Nat. Volatiles & Essent. Oils, 2020;07 (4):120-138

NVEO
Natural Volatiles &
Essential Oils

Synthesis, Spectral Study, Electrochemistry And Reactivity Of Ruthenium(II)-B-Naphthyl-Azo-Imidazole (B-Nair)-Nitro-Nitroso-Terpyridine (TPY)-Complexes.

Prithwiraj Byabartta*

*Departmento de Quimica Inorganica-Instituto de Ciencia deMateriales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza-50009, Spain, Department of Chemistry, Jogesh Chandra Chaudhuri College, 30-Prince Anwar Shah Road, Kolkata-700033; pribatta@rediffmail.com. (Mob-9547775486)

Abstract

Silver assisted aquation of blue [RuCl(tpy)(b-NaiR´)](ClO_4) (**1a**) leads to the synthesis of solvento species, blue-violet [Ru(OH_2)(tpy)(b-NaiR)](ClO_4)**₂** (**2a**), [b-NaiR = b-NaphthylazoImidazole = C_6H_5-N=N-C_4H_3-NN, abbreviated as N,**N´**-chelator] that have been reacted with $NaNO_2$ in warm EtOH resulting in violet nitro complexes of the type, [Ru(NO_2)(tpy)(b-NaiR)](ClO_4) (**3a**). The nitrite complexes are useful synthons of electrophilic nitrosyls, and on triturating the nitro compounds with conc. $HClO_4$ nitrosyl derivatives, [Ru(NO)(tpy)(b-NaiR)](ClO_4)$_3$ are isolated. The diazotization of the primary aromatic amines with a strongly electrophilic mononitrosyl complex in acetonotrile and dichloromethane solution was thoroughly studied.

Keywards. [b-NaiR = b-NaphthylazoImidazole, nitro, nitroso, ruthenium, amines, MLCT, NMR, CV, IR, reactivity.

The development of metal nitrosyl complexes having a high degree of electrophilic character of the coordinated NO function (ν_{NO} > 1900 cm^{-1}) is a formidable challenge, since the electrophilic NO centre is susceptible to fascinating molecular transformations in contact with nucleophiles. Extensive studies have been made on ruthenium nitrosyls and appreciable variation of the electronic aspect of the NO function attached to the metal centre has been observed depanding on the nature of the ancillary groups present. This has prompted me to develop a new class of ruthenium nitrosyl complexes encompassing a combination of strong π-acidic heterochelates. The primary intention is to introduce a high degree of electrophilicity at the nitrosyl centre and subsequently explore the reactivity of this centre to nucleophiles. Until that time, the supposition had been that NO, like its analogues CO and CN-, bound irreversibly to metal centers and therefore functioned as a poison, particular with respect to respiratory processes. The moral, if there is one to be drawn, is that one can always expect surprises in biology, and that apparently well-established theories which lead almost to prejudices have a habit of unraveling, primarily because no one had been able to find examples of, or characterize, the unexpected. This review focuses on the coordination chemistry of NO of particular relevance to topical bio-inorganic systems. It does not deal in detail with metallo biomolecules containing NO, instead concentrating on biomimetic systems which seek to clarify aspects of geometrical and electronic structure, and the biological function of native NO-containing or -activating metallo-bimolecular systems. Consequently, the contents focus extensively on the coordination chemistry of iron, cobalt, and copper with NO. Someother transition metal species are mentioned when appropriate. This article is not intended to provide a comprehensive survey, the intention being to provide information on and some illumination of current problems, preoccupations, and directions in bio mimetic transition metal nitrosyl chemistry. It does not contain a discussion of organometallic nitrosyl species, except where they may be relevant to actual or perceived biomolecular species or processes. For comprehensive accounts of metal nitrosyl chemistry, including details of synthesis, organometallic and cluster chemistry, and the reactivity of coordinated NO, the reader is referred to a selection of reviews.[2-4] The Molecule Nitric oxide is a stable free radical, the molecular orbital diagram of NO showing that the unpaired electron in this molecule resides in a π* molecular orbital. This electronic configuration explains the high reactivity of the NO molecule, in particular the ease of oxidation to the nitrosonium ion (NO+), the probability of reduction to the nitroxide ion (NO-), the facile attack by oxygen leading to formation of NO_2, and reaction with halogens (X_2) affording XNO. NO is isoelectronic with the dioxygen monocation (O^{2+}), and NO^+ is isoelectronic with CO and CN^-, while NO^- is isoelectronic with O_2, having a triplet ground state. The role of biomimicry in metal nitrosyl chemistry is to illuminate molecular and/or electronic structural issues, and to facilitate the understanding of the reactivity of the coordinated NO group. It is convenient to develop by categorizing complexes by generic types: heme analogues and related macrocyclic species, non-heme iron complexes, other iron complexes, and complexes of other metals. The reactivity of coordinated NO has been thoroughly reviewed recently, and so it is not discussed here.[23] Heme Analogues and Related Macrocyclic Complexes Because NO synthase, the enzyme which produces NO in the body, and soluble guanylyl cyclase, the enzymatic receptor for NO, both contain heme, iron nitrosyl porphyrinato complexes have received substantial attention. The iron heme nitrosyls containing $\{Fe(NO)\}^7$ appear, at the time of this writing, to be more prevalent than their oxidized $\{Fe(NO)\}^6$ counterparts. This section also contains brief comments on analogous manganese, ruthenium, and cobalt porphyrins and related complexes. Iron Complexes Iron nitrosyl porphyrins may be five-coordinate or six-coordinate, the sixth ligand in the well-characterized examples of the latter being either a N-hetero cycle, water, alkyl/aryl, or NO^{2-}. The metal-NO bond angles in the diamagnetic $\{Fe(NO)\}^6$ group of com plexes lie between 169° and 180°, i.e. essentially linear, and the Fe-N(O) distances are in the range 1.63-1.67 Å, generally independent of coordination number.[24] Occasionally, a slight off-axis tilt of the Fe-N-O bond system is observed.[25] The nature of the trans axial ligand in the six-coordinate species has relatively little effect on the Fe-N(O) bond length. The NO stretching frequencies of this group, with one significant exception, lie between 1830 and 1937 cm^{-1}, depending on medium, method of preparation, and whether solvent of crystallization is present. The Mo¨ssbauer isomer shifts are in the range δ) 0.02-0.24 mm/s (4.2K), reasonable for diamagnetic complexes of this general class.[26,27,28,29] However, this range is wider than that encountered in iron nitrosyl models of non-heme proteins containing the $\{Fe(NO)\}^6$ core.[30,31] It seems that the electronic structure of this group of complexes, be they five- or six-coordinate, can be sensitive to the nature of the ligand trans to NO,[25] although distortions of the porphyrinato ligand do not seem to have a significant effect on the Fe-N-O bond angle.[29] The major exception to the structural generalities for $\{Fe(NO)\}^6$ porphyrinato complexes referred to above is $[Fe(NO)(oep)(C_6H_4F\text{-}p)]$.[32]

The chemistry of transition-metal-NO complexes, or metal nitrosyls, has taken on added significance in recent years because of the important role that nitric oxide has been found to play as a signaling molecule in biological systems. Recent work has also established that the characteristic chemistry of nitrosyl complexes is often markedly different from that exhibited by their isoelectronic carbonyl analogues. It has been almost 10 years since these complexes were last reviewed in the book *Metal Nitrosyls* and so it seemed to us that an update of this rapidly expanding field would be appropriate at the present time. The principle to all classes of transition-metal-NO complexes, namely the characteristic reactivities of bound NO groups [1-3]. Whenever possible, emphasis is placed on the unique physical and chemical properties imparted to nitrosyl complexes by the presence of the strongly electron-withdrawing NO ligands. Several general articles concerning nitrosyl complexes have appeared between 1991 and 2001. These include theoretical calculations on nitrosyl fragments and submissions concerning electron counting in nitrosyl complexes. Several review articles have also been written concerning a large array of nitrosyl-related topics, such as linkage isomerism. The recent observations of the relevance of nitric oxide (NO) in a wide range of biological and environmental processes have led to a resurgence of interest in the area of nitrosyl chemistry [4-8]. Moreover, the development of metal nitrosyl complexes having a high degree of electrophilic character of the coordinated NO function ($\nu_{NO} > 1900$ cm^{-1}) is a formidable challenge, since the electrophilic NO centre is susceptible to fascinating molecular transformations in contact with nucleophiles. Extensive studies have been made on ruthenium nitrosyls and appreciable variation of the electronic aspect of the NO function attached to the metal centre has been observed depanding on the nature of the ancillary groups present. This has prompted us to develop a new class of ruthenium nitrosyl complexes encompassing a combination of strong π-acidic heterochelates. The primary intention is to introduce a high degree of electrophilicity at the nitrosyl centre and subsequently explore the reactivity of this centre to nucleophiles. Recently, we have developed the arylazoimidazole chemistry of ruthenium and have synthesised chloro, aquo, nitro, nitroso componds and tris chelate species reacting with camphor and hydrazone derivatives. The nitrites are useful synthons of nitrosyls, and mononitrosyl compounds are produced in perchloric acid medium. The diazotozation of primary amines with the nitroso complexes and after all their coupling product were isolated and also were thoroughly examined. The complexes were well characterized by spectral method and reactivity.

