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Synthesis of Mixed Ligand Cationic Rhodium(I) Complexes with Diolefin and Substituted Quinoline *N*-Oxides as Ligands

ARISTIDES CHRISTOFIDES

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

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Abstract

The mixed ligand cationic rhodium(I) complexes of the type $[Rh(COD)LL']ClO_4$ (L = QNO, 2-MeQNO, 4-MeQNO, 4-ClQNO, 2-PhQNO; L′ = 4-NH_2py, 4-NMe_2py, Im, PPh_3) have been prepared and characterized. The reactions of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ with various ligands are also reported.

Introduction

Our work on cationic rhodium(I) complexes bearing substituted quinoline *N*-oxides as ligands has started recently [1]. The publication on the preparation and study of some analogous isoquinoline *N*-oxide rhodium(I) complexes is to appear in the literature soon [2].

In order to complete our work and to understand better the chemistry of some compounds prepared previously [1], we synthesized complexes **I–VII**. An additional motive for undertaking this work was our interest in seeing whether the starting complexes follow the reactivity pattern of their pyridine *N*-oxide counterparts [3], towards N- and P-donor ligands. Moreover, the well known use of soluble rhodium compounds in homogeneous catalysis also led us to the preparation of these compounds, hoping that some of these new complexes may be effective catalysts. Perhaps this is the most important future aspect of the present paper if you consider that rhodium compounds have also been used as catalysts in a diverse range of organic reactions. We hope that we shall be soon able to test their catalytic activity. Herein are also reported and discussed ^1H and ^{31}P NMR spectra of the new complexes as well as of some related species.

Results and Discussion

In a preliminary report we announced some data concerning complexes **I**, **VI** and **VII** [4]. Following the ready preparation of $[Rh(COD)L_2]ClO_4$ (L = QNO, 2-MeQNO, 4-MeQNO) [1]; we have been investigating reactions of these species by adding into their acetone solutions the stoichiometric amount of ligand L′ (L′ = 4-NH_2py, 4-NMe_2py, Im). The addition causes the displacement of one mole of quinoline *N*-oxide and formation of the respective $[Rh(COD)LL']ClO_4$ complexes **I–V**.

$$[Rh(COD)L_2]ClO_4 + L' \rightarrow [Rh(COD)LL']ClO_4 + L \qquad (1)$$

The new complexes are formed in satisfactory yields. They are yellow microcrystalline compounds and their analyses compare well with the expected ones.

Table I displays the analytical and other data for the new complexes **I–VII**. In the ^1H NMR spectra of complexes **I–IV** the resonances due to the $-NH_2$ and $-NMe_2$ groups of the aminopyridine ligands occur at chemical shifts rather similar to those of the free ligands (see Table II). This is an indication that the aminopyridine ligands are attached to the metal atom via the heterocyclic nitrogen [5].

Complexes **VI** and **VII** were prepared by adding L and PPh_3 (1/1 mole ratio) to acetone solutions of the solvated species $[Rh(COD)(Me_2CO)_x]ClO_4$, the latter being generated by treating $[RhCl(COD)]_2$ with $AgClO_4$ [6]. The sequence of the reactions is shown in eqn. (2).

$$\tfrac{1}{2}[RhCl(COD)]_2 \xrightarrow[Me_2CO]{AgClO_4}$$

$$[Rh(COD)(Me_2CO)_x]ClO_4 \xrightarrow{L+PPh_3}$$

$$[Rh(COD)L(PPh_3)]ClO_4 + XMe_2CO \qquad (2)$$

L = 4-ClQNO (**VI**) and 2-PhQNO (**VII**)

The failure of our earlier attempts to prepare $[Rh(COD)(4\text{-}ClQNO)_2]ClO_4$ and $[Rh(COD)(2\text{-}PhQNO)_2]ClO_4$ [1], excludes the possibility of preparing **VI** and **VII** from the above complexes. Complex **VII** is an air-stable compound whereas **VI** decomposes slowly, since it does not give an acceptable analysis after one or two weeks.

