Inorganica Chimica Acta, 128 (1987) 175–178

Substitution Reactions of Chloro(η^5-cyclopentadienyl)bis(triphenylphosphine)-ruthenium(II) with some Thiocarboxa(i)mides

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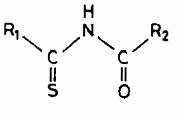
(Received September 8, 1986)

Abstract

Reactions of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ with the ligands of the type $RCSNHCOOC_2H_5$ (R = 2-pyrrole, 2-thiophene or 4-toluene), $RCSNHCONHC_6H_5$ (R = 2-pyrrole) and 2-thiopyrrole-1,2-dicarboximide lead to the formation of diamagnetic compounds of the formula $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ligand)]$. These compounds were characterised by using analytical, magnetic, conductivity and spectroscopic (UV, VIS, IR and proton NMR) data. A distorted octahedral geometry is proposed for the complexes.

Introduction

Recently we have reported the interactions of these ligands with a number of transition and non-transition metal ions and their complexes [1–4]. In continuation of the work, we are reporting here the interaction of ligands containing the thioamide group with $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$. In the past, very little work on the reactivity of this class of ligands has been reported [5–7]. Some of these ligands as well as their complexes are reported or expected to have important pharmacological properties [8, 9]. The names and abbreviations of the ligands reported here are as follows



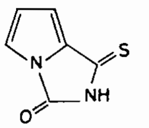
R_1 = 2-pyrrole; R_2 = OC_2H_5, *N*-ethoxycarbonylpyrrole-2-thiocarboxamide (EPT)

R_1 = 2-thiophene; R_2 = OC_2H_5, *N*-ethoxycarbonylthiophene-2-thiocarboxamide (ETT)

R_1 = 4-toluene; R_2 = OC_2H_5, *N*-ethoxycarbonyltoluene-4-thiocarboxamide (ETOT)

R_1 = 2-pyrrole; R_2 = NHC_6H_5, *N*-phenylcarbomoylpyrrole-2-thiocarboxamide (PPT)

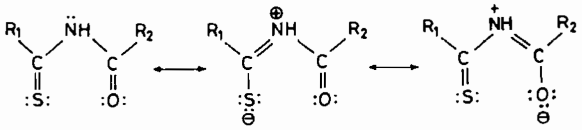
and



2-Thiopyrrole-1,2-dicarboximide (TPD)

Results and Discussion

Analytical data are in good agreement with the stoichiometry proposed for the complexes (Table I). All compounds were found to be diamagnetic and non-ionic in nature. The compounds are, in general, air stable and soluble in most of the organic solvents. The donor ability of this class of ligands can perhaps be best understood in terms of resonance structures given below.



I II III

Ordinarily, only structure **I** is considered but **II** and **III** are also quite valid and may predominate under certain situations. In the case of coordination of the ligand through its thiocarbonyl sulphur atom the ν(C=S), thioamide band IV ($\nu(C\overline{\cdots\cdot}S)$) should shift to a lower wave number and thioamide band I (δ(N–H) + ν(C=N)) [10, 11] should shift to a higher wave number, whereas if coordination is through the N atom, the thioamide band I will shift to a lower wave number. Based on the above criterion a bonding mode has been arrived at (Table II). In all cases the ν(C=O) of the ligands goes to a higher wave number after complexation (Table II), hence coordination through oxygen is ruled out. Coordination through ring nitrogen or sulphur of pyrrole or thiophene is unlikely as they are weakly basic. The thioamide bands II (ν(C=N) + ν(C=S) + δ(C–H)) and III (ν(C–N) + ν(C–S)) [12] do not shift systematically

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TABLE I. Analytical Data of the Complexes $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(\text{ligand})]$