Nitro-{-2-([b-NaiR = b-NaphthylazoImidazole **}-(terpyridine)-ruthenium(II), [Ru(NO$_2$)(tpy) (**[b-NaiR = b-NaphthylazoImidazole**)](ClO$_4$)**

To an EtOH blue-violet solution (15 cm) of [Ru(OH$_2$)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$) (0.1 g, 0.14 mmol) was added 0.019 g (0.27 mmol) of solid $NaNO_2$, 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 water and dried in vacuo over $CaCl_2$. Analytically pure **nitro** complexes were obtained after chromatography over an alumina (neutral) column on eluting the violet band with toluene-acetonitrile (4:1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%). Analysis for [Ru(O$_2$N)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$), **3a,** Found: C, 45.6, H, 3.3, Calcd for [$C_{25}H_{21}N_8RuO_2$](ClO$_4$), C, 45.1, H, 3.2, IR (KBr disk, cm^{-1}) ν(NO$_2$)$_{asy}$ 1300, ν(NO$_2$)$_{sy}$ 1250, ν(N=N) 1371, ν(C=N), 1575, UV-Vis [λ(nm)(10^{-3} ε/dm^3 mol^{-1} cm^{-1})], 510(8009), 320(10913), 220(30032); Cyclic. Voltammetry. [E/V (ΔE$_p$ / mV)], 1.1(80), , -0.68(90), -0.81(80), -1.3(80).

The ground state (GS) contains an NO ligand bound through the nitrogen atom. In the first metastable state (MS1), the nitrosyl group is coordinated through the oxygen atom, and the coordination is η2-M(NO) for the second metastable state (MS2). The metastable states occurrence has been proven for various metals;[93-112] however, the highest thermal stability and population correspond to ruthenium complexes.[4–6,90-112] Factors that influence metastable thermal stability can be divided into two groups. The first group is the nature of the molecule, specifically, the charge and ligand sphere. The second is the nitrosyl group surrounding the crystal structure. It is generally accepted that the nature of the complex and the ligand trans to NO play crucial roles in the MS1 thermal stability. Studies show that the MS1 thermal stability increases in the sequence [RuNO(en)$_2$Br]Br$_2$ (229 K) < [RuNO(en)$_2$Cl]Cl$_2$ (246 K) < [RuNO(en)$_2$(H$_2$O)]Cl$_3$ (267 K) < [RuNO-(en)$_2$(HOx)]Cl$_2$ (277 K). Similar results obtained by Fomitchev and Coppens provide a qualitative correlation between νNO in IR spectra and the MS1 decay temperature (Td). Comparisons between [RuNO(NH$_3$)$_4$X]Cln (X = H$_2$O, NH$_3$, OH−) show an increase in the MS1 thermal stability, while electron donation decreases (NH$_3$ < OH− < H$_2$O) with a 30 K difference in Td for NH$_3$ and H$_2$O complexes.

Preparation of [Ru)(NO)(papm**)(tpy)](ClO$_4$)$_3$ (4a)**

[Ru(NO$_2$)([b-NaiR = b-NaphthylazoImidazole)(tpy)]$^+$ (**3a**) (0.1 g, 0.17 mmol) and conc. $HClO_4$ (3 cm^3) were placed in a small beaker, and the mixture was triturated with a glass rod for 1 h. The mixture immediately changed from violet to orange-red. The pasty mass was extracted with CH_2Cl_2 (4 × 5 cm^3) and concentrated under reduced pressure. The dark red crystalline product was separated by filtration, washed with chilled H_2O containing a few drops of dil. $HClO_4$ and dried in vacuo over P_4O_{10} to yield analytically pure (**4a**), [Yield 0.092 g (70%)]; Analysis for [Ru(ON)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$)$_3$, **4a,** Found: C, 35.6, H, 2.3, Calcd for [$C_{25}H_{21}N_8RuO$](ClO$_4$)$_3$, C, 35.1, H, 2.2, IR (KBr disk, cm^{-1}) ν(NO) 1900, ν(ClO$_4$) 1140,1100,1090,640,625, ν(N=N) 1371, ν(C=N), 1575, UV-Vis, 360(8009), 320(10913), 280(14000), 220(30032); Cyclic Voltammetry, 1.7(80), 0.7(90), 0.04, -0.68(90), -0.81(80), -1.3(80).

Interconversion: [Ru(NO)([b-NaiR = b-NaphthylazoImidazole**)(tpy)](ClO$_4$)$_3$ (4a)→ [Ru(NO$_2$)(** [b-NaiR = b-NaphthylazoImidazole**)(tpy)] (ClO$_4$) (3a)**

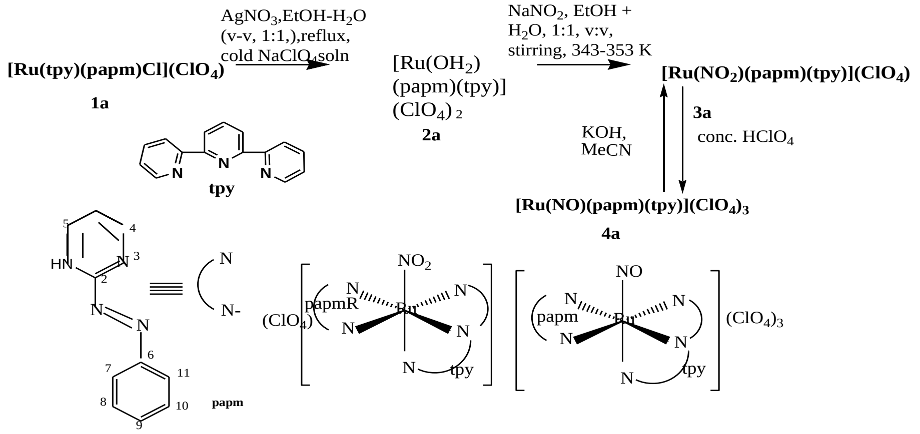
To an aqueous solution of (**4a**) (0.1 g, 0.13 mmol) was added an equivalent amount of KOH in the same solvent. The orange-red solution immediately turned violet, and was extracted with CH_2Cl_2. The solvent was removed by evaporation under reduced pressure and the pasty mass, dissolved in a minimum vol. of CH_2Cl_2, was chromatographed on an alumina (neutral) column. A deep violet band was eluted with toluene-acetonitrile (4:1, v/v). The identity of the product as (**3a**) was checked by comparing properties with an authentic sample.

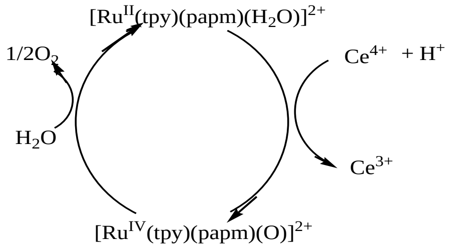
Reaction of Primary Amines with [Ru(NO)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$)$_3$

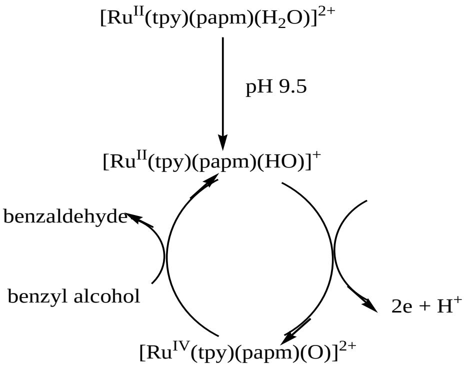
To a acetonitrile solution (20 cm) of [Ru(NO)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO_4)$_3$ (0.2 g, 0.26 mmol) equivalent amounts of aniline (0.054 g, 0.26 mmol) was added, and the mixture was stirred for 30 min at room temp. and then evaporated to dryness using a vacuum pump. The crude pdt was then extracted with 30 cc of ice-cold water and the aquous solution was collected by filtration. To the aquous solution an aquous solution of alkaline b-naphthol was added with continious stirring over a period of 15 min. Red crystal of 1-phenylazo-2-naphthol were separated and recrystalised from methanol. The residue was dried and dissolved in dichloromethane and brown crystal of [Ru(S)([b-NaiR = b-NaphthylazoImidazole)(tpy)]ClO_4 (S = CH_3CN) (**6a**) were obtained.

Results and Discussion

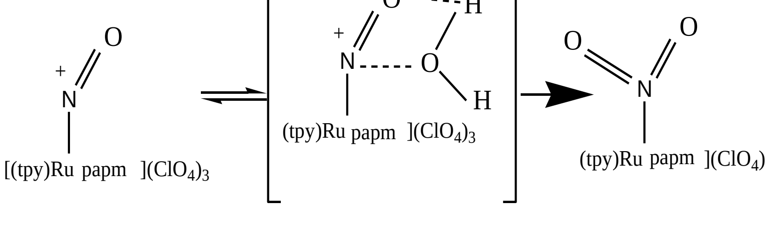
Aquo complexes [Ru(OH_2)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO_4)$_2$, prepared by Ag^+-assisted aquation of [RuCl([b-NaiR = b-NaphthylazoImidazole)(tpy)]$^+$ (**1a**), [papm′ =-C_6H_5-N=N-C_4H_3-NN, abbreviated as N,N′-chelator] were reacted with $NaNO_2$ (excess amount >2 mol) under stirring at 343-353 K in aqueous alcohol to give [Ru(NO_2)([b-NaiR)(tpy)]$^+$ (**3a**) in good yield (65-85%). The synthetic routes are shown below. The nitrites were synthesized in low yield either directly on stirring $NaNO_2$ in ethanol-acetone mixture for 30 h or in situ synthesis of the aquo complex by $AgNO_3$ followed by the reaction with $NaNO_2$. The composition of the complexes is supported by microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic. Trituration of solid [Ru(NO_2)([b-NaiR)(tpy)](ClO_4) in concentrated $HClO_4$ at ambient condition gives an orange-red solution from which the nitrosyl complexes [Ru(NO)([b-NaiR)(tpy)](ClO_4)$_3$ are isolated. In alkaline media nitrosyl complexes, regenerate the corresponding nitrite precursors (**3a**). The reaction of H^+ with coordinated NO^+ group in nitrite complexes and the nucleophilic attack of OH^- on the NO in nitrosyls are the key steps for such reaction. The violet nitrites are soluble in common organic solvents but insoluble in H_2O whereas the orange-red nitrosyls are soluble in H_2O and in a range of common organic solvents viz., methanol, ethanol, partly soluble in acetone, acetonitrile, chloroform, dichloromethane. In MeCN, nitroso behave as 1:3 electrolytes (Λ = 160-190 Ω cmmol) whereas 1:1 electrolytic behaviour is found for type nitrite complexes (Λ = 60-90 Ω cmmol) as indicated by their very low Λ_M values. Chemical oxidation of the aqua complex by excess aqueous ceric solution in 1 (N) H_2SO_4 leads to the spontaneous formation of a yellow colored oxo species and the process follow by oxidising the benzylic alcohol solution.



