INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES
(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com
DOI: 10.22192/ijcrcps Coden: IJCROO(USA) Volume 6, Issue 12 - 2019

Research Article

DOI: http://dx.doi.org/10.22192/ijcrcps.2019.06.12.002

Ru-N3-RaaiR: Homoleptic bis chelates of Ruthenium: CIS-Diazido-Ruthenium(II)-bis-{1-(alkyl)-2-(arylazo)imidazole (RaaiR)} complexes: Synthesis, spectra and electrochemistry.

Prithwiraj Byabartta
Inorganic Chemistry Research Laboratory, ICRL
Department of Chemistry, Jogesh Chandra Chaudhuri College, 30- Prince Anwar Shah Road, Kolkata-700033; prbjcc@gmail.com. (Mob-9547775486)

Abstract

Silver assisted aquation of blue *cis-trans-cis*-$RuC_2l(RaaiR')_2$ (**1**) leads to the synthesis of solvento species, blue-violet *cis-trans-cis*-$[Ru(OH_2)_2(RaaiR')_2](ClO_4)_2$ [RaaiR = *p*-R-C_6H_4- N=N-C_3H^2-NN, (**2**), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, respectively; R = H (**a**), p-Me (**b**), p-Cl (**c**) that have been reacted with NNN^- in warm EtOH resulting in red-violet dithiocyanato complexes of the type, $[Ru(NNN)_2(RaaR)_2]$ (**3-5**). The solution structure and stereoretentive transformation in each step have been established from ^1H n.m.r. results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centred oxidation and successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

Keywords: 1-alkyl-2-(arylazo)imidazole, azido, ruthenium(II), MLCT, NMR, CV, IR.

Introduction

The elimination of functional groups from organic molecules has immense significance in chemistry, including the synthesis of natural products.1,2 In this context, decarbonylation reactions have become an indispensable aspect in the advancement of chemical synthesis. The key challenge of the decarbonylation reaction lies in the high bond dissociation energy of the C−C bond. Complexes of platinum group metals have been used to address this issue, as the metal center destabilizes the C−C bond through single- or two-electrontransfer processes. Hence, the platinum-group metals have drawn considerable attention over the decades.3−5 Among the platinum-group metals, ruthenium exhibits the largest range of stable oxidation states (from −II to + VIII).6 Hence, there is interest in the exploration of new ruthenium-based catalysts capable of decarbonylation reactions, especially after an initial report by Dolphin and co-workers on the stoichiometric decarbonylation using a ruthenium−porphyrin-based complex.7 An iridium-catalyzed decarbonylation method has also been reported by Tsuji and co-workers, wherein a variety of functional groups were tolerated under mild reaction conditions.8 In this way, effective synthetic decarbonylation processes can be beneficial for the generation of fuel-grade alkanes and should be attractive alternatives to existing expensive hydrogenation methodologies.9 Bhattacharya and co-workers,10-33 Jayanthi et al.,11 and Dinger et al.12 have worked on ruthenium complexes wherein in situ solvent oxidation and decarbonylation had led to CO-coordinated Ru(II) complexes. These groups had

© 2019, IJCRCPS. All Rights Reserved

proposed CO generation via either Ruassisted methyl oxidation or solvent oxidation in azo and hydrazone complexes. However, their findings lacked substantial experimental evidence to support the mechanism of Ru-assisted solvent oxidation. Thus, further experimental investigations into the precise mechanism of these Ru-assisted alcohol dehydrogenation reactions and CO coordination are needed.11,12 These literature reports prompted us to synthesize some new ruthenium azo complexes and examine the possiblesolvent oxidation (by using 13C-labeled ethanol) and subsequent decarbonylation. We here focus on the synthesis of organometallic ruthenium complexes (1 & 2) derived from arylazo functionalized ligands, wherein an in situ solvent oxidation and subsequent decarbonylation to generate an alkane would be possible. To further see whether this decarbonylation is specific for ruthenium, we attempted to observe similar in situ decarbonylation in an organoiridium complex (3) using the same organic ligand. However, it is also known that arylazo complexes of the platinum-group metals have been the subject of substantial interest because of their rich redox and spectroscopic behavior, catalytic activities, and isomerization reactions.13−16 By comparison, the anticancer activity of platinum arylazo complexes has received rather limited attention.17a−c While conventional platinum anticancer drugs such as cisplatin, carboplatin, and oxaliplatin are potent against a range of tumors, their side effects like toxicity toward normal tissue and tumor resistance have motivated researchers to develop anticancer agents that diverge from the stereotypical complexes already in use.17d−f In this direction, ruthenium and iridium complexes have emerged as encouraging classes of metallodrug candidates and hold great promise for cancer chemotherapy.18 Moreover, recent reports have revealed ruthenium complexes as remarkable antiproliferative agents, for example, the Ru(III)- based anticancer drugs indazolium trans-[tetrachlorobis(1Hindazole)ruthenate(III)] (KP1019),32-80 its sodium salt analogue sodium trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (NKP-1339),20-32 and the new antimetastasis inhibitor imidazolium trans-[tetrachlorobis(1H-imidazole)(S-dimethyl sulfoxide)-ruthenate(III)] (NAMI-A),21 which all have proceeded into the clinical stages of drug development. Furthermore, iridium complexes have been reported to generate reactive oxygen species and to induce apoptosis by acting on mitochondria as well as exerting anticancer effects through interaction with DNA.22−24 Phenylazo ligands have a crucial role in cytotoxicity against the A2780 ovarian and A549 lung-cancer cell lines as reported by Dougan et al. during investigation of η6 -areneruthenium(II) derivatives containing phenylazo ligands.17a The azo derivatives of ruthenium were found to be more cytotoxic as compared to the oxadiazole derivatives, on human glioblastoma cell lines, inspiring further study of azo-coordinated complexes.17c The redox reactions of the metal-coordinated azo ligands have been known to increase the cytotoxicity of half-sandwich organometallic (arene)-ruthenium(II) complexes.17a,c As compared to the free arylazo ligand, the transitionmetal chelated azo complexes target cancer cells better than normal cells due to increased lipophilicity on chelation; this prompts the design and exploration of more metal-coordinated azo compounds.25 Significant in vitro cytotoxic results of azovanadium complexes have also been reported in our earlier works, which further stimulates us to design and study azofunctionalized complexes.26 Another class of pharmacophoric interest are triphenylphosphine (PPh3)-coordinated metal complexes, as they exhibit excellent potential in chemotherapy by influencing mitochondrial metabolism.27a−g Using hydrophobic PPh3-ligated complexes results in complexes with good cytotoxicity, presumably due to their increasing vehiculation property.27h−j Some ruthenium phosphine complexes are known to inhibit the human topoisomerase IB enzyme (a potential biological target for complexes).27h It has been demonstrated that the presence of a PPh3 ligand is important also to facilitate the binding of the Ru complex to DNA and then distort its secondary and tertiary structure.27j,k Also, wide investigations of platinum, ruthenium, copper, and gold complexes have led to conclusions that mixed-ligand complexes possessing PPh3 are highly cytotoxic in contrast to the phosphine-free ones, which inhibited cell proliferation only in relatively high concentrations.27h,l−q Thus, the wide cytotoxic activity of azo- and PPh3-derived complexes stimulated us to investigate mixed azo- and PPh3-coordinated complexes. Ruthenium is a component of mixed-metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures, and for electrolytic cells for chemical processes such as generating chlorine from salt water. The fluorescence of some ruthenium complexes is quenched by oxygen, which has led to their use as optode sensors for oxygen. Ruthenium red, $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$, is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy. The beta-decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors, mainly malignant melanomas of the uvea. Ruthenium-centered complexes are being researched for possible anticancer properties. Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumors. NAMI-A and KP1019 are two drugs undergoing clinical evaluation against metastatic tumors and colon cancers. Because of its ability to harden platinum and palladium, ruthenium is used in

© 2019, IJCRCPS. All Rights Reserved

platinum and palladium alloys to make wear-resistant electrical contacts. In this application, only thin plated films are used to achieve the necessary wear-resistance. Because of its lower cost and similar properties compared to rhodium, the use as plating material for electric contacts is one of the major applications. The thin coatings are either applied by electroplating or sputtering. Ruthenium dioxide and lead and bismuth ruthenates are used in thick-film chip resistors. These two electronic applications account for 50% of the ruthenium consumption. Only a few ruthenium alloys are used other than those with other platinum group metals. Ruthenium is often used in small quantities in those alloys to improve some of their properties. The beneficial effect on the corrosion resistance of titanium alloys led to the development of a special alloy containing 0.1% ruthenium. Ruthenium is also used in some advanced high-temperature single-crystal superalloys, with applications including the turbine blades in jet engines. Several nickel based superalloy compositions are described in the literature. Among them are EPM-102 (with 3% Ru) and TMS-162 (with 6% Ru), as well as TMS-138 and TMS-174. both containing 6% rhenium. Fountain pen nibs are frequently tipped with alloys containing ruthenium. From 1944 onward, the famous Parker 51 fountain pen was fitted with the "RU" nib, a 14K gold nib tipped with 96.2% ruthenium and 3.8% iridium.

A wide number of ruthenium complexes containing heterocyclic nitrogeneous molecules and related ligands have been reported to date. They are of considerable interest primarily due to variable oxidation states, building blocks for supramolecular assemblies, photo-physical properties, directional electron and energy transfer, potential anticancer property. Modification of heterocyclic ligands may be carried out by incorporating new donor centers, spectator groups, change of ring size and number of Heteroatoms. They can significantly influence the physical and chemical properties of the complex molecules. Since the discovery of important redox, photophysical and photochemical properties of ruthenium complexes having 2,2-bipyridine (bipy) as ligand, there has been continuous research activity in the direction of developing newer ruthenium–bipyridine systems with the perspective of interesting physicochemical properties. In this context different kinds of mixed ligand ruthenium–bipyridine complexes have been synthesized and studied over the last fifteen years [Rasmussen S. C., Thompson D. W., Singh V. and Petersen J. D., (1996 medical aspects)]. The basic strategies behind all these activities are either to incorporate different groups within the bipyridine moiety itself or use other types of donor sites like azoimine function along with the $Ru(bipy)_2$ core to form mixed-ligand tris-chelates to modulate the photo-redox activities of this class of complexes [Santra B. K., Thakur G. A., Ghosh P., Pramanik A. and Lahiri G. K., *Inorg. Chem.*, 1996]. The nature of chemical reactions of organic substrates can vastly be affected by their coordination to metal ions. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species. Thiocyanates, as ligand, have attracted considerable attention in recent years not only because of their versatile coordination abilities but also some of their transition metal complexes have been found to be useful. The ruthenium chemistry of diimine ligands is an area of significant current interest, particularly with regard to the photophysical and photo-chemical properties exhibited by such complexes. Di-imine ligands are strong π-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d^6, *S*=0). As a consequence, an interesting aspect of the ruthenium–diimine chemistry has been to study the remarkable π-interaction between the filled t_2 orbitals of ruthenium(II) and the low-lying vacant π*-orbital of the diimine chromophore. The extent of π-interaction in these complexes depends primarily on the nature of the diimine ligands, which again depends on the nature of the groups linked to the two carbons and the two imine-nitrogens. The presence of other π-acceptor ligands within the coordination sphere may also have significant influence on the π-interaction between the diimine ligands and ruthenium(II)[1-5]. For the last few years, the search for a suitable precursor to synthesize NNN^- complexes is a challenging domain and the compounds are found to be useful in this context [6-8]. Recently, we have developed the arylazopyrimidine as well as arylazoimidazole chemistry of ruthenium(II) and have synthesised dichloro componds and diaquo species. Syntheses of hetero-tris-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, n = 2) from the solvento complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$ /$[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres are reported from Prof. Sinha´s laboratory [8-11]. In this paper, We examine the reaction of NNN^- towards $[Ru(OH_2)_2(RaaiR)_2]^{2+}$ and the reactions of the complexes derived there-from and also studied the dinuclear adduct formation pathway. The complexes were well charecterised by C.H.N, FT-I.R, U.V-Vis, and Cyclic Voltammetrically. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

Experimental

Published methods were used to prepare RaaiR [7-8], *ctc*-$RuCl_2(RaaiR)_2$[7-8], *ctc*-$[Ru(OH_2)_2(RaaiR)_2](ClO_4)_2$. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, India). The purification of MeCN and preparation of [n-

© 2019, IJCRCPS. All Rights Reserved

$Bu_4N][ClO_4]$ respectively used as solvent and supporting electrolyte in electrochemical experiments were done following the literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 spectrophotometer. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^1H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for the junction effect.

Preparation of cis,trans,cis-Dithiocyanato-bis-{1-methyl-2-(p-tolylazoimidazolee} ruthenium(II), ctc-$Ru(NNN)_2(MeaaiMe)_2$

CAUTION ! Perchlorates of heavy metal ions with organic ligands are potentially explosive. The syntheses involve in some cases the use of perchlorate ions. Three independent methods were employed to synthesise.

Method (a). To an EtOH blue-violet solution (15 cm^3) of ctc-$[Ru(OH_2)_2(MeaaiMe)_2](ClO_4)_2$ (0.1 g, 0.14 mmol) was added 0.019 g (0.27 mmol) of solid NH_4NNN, and the mixture was stirred at 343-353 K for 12 h. The violet solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with H_2O and dried in vacuo over $CaCl_2$. Analytically pure (7b) was obtained after chromatography over an alumina (neutral) column on eluting the red-violet band with toluene-acetonitrile (4:1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%).

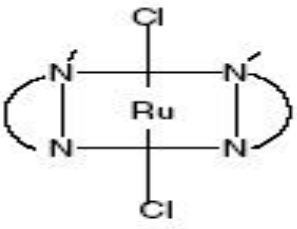
Method (b). To a suspension of ctc-$RuCl_2(MeaaiMe)_2$ (4b) (0.1 g, 0.18 mmol) in EtOH (25 cm^3) was added an aqueous solution of $AgNO_3$ and stirred at room temperature (300 K) for 2 h. The AgCl which precipitated was filtered through a G-4 sintered crucible. An EtOH solution of NH_4NNN (0.025 g, 0.35 mmol) was added to the filtrate, and the resulting mixture was stirred at room temperature for 8 h under a N_2 atmosphere. The violet solution was concentrated by slow evaporation and the precipitate was processed as in Method (a); yield, 0.047 g (45%).

Method (c). To a CH_2Cl_2-Me_2CO (1:1, v/v, 30 cm^3) solution of ctc-$RuCl_2(MeaaiMe)_2$ (4b) (0.1 g, 0.18 mmol) was added an H_2O-Me_2CO solution of NH_4NNN (0.024 g, 0.35 mmol). The mixture was stirred at 343-353 K for 30 h. The resulting violet solution was processed as in method (a) to give analytically pure dithiocyanato complexes; yield, 0.021 g (20%). The high yield in method (a) has prompted us to follow this route for the syntheses of the other complexes (3b-3e). The yields varied in the range 65-85%.

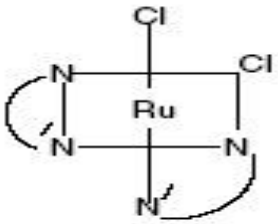
Results and Discussion

Diaquo complexes ctc-$[Ru(OH_2)_2(RaaiR)_2](ClO_4)_2$, prepared by Ag^+-assisted aquation of ctc-$RuCl_2(RaaiR)_2$, were reacted with NH_4NNN (excess amount >3 mol) under stirring at 343-353 K in aqueous alcohol to give $Ru(NNN)_2(RaaiR)_2$ (**3-5**) in good yield (65-85%). The synthetic routes are shown in Scheme 1. The dithiocyanato were synthesized in low yield either directly on stirring in ethanol-acetone mixture for 30 h or in situ synthesis of the aquo complex by $AgNO_3$ followed by the reaction with NH_4NNN. The composition of the complexes is supported by microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t_{2g}^6, S = 0). The violet dithicyanato complexes are soluble in common organic solvents but insoluble in H_2O. In MeCN, they show as non-electrolytic behaviour is found for type complexes as indicated by their very low Λ_M values (10-20 Ω^{-1} cm^{-1} mol^{-1}).

