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Azo-oximate metal-carbonyl to metallocarboxylic acid *via* the intermediate Ir(III) radical congener: quest for co-ligand driven stability of open- and closed-shell complexes †

Soumitra Dinda, [a] Shuvam Pramanik, [b] Jaydeep Basu, [a] Sarat Chandra Patra, [b] Kausikisankar Pramanik *[b] and Sanjib Ganguly *[a]

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Abstract

The redox non-innocent behavior of the diaryl-azo-oxime ligand L^{NOH}**1** has been accentuated *via* the synthesis of metastable anion radical complexes of type *trans*-[Ir($L^{NO\cdot-}$)Cl(CO)(PPh_3)$_2$] **2** (CO is *trans* to azo group of the ligand) by the oxidative coordination reaction of **1** with Vaska's complex. The stereochemical role of co-ligands *vis-à-vis* the interplay of π-bonding has been found to be decisive in controlling the aptitude of the coordinated redox non-innocent ligand to accept or reject an electron. This has been clarified *via* the isolation of quite a few complexes as well as the failure to synthesize some others. The oxidized analogues of type *trans*-[Ir(L^{NO-})Cl(CO)(PPh_3)$_2$]$^+$**2**$^+$ (CO and azo group of the ligand are *trans*) as well as its *cis* isomer *cis*-[Ir(L^{NO-})Cl(CO)(PPh_3)$_2$]$^+$**3**$^+$ (CO and azo group of the ligand are *cis*) have been structurally characterized but the radical anion congener of the latter could not be synthesized. Furthermore, the closed shell complexes [Ir(L^{NO-})Cl$_2$(PPh_3)$_2$] **4** and [Ir(L^{NO-})$_2$Cl(PPh_3)] **5** have been well characterized by diffraction as well as spectral techniques but their corresponding azo anion radical complexes could not be isolated and this is attributed to the *trans* influence of ancillary ligands. The anion

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ARTICLE

Ruthenocycles of benzothiazolyl and pyridyl hydrazones with ancillary PAHs: Synthesis, structure, electrochemistry and antimicrobial activity

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Two types of bivalent ruthenium complexes [RuL^{Py}(CO)Cl(PPh$_3$)$_3$] **3** and [RuL^{Benz}(CO)Cl(PPh$_3$)$_3$] **4** were synthesized starting from [RuH(CO)Cl(PPh$_3$)$_3$] and heterocyclic hydrazoneligands **1** and **2** respectively. X-ray diffraction studies reveal that in both type of complexes, the ligands behave as monoanionic bidentate $N_{hydrazonyl}$ and $N_{pyridyl}$/ $N_{benzothiazolyl}$ donors towards ruthenium(II), thereby furnishing four-membered metallacycles. The multiple transitions in the electronic spectra have been elucidated by Time Dependent Density Functional Theory (TDDFT). The redox active nature of both **3** and **4** have been substantiated from the well-defined oxidative responses and theoretical scrutiny corroborates that one of them is exclusively ligand centred while the other one is chiefly due to the Ru^{II}/Ru^{III} oxidation. Both the type of complexes exhibit a significant antimicrobial activity, although the activity of **4** is more prominent, particularly over *Pseudomonas*. These are analyzed by measuring ZOI, MIC as well as extent of membrane damage and protein leakage studies. The complexes probably cause free-radical facilitated oxidative damage to the bacterial cells during the course of their activity.

Introduction

Among the major advances in medical science has been the development of antimicrobials that are the most indispensable armaments in combating bacterial infections.[1]Consequently, antibacterial substances are imperative in treating infectious diseases caused by pathogenic bacteria like *Enterococcus*, *Staphylococcus*, *Enterobacter*, *Klebsiella pneumoniae*, *Acinetobacter* and *Pseudomonas aeruginosa*.[2] It is owing to the extensive usage of antibiotics that have rendered such pathogenic bacteria progressively more resistant to commercially accessible antimicrobial agents, thereby reducing the competence of treatment and subsequently leading to significant economic losses.[3] The escalating cases of microbial resistance has become a foremost challenge to the scientific community since it may create a global menace to human life.[4]Therefore, the synthesis and exploration for new antimicrobials has become a prime requisite to sustain human life. In the recent past, several hydrazone derivatives have been screened for their analgesic,[5]antiinflammatory,[6] antioxidant,[7]anticonvulsant,[8]antiparasitic,[9] antitubercular,[10] anti-HIV[11] and anticancer[12] as well as antimicrobial[13] activities. Interestingly, the biological activity of hydrazones have been found to be appreciably improved upon coordination to ruthenium(II).This may be attributed to their ability to mimic iron when bound to biomolecules.[14] Thus, the synthesis of new ruthenium hydrazone complexes and exploration of their biological activities is significant for the further advancement in the medicinal research and welfare of the society.