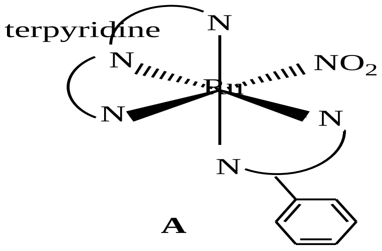




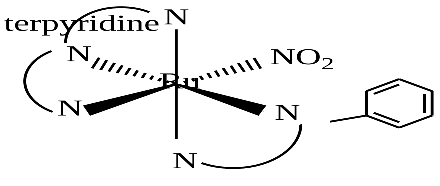
IR spectra of dinitro complexes, [Ru(NO$_2$)([b-NaiR = b-NaphthylazoImidazole)(tpy)] show a 1:1 correspondence to the spectra of the dichloro analogue, *ctc*-[RuCl([b-NaiR = b-NaphthylazoImidazole)(tpy)] except the appearance of intense stretching at 1300-1335 and 1250-1280 cm^{-1} with concomitant loss of ν(Ru-Cl) at 320-340 cm^{-1}. They are assigned as symmetric and asymmetric stretching of NO$_2$ i.e. ν(NO$_2$)asym and ν(NO$_2$)sym, respectively. The ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively. Mono-nitroso-ruthenium(II), [Ru(NO)([b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$)$_2$ show a very strong stretch in the 1910-1925 cm^{-1} range which is conspicuously absent in the spectra of [Ru(NO$_2$)([b-NaiR)(tpy)]. Thus, the present series of Ru-NO complexes are assumed to contain linear NO group. Other important frequencies are ν(HO) at 3350-3400 cm and ν(ClO$_4$) at 1140-1145, 1110-1120 and 1080-1090 cm^{-1} along with weak bands at 640 and 625 cm^{-1}. Triplet splitting pattern of ClO$_4$ may presumably be due to some sort of hydrogen bonding interaction. The solution electronic spectra of these new complexes were recorded in dry acetonitrile. The nitro complexes in MeCN showed three to four bands in the region 719–254 nm (Table 2). All the complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$, arising from the t_{2g}^6 configuration. The excited state terms are $^3T_{1g}$, ^3T_2g, $^1T_{1g}$ and $^1T_{2g}$. Hence four bands corresponding to the transition $^1A_{1g}\rightarrow{}^3T_1g$, $^1A_{1g}\rightarrow{}^3T_{2g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ are possible in order of increasing energy. The electronic spectral bands at around 719–653 nm are assigned to $^1A_{1g}\rightarrow{}^1T_{1g}$. The other high intensity band in the visible region around 504–519 nm has been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled **π*** molecular orbital of the ligand. The high intensity bands around 330–310 nm and 272–254 nm has been designated as **n– π** * and **π – π** * transitions respectively. Nitro complexes (**3a-3i**) exhibit multiple transitions in the uv-visible region. They display intense MLCT transition in the 550-560 nm range along with weak longer wavelength absorption near 750 nm (shoulder). In nitroso derivatives, [Ru(NO)(b-NaiR = b-NaphthylazoImidazole)(tpy)](ClO$_4$)$_3$ the intense absorption bands are further shifted to shorter wavelength, near 420 nm along with a weak band near 600 nm. This is attributed to strong dπ(Ru) → π(NO) back bonding which stabilizes the dπ level and consequently shifts the MLCT band to the lower wavelength region. The nitrosyl complexes are found to be stable only in dry acetonitrile solution. In ordinary acetonitrile or in contact with moister the spectrum spontaneously changes and levels off with the spectrum of precursor nitro derivative. The transformation has been proved through product isolation in one case, and characterized comparing of its properties with an authentic sample. The conversion from nitroso into the nitro complex is followed by the following mechanism.



The ^{1}H NMR spectra of [Ru(NO$_2$)([b-NaiR = b-NaphthylazoImidazole)(tpy)] (**3a**) complexes were assigned on comparing with dichloro precursor. 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 (**3a-3i**) appears as a single signal at 2.30 ppm. The mononitrosyls, [Ru(NO)([b-NaiR = b-NaphthylazoImidazole)(tpy)]$(ClO_4)_3$ exhibit similar pattern of signals in the aromatic portion and the spectra have been shifted to higher field by 0.03-0.15 ppm from those of respective nitro derivatives. It is due to better dπ(Ru) → π^*(NO) charge transfer which increases hardness of Ru(II) leading to strong σ-interaction with the chelator. The solution ^{1}H NMR spectra support at least the presence of two isomers in different proportion.



A



Isomer B

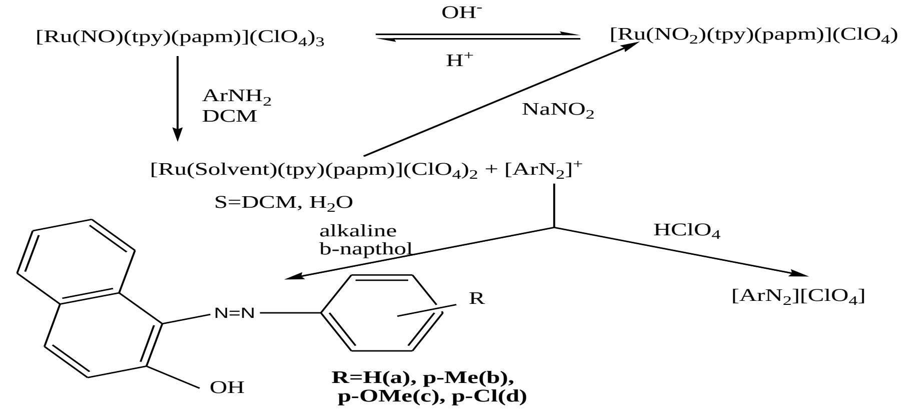
The potential values of the complexes in dry acetonitrile solution are measured. The reduction sweep shows a new wave that has a counter oxidative wave on the second sweep. The first primary redox process (E = 1.3-1.13 V) is assigned to Ru(III)/Ru(II) couple. The nitrosyl complexe exhibit multiple redox responses in the potential range +2.0 V to –2.0 V versus s.c.e. Two quasi-reversible reductive responses in the potential 0.5 to 0.6 V and –0.1 to –0.2 V are seen. The couples IV and V are assigned to successive one-electron reductions of the coordinated NO unit; [Ru-NO → Ru-NO (couple II), Ru-NO → Ru-NO(couple III)]. The couple III is irreversible, indicating instability of the reduced species. High potential voltammetric wave at 1.4-1.5 V (couple 1) (ΔE ≥ 120 mV) is assigned to the Ru(III)/Ru(II) couple. The azo group may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window three reductions were clearly observable. The nitrosyl complexes display multiple redox processes in the experimental potential range (couples I–VI). The first two reductions (couples II and III) are assigned to successive one-electron reductions of the coordinated NO unit, eqns. (1) and (2).

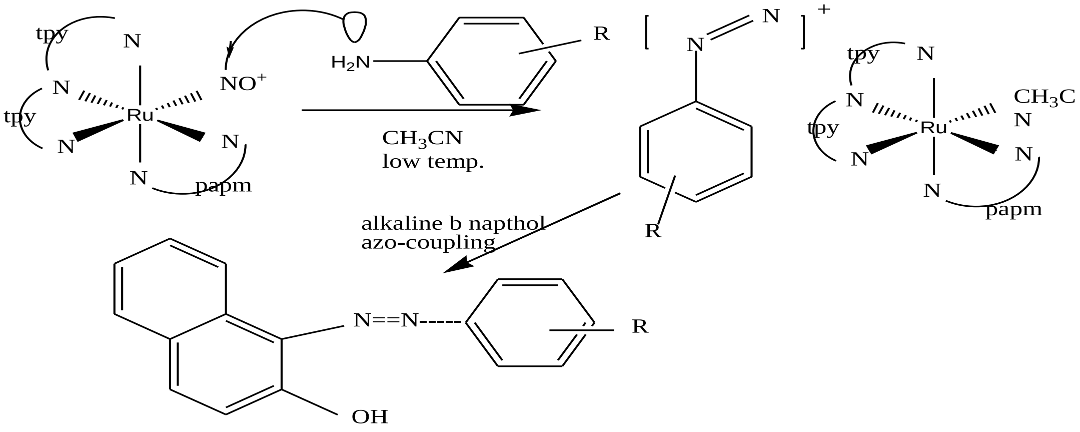
[Ru^{II}([b-NaiR = b-NaphthylazoImidazole)(tpy)(NO)]$^{3+}$ + e = [Ru^{II}([b-NaiR = b-NaphthylazoImidazole)(tpy)(NO)]$^{2+}$..................... (1)

[Ru^{II}([b-NaiR = b-NaphthylazoImidazole)(tpy)(NO)]$^{2+}$ + e = [Ru^{II}([b-NaiR = b-NaphthylazoImidazole)(tpy)(NO)]$^{+}$...................... (2)

The reduction potential of Ru–NO$^-$ → Ru–NO [couple II, eqn. (1)] of nitroso-complexes is close to that of uncoordinated NO (*E*= 0.74 V). Although the first reduction process Ru–NO$^-$.→ Ru–NO (couple II) is stable on the coulometric timescale, the second Ru–NO.→ Ru–NO$^-$ is unstable. Nitrosyl complexes show one additional quasi-reversible oxidation process near 1.60 V. The oxidation process corresponding to it may be assigned to the ruthenium(II)–ruthenium(III) oxidation as all other redox active centres in the complex moiety are only susceptible to reduction.