Compound with the ligand	Colour	Melting point[a]	Analysis, found (calc.) (%)						
			Ru	S	Cl	C	H	N	P
EPT	Red	82	15.6 (15.3)	5.0 (4.8)	5.3 (5.4)	56.0 (56.2)	4.4 (4.5)	4.3 (4.2)	4.5 (4.7)
ETT	Reddish violet	84d	15.0 (14.9)	9.3 (9.4)	5.4 (5.2)	55.0 (54.8)	4.2 (4.3)	2.2 (2.1)	4.7 (4.6)
ETOT	Yellow orange	80	14.8 (14.7)	4.6 (4.7)	5.1 (5.2)	59.5 (59.4)	4.7 (4.8)	2.1 (2.0)	4.3 (4.5)
PPT	Red	88	14.1 (14.3)	4.4 (4.5)	5.1 (5.0)	59.5 (59.3)	4.5 (4.4)	6.0 (5.9)	4.6 (4.4)
TPD	Reddish violet	75	16.3 (16.4)	5.2 (5.2)	5.7 (5.8)	56.3 (56.5)	4.0 (3.9)	4.4 (4.5)	5.2 (5.0)

[a]Melting points are uncorrected; d, decomposes.

TABLE II. Major IR Bands of the Complexes and Ligands

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands				Mode of coordination
				I	II	III	IV	
EPT	3330s 3240m	1735s	1120s	1540sbr	1290m	1020m	870m	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(EPT)]$	3300br	1760s	1100s	1550m	1280m	1010m	850br	S
ETT	3240sbr	1730s	1180s	1510sbr	1360s	1020s	770s	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ETT)]$		1750s	1180s	1480s	1360s	1000w	760s	N
ETOT	3220s	1765s	1130m	1540s	1360s	1030m	850m	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ETOT)]$		1780m	1100s	1620m	1370w	1015m	850m	S
PPT	3410m 3260m 3160m	1720s	1125s	1520s	1350s	1000m	860m	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(PPT)]$	3400w	1750s	1180m	1480s	1360m		860m	N
TPD	3200m	1760m	1140s	1555s	1305s	1000m	750s	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(TPD)]$		1780s	1150s	1490s	1320s	1010m	750s	N

after complexation hence could not be used reliably for deciding a bonding site. The ν(NH) in some of the complexes could not be observed. All the characteristic bands of PPh_3 and η^5-C_5H_5 (820–850 cm^{-1}) [13, 14] were present in the IR spectra of the complexes. The new bands of medium intensity in the region of 350–480 cm^{-1} may be attributed to coupled vibration of ν(Ru–Cl) + ν(Ru–S) or ν(Ru–N) [15].

The proton NMR spectra (Table III) of the complexes display a sharp singlet δ 4.1–4.3 (for η^5-C_5H_5) apart from all characteristic signals of concerned ligands and PPh_3 [16]. However, the NH proton resonance could not be detected in the NMR spectra of the complexes.

The electronic spectra of the complexes as well as the ligands were taken in chloroform. The bands position and their assignment are given in Table III.

The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$ and only two spin allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$, are expected. The band in the region 465–485 nm may be assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ and a shoulder at 525 nm in the ETT complex may be due to $^1A_{1g} \rightarrow {}^1T_{1g}$. Some of the intraligand (IL) bands were present in electronic spectra of respective complexes with small shifts. The intense bands at 240–245 nm and 270–280 nm are assigned to charge transfer (CT) transitions.

The diamagnetism of Ru(II), d^6, systems indicate the spin pairing, hence distorted octahedral structure, assuming that the η^5-C_5H_5 group occupies three coordination sites, is preferred over tetrahedral or distorted tetrahedral [14] as spin pairing is not possible in the latter case.