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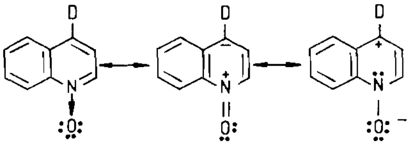
TABLE I. Analytical Results, Molar Conductivities, Yields and IR Data for Complexes $[Rh(COD)LL']ClO_4$

Complex		Found (calc.) (%)			ΛM (ohm^{-1} cm^2 mol^{-1})	Yield (%)	IR bands (cm^{-1})	
		C	H	N			ν(NO)	δ(NO)
I	$[Rh(COD)(QNO)(4\text{-}NH_2py)]ClO_4$	47.89	4.54	7.39	151	55	1225, 1208	802
		(48.06)	(4.58)	(7.64)				
II	$[Rh(COD)(2\text{-}MeQNO)(4\text{-}NH_2py)]ClO_4$	50.07	5.01	7.68	152	78	1185	815
		(48.99)	(4.83)	(7.45)				
III	$[Rh(COD)(2\text{-}MeQNO)(4\text{-}NMe_2py)]ClO_4$	50.03	5.41	7.34	158	84	1188	820
		(50.73)	(5.28)	(7.10)				
IV	$[Rh(COD)(4\text{-}MeQNO)(4\text{-}NMe_2py)]ClO_4$	52.38	5.43	7.50	155	86	1210, 1153	810
		(50.73)	(5.28)	(7.10)				
V	$[Rh(COD)(4\text{-}MeQNO)(Im)]ClO_4$	48.05	4.83	8.01	167	65	1208, 1154	832
		(46.90)	(4.69)	(7.81)				
VI	$[Rh(COD)(4\text{-}ClQNO)(PPh_3)]ClO_4$	55.87	4.42	1.86	205	40	1308, 1265	830
		(54.01)	(4.49)	(1.71)				
VII	$[Rh(COD)(2\text{-}PhQNO)(PPh_3)]ClO_4$	61.95	4.85	1.43	180	71	1303	809
		(62.01)	(4.82)	(1.76)				

TABLE II. ^1H NMR Spectra[a] for Substituted Quinoline *N*-Oxide Complexes

Complex	Aminopyridine ligand Amino	Cyclooctadiene		Substituted quinoline *N*-oxide
		CH	CH_2	CH_3
$[Rh(COD)(QNO)_2]ClO_4$		4	2.5, 1.8	
$[Rh(COD)(QNO)(4\text{-}NH_2py)]ClO_4$	6.5 (NH_2)	–	2.5, 1.8	
$[Rh(COD)(QNO)(PPh_3)]ClO_4$		3.5	2.6, 1.9	
$[Rh(COD)(IQNO)_2]ClO_4$		3.9	2.6, 1.7	
$[Rh(COD)(IQNO)(4\text{-}NMe_2py)]ClO_4$	2.9 (NMe_2)	4.0	2.7, 1.9	
$[Rh(COD)(2\text{-}MeQNO)_2]ClO_4$		3.5	2.5, 1.6	3.0
$[Rh(COD)(2\text{-}MeQNO)(4\text{-}NH_2py)]ClO_4$	7.3 (NH_2)	3.4	2.7, 1.7	3.0
$[Rh(COD)(2\text{-}MeQNO)(4\text{-}NMe_2Py)]ClO_4$	3.0 (NMe_2)	3.8	2.5, 1.9	2.9
$[Rh(COD)(2\text{-}MeQNO)(PPh_3)]ClO_4$		3.4	2.4, 1.6	2.9
$[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$		3.8	2.7, 1.7	2.6
$[Rh(COD)(4\text{-}MeQNO)(4\text{-}NMe_2py)]ClO_4$	2.9 (NMe_2)	3.9	2.6, 1.8	2.6
$[Rh(COD)(4\text{-}MeQNO)(PPh_3)]ClO_4$		3.3	2.4, 1.7	2.6

[a] Measured in $\{^2H_1\}$ chloroform, δ values (ppm).



The ^{31}P NMR spectra of complexes incorporating triphenylphosphines taken in deuterated chloroform, displayed double resonances at *ca.* 28 ppm with rhodium–phosphorous coupling of *ca.* 136 Hz. The spectrum of **VI** also exhibits peaks which may be due to decomposition products as mentioned earlier. The chemical shifts as well as the coupling constant of **VII** are close to those reported for similar rhodium(I) complexes [1, 7]. Interestingly, the coupling constant of **VI** of 128 Hz is lower than those reported earlier for analogous complexes bearing substituted quinoline *N*-oxides with an electron-releasing group (methyl) in the four position [1, 2]. It can be justified by considering the resonance forms B and C of the quinoline *N*-oxide in comparison with that of the basic structure A (D = H).