Reaction of the mononitrosyl complexes with primary amines were studied by the following sequence. To investigate the reaction mechanism it was studied in two solvents, in acetonitrile and in dichloromethane. This monoaquo complex produces the monoacetonitrile complex on treatment with acetonitrile. One real advantage of such reaction is the possibility of developing analytical route for synthetic nitrosation of organic substrate using [Ru(NO)(RaaiMe)(tpy)]$(ClO_4)_3$ as the source of NO under mildly acidic condition.





In conclusion, nitro as well as nitroso complexes of ruthenium(II), [Ru(NO_2)([b-NaiR = b-NaphthylazoImidazole)(tpy)] have been synthesised by stereoretentive reaction of aquo complex [Ru(OH_2)([b-NaiR = b-NaphthylazoImidazole)(tpy)] with nitrite ion. The complexes exhibit strong MLCT transitions. Voltammetric study shows Ru(III)/Ru(II) couple along with successive ligand-based reductions and additionally NO^+ reductions in nitrosyl derivatives. The electrophilic activity of bound NO has been established through diazotization of $ArNH_2$

Acknowledgement

Department of Science and Technology (DST) is thanked for financial support. (FAST TRACK Grand No. **SERB/F/4888/2012-13 Dated 30.11.2012,** Project Title: GOLD(I) & GOLD(III) ARYLAZOIMIDAZOLE (N, N DONAR) & OXO COMPLEXES : SYNTHESIS, STRUCTURE, SPECTRAL STUDY, ELECTROCHEMISTRY AND CHEMICAL REACTIVITY).

References:

1. L. M. Carruthers, C. L. Closken, K. L. Link, S. N. Mahapatro, M. Bikram, J. Du, S. S. Eaton and G. R. Eaton, *Inorg. Chem.*, **38**, 3529,1999; G. Yi, M. A. Khan, D. R. Powell and G. B. Richter-Addo, *Inorg. Chem.*, **37**, 208; 1998, M. K. Ellison and W. R. Scheidt, *Inorg. Chem.*, **37**, 382,1998,; K. M. Miranda, X. Bu, I. Lorkovic and P. C. Ford, *Inorg. Chem.*, **36**, 4838, 1997; A. Wlodarczyk, J. P. Maher, S. Coles, D. V. Hibbs, M. H. B.Hursthouse and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 2597,1997; P. Legzdins, S. J. Rettig, K. M. Smith, V. Tong and V. G. Young, Jr., *J. Chem. Soc., Dalton Trans.*, 3269, 1997.
2. Das, C. J. Jones and J. A. McCleverty, *Polyhedron*, **12**, 327; 1993, J. A. McCleverty, *Chem. Rev.*, **79**, 53,1979; K. K. Pandey, *Coord. Chem. Rev.*, **51**, 69; 1983, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, **23**, 2466; 1984, M. H. Thiemens and W. C. Trogler, *Science*, **251**, 932; 1991, M. Feelisch and J. S. Stamler (Editors), *Methods in Nitric Oxide Research*, Wiley, Chichester, 1996.
3. M. Kawano, A. Ishikawa, Y. Morioka, H. Tomizawa and E. Miki, *J. Chem. Soc., Dalton Trans.*, 781; 2000, M. Kawano, A. Ishikawa, Y. Morioka, H. Tomizawa, E. Miki and Y. Ohashi, *J. Chem. Soc., Dalton Trans.*,

2425; 2000, S. S. S. Broges, C. U. Davanzo, E. E. Castellano, J. Z-Schpector, S. C. Silva and D. W. Franco, *Inorg. Chem.*, **37**, 2670; 1998, P. Homanen, M. Haukka, M. Ahlgren and T. A. Pakkanen, *Inorg. Chem.*, **36**, 3794; 1997, M. R. Rhodes and T. J. Meyer, *Inorg. Chem.*, **27**, 4772; 1988, T. Uchida, R. Irie and T. Katsuki, *Tetrahedron*, **56**, 3501; 2000, F. Bottomley, W. V. F. Brooks, D. E. Paez, P. S. White and M. Mukaida, *J. Chem. Soc.*, *Dalton Trans.*, 2465; 1983, W. R. Murphy, Jr., K. J. Takeuchi and T. J. Meyer, *J. Am. Chem. Soc.*, **104**, 5817; 1982, M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, **103**, 5577; 1981, J. L. Walash, R. M. Bullock and T. J. Meyer, *Inorg. Chem.*, **19**, 865,1980,

4. B. Mondal, M. G. Walawalkar and G. K. Lahiri, *J. Chem. Soc.*, *Dalton Trans.*, 4209; 2000, P. Byabartta, M Laguna Transition Met. Chem., in press, TMCH6669,6670,6699,6700,6709,6710, 6732,6733;
5. B. Mondal H., Paul V. G.Puranik and G. K. Lahiri *J. Chem. Soc., Dalton Trans.,* 481. 2001, P., Byabartta, M Laguna, J. Chem. Sci, 118, 385, 2006; P., Byabartta J Chem. Sci, 118, 2006, 171; P., Byabartta, J. Chem. Sci, 118, 2006, 399-409; P., Byabartta, M Laguna, Rus J. Coord. Chem., 2006, in press,
6. P. Byabartta Transition Met. Chem., 2005, 30, 902, P., Byabartta, Spectrochimica Acta-A., published online on 6th april, 2006,; P., Byabartta, Dyes & Pigment, published online on 16th October, 2006, T. K., Misra, D.Das C., Sinha P. K. Ghosh and C. K.,Pal *Inorg. Chem.,* 37, 1672. 1998,
7. Koshland, D. E. Science 1992, 258, 1861. Richter Addo, G. B.; Legzdins, R. Metal Nitrosyls; Oxford University Press: Oxford, 1992. Richter Addo, G. B.; Legzdins, R.; Burstyn, J. Chem. Rev. 2002, 102, 857. Hayton, T. W.; Legzdins, P.; Sharp, W. B. Chem. Rev. 2002, 102, 935 and references therein. (a) Natalis, P.; Collin, J. E.; Delwiche, J.; Caprace, G.; Hubin, M. J. J. Electron Spectrosc. Relat. Phenom. 1979, 17, 421. (b) Siegel, M. W.; Celotta, R. J.; Hall, J. L.; Levine, J.; Bennett, R. A. Phys. Rev. A 1972, 6, 607. Lee, K. Y.; Kuchnya, D. L.; Kochi, J. K. Inorg. Chem. 1990, 29, 4196. Kim, E.; Kochi, J. K. J. Am. Chem. Soc. 1991, 113, 4962.Stanbury, D. M. Adv. Inorg. Chem. 1989, 33, 69. Bartberger, M. D.; Liu, W.; Ford, E.; Miranda, K. M.; Switzer, C.; Fukuto, J. M.; Farmer, P. J.; Wink, D. A.; Houk, K. N. Proc. Natl. Acad. Sci. U.S.A. 2002, 99, 10958. Jones, K. Comprehensive Inorganic Chemistry; Pergamon: Ox ford, 1973; Vol. 2, Chapter 19. Wong, M. W.; Nobes, R. H.; Bouma, W. J.; Radom, L. Chem. Phys. 1989, 91, 2971. Teillet-Billy, D.; Fiquet-Fayard, F. J. Phys. Chem. 1990, 94, 3450. Teillet-Billy, D.; Fiquet-Fayard, F. J. Phys. 1977, 10B, L111.
8. Lee, J.; Chen, L, West, A. H.; Richter-Addo, G. B. Chem. Rev. 2002, 102, 1019 and references therein.
9. Johnson, B. F. G.; McCleverty, J. A. Prog. Inorg. Chem. 1966, 7, 277. Griffith, W. P. Adv. Organomet. Chem. 1968, 7, 211. Connely, N. G. Inorg. Chim. Acta 1972, 6, 47.
10. Enemark, J. H.; Feltham, R. D. Coord. Chem. Rev. 1974, 13, 339.
11. Mingos, D. M. P. Inorg. Chem. 1973, 12, 1209.
12. Brown, C. A.; Pavolovsky, M. A.; Westre, T. E.; Zhang, Y.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. J. Am. Chem. Soc. 1995, 117, 715.
13. Conradie, J.; Wondimagegn, T.; Ghosh, A. J. Am. Chem. Soc. 2003, 125, 4968. (b) Lorkovic, I.; Ford, P. C. J. Am. Chem. Soc., 2000, 122, 6516.
14. Paul, P. P.; Tyeklar, Z.; Farooq, A.; Karline, K. D.; Liu S.; Zubieta, J. J. Am. Chem. Soc. 1990, 112, 2430.
15. Coppens, P.; Novozhilova, I.: Kovalevsky, A. Chem. Rev. 2002, 102, 861 and references therein.
16. Weichsel, A.; Andersen, J. F.; Roberts, S. A.; Montfort, W. R. Nature Struct. Biol. 2000, 7, 551.
17. Cheng, L.; Novozhilova, I.; Kim, C.; Kovalevsky, A.; Bgley, K. A.; Coppens, P.; Richter-Addo, G. B. J. Am. Chem. Soc. 2000, 122, 7142.
18. Fomitchev, D. V.; Coppens, P.; Li, T.; Bagley, K. A.; Chen, L.; Richter-Addo, G. B. Chem.Commun. 1999, 2013. (21) Ghosh, A.; Wondimagegn, T. J. Am. Chem. Soc. 2000, 122, 8101. Wondimagegn, T.; Ghosh, A. J. Am. Chem. Soc. 2001, 123, 5680.
19. Mason, J.; Larkworthy, L. F.; Moore, E. A. Chem. Rev. 2002, 102, 91
20. McCleverty, J. A. Chem. Rev. 1979, 7, 53. Wolak, M.; van Eldik, R. Chem. Rev. 2002, 102, 263. Ford, P. C.; Lorkovic, I. M. Chem. Rev. 2002, 102, 993.
21. Wyllie, R. A.; Scheidt, W. R. Chem. Rev. 2002, 102, 1067.
22. Ellison, M. K.; Schulz, C. E.; Scheidt, W. R. Inorg. Chem. 2000, 39, 5102.
23. Scheidt, W. R.; Lee, Y. J.; Hatano, K. J. Am. Chem. Soc. 1984, 106, 3191.
24. Ellison, M. K.; Schulz, C. E.; Scheidt, W. R.; Inorg. Chem. 1999, 38, 100.
25. Ellison, M. K.; Scheidt, W. R. J. Am. Chem. Soc. 1999, 121, 5210.
26. Ellison, M. K.; Schulz, C. E.; Scheidt, W. R. J. Am. Chem. Soc. 2002, 124, 13833.