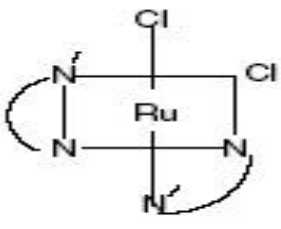
© 2019, IJCRCPS. All Rights Reserved



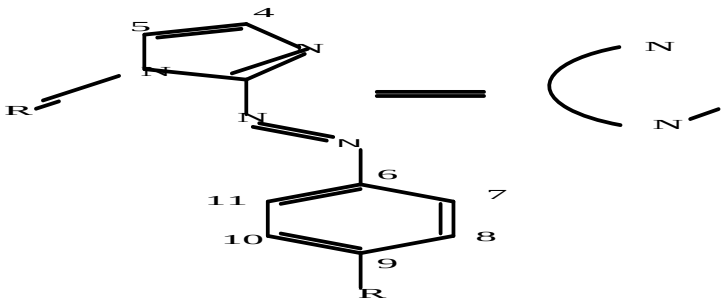
tcc -

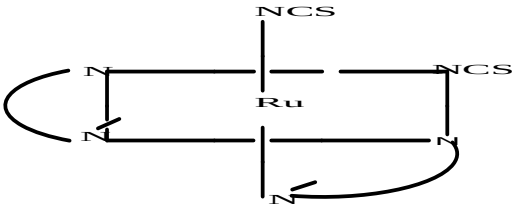


ctc -



ccc -





R = H (a), Me (b), Cl (c)
R'' = Me (4), Et (5), Bz (6)

Table 1. Microanalytical (C.H.N) [a] and FT-IR spectroscopic [b] data

Complexes	C H N	ν(N=N)ν(C=N)ν(C=C)ν(NNN)
$Ru(NNN)_2(H\text{-}aaiMe)_2$, **3a**	42.4 3.5 24.8 (42.3) (3.4) (24.7)	1365 1570 1600 1300
$Ru(NNN)_2(p\text{-}Me\text{-}aaiMe)_2$, **3b**	44.4 4.0 23.6 (44.5) (4.1) (23.7)	1367 1580 1602 1320
$Ru(NNN)_2(p\text{-}Cl\text{-}aaiMe)_2$, **3c**	37.8 2.84 22.1 (37.7) (2.7) (22.0)	1370 1590 1610 1325
$Ru(NNN)_2(H\text{-}aaiEt)_2$, 4a	44.3 4.2 23.5 (44.5) (4.1) (23.7)	1375 1585 1613 1320
$Ru(NNN)_2(p\text{-}Me\text{-}aaiEt)_2$, 4b	37.8 4.84 22.1 (37.7) (2.7) (22.0)	1380 1590 1609 1310
$[Ru(NNN)_2(p\text{-}Cl\text{-}aaiEt)_2]$, **4c**	34.1 4.3 19.9 (34.0) (2.4) (19.8)	1370 1570 1609 1300
$Ru(NNN)_2(H\text{-}aaiBz)_2$, 5[a]	34.0 3.1 18.0 (34.1) (3.0) (18.1)	1365 1575 1606 1310
$Ru(NNN)_2(p\text{-}Me\text{-}aaiBz)_2$, **5b**	31.1 3.81 18.1 (31.2) (1.82) (18.2)	1380 1570 1609 1320
$Ru(NNN)_2(p\text{-}Cl\text{-}aaiBz)_2$, **5c**	34.2 3.2 18.1 (34.1) (3.0) (18.1)	1370 1575 1609 1310

[a] Calculated values are in parenthesis; On KBr disk

© 2019, IJCRCPS. All Rights Reserved

Table 2. UV-Vis[a] and cyclic voltammetric[b] data

Comp Ound	UV-Vis spectra λ_{max}(nm)(10^{-3} ε/dm^3 mol^{-1} cm^{-1})	Cyclic Voltammetric data E/V (ΔE_P / mV) E^{M1}	$-E^{L}$
(**3a**)	551(8.379),421(8.914)[d], 373(18. 3)	1.188(110)	0.388(80), 0.651(130)
(**3b**)	548(6.773), 421(12.271)[d], 379(17.791)	1.101(115)	0.407(95), 0.691(120)
(**3c**)	555(13.919), 424(13.416)[d], 384(40.721)	1.201(107)	0.344(80), 0.673(100)
(**4a**)	550(8.796), 416(10.081)[d], 376(20.755)	1.108(120)	0.377(80), 0.632(75)
(**4b**)	547(8.752), 423(7.149)[d], 380(23.694)	1.011(80)	0.383(85), 0.647(100)
(**4c**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80) 0.711(120)
(**5a**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120)
(**5b**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80), 0.711(120)
(**5c**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120),

[a] Solvent dry MeCN; [d] shoulder; [b] Solvent dry MeCN, supporting electrolyte [^{n}Bu$_4$N][ClO$_4$] (0.1M), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute conc. ~10^{-3} M, scan rate 50 mVs^{-1}, E^{M} : metal oxidation, eqn (3), E^{L} : ligand reductions, ΔE_P = | E_{pa} - E_{pc}| V where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

Table 3. ^{1}H-n.m.r. spectral data, δ (J/Hz), ppm of the complexes in $CDCl_3$

Compd	4-H[c]	5-H[c]	7-H[c]	11-H	8-H	10-H
(3[a])[a]	7.15	7.06	8.03	7.88	7.80	7.86
	(7.5)	(7.5)	(8.1)	(8.91)	(8.1)	(6.1)
(3b)	6.98	6.86	8.17	8.09	8.04	8.01
	(7.5)	(7.5)	(8.1)	(8.1)	(8.1)	(8.01)
(3c)	7.13	7.02	8.15	7.99	7.95	7.92
	(8.1)	(8.1)	(7.8)	(7.0)	(7.8)	(8.8)
(4[a])[a]	7.14	7.00	8.01	7.95	7.85	7.89
	(7.5)	(7.5)	(7.8)	(7.1)	(7.8)	(7.8)
(4b)	7.02	6.94	8.11	8.04	8.04	8.07
	(8.1)	(8.1)	(7.5)	(6.5)	(7.5)	(6.5)
(4c)	7.13	7.06	8.14	8.06	8.06	8.0
	(8.1)	(8.1)	(7.5)	(8.5)	(7.5)	(7.7)
(5[a])[a]	7.06	6.98	8.08	8.10	8.00	7.00
	(7.8)	(7.8)	(8.1)	(8.3)	(8.1)	(8.1)
(5b)	6.97	6.85	8.21	7.80	8.10	8.50
	(8.1)	(8.1)	(8.1)	(8.1)	(8.1)	(8.7)
(5c)	7.11	7.02	8.15	8.00	8.05	7.05
	(7.8)	(7.8)	(8.1)	(6.1)	(8.1)	(8.01)

[a] δ(9-H) 7.60 ppm(m); [b] δ (9-Me); [c] doublet; [d] triplet; [e] N-Bz, AB type sextet, geminal coupling constant,4.98,4.78,; [f] 1-Me, singlet, 1.98; [g] N-Et, AB type quartet, geminal coupling constant, 4.44,4.12.

© 2019, IJCRCPS. All Rights Reserved

I.R. spectra of the complexes, $Ru(NNN)_2(RaaiR)_2$ (**3-5**) show a 1:1 correspondence to the spectra of the dichloro analogue, *ctc*-$RuCl_2(RaaiR)_2$ except the appearance of intense stretching at 1300-1335 and 1250-1280 cm^{-1} with concomitant loss of ν(Ru-Cl) at 320-340 cm^{-1}. They are assigned to $\nu(NNN)_{as}$ and $\nu(NNN)_s$, respectively [5,6,15]. The ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively. The present series of Ru-NO complexes are assumed to contain linear NNN group. Other important frequencies are $\nu(H_2O)$ at 3350-3400 cm^{-1}

The solution electronic spectra of these new complexes were recorded in dry acetonitrile. Dithiocyanato complexes (**3-5**) exhibit multiple transitions in the uv-visible region (*Table 1*). They display intense MLCT transition in the 550-560 nm range . The transitions are blue shifted by ~ 40 nm as compared with corresponding dichloro derivatives, $RuCl_2(RaaiR)_2$ [6,8,11]. The ^1H n.m.r. spectra of $Ru(NNN)_2(RaaiR)_2$ (**3-5**) complexes were unambiguously assigned (Table 2) on comparing with $RuCl_2(RaaiR)_2$ [7-9]. The aryl protons (7-H—11-H) are downfield shifted by 0.1-0.7 ppm as compared to those of the parent dichloro derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9) and C(10)-position. The aryl protons resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The aryl-Me (R = Me) in $Ru(NNN)_2(MeaaiR)_2$ (**3-5**) appears as a single signal at 2.30 ppm and is in consonance with stereoretentive nucleophilic substitution during synthesis of dithiocyanato complexes from *ctc*-$RuCl_2(RaaiR)_2$ via aquo derivatives. Isomerisation of the ctc-isomer may lead to ccc-configuration belonging to C_1-symmetry and would give two equally intense Ar-Me signals, which is however not the case here. The potential values of the complexes in dry acetonitrile solution are set out in Table 1. The dithiocyanato complexes exhibit a quasi-reversible ($\Delta E_P \geq 100$ mV) oxidative response in the potential range 1.0-1.3 V. This is assigned to the Ru(III)/Ru(II) couple. The one-electron stoichiometry of this couple is confirmed by constant potential electrolysis vs SCE and the electron count ratio equals 0.94. The potential $E^M_{1/2}$ is dependent on the substituent type R. The present series of complexes show higher $E^M_{1/2}$ values than that of precursor dichloro derivatives by ~ 0.4 V. The better electron withdrawing property of NNN^- over Cl^- stabilises the dπ shell of the metal and thus shifts the metal-centred redox process to more anodic values. The stronger π-acidic nature of RaaiR′ compared to α-diimine system leads to better stabilisation of Ru(II) in the present series of complexes. The cyclic voltammogram of $Ru(NNN)_2(RaaiR')_2$ exhibit some unusual behaviour on repetitive cycles. The reduction sweep shows a new wave that has a counter oxidative wave on the second sweep. The second and consecutive cycles increase the peak height with subsequent decrease of the primary couple. The assignment is based on earlier observations of similar Ru-bipyridine [21] and Ru-azopyridine [11] systems. The potential values of the present set of complexes lie between bipyridine and azopyridine analogous complexes and follow the order azopyridine > azoimidazole > bipyridine. This is in line of π-acidity order of these different ligand systems. The one-electron stoichiometry of the couples is assigned by comparison of current heights in differential pulse voltammetry experiments. Successive reductions on the negative side of SCE were observable and one-electron nature was confirmed by comparing the current heights of these process with that of couple II in the differential pulse voltammetry experiments and are assigned to the reduction of coordinated ligand. The azo group in RaaiR′ may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable.

Synthesis and Separation of the Linkage Isomers.

$[RuCl_2(RaaiR)_2]$ was prepared according to a previous report in the literature. The violet product of $[Ru(NNN)_2(RaaiR)_2]$ was synthesized by a method as mentioned above. To a DMSO solution of $[RuCl_2(RaaiR)_2]$ (0.2 mmol) was added an aqueous solution containing 2 equiv of $AgNO_3$ (0.068 g) and the reaction mixture stirred at 100 °C for 2 h. A gray precipitate of AgCl was removed by filtration. To the resulting yellow filtrate was added an aqueous solution of excess KNNN (0.104 g, 1 mmol) at ca. 5 °C resulting in the immediate formation of the grey-violet precipitate. The precipitate was filtered and repeatedly washed with water to completely remove all traces of DMSO. This process of washing is very important to avoid the conversion. The violet crystals thus obtained were confirmed to be mostly $[Ru(NNN)_2(RaaiR)_2]$ on the basis of UV-Vis spectral analysis. Recrystallization of the violet product from acetone, acetone/DMSO (99/1 v/v), and DMF formed violet

© 2019, IJCRCPS. All Rights Reserved

crystals of $[Ru(NNN)_2(RaaiR)_2]$, grey-violet crystals of $[Ru(NNN)(NNN)(RaaiR)_2]$, and red-violet crystals of $[Ru(NNN)_2(RaaiR)_2]$, respectively. Due to the change of hard donar centre, N to soft donar centre, S, the HOMO and LUMO gap changes, which shift the MLCT band from high energy to low energy value.

Conclusion

Dithiocyanato complexes of ruthenium(II)–azoimidazole, *ctc*-$Ru(NNN)_2(RaaiR)_2$ have been synthesised by stereoretentive reaction of diaquo complex $[Ru(OH_2)_2(RaaiR)_2]^{2+}$ with thiocyanate ion. The complexes exhibit strong MLCT transitions. Voltammetric study shows Ru(III)/Ru(II) couple along with successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

Acknowledgments

Department of Science and Technology (DST) is thanked for financial support. (FAST TRACK Grand No. **SERB/F/4888/2012-13 Dated 30.11.2012.** Departmento de Quimica Inorganica-Instituto de Ciencia deMateriales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza, 50009, Spain

References

(1) Hartwig, J. F. Organotransition Metal Chemistry, from Bonding to Catalysis; University Science Books: New York, 2010. Tsuji, J. In Organopalladium Chemistry for Organic Synthesis; Negishi, E.-I., Ed.; Wiley: NY, 2002; Vol. 2, pp 2648−2653. Garralda, M. A. Aldehyde C-H activation with late transition metal organometallic compounds. Formation and reactivity of acyl hydrido complexes. Dalton Trans. 2009, 3635−3645. Modak, A.; Deb, A.; Patra, T.; Rana, S.; Maity, S.; Maiti, D. A general and efficient aldehyde decarbonylation reaction by using a palladium catalyst. Chem. Commun. 2012, 48, 4253−4255. Patra, T.; Manna, S.; Maiti, D. Metal Mediated Deformylation Reactions: Synthetic and Biological Avenues. Angew. Chem., Int. Ed. 2011, 50, 12140−12142. Sabo-Etienne, S.; Grellier, M. Ruthenium: Inorganic & Coordination Chemistry. In Encyclopedia of Inorganic Chemistry [Online]; John Wiley & Sons, Ltd, 2006. Domazetis, G.; Tarpey, B.; Dolphin, D.; James, B. R. Catalytic decarbonylation of aldehydes using ruthenium(II) porphyrin systems. J. Chem. Soc., Chem. Commun. 1980, 939−940.

(2) Iwai, T.; Fujihara, T.; Tsuji, Y. The iridium-catalyzed decarbonylation of aldehydes under mild conditions. Chem. Commun. 2008, 6215−6217. (a) Schirmer, A.; Rude, M. A.; Li, X. Z.; Popova, E.; del Cardayre, S. B. Microbial biosynthesis of alkanes. Science 2010, 329, 559−562. (b) Rana, S.; Haque, R.; Santosh, G.; Maiti, D. Decarbonylative Halogenation by a Vanadium Complex. Inorg. Chem. 2013, 52, 2927−2932. (c) Akanksha; Maiti, D. Microwaveassisted palladium mediated decarbonylation reaction: synthesis of eulatachromene. Green Chem. 2012, 14, 2314−2320. (d) Rana, S.; Pandey, B.; Dey, A.; Haque, R.; Rajaraman, G.; Maiti, D. A Doubly Biomimetic Synthetic Transformation: Catalytic Decarbonylation and Halogenation at Room Temperature by Vanadium Pentoxide. ChemCatChem 2016, 8, 3367−3374. (e) Kundu, P. K.; Dhiman, M.; Modak, A.; Chowdhury, A.; Polshettiwar, V.; Maiti, D. Palladium Nanoparticles Supported on Fibrous Silica (KCC-1-PEI/Pd): A suitable Nanocatalyst for Decarbonylation Reactions. ChemPlusChem 2016, 81, 1142−1146. (f) Modak, A.; Rana, S.; Phukan, A. K.; Maiti, D. Palladium-Catalyzed Deformylation Reactions with Detailed Experimental and in Silico Mechanistic Studies. Eur. J. Org. Chem. 2017, 2017, 4168−4174. (g) Modak, A.; Naveen, T.; Maiti, D. An efficient dehydroxymethylation reaction by a palladium catalyst. Chem. Commun. 2013, 49, 252−254. Acharyya, R.; Peng, S.-M.; Lee, G. H.; Bhattacharya, S. An Unprecedented Oxidative Migration of a Methyl Group from 2-(2 ‘, 6 ‘-Dimethylphenylazo)-4-methylphenol Mediated by Ruthenium and Osmium. Inorg. Chem. 2003, 42, 7378−7380. Jayanthi, E.; Kalaiselvi, S.; Padma, V. V.; Bhuvanesh, N. S. P.; Dharmaraj, N. Solvent assisted formation of ruthenium(iii) and ruthenium(ii) hydrazone complexes in one-pot with potential in vitro cytotoxicity and enhanced LDH, NO and ROS release. Dalton Trans. 2016, 45, 1693−1707 and references therein. Dinger, M. B.; Mol, J. C. Degradation of the First-Generation Grubbs Metathesis Catalyst with Primary Alcohols, Water, and Oxygen. Formation and Catalytic Activity of Ruthenium(II) Monocarbonyl Species. Organometallics 2003, 22, 1089−1095.