In this connection and also as a part of our pursuit for new antimicrobials, we have designed and efficaciously synthesized three pyridyl hydrazone ligands of type HL^{Py}**1** and two benzothiazolylhydrazone ligands of type HL^{Benz}**2** containing pendant polyaromatic hydrocarbons(PAHs). The design of the ligands was based upon the well-known biological activity as well as fascinating pharmacological profile of the benzothiazole framework. In fact, benzothiazole is still one of the well understood resourceful group that can exhibit antimicrobial activity[15]and its derivatives are characterized by diverse biological functions. The dangling polyaromatic hydrocarbons, especially the pyrene moiety are known to display remarkable fluorescence and this property may be suitably exploited for biological and bio-imaging investigations.[16] These ligands have been employed to isolate the heterocyclic hydrazone derived four-membered ruthenocycles of type [RuL^{Py}(CO)Cl(PPh$_3$)$_3$] **3** (**3a**, **3b**, **3c**) and [RuL^{Benz}(CO)Cl(PPh$_3$)$_3$] **4** (**4a**, **4b**) upon treating [RuH(CO)Cl(PPh$_3$)$_3$] with **1** and **2** respectively. The complexes

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† Electronic supplementary information (ESI) available: X-ray crystallographic data for **3a**, **3b**, **3c** and **4b**, selected experimental and theoretical bond parameters, absorption spectra, electrochemical data, NMR spectra of all compounds, relevant DFT results. CCDC 1887300(**3a**), 1937129(**3b**), 1948734(**3c**) and 1951462(**4b**).For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

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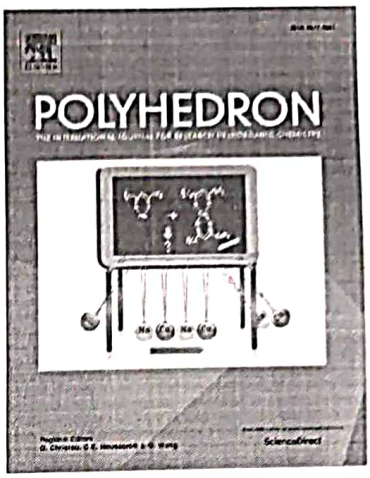

Rhodium assisted *peri*-C–H activation in benzothiazolyl-hydrazone derivatized pyrene

Soumitra Dinda, Sarat Chandra Patra, Tridib Samanta, Ambika Basu, Kausikisankar Pramanik, Sanjib Ganguly

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Rhodium assisted *peri*-C–H activation in benzothiazolyl-hydrazone derivatized pyrene

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Abstract

Benzothiazolyl hydrazones incorporating polyaromatic pyrene moiety, **1** (H_2L^{Pyr}), have been smartly employed as a directing group (DG) to bring about the rhodium assisted C–H bond activation at the peri position of pyrene. The formation of *peri*-metallated $[Rh^{III}(L^{Pyr})(H)(PPh_3)_2]$ **3** is a logical consequence of its co-product, a dihalo complex $[Rh^{III}(HL^{Pyr})Cl_2(PPh_3)_2]$ **2**, in due course of the reaction between the ligand and Wilkinson's catalyst. The initial formation of the complex **2** in the initial stage of the reaction has been envisaged as the driving force for the generation of organometallic complex **3**, where paucity of chloride ion triggers the tridentate coordination mode $[L^{Pyr}]^{2-}$ *via in situ* C–H activation. The underlying mechanism of formation of **3** has been observed to proceed *via* oxidative addition, involving a two electron transfer from the appropriate electron reservoir $[Rh^{I}]$ to the ligand scaffold and this is accompanied by an intramolecular ligand to metal hydride transfer via a PCET pathway. Complexes **2** and **3** have been found to be redox active and are prone to oxidation at moderate potentials where the responses are analyzed to be exclusively ligand-centred in nature. Significantly, cyclometallated complex is more prone to oxidation relative to the non-activated compound, **2**. The redox event has been meticulously scrutinized by DFT, revealing the destabilization of HOMO in **3** by ~0.5 eV in comparison to **2**. Both complexes provide rich optoelectronic features that have been analyzed to be predominantly ^{1}ILCT in nature.

Keywords: Hydrazone, Directing group (DG), C–H activation, Hydride transfer, Electrochemistry.