27. Li, M.; Bonnet, D.; Bill, E.; Neese, F.; Weyhermu¨ ller, T.; Blum, N.; Sellmann, D.; Wieghardt, K. Inorg. Chem. 2002, 41, 3444.
28. Lopez, J. P.; Heinemann, F. W.; Prakash, R.; Hess, B. A.; Horner, O.; Jeandey, C.; Oddou, J.-L.; Latour, J.-M., Grohmann, A. Chem. Eur. J. 2002, 8, 5709.
29. Richter-Addo, G. B.; Wheller, R. A.; Hixson, C. A.; Chen, L.; Khan, M. A.; Ellison, M. K.; Schulz, C. E.; Scheidt, W. R. J. Am. Chem. Soc. 2001, 123, 6314. (33) Guilard, R.; Lagrange, G.; Tabard, A.; Lanc¸on, D.; Kadish, K. M. Inorg. Chem. 1985, 24, 3649.
30. Nasri, H.; Ellison, M. K.; Chen, S.; Huynh, B. H.; Scheidt, W. R. J. Am. Chem. Soc. 1997, 119, 6274. (35) Mu, X. H.; Kadish, K. M. Inorg. Chem. 1988, 27, 4720. Lanc¸on, D.; Kadish, K. M. J. Am. Chem. Soc. 1983, 105, 5610. Mu, X. H.; Kadish, K. M. Inorg. Chem. 1990, 29, 1031.
31. Choi, I.-K.; Liu, Y.; Feng, D. W.; Paeng, K.; Ryan, M. D. Inorg. Chem. 1991, 30, 1832.
32. Kadish, K. M.; Mu, X. H.; Lu, X. Q. Inorg. Chem. 1988, 27, 1489.
33. Kelly, S.; Lanc¸on, D.; Kadish, K. M. Inorg. Chem. 1984, 23, 1451.
34. Choi, I.-K.; Ryan, M. D. Inorg. Chim. Acta 1988, 153, 25.
35. Fujita, E.; Chang, C.-K.; Fajer, J. J. Am. Chem. Soc. 1985, 107, 7665.
36. Westre, T. E.; di Cicco, A.; Filiponi, A.; Natoli, C. R.; Hedman, B.; Solomon, E. I.; Hodgson, K. O. J. Am. Chem. Soc. 1994, 116, 6757.
37. Pohl, K; Wieghardt, K.; Nuber, B.; Weiss, J. J. Chem. Soc., Dalton Trans. 1987, 187.
38. Patra, A. K.; Afshar, R.; Olmstead, M. M.; Mascharak, P. K. Angew. Chem., Int. Ed. 2002, 41, 2512.
39. Hauser, C.; Glaser, T.; Bill, E.; Weyhermu¨ ller, T; Wieghardt, K. J. Am. Chem. Soc. 2000, 122, 4352.
40. Lopes, L. G. F.; Sousa, E. H. S.; Miranda, J. C. V.; Oliveira, C. P.; Carvalho, I. M. M.; Batista, A. A.; Ellena, J.; Castellano, E. E.; Nascimenta, O. R.; Moreira, I. S. J. Chem. Soc., Dalton Trans. 2002, 1903.
41. Hodges, K. D.; Wollmann, R. G.; Kessel, S. L.; Hendrickson, D. N.; van Derveer, D. G.; Barefield, E. K. J. Am. Chem. Soc. 1979, 101, 906.
42. Chiou, Y.-M.; Que, L. Inorg. Chem. 1995, 34, 3270.
43. Weber, R.; Go¨rls, H.; Rudolph, M.; Ja¨ger, E.-G. Inorg. Chim. Acta 2002, 337, 247.
44. Sellmann, D.; Blum, N.; Heinemann, F. W.; Hess, B. A. Chem. Eur. J. 2001, 7, 1874.
45. Schweitzer, D.; Ellison, J. J.; Shoner, S. C.; Lovell, S.; Kovacs, J. A. J. Am. Chem. Soc. 1998, 120, 10996.
46. Grapperhaus, C. A.; Patra, A. K.; Mashuta, M. S. Inorg. Chem. 2002, 41, 1039.
47. Ray, M.; Golombek, A. P.; Hendrich, M. P.; Yap, G. P. A.; Liable Sands, L. M.; Rheingold, A. L.; Borovik, A. S. Inorg. Chem. 1999, 38, 3110.
48. Haller, K. J.; Johnson, P. L.; Feltham, R. D.; Enemark, J. H.; Ferraro, J. R.; Basile, L. Inorg. Chim. Acta 1979, 33, 119.
49. Wells, F. V.; McCann, S. W.; Wickman, H. H.; Kessel, S. L.; Hendrickson, D. N.; Feltham, R. D. Inorg. Chem. 1982, 21, 2306; Fitzsimmons, B. W.; Larkworthy, L. F.; Rogers, K. A. Inorg. Chim. Acta. 1980, 44, L53.
50. Ko¨nig, E.; Ritter, G.; Waigel, J.; Larkworth, L. F.; Thompson, R. M. Inorg. Chem. 1987, 26, 1563.
51. Gerbeleu, N. V.; Arion, V. B.; Simonov, Y. A.; Zavodnik, V. E.; Stavrov, S. S.; Turta, K. I.; Gradinaru, D. I.; Birca, M. S.; Pasynskii, A. A.; Ellert, O. Inorg. Chim. Acta 1992, 202, 173.
52. McCleverty, J. A.; Atherton, N. M.; Locke, J.; Wharton, E. J.; Winscom, C. J. J. Am. Chem. Soc. 1967, 89, 6082. Teschmit, G.; Kirmse, R. Inorg. Chem. Commun. 1999, 2, 465. Rae, A. I. M. Chem. Commun. 1967, 1245.
53. Stobie, K.; Maher, J. P.; McCleverty, J. A.; Ward, M. D.; Bill, E.; Wieghardt, K. Work to be published.
54. Davies, G. R.; Mais, R. H. B.; Owston, P. G. Chem. Commun. 1968, 81. Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G. J. Chem. Soc. A 1970, 1275. Quinby Hunt, M.; Feltham, R. D. Inorg. Chem. 1978, 17, 2515; J. Chem. Phys. 1964, 41, 337; J. Chem. Phys. 1969, 50, 2594.
55. Larkworthy, L. F.; Sengupta, S. K. Inorg. Chim. Acta 1991, 179, 157.
56. Chen, Y.; Lin, F.-T.; Shepherd, R. E. Inorg. Chem. 1999, 38, 973.
57. Ward, M. D.; McCleverty, J. A. J. Chem. Soc., Dalton Trans. 2002, 275. Ghosh, P.; Bill, E.; Weyhermu¨ ller, T.; Wieghardt, K. J. Am. Chem. Soc. 2003, 125, 3967.
58. Wanat, A.; Schneppensieper, T.; Stochel, G.; van Eldik, R.; Bill, E.; Wiehgardt, K. Inorg. Chem. 2002, 41, 4.
59. Butler, A. R.; Megson, I. L. Chem. Rev. 2002, 102, 1155.