When D = Cl it rather results in enhancing contributions from resonance forms such as B. On the other hand structure C predominates in the case of

D = CH_3 [8]. Thus, structure B having less negative charge on the oxygen atom than structure C may exert a different influence over the rhodium atom which in turn lowers the *J*(Rh–P) coupling constant. This is consistent with the observation that chemical shifts and especially the *J*(Rh–P) coupling constants are very sensitive to electron density changes on the rhodium atom [9].

Nelson *et al.* [10] have pointed out that quinoline *N*-oxides have better π-bonding ability than pyridine *N*-oxides, owing to the fact that the former are better acceptors of π-electron density than the latter. However, the difference in their σ-bonding ability is opposite due to the steric interactions arising in the case of quinoline *N*-oxides. In order to find out which of the principal compounds, quinoline or pyridine *N*-oxide, has better coordination ability towards rhodium, we reacted the solvated species $[Rh(COD)(CH_3COCH_3)_x]ClO_4$ with an equimolar mixture of the two ligands. The examination of the reaction product proved that it has the formula $[Rh(COD)(QNO)_2]ClO_4$, thereby indicating the better coordination capacity of QNO compared with that of pyNO.

In this paper we also continue the investigation of the reactivity of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ which we started recently [1].

The displacement of 4-MeQNO from complex $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ can be accomplished by reacting it with an excess of py, one mole of bipy, dpe [1,2bis(diphenylphosphine)] or of two moles of 4-aminopyridine (4-NH_2py), 4-dimethylaminopyridine (4-NMe_2py) and PPh_3. The reaction of $[Rh(COD)(QNO)_2]ClO_4$ with 1,10-phenanthroline works as well as in the case of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ [1].

All the above reactions result in formation of the corresponding previously prepared complexes [5, 11–13]. Addition of an excess of t-BuNC or dpe to solutions of the starting complex leads to the complete displacement of all ligands and formation of $[Rh(t\text{-}BuNC)_4]ClO_4$ [3, 14] or $[Rh(dpe)_2]ClO_4$ [15], respectively, whereas the poorer N-donors 2-CNpy of 4-CNpy do not react [2].

Generally, the molar conductivities of the studied complexes measured in *ca.* 5×10^{-4} acetone solutions suggest the presence of 1:1 electrolytes [16]. However, the value of ΛM of complex **VI** is slightly higher than the expected range. A good reason for this discrepancy may be the presence of decomposition products; **VI** is not very stable as we have noticed before (see Table I).

IR Spectra

The bands at *ca.* 1100 (V_3) and 620 (V_4) cm^{-1} are characteristic of the uncoordinated anion ClO_4^- (Td) [17], and are present in the spectra of all complexes **I**–**VII**.

The values of ν(N–O) and δ(N–O) are listed in Table I. The bands due to ν(N–O) are shifted towards lower wave numbers than those of the free ligands, the exception being complex **VI** having the corresponding bands shifted to higher wavenumbers. In contrast, the values of δ(N–O) are shifted to higher wavenumbers and only in complexes **IV** and **VII** do the respective bands occur at lower frequencies, compared with those of the free ligands [10, 18]. In the IR spectrum of **V** the imidazole ring vibration bands ν_{as}(C=N–C=C) and ν_s(C=N–C=C) occur at 1572 and 1427 cm^{-1}. The former do not exhibit appreciable shifting in comparison with the corresponding band of free imidazole. The latter, however, is shifted to lower frequencies by 18 cm^{-1}, indicating that coordination takes place via the unsaturated nitrogen atom and not through the imino one [19, 20]. A very weak peak at 954 cm^{-1} could be assigned to δ(N–H) and the band at 654 cm^{-1} is probably due to ring vibrations [20]. We have been unable to see any band assignable to ν(Rh–N). For complexes **I** and **II** bands in the 3500–3230 cm^{-1} region are assigned to ν(N–H).

Experimental

Elemental analyses (C, H, N) were obtained with a Perkin-Elmer 240 instrument. Infrared spectra were recorded with Nujol mulls or KBr discs on a Perkin-Elmer 1430 ration recording spectrophotometer (over the range 4000–200 cm^{-1}).