Polyaromatic hydrocarbon derivatized azo-oximes of Cobalt(III): ligand-redox controlled electro-catalytic oxygen reduction reaction

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Coligand driven diverse organometallation in benzothiazolyl-hydrazone derivatized pyrene: ortho vs peri C–H activation

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Benzothiazolyl hydrazones **1** (H_2L^{PAH}) incorporating polycyclic aromatic hydrocarbons (PAHs) have been fabricated as hemilabile scaffolds and elegantly utilized the inbuilt nitrogen donors as proficient directing group (DG) to bring about the ruthenium(II) assisted C–H activation in PAHs at both peri and ortho positions. An isomeric pair of organometallics having formula $[Ru^{II}(L^{Pyr})(CO)(PPh_3)_2]$ (peri: **3a**, ortho: **5a**) have been conveniently prepared by varing the $[Ru^{II}]$ precursors with H_2L^{Pyr}. In contrast, only one type of activated product *viz.* $[Ru^{II}(L^{Anc})(CO)(PPh_3)_2]$ **3b** has been obtained with 9-anthracene derivative of **1**, H_2L^{Anc}, under analogous reaction conditions. The underlying mechanistic aspects have been elucidated by isolating the thermally unstable intermediates *viz.* $[Ru^{II}(HL^{Pyr})Cl(CO)(PPh_3)_2]$ **2a** and $[Ru^{II}(HL^{Pyr})H(CO)(PPh_3)_2]$ **4a** in due course of peri and ortho C–H activation processes, respectively. Coligand (Cl/H) plays a vital role to bring about the C–H activation at desired positions *via* formation of either a four- or five-membered metallacycle in **2a** and **4a**, respectively. The activation process *vis-à-vis* Ru–C bond formation in **3a** can be achieved smoothly from **2a** by thermal transformation route, which proceeds *via* an initial rupture of $Ru–N_{hydrazonyl}$ bond. On the contrary, trans influential hydride coligand prefers a five-membered chelate to avoid confrontation with $N_{hydrazone}$ in **4a**, which in turn furnishes exclusively an ortho activation owing to the close approach of the Ru–H bond towards *ortho*-H in pyrene. The organometallated complexes exhibit oxidative responses at mild potential. EPR and computatinal studies indicate that redox activity originates from the ligand-centered orbitals. The observed rich optoelectronic features are analysed primarily as ^{1}ILCT admixed with ^{1}MLCT component by theoretical means, indicating an apprecible accumulation of electron density over the ligand backbone in their ground states.

Introduction

C – H bond activation is a long-standing issue under the exploration in synthetic organic chemistry, primarily owing to its prospect in simplifying varied chemical conversion in an atom-efficient technique.[1] The efficacy of this ingenious synthetic approach have been efficiently applied to the fabrication of pharmaceuticals[2] and agrochemicals[3] as well as certain materials.[4,5] One of the prime strategy involved in the activation of the aromatic C–H bond is by introducing a directing group (DG) that coordinates a transition metal lying in the vicinity of the aromatic C – H bond, with subsequent activation *via* cyclometallation.[6] Since the C–H bond strength is much higher than that of M–C, the thermodynamic barrier for C–H bond cleavage is expected to be high.[7] Nevertheless, this can be attained with the aid of chelation of a directing group enabled ligand, which in turn affords organometallacycle at target specific position.[8] Although C–H transformation of aldehyde-derived hydrazones are documented,[9] directing ability of benzothiazole blended hydrazones is yet to be explored to bring about aromatic C–H functionalization in polyaromatic hydrocarbons (PAHs). Indeed, the bifunctional groups are enviable for diverse chemical reactivity as they can typically exhibit supplementary flexibility during coordination.

Controlling the site-selectivity of C–H activations is a prime barrier for the advancement of synthetically convenient methodology. In the present work, we report the designed synthesis of a pair of alluring PAH derivatized benzothiazolyl-hydrazone ligands **1**, H_2L^{PAH} (PAH = pyrene and anthracene). They offer two types of nitrogen donors *viz.* $N_{benzothiazole}$ and $N_{hydrazone}$ apart from the $N_{azomethine}$. The directing ability of the benzothiazolyl–hydrazone framework has been skillfully exploited towards the site selective activation of C–H bond in the ancillary PAH. Notably, both ortho and peri activations can be accomplished by inducing a subtle variation in the metal precursors, where coligand Cl/H derived from the respective starting complexes plays a crucial role for the differential fate in activation process. This event thus provides a

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Palladium(II) and platinum(II) complexes of glyoxalbis(N-aryl)osazone: molecular and electronic structures, anti-microbial activities and DNA-binding study