60. Chau, C.-N.; Wojcicki, A. Polyhedron 1992, 11, 851. Chau, C.- N; Wojcicki, A. Polyhedron 1993, 121, 1261.
61. Glidewell, C.; Lambert, R. J. W. Polyhedron 1992, 11, 2803.
62. Bhattacharyya, R. G.; Mallik, M.; Ghosh, P. N. Inorg. Chim. Acta 1990, 168, 141.
63. Reginato, N.; McCrory, C. T. C.; Pervitsky, D.; Li, L. J. Am. Chem. Soc. 1999, 121, 10217.
64. Franz, K. J.; Lippard, S. J. J. Am. Chem. Soc. 1999, 121, 10504.
65. Feig, A. L.; Bautista, M. T.; Lippard, S. J. Inorg. Chem. 1996, 35, 6892.
66. Liauw, W.-F.; Chiang, C.-Y.; Lee, G.-H.; Peng, S.-M.; Lai, C.-H.; Darensbourg, M. Y. Inorg. Chem. 2000, 39, 480.
67. Balutsis, L. M.; Karlin, K. D.; Rabinowitz, H. N.; Dewan, J. C.; Lippard, S. J. Inorg. Chem. 1980, 19, 2627. Osterloh, F.; Saak, W.; Haase, D.; Pohl, S. Chem. Commun. 1997, 979.
68. Smith, M. C.; Barclay, J. E.; Cramer, S. P.; Davies, S. C.; Gu, W.-W.; Hughes, D. L.; Longhurst, S.; Evans, D. J. J. Chem. Soc., Dalton Trans. 2002, 2641.
69. Chen, Y.; Lin, F.-T.; Shepherd, R. E. Inorg. Chem. 1999, 38, 973.
70. Lang, D. R.; Davis, J. A.; Lopes, L. G. F.; Ferro, A. A.; Vasconcellos, L. C. G.; Franco, D. W.; Tfouni, E.; Wieraszko, A.; Clarke, M. J. Inorg. Chem. 2000, 39, 2294.
71. Groombridge, C. J.; Larkworthy, L. F.; Marecaux, A.; Povey, D. C.; Smith, G. W.; Mason, J. J. Chem. Soc., Dalton Trans. 1992, 3125.
72. Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. J. Am. Chem. Soc. 1993, 115, 11285.
73. Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G.; Tolman, W. B. J. Am. Chem. Soc. 1998, 120, 11408
74. K. J. Franz and S. J. Lippard, *Inorg. Chem., 2000,* **39**, 3722; M. K. Ellison, C. E. Schulz and W. R. Scheidt, *Inorg. Chem.*, 1999, **38**, 100; M. Ray, A. P. Golombek, M. C. Hendrich, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold and A. S. Borovik, *Inorg. Chem.*,1999, **38**, 3110; L. M. Carruthers, C. L. Closken, K. L. Link, S. N. Mahapatro, M. Bikram, J. Du, S. S. Eaton and G. R. Eaton, *Inorg. Chem.*, 1999, **38**, 3529; G. Yi, M. A. Khan, D. R. Powell and G. B. Richter-Addo, *Inorg. Chem.*, 1998, **37**, 208; M. K. Ellison and W. R. Scheidt, *Inorg. Chem.*, 1998, **37**, 382; L. Chen, M. A. Khan and G. B. Richter-Addo, *Inorg. Chem.*, 1998, **37**, 533; K. M. Miranda, X. Bu, I. Lorkovic and P. C. Ford, *Inorg. Chem.*, 1997, **36**, 4838; A. Wlodarczyk, J. P. Maher, S. Coles, D. V. Hibbs, M. H. B.Hursthouse and K. M. Abdul Malik, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2597; P. Legzdins, S. J. Rettig, K. M. Smith, V. Tong and V. G. Young, Jr., *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3269.
75. J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53; K. K. Pandey, *Coord. Chem. Rev.*, 1983, **51**, 69; A. Das, C. J. Jones and J. A. McCleverty, *Polyhedron*, 1993, **12**, 327; D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 2466; M. H. Thiemens and W. C. Trogler, *Science*, 1991, **251**, 932; M. Feelisch and J. S. Stamler (Editors), *Methods in Nitric Oxide Research*, Wiley, Chichester, 1996.
76. D. R. Lang, J. A. Davis, L. G. F. Lopes, A. A. Ferro, L. C. G. Vasconcellos, D. W. Franco, E. Tfouni, A. Wieraszko and M. J. Clarke, *Inorg. Chem.*, 2000, **39**, 2294; B. R. McGarvey, A. A. Ferro, E. Tfouni, C. W. B. Bezerra, I. Bagatin and D. W. Franco, *Inorg. Chem.*, 2000, **39**, 3577; M. Kawano, A. Ishikawa, Y. Morioka, H. Tomizawa and E. Miki, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 781; M. Kawano, A. Ishikawa, Y. Morioka, H. Tomizawa, E. Miki and Y. Ohashi, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 2425; S. S. S. Broges, C. U. Davanzo, E. E. Castellano, J. Z-Schpector, S. C. Silva and D. W. Franco, *Inorg. Chem.*, 1998, **37**, 2670; P. Homanen, M. Haukka, M. Ahlgren and T. A. Pakkanen, *Inorg. Chem.*, 1997, **36**, 3794; M. R. Rhodes and T. J. Meyer, *Inorg. Chem.*, 1988, **27**,4772; T. Uchida, R. Irie and T. Katsuki, *Tetrahedron*, 2000, **56**, 3501; A. K. Deb and S. Goswami, *Polyhedron*, 1993, **12**, 1419; F. Bottomley, W. V. F. Brooks, D. E. Paez, P. S. White and M. Mukaida, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 2465; A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 961; W. R. Murphy, Jr., K. J. Takeuchi and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 5817; M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **103**, 5577; J. L. Walash, R. M. Bullock and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 865.
77. B. Mondal, M. G. Walawalkar and G. K. Lahiri, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 4209.
78. B.,Mondal H., Paul V. G.Puranik and G. K.,Lahiri 2001, J. Chem. Soc., Dalton Trans., 481.
79. K., Deb P. C. Paul and S.,Goswami 1988, J. Chem. Soc., Dalton Trans., 2051.
80. K.,Deb and S.,Goswami 1991, Polyhedron, 10, 1799
81. T. K., Misra D.,Das C., Sinha P. K. Ghosh and C. K.,Pal 1998, Inorg. Chem., 37, 1672.

82. P,Byabartta. J, Dinda P K, Santra C, Sinha K,Panneerselvam F –L Liao and T –H, Lu 2001 J. Chem. Soc., Dalton Trans., 2825.
83. T. K.,Misra S P. K.antra and C., Sinha 1999, Transition Met. Chem., 24, 672;
84. S., Pal T. K., Misra C., Sinha A. M. Z. Slawin and J. D., Woolins 2000, Polyhedron, 19, 1925.
85. Hauser, U.; Oestreich, V.; Rohrweck, H. D. On optical dispersion in transparent molecular systems. Z. Phys. A: At. Nucl. 1977, 280 (1), 17−25.
86. Fomitchev, D. V.; Coppens, P. X-ray Diffraction Analysis of Geometry Changes upon Excitation: The Ground-State and MetastableState Structures of K2[Ru(NO2)4(OH)(NO)]. Inorg. Chem. 1996, 35 (24), 7021−7026. Carducci, M. D.; Pressprich, M. R.; Coppens, P. Diffraction studies of photoexcited crystals: Metastable nitrosyl-linkage isomers of sodium nitroprusside. J. Am. Chem. Soc. 1997, 119 (11), 2669−2678.
87. Awasabisah, D.; Richter-Addo, G. B. Chapter One-NOx Linkage Isomerization in Metal Complexes. Adv. Inorg. Chem. 2015, 67, 1−86.
88. Casaretto, N.; Pillet, S.; Bendeif, E. E.; Schaniel, D.; Gallien, A. K.; Klüfers, P.; Woike, T. Multiple light-induced NO linkage isomers in the dinitrosyl complex [RuCl(NO)2(PPh3)2]BF4 unravelled by photocrystallographic and IR analysis. IUCrJ 2015, 2 (1), 35−44. Cormary, B.; Malfant, I.; Buron-Le Cointe, M.; Toupet, L.; Delley, B.; Schaniel, D.; Mockus, N.; Woike, T.; Fejfarova, K.; Petricek, V.; Dusek, M.ˇ [Ru(py)4Cl(NO)](PF6)2·0.5H2O: a model system for structural determination and ab initio calculations of photo-induced linkage NO isomers. Acta Crystallogr., Sect. B: Struct. Sci. 2009, 65
89. 612−623. (5) Schaniel, D.; Woike, T.; Delley, B.; Boskovic, C.; Biner, D.; Kramer,̈ K. W.; Gü del, H. U. Long-lived light-induced metastable states in trans- [Ru(NH3)4(H2O)NO]Cl3·H2O and related compounds. Phys. Chem. Chem. Phys. 2005, 7
90. 1164−1170. (6) Morioka, Y.; Ishikawa, A.; Tomizawa, H.; Miki, E. I. Light-induced metastable states in nitrosyl−ruthenium complexes containing ethylenediamine and oxalate ion ligands. J. Chem. Soc., Dalton Trans. 2000, No. 5, 781−786. Ookubo, K.; Morioka, Y.; Tomizawa, H.; Miki, E. Vibrational spectroscopic study of light-induced metastable states of ethylenediaminenitrosylruthenium (II) complexes. J. Mol. Struct. 1996, 379 (1), 241−247.
91. Fomitchev, D. V.; Coppens, P. Light-induced metastable linkage isomers of transition metal nitrosyls. Comments Inorg. Chem. 1999, 21 (1−3), 131−148.
92. Cormary, B.; Ladeira, S.; Jacob, K.; Lacroix, P. G.; Woike, T.; Schaniel, D.; Malfant, I. Structural Influence on the Photochromic Response of a Series of Ruthenium Mononitrosyl Complexes. Inorg. Chem. 2012, 51 (14), 7492−7501.
93. Zöllner, H.; Krasser, W.; Woike, T.; Haussü hl, S. The existence of light-induced long-lived metastable states in different Xn[Fe(CN)5NO]· yH2O crystals, powders and solutions. Chem. Phys. Lett. 1989, 161 (6), 497−501.
94. Pichkov, V. N.; Zvyagintsev, O.; Sinitsyn, N. Nitrosoruthenium compound RuNO(NO2)2(NH3)2OH. Dokl. Akad. Nauk SSSR 1964, 156 (4), 891−893.
95. Khodashova, T. S.; Sergienko, V. S.; Porai-Koshits, M. A. X-ray structure determination for crystals of dinitrohydroxonitrosodiammineruthenium. J. Struct. Chem. 1971, 12 (3), 439−445. (12) Phillips, A. E.; Cole, J. M.; d'Almeida, T.; Low, K. S. Effects of the reaction cavity on metastable optical excitation in ruthenium-sulfur dioxide complexes. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 82 (15), 155118.
96. Kabin, E. V.; Emel'yanov, V. A.; Tkachev, S. V. Nitrosoruthenium nitrite-nitrate complexes in aqueous and nitric acid solutions as probed by 15N NMR. Russ. J. Inorg. Chem. 2013, 58 (2), 229−238.
97. Emelyanov, V. A.; Fedotov, M. A.; Belyaev, A. V. Study of reverse nitro-nitroso-transformations in the rithenium (II) complexes by the N15, O-17, Ru-99 NMR method. Zh. Neorg. Khim. 1993, 38 (11), 1842−1848. Kabin, E. V.; Emel'yanov, V. A.; Torgov, V. G.; Tkachev, S. V.; Us, T. V.; Korda, T. M. Behavior of nitrite forms of nitrosylruthenium on extraction and back extraction of heterometalic Ru/Zn complexes with trioctylphosphine oxide. Russ. J. Inorg. Chem. 2013, 58 (8), 994−1003.
98. Emel'yanov, V. A.; Baidina, I. A.; Gromilov, S. A.; Vasiliev, A. D.; Belyaev, A. V. Synthesis and Crystal Structure of Nitrosoruthenium Triammino Complex [RuNO(NH3)3Cl(H2O)]Cl2. J. Struct. Chem. 2000, 41 (6), 1030−1034.
99. Il'yin, M. A.; Emel'anov, V. A.; Belyaev, A. V.; Makhinya, A. N.; Tkachev, S. V.; Alferova, N. I. New method for the synthesis of transhydroxotetraamminenitrosoruthenium (II) dichloride and its characterization. Russ. J. Inorg. Chem. 2008, 53 (7), 1070−1076.