(3) (a) Acharyya, R.; Basuli, F.; Wang, R.-Z.; Mak, T. C. W.; Bhattacharya, S. Iridium(III) complexes formed by O-H and/Or C-H activation of 2-(arylazo)phenols. Inorg. Chem. 2004, 43, 704−711. (b) Maiti, N.; Pal, S.; Chattopadhyay, S. Reaction of 2-(Phenylazo)- aniline with Na2PdCl4: Formation of a 2-(Phenylazo)imino Complex of Bivalent Palladium. Inorg. Chem. 2001, 40, 2204−2205. (c) Datta, P.; Sardar, D.; Saha, R.; Mondal, T. K.; Sinha, C. Structure, photophysics, electrochemistry and DFT calculations of [RuH(CO)- (PPh3)2(coumarinyl-azo-imidazole)]. Polyhedron 2013, 53, 193−201.

© 2019, IJCRCPS. All Rights Reserved

(4) Krause, R. A.; Krause, K. Chemistry of bipyridyl-like ligands. Isomeric complexes of ruthenium(II) with 2-(phenylazo)- pyridine. Inorg. Chem. 1980, 19, 2600−2603. (b) Pratihar, J. L.; Bhaduri, S.; Pattanayak, P.; Patra, D.; Chattopadhyay, S. Reactions of 2-(arylazo)aniline with ruthenium substrates: Isolation, characterizations and reactivities of delocalized diazoketiminato and orthometallated Ru(II) chelates. J. Organomet. Chem. 2009, 694, 3401−3408. (c) Basu, S.; Halder, S.; Pal, I.; Samanta, S.; Karmakar, P.; Drew, M. G. B.; Bhattacharya, S. 1-(20-Pyridylazo)-2-naphtholate complexes of ruthenium: Synthesis, characterization, and DNA binding properties. Polyhedron 2008, 27, 2943−2951.

(5) (a) Ghosh, P.; Pramanik, A.; Bag, N.; Chakravorty, A. Bis(N, N) chelated rhenium(III): the [ReL2Cl2]Cl family [L = 2-(arylazo)- pyridine]. J. Chem. Soc., Dalton Trans. 1992, 1883−1886. (b) Lahiri, G. K.; Bhattacharya, S.; Goswami, S.; Chakravorty, A. High-potential isomeric ruthenium(III) complexes of 2-(phenylazo)pyridine. J. Chem. Soc., Dalton Trans. 1990, 561−565. (c) Ghosh, B. K.; Chakravorty, A. Electrochemical studies of ruthenium compounds. (d) Wolfgang, S.; Strekas, T. C.; Gafney, H. D.; Krause, A. R.; Krause, K. Spectral and photophysical properties of ruthenium(II) 2-(phenylazo)pyridine complexes. Inorg. Chem. 1984, 23, 2650−2655. (e) Goswami, S.; Mukherjee, R. N.; Chakravorty, A. Chemistry of ruthenium. 12. Reactions of bidentate ligands with diaquabis[2- (arylazo)pyridine]ruthenium(II) cation. Stereoretentive synthesis of tris chelates and their characterization: metal oxidation, ligand reduction, and spectroelectrochemical correlation. Inorg. Chem. 1983, 22, 2825−2832. (f) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. Chemistry of ruthenium. 7. Aqua complexes of isomeric bis[(2-arylazo)pyridine]ruthenium(II) moieties and their reactions: solvolysis, protic equilibriums, and electrochemistry. Inorg. Chem. 1983, 22, 602−609.

(6) (a) Ghosh, A. K.; Majumdar, P.; Falvello, L. R.; Mostafa, G.; Goswami, S. Novel Examples of Simultaneous Reductive Azo Cleavage and Oxidative Aromatic Ring Amination in Rhodium Complexes of 2-(Arylazo)pyridine. Organometallics 1999, 18, 5086− 5090. (b) Lahiri, G. K.; Goswami, S.; Falvello, L. R.; Chakravorty, A. A new family of semibent rhenium(V) arylimides formed by azo splitting. Structure, bonding, and electrooxidation to rhenium(VI) congeners. Inorg. Chem. 1987, 26, 3365−3370. (c) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. The aquaruthenium(II)-oxoruthenium(IV) couple in a ruthenium complex of 2-(phenylazo)- pyridine: homogeneous catalysis of the oxidation of water to dioxygen. J. Chem. Soc., Chem. Commun. 1982, 1288−1289. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. Chemistry of ruthenium. 5. Reaction of trans-dihalobis[2-(arylazo)pyridine]-ruthenium(II) with tertiary phosphines: chemical, spectroelectrochemical, and mechanistic characterization of geometrically isomerized substitution products. Inorg. Chem. 1982, 21, 2737−2742.

(7) (a) Dougan, S. J.; Habtemariam, A.; McHale, S. E.; Parsons, S.; Sadler, P. J. Catalytic organometallic anticancer complexes. Proc. Natl. Acad. Sci. U. S. A. 2008, 105, 11628−11633. (b) Pazinato, J.; Cruz, O. M.; Naidek, K. P.; Pires, A. R. A.; Westphal, E.; Gallardo, H.; Baubichon-Cortay, H.; Rocha, M. E. M.; Martinez, G. R.; Winnischofer, S. M. B.; Di Pietro, A.; Winnischofer, H. Cytotoxicity of η6 -areneruthenium-based molecules to glioblastoma cells and their recognition by multidrug ABC transporters. Eur. J. Med. Chem. 2018, 148, 165−177. (c) Dougan, S. J.; Melchart, M.; Habtemariam, A.; Parsons, S.; Sadler, P. J. Phenylazopyridine and Phenylazo-pyrazole Chlorido Ruthenium(II) Arene Complexes: Arene Loss, Aquation, and Cancer Cell Cytotoxicity. Inorg. Chem. 2006, 45, 10882−10894. (d) Wang, D.; Lippard, S. J. Cellular Processing of platinum anticancer drugs. Nat. Rev. Drug Discovery 2005, 4, 307−320. (e) Dabrowiak, J. C. Metals in Medicine; John Wiley & Sons: Hoboken, NJ, 2013; pp 151−161. (f) Yao, X.; Panichpisal, K.; Kurtzman, N.; Nugent, K. Cisplatin Nephrotoxicity: A Review. Am. J. Med. Sci. 2007, 334, 115−124.

(8) (a) Kostova, I. Ruthenium complexes as anticancer agents. Curr. Med. Chem. 2006, 13, 1085−1107. (b) Gothe, Y.; Marzo, T.; Messori, L.; Metzler-Nolte, N. Cytotoxic activity and protein binding through an unusual oxidative mechanism by an iridium(I)-NHC complex. Chem. Commun. 2015, 51, 3151−3153. (c) Gothe, Y.; Marzo, T.; Messori, L.; Metzler-Nolte, N. Iridium(I) Compounds as Prospective Anticancer Agents: Solution Chemistry, Antiproliferative Profiles and Protein Interactions for a Series of Iridium(I) NHeterocyclic Carbene Complexes. Chem. - Eur. J. 2016, 22, 12487− 12494. (d) Gothe, Y.; Romero-Canelon, I.; Marzo, T.; Sadler, P. J.; Messori, L.; Metzler-Nolte, N. Synthesis and Mode of Action Studies on Iridium(I)-NHC Anticancer Drug Candidates. Eur. J. Inorg. Chem. 2018, 2018, 2461−2470.

© 2019, IJCRCPS. All Rights Reserved

(9) Hartinger, C. G.; Jakupec, M. A.; Zorbas-Seifried, S.; Groessl, M.; Egger, A.; Berger, W.; Zorbas, H.; Dyson, P. J.; Keppler, B. K. KP1019, a new redox-active anticancer agent–preclinical development and results of a clinical phase I study in tumor patients. Chem. Biodiversity 2008, 5, 2140−2155. Dickson, N. R.; Jones, S. F.; Burris, H. A.; Ramanathan, R. K.; Weiss, G. J.; Infante, J. R.; Bendell, J. C.; McCulloch, W.; Von Hoff, D. D. A Phase I Dose Escalation Study of NKP-1339 in Patients with Advanced Solid Tumors Refractory to Treatment. J. Clin. Oncol. 2011, 29, 2607 (suppl., abstr.). Enzo Alessio; Giovanni Mestroni; Alberta Bergamo; Gianni Sava. Ruthenium antimetastatic agents. Curr. Top. Med. Chem. 2004, 4, 1525−1535. (22) Henze, K.; Martin, W. Evolutionary biology: essence of mitochondria. Nature 2003, 426, 127−128. (23) McBride, H. M.; Neuspiel, M.; Wasiak, S. Mitochondria: more than just a powerhouse. Curr. Biol. 2006, 16, 551−560. Youle, R. J.; Narendra, D. P. Mechanisms of mitophagy. Nat. Rev. Mol. Cell Biol. 2011, 12, 9−14.

(10) (a) Ganguly, D.; Jain, C. K.; Santra, R. C.; Roychoudhury, S.; Majumder, H. K.; Das, S. The biological in vitro effect and selectivity shown by a CoII complex of 2-(2-hydroxyphenylazo)-indole-3′-acetic acid on three distinctly different cancer cells. RSC Adv. 2017, 7, 3428−3428. (b) Venugopal, N.; Krishnamurthy, G.; Bhojyanaik, H. S.; Giridhar, M. Novel bioactive azo-azomethine based Cu (II), Co (II) and Ni(II) complexes, structural determination and biological activity. J. Mol. Struct. 2019, 1191, 85−94.

(11) (a) Roy, S.; Böhme, M.; Dash, S. P.; Mohanty, M.; Buchholz, A.; Plass, W.; Majumder, S.; Kulanthaivel, S.; Banerjee, I.; Reuter, H.; Kaminsky, W.; Dinda, R. Anionic Dinuclear Oxidovanadium(IV) Complexes with Azo Functionalized Tridentate Ligands and μEthoxido Bridge Leading to an Unsymmetric Twisted Arrangement: Synthesis, X-ray Structure, Magnetic Properties, and Cytotoxicity. Inorg. Chem. 2018, 57, 5767−5781. (b) Lima, S.; Banerjee, A.; Mohanty, M.; Sahu, G.; Kausar, C.; Patra, S. K.; Garribba, E.; Kaminsky, W.; Dinda, R. Synthesis, structure and biological evaluation of mixed ligand oxidovanadium(IV) complexes incorporating 2- (arylazo)phenolates. New J. Chem. 2019, 43, 17711−17725.

(12) (a) Li, S.; Zhao, J.; Guo, Y.; Mei, Y.; Yuan, B.; Gan, N.; Zhang, J.; Hu, J.; Hou, H. Influence of the introduction of a mitochondriontargeting group on the anticancer activity of a copper complex. J. Inorg. Biochem. 2020, 210, 111102−111111. (b) Chen, Z. G.; Kang, X. X.; Wu, Y. X.; Xiao, H. H.; Cai, X. Z.; Sheng, S. H.; Wang, X. F.; Chen, S. G. A Mitochondria Targeting Artesunate Prodrug Loaded Nanoparticle Exerting Anticancer Activity via Iron-Mediated Generation of Reactive Oxygen Species. Chem. Commun. 2019, 55, 4781−4784. (c) Wang, K.; Zhu, C. C.; He, Y. F.; Zhang, Z. Q.; Zhou, W.; Muhammad, N.; Guo, Y.; Wang, X. Y.; Guo, Z. J. Restraining Cancer Cells by Dual-Metabolic Inhibitions with a Mitochondrion-Targeted Platinum(II) Complex. Angew. Chem., Int. Ed. 2019, 58, 4638−4643. (d) Chrysouli, M.P.; Banti, C.N.; Kourkoumelis, N.; Panayiotou, N.; Markopoulos, G.S.; Tasiopoulos, A.J.; Hadjikakou, S.K. Chloro-(triphenylphosphine)gold(I) a forefront reagent in gold chemistry as apoptotic agent for cancer cell. J. Inorg. Biochem. 2018, 179, 107−120. (e) De Nisi, A.; Bergamini, C.; Leonzio, M.; Sartor, G.; Fato, R.; Naldi, M.; Monari, M.; Calonghi, N.; Bandini, M. Synthesis, cytotoxicity and anticancer activity of new alkynyl-gold(I) complexes. Dalton Trans. 2016, 45, 1546−1553. (f) Castonguay, A.; Doucet, C.; Juhas, M.; Maysinger, D. New Ruthenium(II)-Letrozole Complexes as Anticancer Therapeutics. J. Med. Chem. 2012, 55, 8799−8806. (g) Jin, S. X.; Hao, Y. G.; Zhu, Z. Z.; Muhammad, N.; Zhang, Z. Q.; Wang, K.; Guo, Y.; Guo, Z. J.; Wang, X. Y. Impact of MitochondrionTargeting Group on the Reactivity and Cytostatic Pathway of Platinum(IV) Complexes. Inorg. Chem. 2018, 57, 11135−11145. (h) Ribeiro, G. H.; Colina-Vegas, L.; Clavijo, J. C.T.; Ellena, J.; Cominetti, M. R.; Batista, A. A. Ru(II)/N-N/PPh3 complexes as potential anticancer agents against MDAMB-231 cancer cells (N-N = diimine or diamine). J. Inorg. Biochem. 2019, 193, 70−83 and references therein. (i) Villarreal, W.; Colina-Vegas, L.; Rodrigues de Oliveira, C.; Tenorio, J. C.; Ellena, J.; Gozzo, F. C.; Cominetti, M. R.; Ferreira, A. G.; Ferreira, M. A. B.; Navarro, M.; Batista, A. A. Chiral Platinum(II) Complexes Featuring Phosphine and Chloroquine Ligands as Cytotoxic and Monofunctional DNA-Binding Agents. Inorg. Chem. 2015, 54, 11709−11720. (j) Saez, R.; Lorenzo, J.; Prieto, M. J.; Font-Bardia, M.; Calvet, T.; Omenaca, N.; Vilaseca, M.; Moreno, V. Influence of PPh3 moiety in the anticancer activity of new12. (k) Bomfim, L. M.; de Araujo, F. A.; Dias, R. B.; Sales, C. B. S.; Rocha, C. A. G.; Correa, R. S.; Soares, M. B. P.; Batista, A. A.; Bezerra, D. P. Ruthenium(II) complexes with 6-methyl-2-thiouracil selectively reduce cell proliferation, cause DNA double-strand break and trigger caspase-mediated apoptosis through JNK/p38 pathways in human acute promyelocytic leukemia cells. Sci. Rep. 2019, 9, 11483. (l) Papazoglou, I.; Cox, P. J.; Hatzidimitriou, A. G.; Kokotidou, C.; Choli-

© 2019, IJCRCPS. All Rights Reserved

Papadopoulou, T.; Aslanidis, P. Copper(I) halide complexes of 5-carbethoxy-2-thiouracil: Synthesis, structure and in vitro cytotoxicity. Eur. J. Med. Chem. 2014, 78, 383−391. (m) Hadjikakou, S. K.; Aslanidis, P.; Karagiannidis, P.; Kojic-Prodic, B.; Luic, M. Preparation and spectral studies of dinuclear mixed-ligand copper(I) complexes. The crystal structure of bis[m-s(pyridine-2-thione)(tmtp) copper(I) bromide]. Polyhedron 1994, 13, 3119−3125. (n) Gonzalez-A´´ lvarez, M.; Alzuet, G.; Borras, J.; García-Granda, S.; Montejo- Bernardo, J. M.´ Structural and functional models for the dinuclear copper active site in catechol oxidases. Synthesis, X-ray crystal structures, magnetic and spectroscopic properties of m-methoxo-bridged dinuclear copper(II) complexes with N-substituted sulfonamide ligands. J. Inorg. Biochem. 2003, 96, 443−451. (o) Stromyer, M. L.; Southerland, M. R.; Satyal, U.; Sikder, R. K.; Weader, D. J.; Baughman, J. A.; Youngs, W. J.; Abbosh, P. H. Synthesis, characterization, and biological activity of a triphenylphosphonium-containing imidazolium salt against select bladder cancer cell lines. Eur. J. Med. Chem. 2020, 185, 111832− 111841. (p) Biancalana, L.; Zacchini, S.; Ferri, N.; Lupo, M. G.; Pampaloni, G.; Marchetti, F. Tuning the cytotoxicity of ruthenium(II) paracymene complexes by mono-substitution at a triphenylphosphine/phenoxydiphenylphosphine ligand. Dalton Trans. 2017, 46, 16589−16604. (q) Barreiro, E.; Casas, J. S.; Couce, M. D.; Sanchez,´ A.; Sanchez-Gonza´ lez, A.; Sordo, J.; Varela, J. M.; Vazquez Lo´ pez, E.´ M. Dinuclear triphenylphosphinegold(I) sulfanylcarboxylates: Synthesis, structure and cytotoxic activity against cancer cell lines. J. Inorg. Biochem. 2010, 104, 551−559. Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. Tetrakis-(triphenylphosphine)dichlororuthenium(II) and Tris- (triphenylphosphine)dichlororuthenium(II). In Inorganic Syntheses; John Wiley & Sons, Inc., 2007; pp 237−240. Baksi, S.; Acharyya, R.; Dutta, S.; Blake, A. J.; Drew, M. G. B.; Bhattacharya, S. Interaction of 2-(arylazo) phenols with rhodium. Usual coordination vs. C-H and C-C activation. J. Organomet. Chem. 2007, 692, 1025−1032 and references therein. SAINT; Bruker AXS Inc.: Madison, WI, 2008. SADABS; Bruker AXS Inc.: Madison, WI, 2008. Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Cryst. 2015 C71, 3−8. Wang, X.; Tanaka, M.; Krstin, S.; Peixoto, H. S.; Moura, C. C. d. M.; Wink, M. Cytoskeletal interference - A new mode of action for the anticancer drugs camptothecin and topotecan. Eur. J. Pharmacol. 2016, 789, 265−274.