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Palladium (II) and platinum(II) complexes of types $[Pd(L^{NHPh}H_2)Cl_2]$ (**1**), $[Pd(L^{NH(ClPh)}H_2)Cl_2]$ (**2**), $[Pt(L^{NHPh}H_2)Cl_2]$ (**3**) and $[Pt(L^{NH(ClPh)}H_2)Cl_2]$ (**4**) were successfully isolated, where $L^{NHPh}H_2$ and $L^{NH(ClPh)}H_2$ are osazone ligands. Molecular and electronic structures of **1-4** and their reduced analogues were confirmed by single crystal X-ray crystallography, EPR spectroscopy, and DFT calculations. Osazone is a redox non-innocent ligand and the redox activities of **1-4** were investigated by cyclic voltammetry. The redox activities of **1-4** are solvent dependent. In cyclic voltammetry, no redox wave of **1-4** is discernible in CH_3CN, while in less polar CH_2Cl_2 solvent, the cathodic waves of **3** and **4** gain some reversibility. Mulliken spin density analyses and EPR spectral data reveal that the unpaired electron of $[3]^-$ and $[4]^-$ ions is dominantly localized on the diimine fragment of osazone ligands. Cell viability performed by MTT assay against leishmania promastigote shows that these compounds are strong leishmanicidal agents while they are little responsive towards anti-bacterial and anti-fungal activities. All the reported compounds are completely non-cytotoxic within the limit of 0-50 μM upto 72 hr revealing their potentiality in therapeutic measure. The leishmanicidal activity of **1** and **3** are found to be higher than the ligands as well as **2** and **4**. Furthermore, the interaction of **1** and **3** with DNA has been assessed as possibly intercalating in nature that correlates with one of the requisite modes for anti-leishmanial activity.

Introduction

Square planar palladium(II) and platinum(II) complexes with heterocyclic α-diimine ligands have been investigated over last few decades owing to their attractive redox activity[1], rich photoluminescence properties[2] and high antiproliferative profile.[3] Although their aliphatic analogues[4] those are less documented in literature, have parallel remarkable chemistry. Osazones represent a special class of α-diimine ligands containing a RNN=CH-CH=NNR moiety and the chemistry of it is different from that of α-diimine ligands containing RN=CH-CH=NR fragment. In our previous investigation on osazone complexes, we reported that osazones are redox active[5] and phenyl osazone ($L^{NHPh}H_2$) is a better π-acceptor [$E_{\pi^*}(L^{NHPh}H_2)$ = −2.613 eV] than that of phenyl diimine ligand [$E_{\pi^*}(L^{Ph}H_2)$ = −1.421 eV].[5a] Thus, osazones have been considered to generate tunable $Pd^{II}N_2Cl_2$ and $Pt^{II}N_2Cl_2$ coordination spheres. In the early 1970's, Vigato et al. reported some complexes of osazones[6] of the types $[M^{II}(L_1)Cl_2]$, $[M^{II}(L_2)Cl_2]$ (M = Pd, Pt), $[Pd_2(L_2\text{-}H)_2Cl_2]$, and $[Pd^{II}(L_2)Cl]$, where L_1 = cyclohexane-1, 2-dionebisphenylhydrazone, L_2 = biacetylbis-(N-methyl, N-phenyl)hydrazone. However, a detailed molecular and electronic structures of the complexes of general formula $M^{II}(N^{\frown}N)Cl_2$ (M = Pd, Pt) with parent osazones is under-explored. The –C=NNHR moiety in osazones closely resembles with that of semicarbazone and thiosemicarbazones. The anti-leishmanial activity of platinum and palladium complexes containing bioactive nitrofuryl thiosemicarbazones[7] is well established and the same with hydrazone ligands[8] is rare. Navarro et al. reported a series of palladium(II) polypyridyl complexes[9] of types $[PdCl_2(phen)]$, $[PdCl_2(biquinoline)]$ and $[PdCl_2(phendiamine)]$ which exhibit leishmanistatic effect, particularly inhibiting the growth rate. $[PdCl_2(phendiamine)]$ was found to be the most effective causing 58 % growth inhibition. The investigation provides an useful information that the hetrocyclic α-diimine complexes of palladium(II) and platinum(II) are potential leishmanicidal agent and in this study we have been persuaded to explore such activity with **1-4**.

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X-ray cystallographic CIF, materials and physical measurements, DFT calculations, cyclic voltammograms, EPR spectra $[3]^-$ and $[4]^-$, Mulliken spin density of $[3]^*$, gas phase optimized geometries, FMOs of **1-4**, comparative study of IC_{50} values, anti-leishmanial activity of the compounds **1** and **3**, minimum inhibitory concentration (MIC) of **1** and **3** in bacterial system, antifungal activity (MIC) of **1** and **3**, optimized coordinates. See DOI: 10.1039/x0xx00000x.

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