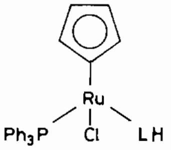
Thus, on the basis of analytical, conductance and spectroscopic (IR, UV, VIS and proton NMR) and

TABLE III. Electronic Spectra of the Complexes in Chloroform and Proton NMR in $CDCl_3$

Compound	Bands position[a] λ_{max} (nm)	Assignment	NMR signals with assignments (δ)
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(EPT)]$	475	$^1A_{1g} \rightarrow {}^1T_{2g}$	1.3 (t, 3, $-CH_3$), 4.1 (S, 5, $\eta^5\text{-}C_5H_5$) 4.3 (q, 2, $-OCH_2$), 7.2–7.4 (m, 18, aromatic)
	355(–10)	IL ($\pi \rightarrow \pi^*$)	
	270	CT	
	240	CT	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ETT)]$	525sh	$^1A_{1g} \rightarrow {}^1T_{1g}$	1.3 (t, 3, $-CH_3$), 4.1 (S, 5, $\eta^5\text{-}C_5H_5$), 4.3 (m, 2, $-OCH_2$) 7.0–7.7 (m, 18, aromatic)
	465	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	335(–15)	IL ($n \rightarrow \pi^*$)	
	245	CT	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ETOT)]$	375br	IL or CT	1.2 (t, 3, $-CH_3$), 2.2 (br, 3, ring $-CH_3$), 4.2 (S, 5, $\eta^5\text{-}C_5H_5$), 4.4 (br, 2, $-OCH_2$) 7.1–7.4 (m, 19, aromatic)
	325sh(+15)	IL ($\pi \rightarrow \pi^*$)	
	245	CT	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(PPT)]$	485	$^1A_{1g} \rightarrow {}^1T_{2g}$	4.1 (S, 5, $\eta^5\text{-}C_5H_5$), 7.0–7.6 (m, 23, aromatic)
	355	IL or CT	
	240	CT	
$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(TPD)]$	468	$^1A_{1g} \rightarrow {}^1T_{2g}$	4.1 (S, 5, $\eta^5\text{-}C_5H_5$), 7.0–7.5 (m, 18, aromatic)
	360(–10)	IL ($n \rightarrow \pi^*$)	
	325sh(+5)	IL ($\pi \rightarrow \pi^*$)	
	310	CT	
	280sh(–5)	CT	
	270(–5)	CT	
	240	CT	

[a] br = broad, sh = shoulder. The values given in parentheses indicate the shift in the position of respective ligand's band [1, 2, 5–7] after complexation.

magnetic measurement studies, a distorted octahedral geometry, is suggested for the complexes



Experimental

All the chemicals used were either of Analar or chemically pure grade. Solvents were dried before use and all the reactions were carried out under dry N_2. The ligands were prepared by literature methods [16]. Sulphur, chloride and phosphorus were estimated gravimetrically. Ruthenium was estimated on a IL-751 atomic absorption spectrophotometer after the complex had been decomposed by heating with a mixture of H_2SO_4 and HNO_3. C, H, and N analyses were done at the Microanalytical Laboratory, I.I.T., Kanpur. The IR spectra were recorded in KBr in the range 4000–250 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. The electronic spectra were recorded on a Shimadzu double beam UV-190 spectrophotometer. ^1H NMR spectra were recorded on an EM-390 90 MHz spectrometer in the range δ 0–20 ppm in $CDCl_3$ using TMS as calibrant. The magnetic susceptibilities were determined on a parallel field vibrating sample magnetometer (VSM) model 150 A. Melting points were recorded on a Fisher-John melting point apparatus. Conductivity was checked by an Elico conductivity meter type CM-80. The parent compound $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ was prepared by the literature method [17].

Preparation of the Compound [(η^5-C_5H_5)RuCl(PPh$_3$)(ligand)]

In about 40 ml methanol solution containing $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ (0.181 g, 0.25 mmol), 25 ml methanol solution of the appropriate ligand (0.35 mmol) was added under N_2. The resulting mixture was refluxed for 3–4 h. The resulting solution was filtered if needed, then almost dried at reduced pressure, the residue was dissolved in minimum quantity of CH_2Cl_2 followed by an addition of excess petroleum ether (60–80°). On scratching the walls of the beaker with a glass rod and standing for 1–2 h, the precipitate settled down. It was centrifuged, washed several times with petroleum ether (60–80°) and dried *in vacuo*. The yield was in the range 50–60% for all the complexes

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