



Complexes of *cis*-bis(triphenylphosphine)ruthenium(II) with N,S-donor thiobenzhydrazones of polycyclic aromatic aldehydes: Synthesis, properties and structures



Koppanathi Nagaraju, Samudranil Pal*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

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ABSTRACT

Reactions of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$, H_2L^n (polycyclic aromatic aldehyde thiobenzhydrazones $\text{ArCH}=\text{NNHC}(=\text{S})\text{Ph}$, $n = 1-4$ for $\text{Ar} = 1$ -naphthalenyl, 9-anthracenyl, 9-phenanthryl and 1-pyrenyl, respectively) and NaOAc in 1:2:2 mol ratio in methanol produces ruthenium(II) complexes of formula *cis*- $[\text{Ru}(\text{PPh}_3)_2(\text{HL}^n)_2]$ (**1–4**) in ~80% yields. Microanalysis (CHN), magnetic susceptibility, solution conductivity, spectroscopic (IR, UV–Vis, NMR and fluorescence) and cyclic voltammetric measurements have been used for the characterization of **1–4**. The complexes are non-electrolytic and diamagnetic. In the electronic spectra, the complexes display multiple absorptions within 505–245 nm due to metal-to-ligand charge transfer and ligand centred transitions. The emission spectral features of **1–4** indicate ligand centred emissive states. Molecular structures of **3** and **4** have been determined by X-ray crystallography. In each of **3** and **4**, two thioamidate-N,S coordinating $(\text{HL}^n)^-$ and two mutually *cis* oriented PPh_3 molecules assemble a distorted octahedral $\text{N}_2\text{S}_2\text{P}_2$ coordination sphere around the metal centre. Cyclic voltammograms of **1–4** show an oxidation response within $E_{1/2} = 0.76-0.86$ V ($\Delta E_p = 90-100$ mV) versus Ag/AgCl .

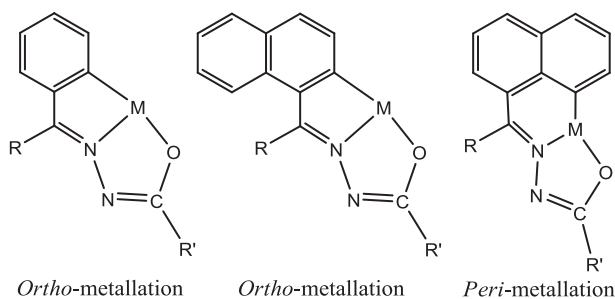
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1. Introduction

Cyclometallation reactions and cyclometallates are of considerable contemporary interest due to their applications in a wide variety of research areas such as organic synthesis, catalysis, photochemistry, biological and pharmaceutical chemistry and materials science [1–21]. Among various types of cyclometallates, pincer complexes are of particular interest because of their reactivity and catalytic efficiency [16–19]. The rigid sterically and electronically easily tunable meridional pincer ligands provide proximate coordination sites for the reactant molecules and hence better reactivity in catalytic reactions. In recent times, redox active and emissive cycloruthenates have also attracted significant attention for their potentials as light harvesting materials [20,21]. We have been examining the cyclometallation of the pendant aryl moiety (Ar) in the acid hydrazones ($\text{ArCR}=\text{NNHC}(=\text{O})\text{R}'$) of various mono- and polycyclic aromatic aldehydes using platinum metals for the past several years [22–30]. The aryl group in the $\text{Ar}-\text{C}(\text{R})=\text{N}-$ ($\text{R} = \text{H}$ or Me) fragment of a monocyclic aromatic aldehyde acid hydrazone provides only the *ortho*-C for metallation [22–25]. On the other hand, in case of a polycyclic aromatic

aldehyde acid hydrazone, there is a choice between the *ortho* and the *peri* position of the aryl group for metallation depending upon the position of the $-\text{C}(\text{R})=\text{N}-$ on it (Scheme 1) [26,28–30]. In the resulting complex, the acid hydrazone acts as a CNO pincer like ligand and forms 5,5- or 6,5-membered fused chelate rings for *ortho*- or *peri*-metallation, respectively. In general, with the acid hydrazones of polycyclic aromatic aldehydes, we have found that palladation occurs at the *peri* position [26,28], while, ruthenation occurs at the *ortho*-position [29,30] of the pendant aryl moiety. In the present work, we have studied the ruthenium chemistry of thiobenzhydrazones of some polycyclic aromatic aldehydes (H_2L^{1-4} , the two H of the formula represent the aryl C–H and the thioamide N–H protons; Scheme 2). Among the four Schiff bases chosen, except for H_2L^2 the remaining three provide the scope for either the *ortho*- or the *peri*-ruthenation. The purpose was to prepare new cycloruthenates with CNS pincer like ligands and explore whether regioselective *ortho*-ruthenation and formation of fused 5,5-membered fused chelates (with H_2L^1 , H_2L^3 and H_2L^4) as observed for analogous polycyclic aromatic aldehyde benzhydrazones occur or not. Interestingly, no cycloruthenation is taking place at the polycyclic aryl moiety of any of the thiobenzhydrazones. Instead, a series of complexes with the formula *cis*- $[\text{Ru}(\text{PPh}_3)_2(\text{HL}^n)_2]$, where $(\text{HL}^n)^-$ acts as four-membered chelate ring forming thioamidate-N,S donor, has been isolated (Scheme 2). Herein, we describe

* Corresponding author. Tel.: +91 40 2313 4829; fax: +91 40 2301 2460.
E-mail address: spal@uohyd.ac.in (S. Pal).