Conductivities were measured in *ca.* 5×10^{-4} M acetone solutions with an Industrial conductance bridge, model RC 216 B2.

The ^1H and ^{31}P NMR spectra were obtained by using a JEOL FX-90 QFT spectrometer. $[RhCl(COD)]_2$ [21], quinoline *N*-oxide and its derivatives were prepared by published procedures [22–24] and recrystallized prior to use; 2-MeQNO and 4-MeQNO were prepared by applying Ochiai's method [22] employed for QNO. All reactions were performed at room temperature in air.

Preparation of Complexes of the Type [Rh(COD)LL']ClO$_4$ (L' = 4-NH$_2$py, 4-NMe$_2$py and Im) (I)–(V)

A solution of complex $[Rh(COD)(QNO)_2]ClO_4$ (0.06 g, 0.1 mmol) in acetone (20 ml) was treated with 4-NH_2py (0.0095 g, 0.1 mmol), the latter being added slowly with stirring. After a rapid change in colour and further stirring (0.5 h), the solution was filtered. The filtrate was concentrated to a small volume (*ca.* 2 ml) and diethylether (10 ml) was added affording orange crystals of $[Rh(COD)(QNO)(4\text{-}NH_2py)]ClO_4$ (**I**) (0.03 g), which were dried *in vacuo*.

Preparation of Complexes of the Type $[Rh(COD)LPPh_3]ClO_4$ *(VI) and (VII)*

An acetone solution (60 ml) of $[RhCl(COD)]_2$ (0.061 g, 0.12 mmol) was treated with $AgClO_4$ (0.052 g, 0.25 mmol). The resultant precipitate (AgCl) was removed by filtration and 4-ClQNO (0.44 g, 0.25 mmol) and PPh_3 (0.065 g, 0.25 mmol) were added successively under constant stirring. After a rapid change in colour the solution was reduced *in vacuo* to *ca.* 3 ml and diethylether (10 ml) added. The solution became cloudy and the stirring was continued for a while to help the formation of the residue. The supernatant liquid was decanted and the brown precipitate washed with diethylether (2 × 5 ml) giving microcrystals of $[Rh(COD)(4\text{-}ClQNO)(PPh_3)]ClO_4$ (**VI**) (0.075 g), dried *in vacuo*. The ^{31}P NMR spectra of **VI** and **VII** in $\{^2H_1\}$ chloroform exhibited double resonances at 29.8 (J(RhP) = 128 Hz) and 26.3(J(RhP) = 145 Hz), respectively.

For complex **VII** the ligands 2-PhQNO and PPh_3 were added together dissolved in acetone (10 ml).

Reactions of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$

(i) Addition of $4\text{-}NH_2py$ (0.2 mmol), $4\text{-}NMe_2py$ (0.2 mmol), bipy (0.1 mmol), dpe (0.1 mmol), PPh_3 (0.2 mmol) and py (0.6 ml) to acetone of dichloromethane solutions of 0.1 mmol of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ caused the complete displacement of 4-MeQNO; concentration under vacuum and addition of diethylether afforded microcrystals of $[Rh(COD)(4\text{-}NH_2py)_2]ClO_4$ [5], $[Rh(COD)(4\text{-}NMe_2py)_2]ClO_4$ [5], $[Rh(COD)(bipy)]ClO_4$ [12], $[Rh(COD)(dpe)]ClO_4$ [13], $[Rh(COD)(PPh_3)_2]ClO_4$ [13] and $[Rh(COD)(py)_2]ClO_4$ [11].

$[Rh(COD)(QNO)_2]ClO_4$ (0.1 mmol) reacts similarly with phen (0.1 mmol) affording $[Rh(COD)Phen]ClO_4$ also previously reported [12].

(ii) Treatment of acetone or dichloromethane solutions of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ (0.1 mmol) with t-BuNC (0.1 ml, 8.85 mmol) of dpe (solid 0.2 mol) caused the displacement of all the ligands of the starting complex. Evaporation to a small volume and addition of diethylether gave $[Rh(t\text{-}BuNC)_4]ClO_4$ [13, 14] and $[Rh(dpe)_2]ClO_4$ [15].

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