(13) (a) Gupta, P.; Dutta, S.; Basuli, F.; Peng, S.-M.; Lee, G.-H.; Bhattacharya, S. Ruthenium Mediated C- H Activation of 2-(Arylazo) phenols: Characterization of an Intermediate and the Final Organoruthenium Complex. Inorg. Chem. 2006, 45, 460−467. (b) Mandal, S.; Samanta, S.; Mondal, T. K.; Goswami, S. Activation in ortho-CaromaticN Bond Fusion in Substituted Anilines Using Ruthenium(II) Mediators: Isolation and Characterization of Unusual Ru2 Complexes. Organometallics 2012, 31, 5282−5293. (c) Acharyya, R.; Basuli, F.; Peng, S.-M.; Lee, G.-H.; Wang, R.-Z.; Mak, T. C. W.; Bhattacharya, S. Iridium mediated methyl and phenyl C-H activation of 2-(arylazo)- phenols. Synthesis, structure, and spectral and electrochemical properties of some organoiridium complexes. J. Organomet. Chem. 2005, 690, 3908−3917. Nag, S.; Gupta, P.; Butcher, R. J.; Bhattacharya, S. Unprecedented Migration of a Methyl Group in 2-(2 ‘, 6 ‘-Dimethylphenylazo)-4-methylphenol Mediated by Ruthenium. Inorg. Chem. 2004, 43, 4814−4816. Acharyya, R.; Peng, S.-M.; Lee, G.-H.; Bhattacharya, S. Iridium mediated phenolic OH activation and cyclometalation of 2-(naphthyl1’-azo)-4-methylphenol Formation of organoiridium complexes. J. Chem. Sci. 2009, 121, 387−395. (37) Yi, C. S.; Lee, D. W.; Chen, Y. Hydrovinylation and [2+ 2] Cycloaddition Reactions of Alkynes and Alkenes Catalyzed by a WellDefined Cationic Ruthenium-Alkylidene Complex. Organometallics 1999, 18, 2043−2045.

(14) (a) Ghosh, P.; Bag, N.; Chakravorty, A. Decarbonylative Metalation of Diformylphenol Schiff Bases: New Osmium and Ruthenium Organometallics Incorporating the Iminium-Phenolato Zwitterionic Motif. Organometallics 1996, 15, 3042−3047. (b) Bag, N.; Choudhury, S. B.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. Ruthenium (II) phenolates. Synthesis and characterization of a novel four-membered metallacycle. Inorg. Chem. 1990, 29, 5013−5014.

(15) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. The mechanism for the rhodium-catalyzed decarbonylation of aldehydes: a combined experimental and theoretical study. J. Am. Chem. Soc. 2008, 130, 5206−5215. Modak, A.; Maiti, D. Metal catalyzed defunctionalization reactions. Org. Biomol. Chem. 2016, 14, 21−35. Halder, S.; Drew, M. G. B.; Bhattacharya, S. Palladium and platinum complexes of 2-(2’-carboxyphenylazo)-4-methylphenol: Synthesis, structure and spectral properties. J. Chem. Sci. 2008, 120, 441−446. Panda, M.; Paul, N. D.; Joy, S.; Hung, C.-H.; Goswami, S. Hydrido iridium (III) complexes of azoaromatic ligands. Isolation, structure and studies of their

© 2019, IJCRCPS. All Rights Reserved

physicochemical properties. Inorg. Chim. Acta 2011, 372, 168−174. Lo, K. K. -W.; Chung, C.-K.; Zhu, N. Synthesis, Photophysical and Electrochemical Properties, and Biological Labeling Studies of Cyclometalated Iridium(III) Bis(pyridylbenzaldehyde) Complexes: Novel Luminescent Cross Linkers for Biomolecules. Chem. - Eur. J. 2003, 9, 475−483. Djukic, M.; Jeremic, M. S.; Jelic, R.; Klisuric, O.; Kojic, V.; Jakimov, D.; Djurdjevic, P.; Matovic, Z. D. Further insights into ruthenium(II) piano-stool complexes with N-alkylimidazoles. Inorg. Chim. Acta 2018, 483, 359−370. Chang, S. W.; Lewis, A. R.; Prosser, K. E.; Thompson, J. R.; Gladkikh, M.; Bally, M. B.; Warren, J. J.; Walsby, C. J. CF3 Derivatives of the Anticancer Ru(III) Complexes KP1019, NKP-1339, and Their Imidazole and Pyridine Analogues Show Enhanced Lipophilicity, Albumin Interactions, and Cytotoxicity. Inorg. Chem. 2016, 55, 4850−4863. Yang, Y.; Ge, X.; Guo, L.; Zhu, T.; Tian, Z.; Zhang, H.; Du, Q.; Peng, H.; Ma, W.; Liu, Z. Zwitterionic and cationic half-sandwich iridium(iii) ruthenium(ii) complexes bearing sulfonate groups: synthesis, characterization and their different biological activity. Dalton Trans. 2019, 48, 3193−3197.

(16) Ma, W.; Zhang, S.; Tian, Z.; Xu, Z.; Zhang, Y.; Xia, X.; Chen, X.; Liu, Z. Potential anticancer agent for selective damage to mitochondria or lysosomes: Naphthalimide-modified fluorescent biomarker half-sandwich iridium (III) and ruthenium (II) complexes. Eur. J. Med. Chem. 2019, 181, 111599−111608. Avaji, P. G.; Vinod Kumar, C. H.; Patil, S. A.; Shivananda, K. N.; Nagaraju, C. Synthesis, spectral characterization, in-vitro microbiological spectral evaluation and cytotoxic activities of novel macrocyclic bis hydrazone. Eur. J. Med. Chem. 2009, 44, 3552−3559. (a) Saswati, S.; Adao, P.; Majumder, S.; Dash, S. P.; Roy, S.; ˜Kuznetsov, M.; Costa Pessoa, J.; Gomes, C. S. B.; Hardikar, M. R.; Tiekink, E. R.T.; Dinda, R. Synthesis, structure, solution behavior, reactivity and biological evaluation of oxidovanadium(IV/V) thiosemicarbazone complexes. Dalton Trans. 2018, 47, 11358−11374. (b) Majumder, S.; Pasayat, S.; Panda, A. K.; Dash, S. P.; Roy, S.; Biswas, A.; Varma, M. E.; Joshi, B. N.; Garribba, E.; Kausar, C.; Patra, S. K.; Kaminsky, W.; Crochet, A.; Dinda, R. Monomeric and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, and DNA Interaction Studies: Molybdenum Assisted C = N Bond Cleavage of Salophen Ligands. Inorg. Chem. 2017, 56, 11190−11210 and references therein. (c) Roy, S.; Mohanty, M.; Pasayat, S.; Majumder, S.; Senthilguru, K.; Banerjee, I.; Reichelt, M.; Reuter, H.; Sinn, E.; Dinda, R. Synthesis, structure and cytotoxicity of a series of Dioxidomolybdenum(VI) complexes featuring Salan ligands. J. Inorg. Biochem. 2017, 172, 110−121. (d) Dash, S. P.; Pasayat, S.; Bhakat, S.; Roy, S.; Dinda, R.; Tiekink, E. R. T.; Mukhopadhyay, S.; Bhutia, S. K.; Hardikar, M. R.; Joshi, B. N.; Patil, Y. P.; Nethaji, M. Highly Stable Hexacoordinated Nonoxidovanadium(IV) Complexes of Sterically Constrained Ligands: Syntheses, Structure, and Study of Antiproliferative and Insulin Mimetic Activity. Inorg. Chem. 2013, 52, 14096− 14107.

(17) (a) Ruiz, J.; Rodriguez, V.; Cutillas, N.; Samper, K. G.; Capdevila, M.; Palacios, O.; Espinosa, A. Novel C, N-chelate rhodium(III) and iridium(III) antitumor complexes incorporating a lipophilic steroidal conjugate and their interaction with DNA. Dalton Trans. 2012, 41, 12847−12856. (b) El-Ghamry, H. A.; Fathalla, S. K.; Gaber, M. Synthesis, structural characterization and molecular modelling of bidentate azo dye metal complexes: DNA interaction to antimicrobial and anticancer activities. Appl. Organomet. Chem. 2018, 32, 4136−4148.

(18) (a) Reytman, L.; Braitbard, O.; Tshuva, E. Y. Highly cytotoxic vanadium(v) complexes of salan ligands; insights on the role of hydrolysis. Dalton Trans. 2012, 41, 5241−5247 and references therein. (b) Stockert, A.; Kinder, D.; Christ, M.; Amend, K.; Aulthouse, A. Improving the Efficacy of Cisplatin in Colon Cancer HT-29 Cells via Combination Therapy with Selenium. Austin J. Pharmacol. Ther. 2014, 2, 6−12. (c) Lewis, A. D.; Forrester, L. M.; Hayes, J. D.; Wareing, C. J.; Carmichael, J.; Harris, A. L.; Mooghen, M.; Wolf, C. R. Glutathione S-transferase isoenzymes in human tumors and tumor derived cell-lines. Br. J. Cancer 1989, 60, 327−331. (d) Takara, K.; Sakaeda, T.; Yagami, T.; Kobayashi, H.; Ohmoto, N.; Horinouchi, M.; Nishiguchi, K.; Okumura, K. Cytotoxic effects of 27 anticancer drugs in HeLa and MDR1-overexpressing derivative cell lines. Biol. Pharm. Bull. 2002, 25, 771−778. (e) Petinari, L.; Kohn, L. K.; de Carvalho, J. E.; Genari, S. C. Cytotoxicity of tamoxifen in normal and tumoral cell lines and its ability to induce cellular transformation in vitro. Cell Biol. Int. 2004, 28, 531−539.

(19) Ziegler, U.; Groscurth, P. Morphological features of cell death. Physiology 2004, 19, 124−128. Bezabeh, T.; Mowat, M. R. A.; Jarolim, L.; Greenberg, A. H.; Smith, I. C. P. Detection of drug-induced apoptosis and necrosis in human cervical carcinoma cells using 1 H NMR spectroscopy. Cell Death Differ. 2001, 8, 219−224.

© 2019, IJCRCPS. All Rights Reserved

(1) De Sousa, S.; Lyu, S.; Ducasse, L.; Toupance, T.; Olivier, C. Tuning visible-light absorption properties of Ru-diacetylide complexes: simple access to colorful efficient dyes for DSSCs. J. Mater. Chem. A 2015, 3, 18256−18264. Pashaei, B.; Shahroosvand, H.; Graetzel, M.; Nazeeruddin, M. K. Influence of Ancillary Ligands in Dye-Sensitized Solar Cells. Chem. Rev. 2016, 116, 9485−9564. Shalini, S.; Balasundaraprabhu, R.; Kumar, T. S.; Prabavathy, N.; Senthilarasu, S.; Prasanna, S. Status and outlook of sensitizers/dyes used in dye sensitized solar cells (DSSC): a review. Int. J. Energy Res. 2016, 40, 1303−1320. Nazeeruddin, M. K.; Zakeeruddin, S.; Lagref, J.-J.; Liska, P.; Comte, P.; Barolo, C.; Viscardi, G.; Schenk, K.; Gratzel, M. Stepwise¨ assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell. Coord. Chem. Rev. 2004, 248, 1317−1328. Bolink, H. J.; Cappelli, L.; Coronado, E.; Graetzel, M.; Nazeeruddin, M. K. Efficient and Stable Solid-State Light-Emitting Electrochemical Cell Using Tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) Hexafluorophosphate. J. Am. Chem. Soc. 2006, 128, 46− 47. Marin, V.; Holder, E.; Hoogenboom, R.; Schubert, U. S. Functional ruthenium(II)- and iridium(III)-containing polymers for potential electro-optical applications. Chem. Soc. Rev. 2007, 36, 618−635. Nemati Bideh, B.; Roldan-Carmona, C.; Shahroosvand, H.; Nazeeruddin, M. K. Low-voltage, high-brightness and deep-red lightemitting electrochemical cells (LECs) based on new ruthenium(II) phenanthroimidazole complexes. Dalton Trans. 2016, 45, 7195−7199. Puodziukynaite, E.; Oberst, J. L.; Dyer, A. L.; Reynolds, J. R. Establishing Dual Electrogenerated Chemiluminescence and Multicolor Electrochromism in Functional Ionic Transition-Metal Complexes. J. Am. Chem. Soc. 2012, 134, 968−978. Xie, S.; Lu, Y.; Zhang, S.; Wang, L.; Zhang, X. Electro-optical Gas Sensor Based on a Planar Light-Emitting Electrochemical Cell Microarray. Small 2010, 6, 1897−1899. Zysman-Colman, E.; Slinker, J. D.; Parker, J. B.; Malliaras, G. G.; Bernhard, S. Improved Turn-On Times of Light-Emitting Electrochemical Cells. Chem. Mater. 2008, 20, 388−396. (20) Zhao, C.-Z.; Egashira, N.; Kurauchi, Y.; Ohga, K. Electrochemiluminescence oxalic acid sensor having a platinum electrode coated with chitosan modified with a ruthenium (II) complex. Electrochim. Acta 1998, 43, 2167−2173. Chao, H.; Zhang, P.; Ji, L. Preparation method and application of anthraquinone polypyridine ligand and ruthenium-anthraquinone complex. CN103012401A, 2013. Das, A.; Kundu, T.; Mobin, S. M.; Priego, J. L.; JimenezAparicio, R.; Lahiri, G. K. Influence of ancillary ligands on the electronic structure and anion sensing features of ligand bridged diruthenium complexes. Dalton Trans. 2013, 42, 13733−13746. Khatua, S.; Samanta, D.; Bats, J. W.; Schmittel, M. Rapid and Highly Sensitive Dual-Channel Detection of Cyanide by Bisheteroleptic Ruthenium(II) Complexes. Inorg. Chem. 2012, 51, 7075−7086Li, M.-J.; Wong, K. M.-C.; Yi, C.; Yam, V. W.-W. New Ruthenium(II) Complexes Functionalized with Coumarin Derivatives: Synthesis, Energy-Transfer-Based Sensing of Esterase, Cytotoxicity, and Imaging Studies. Chem. - Eur. J. 2012, 18, 8724−8730. Mardanya, S.; Karmakar, S.; Maity, D.; Baitalik, S. Ruthenium- (II) and Osmium(II) Mixed Chelates Based on Pyrenyl-Pyridylimidazole and 2,2′-Bipyridine Ligands as Efficient DNA Intercalators and Anion Sensors. Inorg. Chem. 2015, 54, 513−526. Saha, D.; Das, S.; Bhaumik, C.; Dutta, S.; Baitalik, S. Monometallic and Bimetallic Ruthenium(II) Complexes Derived from 4,5-Bis(benzimidazol-2-yl)imidazole (H3Imbzim) and 2,2′- Bipyridine as Colorimetric Sensors for Anions: Synthesis, Characterization, and Binding Studies. Inorg. Chem. 2010, 49, 2334−2348. Yue, X.; Zhu, Z.; Zhang, M.; Ye, Z. Reaction-Based Turn-on Electrochemiluminescent Sensor with a Ruthenium(II) Complex for Selective Detection of Extracellular Hydrogen Sulfide in Rat Brain. Anal. Chem. 2015, 87, 1839−1845. Zheng, Z.-B.; Wu, Y.-Q.; Wang, K.-Z.; Li, F. pH luminescence switching, dihydrogen phosphate sensing, and cellular uptake of a heterobimetallic ruthenium(II)-rhenium(I) complex. Dalton Trans. 2014, 43, 3273−3284 Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. trans-[RuCl2 (phosphane) 2 (1, 2-diamine)] and Chiral trans-[RuCl2 (diphosphane)(1, 2-diamine)]: Shelf-Stable Precatalysts for the Rapid, Productive, and Stereoselective Hydrogenation of Ketones. Angew. Chem., Int. Ed. 1998, 37, 1703−1707. Au, S.-M.; Huang, J.-S.; Che, C.-M.; Yu, W.-Y. Amidation of unfunctionalized hydrocarbons catalyzed by ruthenium cyclic amine or bipyridine complexes. J. Org. Chem. 2000, 65, 7858−7864. Clapham, S. E.; Hadzovic, A.; Morris, R. H. Mechanisms of the H 2-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes. Coord. Chem. Rev. 2004, 248, 2201−2237. Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-catalyzed living radical polymerization. Chem. Rev. 2001, 101, 3689−3746. Canterbury, T. R.; Arachchige, S.