100. Sinitsyn, N. M.; Pichkov, V. N.; Zvyagintsev, O. E. Extraction of ruthenium nitrosonitro complexes by amines. Radiokhimiya 1966, 8, 545−555.
101. Plyusnina, O. A.; Emel'yanov, V. A.; Baidina, I. A.; Korol'kov, I. V.; Gromilov, S. A. Synthesis, structure, and properties of [RuNO- (NH3)4OH][PtCl4] and [RuNO(NH3)4OH][PdCl4]. J. Struct. Chem. 2007, 48 (1), 114−121. Vorobyev, V.; Kabin, E. V.; Emelyanov, V. A.; Baidina, I. A.; Korolkov, I. V. Synthesis and crystal structure of mernitroaquatriamminenitrosylruthenium (II) nitrate [RuNO- (NH3)3(NO2)(H2O)](NO3)2. Inorg. Chem. Commun. 2016, 68, 1−3.
102. Emel'yanov, V. A.; Baidina, I. A.; Gromilov, S. A.; Virovets, A. V. Synthesis and crystal structure of mixed-cation salt of transhydroxotetranitronitrosoruthenium (II) complex, KNa[Ru(NO) (NO2)4(OH)]·H2O. J. Struct. Chem. 2006, 47 (1), 63−70. (20) Il'in, M. A.; Kabin, E. V.; Emel'yanov, V. A.; Baidina, I. A.; Vorob'yov, V. A. trans-dinitro-and trans-dinitratoruthenium complexes [RuNO(NH3)2(NO2)2(OH)] and [RuNO(NH3)2(H2O) (NO3)2]- NO3·H2O. J. Struct. Chem. 2009, 50 (2), 328−334.
103. Ohashi, Y.; Yanagi, K.; Kurihara, T.; Sasada, Y.; Ohgo, Y. Crystalline state reaction of cobaloxime complexes by x-ray exposure. 1. Direct observation of cobalt-carbon bond cleavage in [(R)-1-cyanoethyl][(S)-(−)-.alpha.-methylbenzylamine] bis- (dimethylglyoximato)cobalt(III). J. Am. Chem. Soc. 1981, 103 (19), 5805−5812.
104. Bondi, A. van der Waals volumes and radii. J. Phys. Chem. 1964, 68, 441−451.
105. Fomitchev, D. V.; Novozhilova, I.; Coppens, P. Photo-induced linkage isomerism of transition metal nitrosyl and dinitrogen complexes studied by photocrystallographic techniques. Tetrahedron 2000, 56 (36), 6813−6820.
106. Emel'yanov, V. A.; Baidina, I. A.; Il'in, M. A.; Gromilov, S. A. Synthesis and crystal structure of nitrosoruthenium aquadiammine complex, [Ru(NO) (NH3)2Cl2(H2O)]Cl·H2O. J. Struct. Chem. 2006, 47 (2), 380−382.
107. Kostin, G. A.; Borodin, A. O.; Mikhailov, A. A.; Kuratieva, N. V.; Kolesov, B. A.; Pishchur, D. P.; Woike, T.; Schaniel, D. Photocrystallographic, Spectroscopic, and Calorimetric Analysis of Light-Induced Linkage NO Isomers in [RuNO(NO2)2(pyridine)2OH]. Eur. J. Inorg. Chem. 2015, 29, 4905−4913.
108. Emel'yanov, V. A.; Gromilov, S. A.; Baidina, I. A. Synthesis and Crystal Structure of Nitrotriammine Complex of Nitrosoruthenium (II) [RuNO(NH3)3(NO2) (OH)]Cl·0.5H2O. J. Struct. Chem. 2004, 45 (5), 879−888.
109. Sanz García, J.; Alary, F.; Boggio-Pasqua, M.; Dixon, I. M.; Malfant, I.; Heully, J. L. Establishing the Two-Photon Linkage Isomerization Mechanism in the Nitrosyl Complex trans-[RuCl(NO) (py)4]2+ by DFT and TDDFT. Inorg. Chem. 2015, 54 (17), 8310−8318. Khadeeva, L.; Kaszub, W.; Lorenc, M.; Malfant, I.; Buron-Le Cointe, M. Two-Step Photon Absorption Driving the Chemical Reaction in the Model Ruthenium Nitrosyl System [Ru(py)4Cl(NO)](PF6)2·1/2H2O. Inorg. Chem. 2016, 55 (9), 4117−4123.
110. Te Velde, G.; Baerends, E. J. Precise density-functional method for periodic structures. Phys. Rev. B: Condens. Matter Mater. Phys. 1991, 44 (15), 7888−7903. Wiesenekker, G.; Baerends, E. J. Quadratic integration over the three-dimensional Brillouin zone. J. Phys.: Condens. Matter 1991, 3 (35), 6721−6742. Franchini, M.; Philipsen, P. H. T.; Visscher, L. The Becke fuzzy cells integration scheme in the Amsterdam Density Functional program suite. J. Comput. Chem. 2013, 34 (21), 1819−1827. BAND2013, SCM, Theoretical Chemistry; Vrije Universiteit: Amsterdam, The Netherlands, 2013; http://www.scm.com. Kadantsev, E. S.; Klooster, R.; De Boeij, P. L.; Ziegler, T. The formulation and implementation of analytic energy gradients for periodic density functional calculations with STO/
111. Christianson, D. W.; Cox, J. D. Catalysis by metal-activated hydroxide in zinc and manganese metalloenzymes. Annu. Rev. Biochem. 1999, 68, 33−57.
112. Borovik, A. S. Bioinspired Hydrogen Bond Motifs in Ligand Design: The Role of Noncovalent Interactions in Metal Ion Mediated Activation of Dioxygen. Acc. Chem. Res. 2005, 38, 54−61. (b) Borovik, A. S. Role of metal−oxo complexes in the cleavage of C−H bonds. Chem. Soc. Rev. 2011, 40, 1870−1874. (c) Cook, S. A.; Borovik, A. S. Molecular Designs for Controlling the Local Environments around Metal Ions. Acc. Chem. Res. 2015, 48, 2407−2414. (113) (a) Marshall, L. J.; de Mendoza, J. Self-Assembled Squares and Triangles by Simultaneous Hydrogen Bonding and Metal Coordination. Org. Lett. 2013, 15, 1548−1551. (b) Lin, R. B.; He, Y.; Li, P.; Wang, H.; Zhou, W.; Chen, B. Multifunctional porous hydrogenbonded organic framework materials. Chem. Soc. Rev. 2019, 48, 1362−1389. (c) Nasser, N.; Borecki, A.; Boyle,

P. D.; Puddephatt, R. J. A Versatile Diphosphine Ligand: cis and trans Chelation or Bridging, with Self Association through Hydrogen Bonding. Inorg. Chem. 2013, 52, 7051−7060.

113.Chang, C. J.; Chng, L. L.; Nocera, D. G. Proton-Coupled O−O Activation on a Redox Platform Bearing a Hydrogen-Bonding Scaffold. J. Am. Chem. Soc. 2003, 125, 1866−1876. (b) Lopez, N.; Graham, D. J.; McGuire, R., Jr.; Alliger, G. E.; Horn-Shao, Y.; Cummns, C. C.; Nocera, D. G. Reversible Reduction of Oxygen to Peroxide Facilitated by Molecular Recognition. Science 2012, 335, 450−453.

114.Nath, I.; Chakraborty, J.; Verpoort, F. Metal organic frameworks mimicking natural enzymes: a structural and functional analogy. Chem. Soc. Rev. 2016, 45, 4127−4170.

115.Galan, A.; Ballester, P. Stabilization of reactive species by supramolecular encapsulation. Chem. Soc. Rev. 2016, 45, 1720−1737.

116.Dydio, P.; Reek, J. N. H. Supramolecular control of selectivity in transition metal catalysis through substrate preorganization. Chem. Sci. 2014, 5, 2135−2145. (b) Kuninobu, Y.; Torigoe, T. Recent Progress on Transition Metal-catalysed Regioselective C-H Transformations Based on Noncovalent Interactions. Org. Biomol. Chem. 2020, 18, 4126−4134. (c) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. Supramolecular Catalysis in Metal-Ligand Cluster Hosts. Chem. Rev. 2015, 115, 3012−3035. (d) Ballester, P.; van Leeuwen, P. W. N. M.; Vidal, A. In Supramolecular Catalysis. Compre. Inorg. Chem. II 2013, 6, 457−486.

