$_4$ (0.06 g, 0.1 mmol) in 30 ml of acetone, 4-NH$_2$py (0.0094 g, 0.1 mmol) was added. The yellow solution was concentrated under vacuum to a small volume (*ca.* 3 ml) and Et$_2$O (5 ml) was added. The solid was filtered off, washed with ether (2 × 3 ml) and air-dried affording yellow crystals of [Rh(COD)(IQNO)(4-NH$_2$py)]ClO$_4$ (**II**) (0.033 g).

Sometimes complexes **II** and **III** give amorphous solids which are crystallized by prolonged stirring and scratching with a spatula.

Reactions of [Rh(COD)(IQNO)$_2$]ClO$_4$

(i) Addition of 4-NH$_2$py (0.2 mmol), 4-NMe$_2$py (0.2 mmol), bipy (0.1 mmol), phen (0.1 mmol) and py (0.6 ml) to acetone or dichloromethane solutions of 0.1 mmol of [Rh(COD)(IQNO)$_2$]ClO$_4$ led to the complete displacement of isoquinoline *N*-oxide. Concentration under vacuum and addition of diethylether gave microcrystals of [Rh(COD)(4-NH$_2$py)$_2$]ClO$_4$ [17], [Rh(COD)(4-NMe$_2$py)$_2$]ClO$_4$ [17], [Rh(COD)-(bipy)]ClO$_4$ [15], [Rh(COD)(phen)]ClO$_4$ [15], [Rh-(COD)(py)$_2$]ClO$_4$ [14].

(ii) Addition of t-BuNC (0.1 ml, 8.85 mmol) or dpe (solid, 0.2 mmol) to acetone or dichloromethane solutions of 0.1 mmol of [Rh(COD)(IQNO)$_2$]ClO$_4$ resulted in displacement of all the ligands of the reacting complex. Evaporation to a small volume and addition of diethylether gave [Rh(t-BuNC)$_4$]ClO$_4$ [11, 18] and [Rh(dpe)$_2$]ClO$_4$ [19].

(iii) Addition of 0.2 mmol of imidazole to 0.2 mmol of [Rh(COD)(IQNO)$_2$]ClO$_4$ in 60 ml of acetone gave yellow solutions, which after concentration to a small volume and addition of diethylether afforded yellow crystals of [Rh(COD)(IQNO)(Im)]-ClO$_4$. *Anal.* Found: C, 48.00; H, 4.17; N, 7.64. Calc. for $C_{20}H_{23}N_3O_5ClRh$: C, 46.86; H, 4.43, N, 8.02%. Sometimes it has to be recrystallized in order to give an acceptable analysis.

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