© 2019, IJCRCPS. All Rights Reserved

M.; Moore, R. B.; Brewer, K. J. Increased Water Reduction Efficiency of Polyelectrolyte-Bound Trimetallic [Ru,Rh,Ru] Photocatalysts in Air-Saturated Aqueous Solutions. Angew. Chem., Int. Ed. 2015, 54, 12819−12822. Limburg, B.; Bouwman, E.; Bonnet, S. Rate and Stability of Photocatalytic Water Oxidation using [Ru(bpy)3]2+ as Photosensitizer. ACS Catal. 2016, 6, 5273−5284. (26) Concepcion, J. J.; Tsai, M.-K.; Muckerman, J. T.; Meyer, T. J. Mechanism of water oxidation by single-site ruthenium complex catalysts. J. Am. Chem. Soc. 2010, 132, 1545−1557. Geletii, Y. V.; Huang, Z.; Hou, Y.; Musaev, D. G.; Lian, T.; Hill, C. L. Homogeneous light-driven water oxidation catalyzed by a tetraruthenium complex with all inorganic ligands. J. Am. Chem. Soc. 2009, 131, 7522−7523. Concepcion, J. J.; Jurss, J. W.; Norris, M. R.; Chen, Z.; Templeton, J. L.; Meyer, T. J. Catalytic water oxidation by single-site ruthenium catalysts. Inorg. Chem. 2010, 49, 1277−1279. Gill, M. R.; Thomas, J. A. Ruthenium (II) polypyridyl complexes and DNA□from structural probes to cellular imaging and therapeutics. Chem. Soc. Rev. 2012, 41, 3179−3192. Lo, K. K.-W.; Hui, W.-K.; Chung, C.-K.; Tsang, K. H.-K.; Ng, D. C.-M.; Zhu, N.; Cheung, K.-K. Biological labelling reagents and probes derived from luminescent transition metal polypyridine complexes. Coord. Chem. Rev. 2005, 249, 1434−1450. Zhu, B.-Z.; Chao, X.-J.; Huang, C.-H.; Li, Y. Delivering the cellimpermeable DNA 'light-switching'Ru (ii) complexes preferentially into live-cell nucleus via an unprecedented ion-pairing method. Chem. Sci. 2016, 7, 4016−4023. Pierroz, V.; Rubbiani, R.; Gentili, C.; Patra, M.; Mari, C.; Gasser, G.; Ferrari, S. Dual mode of cell death upon photo-irradiation of a RuII polypyridyl complex in interphase or mitosis. Chem. Sci. 2016, 7, 6115−6124. Friedman, A. E.; Chambron, J. C.; Sauvage, J. P.; Turro, N. J.; Barton, J. K. A molecular light switch for DNA: Ru (bpy) 2 (dppz)2+. J. Am. Chem. Soc. 1990, 112, 4960−4962. Erkkila, K. E.; Odom, D. T.; Barton, J. K. Recognition and reaction of metallointercalators with DNA. Chem. Rev. 1999, 99, 2777−2796. Boynton, A. N.; Marcélis, L.; Barton, J. K. [Ru (Me4phen)2dppz]2+, a Light Switch for DNA Mismatches. J. Am. Chem. Soc. 2016, 138, 5020−5023. Padilla, R.; Rodriguez-Corrales, J. A.; Donohoe, L. E.; Winkel, B. S.; Brewer, K. J. A new class of Ru (II) polyazine agents with potential for photodynamic therapy. Chem. Commun. 2016, 52, 2705−2708. Puckett, C. A.; Barton, J. K. Mechanism of Cellular Uptake of a Ruthenium Polypyridyl Complex. Biochemistry 2008, 47, 11711− 11716. Gill, M. R.; Garcia-Lara, J.; Foster, S. J.; Smythe, C.; Battaglia, G.; Thomas, J. A. A ruthenium (II) polypyridyl complex for direct imaging of DNA structure in living cells. Nat. Chem. 2009, 1, 662− 667. Wragg, A.; Gill, M. R.; Turton, D.; Adams, H.; Roseveare, T. M.; Smythe, C.; Su, X.; Thomas, J. A. Tuning the cellular uptake properties of luminescent heterobimetallic iridium (III)−ruthenium (II) DNA imaging probes. Chem. - Eur. J. 2014, 20, 14004−14011.

(21) De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; von Zelewsky, A.; Frank, M.; Voegtle, F. Photoinduced energy and electron transfer processes in supramolecular species, tris (bipyridine) complexes of ruthenium (II)/osmium (II), Ru (II)/Ru (III), Os (II)/ Os (III), and Ru (II)/Os (III) separated by a rigid spacer. Inorg. Chem. 1993, 32, 5228−5238. Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. Intramolecular, photoinduced electron transfer in ruthenium (II) bipyridine-quinone complexes. Inorg. Chem. 1994, 33, 5295−5301. Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. Electron transfer on the infrared vibrational time scale in the mixed valence state of 1, 4-pyrazine-and 4, 4′-bipyridine-bridged ruthenium cluster complexes. J. Am. Chem. Soc. 1999, 121, 4625−4632. Ortmans, I.; Moucheron, C.; Kirsch-De Mesmaeker, A. Ru(II) polypyridine complexes with a high oxidation power. Comparison between their photoelectrochemistry with transparent SnO2 and their photochemistry with desoxyribonucleic acids. Coord. Chem. Rev. 1998, 168, 233−271. Lecomte, J.-P.; Kirsch-De Mesmaeker, A.; Feeney, M. M.; Kelly, J. M. Ruthenium (II) complexes with 1, 4, 5, 8, 9, 12-hexaazatriphenylene and 1, 4, 5, 8-tetraazaphenanthrene ligands: key role played by the photoelectron transfer in DNA cleavage and adduct formation. Inorg. Chem. 1995, 34, 6481−6491. Pourtois, G.; Beljonne, D.; Moucheron, C.; Schumm, S.; KirschDe Mesmaeker, A.; Lazzaroni, R.; Bredas, J.-L. Photophysical´ properties of ruthenium (II) polyazaaromatic compounds: A theoretical insight. J. Am. Chem. Soc. 2004, 126, 683−692. Patra, S.; Sarkar, B.; Ghumaan, S.; Fiedler, J.; Kaim, W.; Lahiri, G. K. The triruthenium complex [{(acac)2RuII}3(L)] containing a conjugated diquinoxaline [2, 3-a: 2′, 3′-c] phenazine (L) bridge and acetylacetonate (acac) as ancillary ligands. Synthesis, spectroelectrochemical and EPR investigation. Dalton Trans. 2004, 754−758. Chen, L.; Chao, H.; Zhao, Q.; Zheng, X.; Li, H. Photoluminescence quenching of [Ru (bpy)2(atatp)]2+ bound to a condensed DNA matrix. J. Inorg. Biochem. 2016, 154, 1−6. Sun, Y.; Lutterman, D. A.; Turro, C. Role of electronic

© 2019, IJCRCPS. All Rights Reserved

structure on DNA light-switch behavior of Ru (II) intercalators. Inorg. Chem. 2008, 47, 6427−6434. Liu, Y.; Chouai, A.; Degtyareva, N. N.; Lutterman, D. A.; Dunbar, K. R.; Turro, C. Chemical control of the DNA light switch: cycling the switch ON and OFF. J. Am. Chem. Soc. 2005, 127, 10796− 10797.

(22) Lutterman, D. A.; Chouai, A.; Liu, Y.; Sun, Y.; Stewart, C. D.; Dunbar, K. R.; Turro, C. Intercalation is not required for DNA lightswitch behavior. J. Am. Chem. Soc. 2008, 130, 1163−1170. Sun, Y.; Liu, Y.; Turro, C. Ultrafast dynamics of the low-lying 3MLCT states of [Ru (bpy)2(dppp2)]2+. J. Am. Chem. Soc. 2010, 132, 5594−5595. Sun, Y.; Joyce, L. E.; Dickson, N. M.; Turro, C. Efficient DNA photocleavage by [Ru (bpy)2(dppn)]2+ with visible light. Chem. Commun. 2010, 46, 2426−2428. Treadway, J. A.; Strouse, G. F.; Ruminski, R. R.; Meyer, T. J. Long-lived near-infrared MLCT emitters. Inorg. Chem. 2001, 40, 4508−4509. Paul, F.; Lapinte, C. Organometallic molecular wires and other nanoscale-sized devices: an approach using the organoiron (dppe) Cp* Fe building block. Coord. Chem. Rev. 1998, 178, 431−509. Sathyaraj, G.; Nair, B. U. Unusual solvent dependent emission property of two new ruthenium (II) complexes. Inorg. Chim. Acta 2013, 402, 75−82. Tripathy, S. K.; De, U.; Dehury, N.; Pal, S.; Kim, H. S.; Patra, S. Dinuclear [{(p-cym)RuCl}2(μ-phpy)](PF6)2 and heterodinuclear [(ppy)2Ir(μ-phpy)Ru(p-cym)Cl](PF6)2 complexes: synthesis, structure and anticancer activity. Dalton Trans. 2014, 43, 14546−14549. Lu, X.-H.; Shi, S.; Yao, J.-L.; Gao, X.; Huang, H.-L.; Yao, T.-M. Two structurally analogous ruthenium complexes as naked-eye and reversible molecular "light switch" for G-quadruplex DNA. J. Inorg. Biochem. 2014, 140, 64−71.

(23) Anzenbacher, P.; Tyson, D. S.; Jursíkova, K.; Castellano, F. N.́ Luminescence Lifetime-Based Sensor for Cyanide and Related Anions. J. Am. Chem. Soc. 2002, 124, 6232−6233. Tripathy, S. K.; De, U.; Dehury, N.; Laha, P.; Panda, M. K.; Kim, H. S.; Patra, S. Cyclometallated iridium complexes inducing paraptotic cell death like natural products: synthesis, structure and mechanistic aspects. Dalton Trans. 2016, 45, 15122−15136. Novotny, C´ˇ.; Dias, N.; Kapanen, A.; Malachova, K.;´ Vandrovcova´ , M.; Ita´ vaara, M.; Lima, N. Comparative use of bacterial,¨ algal and protozoan tests to study toxicity of azo-and anthraquinone dyes. Chemosphere 2006, 63, 1436−1442. Carneiro, P. A.; Umbuzeiro, G. A.; Oliveira, D. P.; Zanoni, M. V. B. Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. J. Hazard. Mater. 2010, 174, 694−699. Chandra, F.; Kumar, P.; Tripathi, S. K.; Patra, S.; Koner, A. L. Iridium Complexes as a Roadblock for DNA Polymerase during Amplification. ChemMedChem 2016, 11, 1410−1414. Bhat, S. S.; Kumbhar, A. S.; Lonnecke, P.; Hey-Hawkins, E. SelfAssociation of Ruthenium(II) Polypyridyl Complexes and Their Interactions with Calf Thymus DNA. Inorg. Chem. 2010, 49, 4843−4853. Cardinaels, T.; Ramaekers, J.; Driesen, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Goderis, B.; Binnemans, K. Thermotropic Ruthenium(II)-Containing Metallomesogens Based on Substituted 1,10-Phenanthroline Ligands. Inorg. Chem. 2009, 48, 2490−2499. Foxon, S. P.; Green, C.; Walker, M. G.; Wragg, A.; Adams, H.; Weinstein, J. A.; Parker, S. C.; Meijer, A. J. H. M.; Thomas, J. A. Synthesis, Characterization, and DNA Binding Properties of Ruthenium(II) Complexes Containing the Redox Active Ligand Benzo[i]dipyrido[3,2-a:2′,3′-c]phenazine-11,16-quinone. Inorg. Chem. 2012, 51, 463−471Nayak, A.; Patra, S.; Sarkar, B.; Ghumaan, S.; Puranik, V. G.; Kaim, W.; Lahiri, G. K. Tetrazine derived mononuclear RuII (acac)2(L)(1),[RuII(bpy)2(L)](ClO4)2(2) and [RuII(bpy)(L)2]- (ClO4)2 (3)(L= 3-amino-6-(3, 5-dimethylpyrazol-1-yl)-1, 2, 4, 5- tetrazine, acac= acetylacetonate, bpy= 2, 2′-bipyridine): syntheses, structures, spectra and redox properties. Polyhedron 2005, 24, 333− 342. Sarkar, B.; Laye, R. H.; Mondal, B.; Chakraborty, S.; Paul, R. L.; Jeffery, J. C.; Puranik, V. G.; Ward, M. D.; Lahiri, G. K. Synthesis, structure and spectroelectrochemical properties of a dinuclear ruthenium complex exhibiting a strong electronic interaction across a 1,2,4,5-tetrazine bridging ligand. J. Chem. Soc., Dalton Trans. 2002, 2097−2101. Friebe, C.; Gö rls, H.; Jager, M.; Schubert, U. S. Linear¨ Metallopolymers from Ruthenium (II)-2, 6-di (quinolin-8-yl) pyridine Complexes by Electropolymerization−Formation of Redox-Stable and Emissive Films. Eur. J. Inorg. Chem. 2013, 2013, 4191−4202. Charlot, M.-F.; Pellegrin, Y.; Quaranta, A.; Leibl, W.; Aukauloo, A. A Theoretical Investigation into the Photophysical Properties of Ruthenium Polypyridine-Type Complexes. Chem. - Eur. J. 2006, 12, 796−812. Monat, J. E.; Rodriguez, J. H.; McCusker, J. K. Ground-and excited-state electronic structures of the solar cell sensitizer bis (4, 4′- dicarboxylato-2, 2′-bipyridine) bis (isothiocyanato) ruthenium (II). J. Phys. Chem. A 2002, 106, 7399−7406. Van Houten, J.; Watts, R. Temperature dependence of the photophysical and photochemical properties of the tris (2, 2′- bipyridyl) ruthenium (II) ion in aqueous solution. J. Am. Chem. Soc. 1976, 98,

© 2019, IJCRCPS. All Rights Reserved

4853−4858. Sullivan, B.; Salmon, D.; Meyer, T. J. Mixed phosphine 2, 2′- bipyridine complexes of ruthenium. Inorg. Chem. 1978, 17, 3334−3341. Chen, J.; Li, X. Canon Kabushiki Kaisha, Japan, 2004.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, U.S., 2009. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648−5652. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785. Vosko, S.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 1980, 58, 1200−1211. Stephens, P.; Devlin, F.; Chabalowski, C.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem. 1994, 98, 11623− 11627. Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. Theor. Chim. Acta 1973, 28, 213−222. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. J. Chem. Phys. 1982, 77, 3654−3665. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 1985, 82, 270−283. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. 1985, 82, 299−310. Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. 1985, 82, 284−298. Bauernschmitt, R.; Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. Chem. Phys. Lett. 1996, 256, 454−464. Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules. J. Chem. Phys. 1998, 109, 8218−8224.