Scheme 1. Possible cyclometallation sites.

the synthesis, characterization and physical properties of these complexes with the molecular structures of two representative complexes determined by X-ray crystallography.

2. Experimental

2.1. Materials

Thiobenzhydrazones of polycyclic aromatic aldehydes (H_2L^{1-4} (Scheme 2)) were synthesised by following a procedure similar to that reported for analogous compounds [31,32]. $[Ru(PPh_3)_3Cl_2]$ was prepared according to the literature method [33]. All other chemicals were of analytical grade available commercially and were used as supplied without further purification. Purification of the solvents used was performed by following standard methods [34].

2.2. Physical measurements

Microanalysis (CHN) data were obtained with a Thermo Finnigan Flash EA1112 series elemental analyzer. Magnetic measurements were performed with the help of a Sherwood scientific balance. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification of the Schiff bases. A Bruker Maxis HRMS (ESI-TOF analyzer) spectrometer was used to record the mass spectra of the complexes. The infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. The electronic spectra were recorded on a Cary 100 Conc UV/Vis spectrophotometer. The fluorescence spectra were recorded on a Spex FluoroMax-3 spectrofluorimeter. The NMR spectra of the Schiff bases (in $(CD_3)_2SO$) and the complexes (in $CDCl_3$) were collected with the help of a Bruker 400 MHz NMR spectrometer. Cyclic voltammograms of the complexes in dimethylformamide containing tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte were recorded with a CH-Instruments

model 620A electrochemical analyser. The measurements were carried out with a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode at 298 K under nitrogen atmosphere. The ferrocenium/ferrocene couple was observed at $E_{1/2} = 0.65$ V under identical conditions.

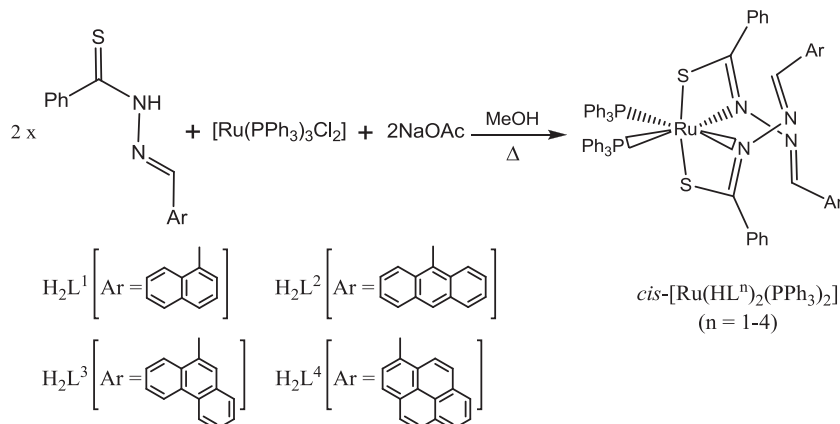
2.3. Synthesis of $cis-[Ru(PPh_3)_2(HL^1)_2]$ (**1**)

Solid $[Ru(PPh_3)_3Cl_2]$ (200 mg, 0.21 mmol) was added to a methanol solution (30 ml) of H_2L^1 (153 mg, 0.42 mmol) and NaOAc (35 mg, 0.42 mmol). The mixture was boiled under reflux for 1 h and then cooled to room temperature. The red solid deposited was collected by filtration and dried in air. This material was dissolved in minimum amount of dichloromethane and transferred to a silica gel column packed with dichloromethane. The first yellow band moved with the eluent 1:4 mixture of dichloromethane/*n*-hexane was discarded. The following red band containing the complex **1** was eluted with a 2:3 mixture of dichloromethane/*n*-hexane. The red solution thus obtained was evaporated to dryness and the complex was collected as a dark red solid. The yield was 220 mg (78%).

The remaining three complexes **2–4** with the general formula $cis-[Ru(PPh_3)_2(HL^n)_2]$ ($n = 2-4$) were synthesised in 77–81% yields using $[Ru(PPh_3)_3Cl_2]$, NaOAc and the corresponding Schiff bases in 1:2:2 mol ratio by following procedures very similar to that used for **1**.

2.4. X-ray crystallography

X-ray quality single crystals of **3** and **4** were obtained by slow evaporation of the respective dichloromethane-acetonitrile (1:1) solutions. **3** crystallizes as it is in the space group $P\bar{1}$, while **4** crystallizes with a dichloromethane molecule in the space group $P2_1/c$. Determination of the unit cell parameters and intensity data collection at 298 K for **3** were performed on a Bruker-Nonius SMART APEX CCD single crystal diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The SMART and the SAINT-Plus programs [35] were used for data acquisition and data extraction, respectively. The SADABS program [36] was used for absorption correction. Unit cell parameters and the intensity data at 298 K for **4**· CH_2Cl_2 were obtained using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) with the help of an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer. The CrysAlisPro software [37] was used for data collection, reduction and absorption correction. The structures of both complexes were solved by direct method and refined on F^2 by full-matrix least-squares procedures. In the case of **3**, the 9-phenanthryl moiety of one of the two $(HL^3)^-$ is refined with geometrical and thermal restraints due to severe disorder. Due to the restrained



Scheme 2. The thiobenzhydrazones (H_2L^{1-4}) and synthesis of $cis-[Ru(HL^{1-4})_2(PPh_3)_2]$ (**1–4**).

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