(25) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular excitation energies to high-lying bound states from timedependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold. J. Chem. Phys. 1998, 108, 4439−4449. O'boyle, N. M.; Tenderholt, A. L.; Langner, K. M. Cclib: a library for package-independent computational chemistry algorithms. J. Comput. Chem. 2008, 29, 839−845. Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112−122. Zarkesh, R. A.; Ichimura, A. S.; Monson, T. C.; Tomson, N. C.; Anstey, M. R. Voltage Clustering in Redox-Active Ligand Complexes: Mitigating Electronic Communication through Choice of Metal Ion. Dalton Trans. 2016, 45 (24), 9962−9969. Ketterer, N. A.; Fan, H.; Blackmore, K. J.; Yang, X.; Ziller, J. W.; Baik, M.-H.; Heyduk, A. F. π • −π • Bonding Interactions Generated by Halogen Oxidation of Zirconium(IV) Redox-Active Ligand Complexes. J. Am. Chem. Soc. 2008, 130 (13), 4364−4374, Cameron, L. A.; Ziller, J. W.; Heyduk, A. F. Near-IR Absorbing Donor−Acceptor Ligand-to-Ligand Charge-Transfer Complexes of Nickel(II). Chem. Sci. 2016, 7 (3), 1807−1814. Kalia, K. C.; Chakravorty, A. Complexes of Arylazooximes. I. Structure of Ligands and Cobalt(III) Chelates. Inorg. Chem. 1968, 7 (10), 2016−2020. Kalia, K. C.; Chakravorty, A. Complexes of Arylazo Oximes. II. Rhodium(III) and Palladium(II) Chelates. Inorg. Chem. 1969, 8 (12), 2586−2590. (10) Mascharak, P. K.; Chakravorty, A. Selective Cleavage of the Two Types of Pd−N Bonds in Di-μ-Halogeno-Bis[ArylazoOximatopalladium(II)]. J. Chem. Soc., Dalton Trans. 1980, 1698− 1702. Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. Bis(Arylazo-Oximato)Palladium(II); Synthesis, Palladium−Nitrogen Bond Lability, and Redox

© 2019, IJCRCPS. All Rights Reserved

Activity. J. Chem. Soc., Dalton Trans. 1981, 623−627. Kalia, K. C.; Singla, M.; Kumar, A. The Reaction of PPh3 with Di-μ-Chlorobis(Arylazooximato)Dipalladium(II). Transition Met. Chem. 1982, 7 (3), 151−153. Chakravarty, A. R.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Ghosh, B. K.; Tomas, M. Cis-Dihalobis(Arylazo Oxime)- Ruthenium(II): Synthesis, Structure and Reactions. Inorg. Chem. 1983, 22 (13), 1892−1896. Manivannan, V.; Chattopadhyay, S.; Basu, P.; Chakravorty, A. Synthesis, Structure, Spectra and Metal Redox of Imidazolium Tris(Arylazo Oximato)Iron(II): The Association of Imidazole with a Tris Chelate Oximato Face and Analogy with Distal Iron···imidazole Disposition. Polyhedron 1993, 12 (22), 2725−2730. Pal, C. K.; Chattopadhyay, S.; Sinha, C.; Chakravorty, A. Synthesis, Structure, and Solution Equilibria of Diamagnetic and Paramagnetic Azooximates of Bivalent Platinum. Geometrical Change Associated with Ligand-Based Electroprotic Reactions. Inorg. Chem. 1994, 33 (26), 6140−6147. Manivannan, V.; Dirghangi, B. K.; Pal, C. K.; Chakravorty, A. Hydrogen-Bonded Oximate−Oxime Chelation and Variable Metal Valence. Syntheses and Structures of RuCl2(L)(HL)z (HL = PhC(NOH)NNPh; z = 1−, 0. Inorg. Chem. 1997, 36 (7), 1526−1528. Ganguly, S.; Manivannan, V.; Chakravorty, A. Synthesis and Structure of Bis(Azooximates) of Dichlororhodium(III): The Oxime−Oximate O−H ··· O Bridge and the Effect of Its Deprotonation. J. Chem. Soc., Dalton Trans. 1998, 461−466. (18) Ganguly, S.; Chattopadhyay, S.; Sinha, C.; Chakravorty, A. Synthesis and Structure of Dimeric Silver Azooximates. Hydrogen Bonding and Nonbonded Ag···Ag Interaction. Inorg. Chem. 2000, 39 (13), 2954−2956. Chakraborty, I.; Panda, B. K.; Gangopadhyay, J.; Chakravorty, A. Rhenium Chemistry of Azooximes: Oxygen Atom Transfer, Azoimine Chelation, and Imine−Oxime Contrast. Inorg. Chem. 2005, 44 (4), 1054−1060. Pramanik, S.; Roy, S.; Ghorui, T.; Ganguly, S.; Pramanik, K. Iridium(III) Mediated Reductive Transformation of Closed-Shell Azo-Oxime to Open-Shell Azo-Imine Radical Anion: Molecular and Electronic Structure, Electron Transfer, and Optoelectronic Properties. Inorg. Chem. 2016, 55 (4), 1461−1468. Pal, S.; Melton, T.; Mukherjee, R.; Chakravarty, A. R.; Tomas, M.; Falvello, L. R.; Chakravorty, A. Trinucleation of Arylazo Oxime Ensembles: Structure and Reactions of Novel Linear FeIIFeIIIFeII Species. Inorg. Chem. 1985, 24 (8), 1250−1257. Basu, P.; Pal, S.; Chakravorty, A. New Binuclear Iron− Vanadium Complexes of Arylazo Oximates. Crystal Structure of [Fe(PhN = NCPh = NO)3VO(Bipy)]PF6 (Bipy = 2,2′-Bipyridine). J. Chem. Soc., Dalton Trans. 1991, 3217−3221. Manivannan, V.; Dutta, S.; Basu, P.; Chakravorty, A. Binding of Copper(I) and Copper(II) to the Pendent O3-Face of Iron Arylazo Oximates: Synthesis and Structure of CuI FeII and CuIIFeII 2 Families. Inorg. Chem. 1993, 32 (22), 4807−4811. Bhattacharyya, I.; Ganguly, S.; Panda, B. K.; Chakravorty, A. Oximato Bridged RhIII2MII and RhIIIMI Species (MII = Mn, Co, Ni; MI = Cu, Ag). Proc. - Indian Acad. Sci., Chem. Sci. 2008, 120 (1), 87− 93. Pal, C. K.; Chattopadhyay, S.; Sinha, C.; Chakravorty, A. A Bis(Azo−imine)Palladium(II) System with 10 Ligand π Electrons. Synthesis, Structure, Serial Redox, and Relationship to Bis-(Azooximates) and Other Species. Inorg. Chem. 1996, 35 (9), 2442−2447. Chang, M.-C.; Otten, E. Reduction of (Formazanate)Boron Difluoride Provides Evidence for an N -Heterocyclic B(I) Carbenoid Intermediate. Inorg. Chem. 2015, 54 (17), 8656−8664. Barbon, S. M.; Reinkeluers, P. A.; Price, J. T.; Staroverov, V. N.; Gilroy, J. B. Structurally Tunable 3-Cyanoformazanate Boron Difluoride Dyes. Chem. - Eur. J. 2014, 20 (36), 11340−11344. Barbon, S. M.; Buddingh, J. V.; Maar, R. R.; Gilroy, J. B. Boron Difluoride Adducts of a Flexidentate Pyridine-Substituted Formazanate Ligand: Property Modulation via Protonation and Coordination Chemistry. Inorg. Chem. 2017, 56 (19), 12003−12011. Barbon, S. M.; Price, J. T.; Reinkeluers, P. A.; Gilroy, J. B. Substituent-Dependent Optical and Electrochemical Properties of Triarylformazanate Boron Difluoride Complexes. Inorg. Chem. 2014, 53 (19), 10585−10593. Travieso-Puente, R.; Chang, M.-C.; Otten, E. Alkali Metal Salts of Formazanate Ligands: Diverse Coordination Modes as a Result of the Nitrogen-Rich [NNCNN] Ligand Backbone. Dalton Trans. 2014, 43 (48), 18035−18041. Chang, M.-C.; Dann, T.; Day, D. P.; Lutz, M.; Wildgoose, G. G.; Otten, E. The Formazanate Ligand as an Electron Reservoir: Bis(Formazanate) Zinc Complexes Isolated in Three Redox States. Angew. Chem., Int. Ed. 2014, 53 (16), 4118−4122. Hong, S.; Hill, L. M. R.; Gupta, A. K.; Naab, B. D.; Gilroy, J. B.; Hicks, R. G.; Cramer, C. J.; Tolman, W. B. Effects of ElectronDeficient β-Diketiminate and Formazan Supporting Ligands on Copper(I)-Mediated Dioxygen Activation. Inorg. Chem. 2009, 48 (10), 4514−4523. Mandal, A.; Schwederski, B.; Fiedler, J.; Kaim, W.; Lahiri, G. K. Evidence for Bidirectional Noninnocent Behavior of a Formazanate Ligand in Ruthenium Complexes. Inorg. Chem. 2015, 54 (16), 8126−8135. (34) Gilroy, J. B.; Patrick, B. O.; McDonald, R.; Hicks, R. G. Transition Metal

© 2019, IJCRCPS. All Rights Reserved

Complexes of 3-Cyano- and 3-Nitroformazans. Inorg. Chem. 2008, 47 (4), 1287−1294. Gilroy, J. B.; Ferguson, M. J.; McDonald, R.; Hicks, R. G. Synthesis and Characterization of Palladium Complexes of 3- Nitroformazans. Inorg. Chim. Acta 2008, 361 (12−13), 3388−3393. Travieso-Puente, R.; Broekman, J. O. P.; Chang, M.-C.; Demeshko, S.; Meyer, F.; Otten, E. Spin-Crossover in a PseudoTetrahedral Bis(Formazanate) Iron Complex. J. Am. Chem. Soc. 2016, 138 (17), 5503−5506.

(26) Kabir, E.; Wu, C.-H.; Wu, J. I.-C.; Teets, T. S. Heteroleptic Complexes of Cyclometalated Platinum with Triarylformazanate Ligands. Inorg. Chem. 2016, 55 (2), 956−963. Chang, M.-C.; Otten, E. Intramolecular Hydride Transfer Reactions in (Formazanate)Boron Dihydride Complexes. Organometallics 2016, 35 (4), 534−542. Compounds of General Interest. In Inorganic Syntheses; Coucouvanis, D., Ed.; John Wiley & Sons, Inc.: New York, USA, 2002; Vol. 33, pp 171−245. Samanta, S.; Ghosh, P.; Goswami, S. Recent Advances on the Chemistry of Transition Metal Complexes of 2-(Arylazo)Pyridines and Its Arylamino Derivatives. Dalton Trans. 2012, 41 (8), 2213−2226. (b) Sarkar, B.; Patra, S.; Fiedler, J.; Sunoj, R. B.; Janardanan, D.; Mobin, S. M.; Niemeyer, M.; Lahiri, G. K.; Kaim, W. Theoretical and Experimental Evidence for a New Kind of SpinCoupled Singlet Species: Isomeric Mixed-Valent Complexes Bridged by a Radical Anion Ligand. Angew. Chem., Int. Ed. 2005, 44, 5655−5658. (a) Das, A.; Scherer, T.; Maji, S.; Mondal, T. K.; Mobin, S. M.; Urbanos, F. A.; Jimenez-Aparicio, R.; Kaim, W.; Lahiri, G. K.́ Reductive Approach to Mixed Valency (n = 1−) in the Pyrazine Ligand-Bridged [(acac)2Ru(μ-L2−)Ru(acac)2]n (L2− = 2,5-Pyrazinedicarboxylate) Through Experiment and Theory. Inorg. Chem. 2011, 50, 7040−7049. (b) Kundu, T.; Sarkar, B.; Mondal, T. P.; Mobin, S. M.; Urbanos, F. A.; Fiedler, J.; Jimenez-Aparicio, R.; Kaim, W.; Lahiri,́ G. K. Redox-Rich Spin-Spin Coupled Semiquinoneruthenium Dimers with intense Near-IR Absorption. Inorg. Chem. 2011, 50, 4753−4763. Kahn, O. Molecular Magnetism; VCH: New York, 1993; p 107.

(22) (a) Kahn, O. Molecular Magnetism; VCH: New York, 1993; p 257. (b) Weng, C. Y. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, 1968.

(27) (a) Camacho Gonzalez, J.; Morales-Verdejo, C.; MunozCastro, A. Variation of through-space magnetic response properties upon the formation of cation−π interactions: a survey of [Ag(ηCH2CH2)3] + via DFT calculations. New J. Chem. 2015, 39, 4244− 4248. (b) Wang, J.; Hou, L.; Browne, W. R.; Feringa, B. L. Photoswitchable Intramolecular Through-Space Magnetic Interaction. J. Am. Chem. Soc. 2011, 133, 8162−8164. (c) Butcher, R. T.; Novoa, J. J.; Ribas-Ariño, J.; Sandvik, A. W.; Turnbull, M. M.; Landee, C. P.; Wells, B. M.; Awwadi, F. F. Strong through-space two-halide magnetic exchange of − 234 K in (2,5-dimethylpyrazine)copper(II) bromide. Chem. Commun. 2009, 1359−1361. (d) Barral, M. C.; Jimenez-́ Aparicio, R.; Perez-Quintanilla, D.; Priego, J. L.; Royer, E. C.; Torres,́ M. R.; Urbanos, F. A. Magnetic Properties of Diruthenium(II,III) Carboxylate Compounds. Crystal Structures of Ru2Cl(μ-O2CCH□CHCH□CHMe)4 and Ru2Cl(μ-O2CCH2OMe)4. Inorg. Chem. 2000, 39, 65−70. (24) O'Connor, C. J. Magnetochemistry- Advances in Theory and Experimentation. Prog. Inorg. Chem. 2007, 29, 203−283.

(28) (a) Roy, S.; Sarkar, B.; Imrich, H.-G.; Fiedler, J.; Zališ , S.;̌ Jimenez-Aparicio, R.; Urbanos, F. A.; Mobin, S. M.; Lahiri, G. K.́ Charged, but Found "Not Guilty": Innocence of the Suspect Bridging Ligands [RO(O)CNNC(O)OR]2− = L2− in [(acac)2Ru(μ-L)Ru- (acac)2]n , n = + , 0, − , 2−. Inorg. Chem. 2012, 51, 9273−9281. (b) Das, D.; Sarkar, B.; Kumbhakar, D.; Mondal, T. K.; Mobin, S. M.; Fiedler, J.; Urbanos, F. A.; Jimenez-Aparicio, R.; Kaim, W.; Lahiri, G.́ K. Bis(acetylacetonato)ruthenium Complexes of Noninnocent 1,2- Dioxolene Ligands: Qualitatively Different Bonding in Relation to Monoimino and Diimino Analogues. Chem. - Eur. J. 2011, 17, 11030− 11040.

(29) (a) Creutz, C. Prog. Inorg. Chem. 1983, 30, 1−73. (b) Ansari, M. A.; Mandal, A.; Beyer, K.; Paretzki, A.; Schwederski, B.; Kaim, W.; Lahiri, G. K. Non-innocence and mixed valency in triand tetranuclear ruthenium complexes of a heteroquinone bridging ligand. Dalton Trans. 2017, 46, 15589−15598.

(30) (a) Miller, J.; Min, K. S. Oxidation Leading to Reduction: Redox-Induced Electron Transfer (RIET). Angew. Chem., Int. Ed. 2009, 48, 262−272. (b) Ghumaan, S.; Sarkar, B.; Patra, S.; van Slageren, J.; Fiedler, J.; Kaim, W.; Lahiri, G. K. Sensitive Oxidation State Ambivalence in Unsymmetrical Three-Center (M/Q/M) Systems [(acac)2Ru(μ-Q)Ru(acac)2] n , Q = 1,10-Phenanthroline-5,6- dione or 1,10-Phenanthroline-5,6-diimine (n = + , 0, − , 2−). Inorg. Chem. 2005, 44, 3210−3214. Das, A.; Kundu, T.; Mobin, S. M.; Priego, J. L.; Jimenez-́ Aparicio, R.; Lahiri, G. K. Influence of ancillary ligands on the electronic structure and anion sensing features of ligand bridged diruthenium complexes. Dalton Trans. 2013, 42, 13733−13746. Ghumaan, S.; Sarkar, B.; Maji,

© 2019, IJCRCPS. All Rights Reserved

S.; Puranik, V. G.; Fiedler, J.; Urbanos, F. A.; Jimenez-Aparicio, R.; Kaim, W.; Lahiri, G. K. Valence- ´ State Analysis through Spectroelectrochemistry in a Series of Quinonoid-Bridged Diruthenium Complexes [(acac)2Ru(μ-L)Ru- (acac)2]n (n = + 2, + 1, 0, − 1, − 2). Chem. - Eur. J. 2008, 14, 10816−10828. Gayathri, P.; Kumar, A. S.; Kamraj, S. An Unusual Electrochemical Reductive Cleavage of Azo Dye into Highly Redox Active Copolymeric Aniline Derivatives on a MWCNT Modified Electrode Surface at Neutral pH and Its Electroanalytical Features. J. Phys. Chem. C 2015, 119, 7791−7801. Kumbhakar, D.; Sarkar, B.; Das, A.; Das, A. K.; Mobin, S. M.; Fiedler, J.; Kaim, W.; Lahiri, G. K. Valence structures of the diastereomeric complexes meso- and rac-[Ru2(acac)4(μ-Q)]n (n = 2-, 1-, 0, 1+, 2+) with the multiple quinonoid bridging ligand Q = 1,2,4,5- tetraimino-3,6-diketocyclohexane. Dalton Trans. 2009, 9645−9652. Kaim, W. Concepts for metal complex chromophors absorbing in the near infrared. Coord. Chem. Rev. 2011, 255, 2503−2513. Kobayashi, T.; Nishina, Y.; Shimizu, K. G.; Satô, G. P. Diacetonitrilebis(β-diketonato)ruthenium(II) Complexes. Their Preparation and Use as Intermediates for the Synthesis of Mixedligand β- Diketonato Ruthenium(III) Complexes. Chem. Lett. 1988, 17, 1137−1140. Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. Mixed Phosphine 2,2′- bipyridine Complexes of Ruthenium. Inorg. Chem. 1978, 17, 3334−3341. Goswami, S.; Chakravarty, A. R.; Chakravorty, A. Chemistry of Ruthenium. 7. Aqua Complexes of Isomeric Bis[(2-arylazo)pyridine]- ruthenium(II) Moieties and Their Reactions: Solvolysis, Protic Equilibriums, and Electrochemistry. Inorg. Chem. 1983, 22, 602−609. Das, P.; Biswas, A. N. 1-Phenyldiazenyl-8-Phenylhydrazononaphthalene-7(8H)-One-2- ol: Co-Existence of Azo-Hydroxy and Hydrazo-Keto Forms. J. Chem. Crystallogr. 2010, 40, 1167−1169. Krejcik, M.; Danek, M.; Hartl, F. Simple Construction of An Infrared Optically Transparent Thin-layer Electrochemical Cell Applications to the Redox Reactions of Ferrocene, Mn2(CO)10 and Mn(CO)3,(3,5-di-t-butyl-catecholate)−. J. Electroanal. Chem. Interfacial Electrochem. 1991, 317, 179−187. (a) Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112−122. (b) Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1997. van der Sluis, P.; Spek, A. L. BYPASS: An Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. Acta Crystallogr., Sect. A: Found. Crystallogr. 1990, 46, 194− 201. Lee, C.; Yang, W.; Parr, R. G. Development of the ColicSalvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785− 789.

(31) (a) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy-Adjusted ab initio Pseudopotentials for the Second and Third Row Transition Elements. Theor. Chim. Acta 1990, 77, 123− 141. (b) Fuentealba, P.; Preuss, H.; Stoll, H.; von Szentpaly, L. A Proper Account of Core-Polarization with Pseudopotentials: Single Valence-Electron Alkali Compounds. Chem. Phys. Lett. 1982, 89, 418−422. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 (Revision A.02); Gaussian, Inc., Wallingford, CT, 2009.

(32) (a) Bauernschmitt, R.; Ahlrichs, R. Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory. Chem. Phys. Lett. 1996, 256, 454−464. (b) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An Efficient Implementation of Time-Dependent Density-Functional Theory for the Calculation of Excitation Energies of Large Molecules. J. Chem. Phys. 1998, 109, 8218−8225. (c) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. J. Chem. Phys. 1998, 108, 4439−4450.

(33) (a) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. J. Phys. Chem. A 1998, 102, 1995−2001. (b) Cossi, M.; Barone, V. Time-Dependent Density Functional

© 2019, IJCRCPS. All Rights Reserved

Theory for Molecules in Liquid Solutions. J. Chem. Phys. 2001, 115, 4708− 4718. (c) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the CPCM Solvation Model. J. Comput. Chem. 2003, 24, 669−681. (45) Leonid, S. Chemissian 1.7; 2005−2010. Available at http:// www.chemissian.com. (46) Zhurko, D. A.; Zhurko, G. A. ChemCraft 1.5; Plimus, San Diego, CA. Available at http://www.chemcraftprog.com.

(34) Noffke, A. L.; Habtemariam, A.; Pizarro, A. M.; Sadler, P. J. Designing organometallic compounds for catalysis and therapy. Chem. Commun. 2012, 48 (43), 5219−5246. Hanif, M.; Hartinger, C. G. Anticancer metallodrugs: where is the next cisplatin? Future Med. Chem. 2018, 10 (6), 615−617. (3) Kenny, R. G.; Marmion, C. J. Toward Multi-Targeted Platinum and Ruthenium Drugs-A New Paradigm in Cancer Drug Treatment Regimens? Chem. Rev. 2019, 119 (2), 1058−1137. Murray, B. S.; Menin, L.; Scopelliti, R.; Dyson, P. J. Conformational control of anticancer activity: the application of arene-linked dinuclear ruthenium(ii) organometallics. Chem. Sci. 2014, 5 (6), 2536−2545. Clavel, C. M.; Paunescu, E.; Nowak-Sliwinska, P.; Griffioen, A. W.; Scopelliti, R.; Dyson, P. J. Modulating the Anticancer Activity of Ruthenium(II)-Arene Complexes. J. Med. Chem. 2015, 58 (8), 3356− 3365. Kubanik, M.; Kandioller, W.; Kim, K.; Anderson, R. F.; Klapproth, E.; Jakupec, M. A.; Roller, A.; Sohnel, T.; Keppler, B. K.; Hartinger, C. G. Towards targeting anticancer drugs: ruthenium(II)- arene complexes with biologically active naphthoquinone-derived ligand systems. Dalton Trans. 2016, 45 (33), 13091−13103. Meier-Menches, S. M.; Gerner, C.; Berger, W.; Hartinger, C. G.; Keppler, B. K. Structure-activity relationships for ruthenium and osmium anticancer agents - towards clinical development. Chem. Soc. Rev. 2018, 47 (3), 909−928. Wang, X.; Wang, X.; Jin, S.; Muhammad, N.; Guo, Z. StimuliResponsive Therapeutic Metallodrugs. Chem. Rev. 2019, 119 (2), 1138−1192. Lameijer, L. N.; Hopkins, S. L.; Breve, T. G.; Askes, S. H. C.; Bonnet, S. D-Versus L-Glucose Conjugation: Mitochondrial Targeting of a Light-Activated Dual-Mode-of-Action RutheniumBased Anticancer Prodrug. Chem. - Eur. J. 2016, 22 (51), 18484− 18491. Garci, A.; Dobrov, A. A.; Riedel, T.; Orhan, E.; Dyson, P. J.; Arion, V. B.; Therrien, B. Strategy to Optimize the Biological Activity of Arene Ruthenium Metalla-Assemblies. Organometallics 2014, 33 (14), 3813−3822. Barry, N. P. E.; Sadler, P. J. Dicarba-closo-dodecarboranecontaining half-sandwich complexes of ruthenium, osmium, rhodium and iridium: biological relevance and synthetic strategies. Chem. Soc. Rev. 2012, 41 (8), 3264−3279. Liu, Z.; Sadler, P. J. Organoiridium Complexes: Anticancer Agents and Catalysts. Acc. Chem. Res. 2014, 47 (4), 1174−1185. Johnstone, T. C.; Suntharalingam, K.; Lippard, S. J. The Next Generation of Platinum Drugs: Targeted Pt(II) Agents, Nanoparticle Delivery, and Pt(IV) Prodrugs. Chem. Rev. 2016, 116 (5), 3436− 3486. Pizarro, A. M.; Sadler, P. J. Cancer chemistry: designing new drugs for cancer treatment. Mol. Biol. Cancer 2013, 438−460. Li, Y.-Q.; Yin, J.-Y.; Liu, Z.-Q.; Li, X.-P. Copper efflux transporters ATP7A and ATP7B: Novel biomarkers for platinum drug resistance and targets for therapy. IUBMB Life 2018, 70 (3), 183− 191. Burger, H.; Loos, W. J.; Eechoute, K.; Verweij, J.; Mathijssen, R. H. J.; Wiemer, E. A. C. Drug transporters of platinum-based anticancer agents and their clinical significance. Drug Resist. Updates 2011, 14 (1), 22−34. Katano, K.; Safaei, R.; Samimi, G.; Holzer, A.; Rochdi, M.; Howell, S. B. The copper export pump ATP7B modulates the cellular pharmacology of carboplatin in ovarian carcinoma cells. Mol. Pharmacol. 2003, 64 (2), 466−473. Leonhardt, K.; Gebhardt, R.; Moessner, J.; Lutsenko, S.; Huster, D. Functional Interactions of Cu-ATPase ATP7B with Cisplatin and the Role of ATP7B in the Resistance of Cells to the Drug. J. Biol. Chem. 2009, 284 (12), 7793−7802. Komatsu, M.; Sumizawa, T.; Mutoh, M.; Chen, Z.-S.; Terada, K.; Furukawa, T.; Yang, X.-L.; Gao, H.; Miura, N.; Sugiyama, T.; Akiyama, S.-I. Copper-transporting P-type adenosine triphosphatase (ATP7B) is associated with cisplatin resistance. Cancer Res. 2000, 60 (5), 1312−1316. Safaei, R.; Adams, P. L.; Maktabi, M. H.; Mathews, R. A.; Howell, S. B. The CXXC motifs in the metal binding domains are required for ATP7B to mediate resistance to cisplatin. J. Inorg. Biochem. 2012, 110, 8−17. Mangala, L. S.; Zuzel, V.; Schmandt, R.; Leshane, E. S.; Halder, J. B.; Armaiz-Pena, G. N.; Spannuth, W. A.; Tanaka, T.; Shahzad, M. M. K.; Lin, Y. G.; Nick, A. M.; Danes, C. G.; Lee, J.-W.; Jennings, N. B.; Vivas-Mejia, P. E.; Wolf, J. K.; Coleman, R. L.; Siddik, Z. H.; Lopez-Berestein, G.; Lutsenko, S.; Sood, A. K. Therapeutic Targeting of ATP7B in Ovarian Carcinoma. Clin. Cancer Res. 2009, 15 (11), 3770−3780. Forbes, J. R.; Cox, D. W. Copper-dependent trafficking of Wilson disease mutant ATP7B proteins. Hum. Mol. Genet. 2000, 9 (13), 1927−1935. Strausak, D.; La Fontaine, S.; Hill, J.; Firth, S. D.; Lockhart, P. J.; Mercer, J. F. B. The role of GMXCXXC metal binding sites

© 2019, IJCRCPS. All Rights Reserved

in the copper-induced redistribution of the Menkes protein. J. Biol. Chem. 1999, 274 (16), 11170−11177. Schaefer, M.; Hopkins, R. G.; Failla, M. L.; Gitlin, J. D. Hepatocyte-specific localization and copper-dependent trafficking of the Wilson's disease protein in the liver. Am. J. Physiol. 1999, 276 (3), G639−G646. Nakayama, K.; Miyazaki, K.; Kanzaki, A.; Fukumoto, M.; Takebayashi, Y. Expression and cisplatin sensitivity of coppertransporting P-type adenosine triphosphatase (ATP7B) in human solid carcinoma cell lines. Oncol. Rep. 2001, 8 (6), 1285−1287. Nakayama, K.; Kanzaki, A.; Ogawa, K.; Miyazaki, K.; Neamati, N.; Takebayashi, Y. Copper-transporting P-type adenosine triphosphatase (ATP7B) as a cisplatin based chemoresistance marker in ovarian carcinoma: Comparative analysis with expression of MDR1, MRP1, MRP2, LRP and BCRP. Int. J. Cancer 2002, 101 (5), 488− 495. Kanzaki, A.; Toi, M.; Neamati, N.; Miyashita, H.; Oubu, M.; Nakayama, K.; Bando, H.; Ogawa, K.; Mutoh, M.; Mori, S.; Terada, K.; Sugiyama, T.; Fukumoto, M.; Takebayashi, Y. Copper-transporting P-type adenosine triphosphatase (ATP7B) is expressed in human breast carcinoma. Jpn. J. Cancer Res. 2002, 93 (1), 70−77. Higashimoto, M.; Kanzaki, A.; Shimakawa, T.; Konno, S.; Naritaka, Y.; Nitta, Y.; Mori, S.; Shirata, S.; Yoshida, A.; Terada, K.; Sugiyama, T.; Ogawa, K.; Takebayashi, Y. Expression of coppertransporting P-type adenosine triphosphatase in human esophageal carcinoma. Int. J. Mol. Med. 2003, 11 (3), 337−341. Miyashita, H.; Nitta, Y.; Mori, S.; Kanzaki, A.; Nakayama, K.; Terada, K.; Sugiyama, T.; Kawamura, H.; Sato, A.; Morikawa, H.; Motegi, K.; Takebayashi, Y. Expression of copper-transporting P-type adenosine triphosphatase (ATP7B) as a chemoresistance marker in human oral squamous cell carcinoma treated with cisplatin. Oral Oncol. 2003, 39 (2), 157−162. Ohbu, M.; Ogawa, K.; Konno, S.; Kanzaki, A.; Terada, K.; Sugiyama, T.; Takebayashi, Y. Copper-transporting P-type adenosine triphosphatase (ATP7B) is expressed in human gastric carcinoma. Cancer Lett. 2003, 189 (1), 33−38. (Samimi, G.; Varki, N. M.; Wilczynski, S.; Safaei, R.; Alberts, D. S.; Howell, S. B. Increase in expression of the copper transporter ATP7A during platinum drug-based treatment is associated with poor survival in ovarian cancer patients. Clin. Cancer Res. 2003, 9 (16), 5853−5859. Samimi, G.; Safaei, R.; Katano, K.; Holzer, A. K.; Rochdi, M.; Tomioka, M.; Goodman, M.; Howell, S. B. Increased expression of the copper efflux transporter ATP7A mediates resistance to cisplatin, carboplatin, and oxaliplatin in ovarian cancer cells. Clin. Cancer Res. 2004, 10 (14), 4661−4669. Samimi, G.; Katano, K.; Holzer, A. K.; Safaei, R.; Howell, S. B. Modulation of the cellular pharmacology of cisplatin and its analogs by the copper exporters ATP7A and ATP7B. Mol. Pharmacol. 2004, 66 (1), 25−32.

(34) Thota, S.; Rodrigues, D. A.; Crans, D. C.; Barreiro, E. J. Ru(II) Compounds: Next-Generation Anticancer Metallotherapeutics? J. Med. Chem. 2018, 61 (14), 5805−5821.

(35) Lenis-Rojas, O. A.; Robalo, M. P.; Tomaz, A. I.; Carvalho, A.; Fernandes, A. R.; Marques, F.; Folgueira, M.; Yanez, J.; VazquezGarcia, D.; Lopez Torres, M.; Fernandez, A.; Fernandez, J. J. Ru(II)(p-cymene) Compounds as Effective and Selective Anticancer Candidates with No Toxicity in Vivo. Inorg. Chem. 2018, 57 (21), 13150−13166.

(36) Lenis-Rojas, O. A.; Robalo, M. P.; Tomaz, A. I.; Carvalho, A.; Fernandes, A. R.; Marques, F.; Folgueira, M.; Yanez, J.; VazquezGarcia, D.; Lopez Torres, M.; Fernandez, A.; Fernandez, J. J. RuII(pcymene) Compounds as Effective and Selective Anticancer Candidates with No Toxicity in Vivo. Inorg. Chem. 2018, 57 (21), 13150−13166.

(37) Li, J.; Tian, M.; Tian, Z.; Zhang, S.; Yan, C.; Shao, C.; Liu, Z. Half-Sandwich Iridium(III) and Ruthenium(II) Complexes Containing P-P-Chelating Ligands: A New Class of Potent Anticancer Agents with Unusual Redox Features. Inorg. Chem. 2018, 57 (4), 1705−1716.

(38) Pettinari, R.; Marchetti, F.; Di Nicola, C.; Pettinari, C.; Galindo, A.; Petrelli, R.; Cappellacci, L.; Cuccioloni, M.; Bonfili, L.; Eleuteri, A. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. Ligand Design for N,O- or N,N-Pyrazolone-Based Hydrazones Ruthenium- (II)-Arene Complexes and Investigation of Their Anticancer Activity. Inorg. Chem. 2018, 57 (22), 14123−14133.

(39) Zhao, J.; Li, W.; Gou, S.; Li, S.; Lin, S.; Wei, Q.; Xu, G. Hypoxia-Targeting Organometallic Ru(II)-Arene Complexes with Enhanced Anticancer Activity in Hypoxic Cancer Cells. Inorg. Chem. 2018, 57 (14), 8396−8403. (40) Mohamed Kasim, M. S.; Sundar, S.; Rengan, R. Synthesis and structure of new binuclear ruthenium(II) arene benzil bis- (benzoylhydrazone) complexes: investigation on antiproliferative activity and apoptosis induction. Inorg. Chem. Front. 2018, 5 (3), 585−596.

(41) Du, Q.; Guo, L.; Tian, M.; Ge, X.; Yang, Y.; Jian, X.; Xu, Z.; Tian, Z.; Liu, Z. Potent Half-Sandwich Iridium(III) and Ruthenium- (II) Anticancer Complexes Containing a Pˆ O-Chelated Ligand. Organometallics 2018, 37 (17), 2880−2889.

© 2019, IJCRCPS. All Rights Reserved

(42) Gatti, A.; Habtemariam, A.; Romero-Canelon, I.; Song, J.-I.; Heer, B.; Clarkson, G. J.; Rogolino, D.; Sadler, P. J.; Carcelli, M. HalfSandwich Arene Ruthenium(II) and Osmium(II) Thiosemicarbazone Complexes: Solution Behavior and Antiproliferative Activity. Organometallics 2018, 37 (6), 891−899.

(43) Aird, R. E.; Cummings, J.; Ritchie, A. A.; Muir, M.; Morris, R. E.; Chen, H.; Sadler, P. J.; Jodrell, D. I. In vitro and in vivo activity and cross resistance profiles of novel ruthenium (II) organometallic arene complexes in human ovarian cancer. Br. J. Cancer 2002, 86 (10), 1652−1657.

(44) Habtemariam, A.; Melchart, M.; Fernandez, R.; Parsons, S.; Oswald, I. D. H.; Parkin, A.; Fabbiani, F. P. A.; Davidson, J. E.; Dawson, A.; Aird, R. E.; Jodrell, D. I.; Sadler, P. J. Structure-Activity Relationships for Cytotoxic Ruthenium(II) Arene Complexes Containing N,N-, N,O-, and O, O-Chelating Ligands. J. Med. Chem. 2006, 49 (23), 6858−6868.

(45) van Rijt, S. H.; Hebden, A. J.; Amaresekera, T.; Deeth, R. J.; Clarkson, G. J.; Parsons, S.; McGowan, P. C.; Sadler, P. J. Amide linkage isomerism as an activity switch for organometallic osmium and ruthenium anticancer complexes. J. Med. Chem. 2009, 52 (23), 7753−7764.

(46) Grozav, A.; Balacescu, O.; Balacescu, L.; Cheminel, T.; Berindan-Neagoe, I.; Therrien, B. Synthesis, Anticancer Activity, and Genome Profiling of Thiazolo Arene Ruthenium Complexes. J. Med. Chem. 2015, 58 (21), 8475−8490.

(47) Lord, R. M.; Hebden, A. J.; Pask, C. M.; Henderson, I. R.; Allison, S. J.; Shepherd, S. L.; Phillips, R. M.; McGowan, P. C. Hypoxia-Sensitive Metal β-Ketoiminato Complexes Showing Induced Single-Strand DNA Breaks and Cancer Cell Death by Apoptosis. J. Med. Chem. 2015, 58 (12), 4940−4953.

(48) Yellol, J.; Perez, S. A.; Buceta, A.; Yellol, G.; Donaire, A.; Szumlas, P.; Bednarski, P. J.; Makhloufi, G.; Janiak, C.; Espinosa, A.; Ruiz, J. Novel C,N-Cyclometalated Benzimidazole Ruthenium(II) and Iridium(III) Complexes as Antitumor and Antiangiogenic Agents: A Structure-Activity Relationship Study. J. Med. Chem. 2015, 58 (18), 7310−7327.

(49) Chow, M. J.; Licona, C.; Pastorin, G.; Mellitzer, G.; Ang, W. H.; Gaiddon, C. Structural tuning of organoruthenium compounds allows oxidative switch to control ER stress pathways and bypass multidrug resistance. Chem. Sci. 2016, 7 (7), 4117−4124.

(50) Weiss, A.; Berndsen, R. H.; Dubois, M.; Muller, C.; Schibli, R.; Griffioen, A. W.; Dyson, P. J.; Nowak-Sliwinska, P. In vivo anti-tumor activity of the organometallic ruthenium(II)-arene complex [Ru(η6-pcymene)Cl2(pta)] (RAPTA-C) in human ovarian and colorectal carcinomas. Chem. Sci. 2014, 5 (12), 4742−4748. (51) Gupta, A.; Das, S.; Ray, K. A glimpse into the regulation of the Wilson disease protein, ATP7B, sheds light on the complexity of mammalian apical trafficking pathways. Metallomics 2018, 10 (3), 378−387.

(52) Nakayama, K.; Kanzaki, A.; Terada, K.; Mutoh, M.; Ogawa, K.; Sugiyama, T.; Takenoshita, S.; Itoh, K.; Yaegashi, N.; Miyazaki, K.; Neamati, N.; Takebayashi, Y. Prognostic value of the Cu-transporting ATPase in ovarian carcinoma patients receiving cisplatin-based chemotherapy. Clin. Cancer Res. 2004, 10 (8), 2804−2811. (53) Purkait, K.; Karmakar, S.; Bhattacharyya, S.; Chatterjee, S.; Dey, S. K.; Mukherjee, A. A hypoxia efficient imidazole-based RuII arene anticancer agent resistant to deactivation by glutathione. Dalton Trans. 2015, 44 (13), 5969−5973.

(54) Purkait, K.; Chatterjee, S.; Karmakar, S.; Mukherjee, A. Alteration of steric hindrance modulates glutathione resistance and cytotoxicity of three structurally related RuII-p-cymene complexes. Dalton Trans. 2016, 45 (20), 8541−8555.

(55) Moon, S.; Hanif, M.; Kubanik, M.; Holtkamp, H.; Soehnel, T.; Jamieson, S. M. F.; Hartinger, C. G. Organoruthenium and Osmium Anticancer Complexes Bearing a Maleimide Functional Group: Reactivity to Cysteine, Stability, and Cytotoxicity. ChemPlusChem 2015, 80 (1), 231−236.

(56) Betanzos-Lara, S.; Novakova, O.; Deeth, R. J.; Pizarro, A. M.; Clarkson, G. J.; Liskova, B.; Brabec, V.; Sadler, P. J.; Habtemariam, A. Bipyrimidine ruthenium(II) arene complexes: structure, reactivity and cytotoxicity. JBIC, J. Biol. Inorg. Chem. 2012, 17, 1033−1051.

(57) Bugarcic, T.; Habtemariam, A.; Deeth, R. J.; Fabbiani, F. P. A.; Parsons, S.; Sadler, P. J. Ruthenium(II) Arene Anticancer Complexes with Redox-Active Diamine Ligands. Inorg. Chem. 2009, 48 (19), 9444−9453.

(58) Dougan, S. J.; Habtemariam, A.; McHale, S. E.; Parsons, S.; Sadler, P. J. Catalytic organometallic anticancer complexes. Proc. Natl. Acad. Sci. U. S. A. 2008, 105 (33), 11628−11633.

© 2019, IJCRCPS. All Rights Reserved

(59) Romero-Canelon, I.; Salassa, L.; Sadler, P. J. The Contrasting Activity of Iodido versus Chlorido Ruthenium and Osmium Arene Azo- and Imino-pyridine Anticancer Complexes: Control of Cell Selectivity, Cross-Resistance, p53 Dependence, and Apoptosis Pathway. J. Med. Chem. 2013, 56 (3), 1291−1300. (

60) Romero-Canelon, I.; Pizarro, A. M.; Habtemariam, A.; Sadler, P. J. Contrasting cellular uptake pathways for chlorido and iodido iminopyridine ruthenium arene anticancer complexes. Metallomics 2012, 4 (12), 1271−1279. (61) Sarkar, A.; Acharya, S.; Khushvant, K.; Purkait, K.; Mukherjee, A. Cytotoxic RuII-p-cymene complexes of an anthraimidazoledione: halide dependent solution stability, reactivity and resistance to hypoxia deactivation. Dalton Trans. 2019, 48, 7187−7197.

(62) Perrin, D. D.; Armarego, W. L. F. Purification of Laboratory Chemicals, 3rd ed.; Pergamon Press: Oxford, U.K., 1988; p 391 pp.

(63) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K.; Ittel, S.; Nickerson, W. (η6-Hexamethylbenzene)ruthenium complexes. Inorg. Synth. 2007, 21, 74−78.

(64) Palatinus, L.; Chapuis, G. SUPERFLIP. A computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J. Appl. Crystallogr. 2007, 40 (4), 786−790.

(65) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008 , 64, 112 −122.

(66) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 2009 , 42 (2), 339 −341.

(67) Sheldrick, G. M. Tutorial on automated Patterson interpretation to find heavy atoms. Int. Union Crystallogr., Crystallogr. Symp. 1991 , 5, 145 −157.

(68) Lokeshwar, B. L.; Escatel, E.; Zhu, B. Cytotoxic activity and inhibition of tumor cell invasion by derivatives of a chemically modified tetracycline CMT-3 (COL-3). Curr. Med. Chem. 2001 , 8 (3), 271 −279.

(69) Alley, M. C.; Scudiero, D. A.; Monks, A.; Hursey, M. L.; Czerwinski, M. J.; Fine, D. L.; Abbott, B. J.; Mayo, J. G.; Shoemaker, R. H.; Boyd, M. R. Feasibility of drug screening with panels of human tumor cell lines using a microculture tetrazolium assay. Cancer Res. 1988 , 48 (3), 589 −601.

(70) Braiterman, L.; Nyasae, L.; Guo, Y.; Bustos, R.; Lutsenko, S.; Hubbard, A. Apical targeting and Golgi retention signals reside within a 9-amino acid sequence in the copper-ATPase, ATP7B. Am. J. Physiol. 2009 , 296 (2), G433 −G444.

(71) Ashraf, A.; Hanif, M.; Kubanik, M.; Sohnel, T.; Jamieson, S. M. F.; Bhattacharyya, A.; Hartinger, C. G. Aspirin-inspired organometallic compounds: Structural characterization and cytotoxicity. J. Organomet. Chem. 2017 , 839, 31 −37.

(72) Pantic, D. N.; Arandelovic, S.; Radulovic, S.; Roller, A.; Arion, V. B.; Grguric-Sipka, S. Synthesis, characterisation and cytotoxic activity of organoruthenium(II)-halido complexes with 1H-benzimidazole-2-carboxylic acid. J. Organomet. Chem. 2016, 819, 61−68.

(73) Berger, I.; Hanif, M.; Nazarov, A. A.; Hartinger, C. G.; John, R. O.; Kuznetsov, M. L.; Groessl, M.; Schmitt, F.; Zava, O.; Biba, F.; Arion, V. B.; Galanski, M.; Jakupec, M. A.; Juillerat-Jeanneret, L.; Dyson, P. J.; Keppler, B. K. In vitro anticancer activity and biologically relevant metabolization of organometallic ruthenium complexes with carbohydrate-based ligands. Chem. - Eur. J. 2008 , 14 (29), 9046 − 9057.

(74) Koch, S.; Mayer, F.; Honecker, F.; Schittenhelm, M.; Bokemeyer, C. Efficacy of cytotoxic agents used in the treatment of testicular germ cell tumours under normoxic and hypoxic conditions in vitro. Br. J. Cancer 2003 , 89 (11), 2133 −2139.

(75) Katano, K.; Kondo, A.; Safaei, R.; Holzer, A.; Samimi, G.; Mishima, M.; Kuo, Y.-M.; Rochdi, M.; Howell, S. B. Acquisition of resistance to cisplatin is accompanied by changes in the cellular pharmacology of copper. Cancer Res. 2002 , 62 (22), 6559 −6565.

(76) Chandel, N. S.; Maltepe, E.; Goldwasser, E.; Mathieu, C. E.; Simon, M. C.; Schumacker, P. T. Mitochondrial reactive oxygen species trigger hypoxia-induced transcription. Proc. Natl. Acad. Sci. U. S. A. 1998 , 95 (20), 11715 −11720.

(77) Wang, G. L.; Semenza, G. L. Characterization of hypoxiainducible factor 1 and regulation of DNA binding activity by hypoxia. J. Biol. Chem. 1993 , 268 (29), 21513 −21518.

(78) Wang, G. L.; Semenza, G. L. Desferrioxamine induces erythropoietin gene expression and hypoxia-inducible factor 1 DNA-binding activity: implications for models of hypoxia signal transduction. Blood 1993 , 82 (12), 3610 −3615.

(79) Polishchuk, E. V.; Concilli, M.; Iacobacci, S.; Chesi, G.; Pastore, N.; Piccolo, P.; Paladino, S.; Baldantoni, D.; van Ijzendoorn, S. C. D.; Chan, J.; Chang, C. J.; Amoresano, A.; Pane, F.; Pucci, P.; Tarallo, A.; Parenti, G.; Brunetti-Pierri, N.; Settembre, C.; Ballabio, A.; Polishchuk, R. S. Wilson Disease Protein ATP7B Utilizes Lysosomal Exocytosis to Maintain Copper Homeostasis. Dev. Cell 2014 , 29 (6), 686 −700.

© 2019, IJCRCPS. All Rights Reserved

(80) Dolgova, N. V.; Olson, D.; Lutsenko, S.; Dmitriev, O. Y. The soluble metal-binding domain of the copper transporter ATP7B binds and detoxifies cisplatin. Biochem. J. 2009 , 419 (1), 51 −56.

Access this Article in Online

Website: www.ijcrcps.com

Subject: Chemistry

Quick Response Code

DOI: 10.22192/ijcrcps.2019.06.12.002

How to cite this article:
Prithwiraj Byabartta. (2019). Ru-N3-RaaiR: Homoleptic bis chelates of Ruthenium: CIS-Diazido-Ruthenium(II)-bis-{1-(alkyl)-2-(arylazo)imidazole (RaaiR)} complexes: Synthesis, spectra and electrochemistry. Int. J. Curr. Res. Chem. Pharm. Sci. 6(12): 12-35.
DOI: http://dx.doi.org/10.22192/ijcrcps.2019.06.12.002

© 2019, IJCRCPS. All Rights Reserved