117.Š mejkal, T.; Breit, B. A Supramolecular Catalyst for Regioselective Hydroformylation of Unsaturated Carboxylic Acids. Angew. Chem., Int. Ed. 2008, 47, 311−315.

118.Hoke, T.; Herdtweck, E.; Bach, T. Hydrogen-bond mediated regio- and enantioselectivity in a C−H amination reaction catalysed by a supramolecular Rh(II) complex. Chem. Commun. 2013, 49, 8009−8011.

119.Huang, Z.; Chen, Z.; Lim, L. H.; Quang, G. C. P.; Hirao, H.; Zhou, J. Weak Arene C-H···O Hydrogen Bonding in PalladiumCatalyzed Arylation and Vinylation of Lactones. Angew. Chem., Int. Ed. 2013, 52, 5807−5812. (b) Fackler, P.; Berthold, C.; Voss, F.; Bach, T. Hydrogen-Bond-Mediated Enantio- and Regioselectivity in a RuCatalyzed Epoxidation Reaction. J. Am. Chem. Soc. 2010, 132, 15911− 15913. (c) Grotjahn, D. B.; Incarvito, C. D.; Rheingold, A. L. Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes. Angew. Chem., Int. Ed. 2001, 40, 3884−3887. (d) Fackler, P.; Huber, S. M.; Bach, T. Enantio- and Regioselective Epoxidation of Olefinic Double Bonds in Quinolones, Pyridones, and Amides Catalyzed by a Ruthenium Porphyrin Catalyst with a Hydrogen Bonding Site. J. Am. Chem. Soc. 2012, 134, 12869− 12878. (e) Kuninobu, Y.; Ida, H.; Nishi, M.; Kanai, M. A metaselective C−H borylation directed by a secondary interaction between ligand and substrate. Nat. Chem. 2015, 7, 712−717. (f) Bai, S. T.; Bheeter, C. B.; Reek, J. N. H. Hydrogen Bond Directed orthoSelective C-H Borylation of Secondary Aromatic Amides. Angew. Chem., Int. Ed. 2019, 58, 13039−13043. (g) Grotjahn, D. B.; Lev, D. A. A General Bifunctional Catalyst for the Anti-Markovnikov Hydration of Terminal Alkynes to Aldehydes Gives Enzyme-Like Rate and Selectivity Enhancements. J. Am. Chem. Soc. 2004, 126, 12232−12233.

120.Bansal, D.; Kumar, G.; Hundal, G.; Gupta, R. Mononuclear complexes of amide-based ligands containing appended functional groups: Role of secondary coordination spheres on catalysis. Dalton Trans. 2014, 43, 14865−14875. (b) Bansal, D.; Gupta, R. HydroxideBridged Dicopper Complexes: The Influence of Secondary Coordination Sphere on Structure and Catecholase Activity. Dalton Trans. 2017, 46, 4617−4627. (c) Bansal, D.; Gupta, R. Selective sensing of ATP by hydroxide-bridged dizinc(II) complexes offering a hydrogen bonding cavity. Dalton Trans. 2019, 48, 14737−14747.

121.Kumar, G.; Gupta, R. Three dimensional {Co3+-Zn2+} and {Co3+-Cd2+} networks originated from carboxylate-rich building blocks: Syntheses, structures, and heterogeneous catalysis. Inorg. Chem. 2013, 52, 10773−10787. (b) Kumar, G.; Aggarwal, H.; Gupta, R. Cobalt complexes appended with para- and meta-arylcarboxylic acids: Influence of cation, solvent, and symmetry on hydrogenbonded assemblies. Cryst. Growth Des. 2013, 13, 74−90. (c) Ali, A.; Hundal, G.;

Gupta, R. Co3+-based building blocks with appended phenol and catechol groups: Examples of placing hydrogen-bond donors and acceptors in a single molecule. Cryst. Growth Des. 2012, 12, 1308−1319. (d) Srivastava, S.; Gupta, B. K.; Gupta, R. Lanthanide-Based Coordination Polymers for the Size-Selective Detection of Nitroaromatics. Cryst. Growth Des. 2017, 17, 3907− 3916.

122. Kumar, G.; Pachisia, S.; Kumar, P.; Kumar, V.; Gupta, R. Znand Cd-based Coordination Polymers Offering H-Bonding Cavities: Highly Selective Sensing of S2O7 2 and Fe3+ Ions. Chem. - Asian J. 2019, 14, 4594−4600.
123. Kumar, S.; Kishan, R.; Kumar, P.; Pachisia, S.; Gupta, R. SizeSelective Detection of Picric Acid by Fluorescent Palladium Macrocycles. Inorg. Chem. 2018, 57, 1693−1697.
124. Pachisia, S.; Gupta, R. Two Hg(II)-Based Macrocycles Offering Hydrogen Bonding Cavities: Influence of Cavity Structure on Heterogeneous Catalysis. Cryst. Growth Des. 2019, 19, 6039−6047.
125. Kumar, P.; Gupta, R. K.; Pandey, D. S. Half-sandwich arene ruthenium complexes: synthetic strategies and relevance in catalysis. Chem. Soc. Rev. 2014, 43, 707−733. (b) Gunanathan, C.; Milstein, D. Bond Activation and catalysis by Ruthenium Pincer Complexes. Chem. Rev. 2014, 114, 12024−12087. (c) Ogba, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H. Recent advances in ruthenium-based olefin metathesis. Chem. Soc. Rev. 2018, 47, 4510−4544. (d) Zhang, J.; Balaraman, E.; Leitus, G.; Milstein, D. Electron-Rich PNP- and PNN-Type Ruthenium (II) Hydrido Borohydride Pincer Complexes. Synthesis, Structure, and Catalytic Dehydrogenation of Alcohols and Hydrogenation of Esters. Organometallics 2011, 30, 5716−5724. (e) Jia, W. G.; Cheng, M. X.; Gao, L. L.; Tan, S. M.; Wang, C.; Liu, X.; Lee, R. A ruthenium bisoxazoline complex as a photoredox catalyst for nitro compound reduction under visible light. Dalton Trans. 2019, 48, 9949−9953.
126. Romain, S.; Vigara, L.; Llobet, A. Oxygen-Oxygen Bond Formation Pathways Promoted by Ruthenium Complexes. Acc. Chem. Res. 2009, 42, 1944−1953. (b) Shaffer, D. W.; Xie, Z.; Concepcion, J. J. O−O bond formation in ruthenium-catalyzed water oxidation: single-site nucleophilic attack vs. O−O radical coupling. Chem. Soc. Rev. 2017, 46, 6170−6193.
127. Donthireddy, S. N. R.; Illam, P. M.; Rit, A. Ruthenium(II) Complexes of Heteroditopic N-Heterocyclic Carbene Ligands: Efficient Catalysts for C−N Bond Formation via a Hydrogen Borrowing Strategy under Solvent-Free Conditions. Inorg. Chem. 2020, 59, 1835−1847. (b) MacDougall, T. J.; Trepanier, S. J.; Dutton, J. L.; Ferguson, M. J.; McDonald, R.; Cowie, M. Facile Carbon− Carbon Bond Formation and Multiple Carbon−Hydrogen Bond Activations Promoted by Methylene-Bridged Iridium/Ruthenium Complexes. Organometallics 2011, 30, 5882−5893. (c) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. Ruthenium(II) Catalyzed C−H Bond Activation and Functionalization. Chem. Rev. 2012, 112, 5879−5918.
128. Hamelin, O.; Menage, S.; Charnay, F.; Chavarot, M.; Pierre, J. l.; Pecaut, J.; Fontecave, M. New Polydentate Ligand and Catalytic Properties of the Corresponding Ruthenium Complex During Sulfoxidation and Alkene Epoxidation. Inorg. Chem. 2008, 47, 6413−6420. (b) Duliere, E.; Devillers, M.; Marchand-Brynaert, J. Novel Phosphinite−Ruthenium Complexes Covalently Bound on Silica: Synthesis, Characterization, and Catalytic Behavior versus Oxidation Reactions of Alcohols into Aldehydes. Organometallics 2003, 22, 804−811. (c) Naota, T.; Takaya, H.; Murahashi, S. I. Ruthenium-Catalyzed Reactions for Organic Synthesis. Chem. Rev. 1998, 98, 2599−2660.
129. Jia, W. G.; Ling, S.; Zhang, H. N.; Sheng, E. H.; Lee, R. Half-Sandwich Ruthenium Phenolate−Oxazoline Complexes: Experimental and Theoretical Studies in Catalytic Transfer Hydrogenation of Nitroarene. Organometallics 2018, 37, 40−47. (b) Jia, W. G.; Zhang, H.; Zhang, T.; Xie, D.; Ling, S.; Sheng, E. H. Half-Sandwich Ruthenium Complexes with Schiff-Base Ligands: Syntheses, Characterization, and Catalytic Activities for the Reduction of Nitroarenes. Organometallics 2016, 35, 503−512. (c) Sathishkumar, P. N.; Raveendran, N.; Bhuvanesh, N. S. P.; Karvembu, R. Chemoselective transfer hydrogenation of nitroarenes, ketones and aldehydes using acylthiourea based Ru(II)(p-cymene) complexes as pre-catalysts. J.

Organomet. Chem. 2018, 876, 57−65. (d) Huang, C. Y.; Kuan, K.-Y.; Liu, Y. H.; Peng, S. M.; Liu, S. T. Synthesis and Catalytic Activity of Water-Soluble Ruthenium(II) Complexes Bearing a Naphthyridine− Carboxylate Ligand. Organometallics 2014, 33, 2831−2836. (e) L'Eplattenier, F.; Matthys, P.; Calderazzo, F. Homogeneous rutheniumcatalyzed reduction of nitrobenzene. Inorg. Chem. 1970, 9, 342−345.

130. Ono, N. The Nitro Group in Organic Synthesis; Wiley-VCH: New York, 2001. (b) Mitchell, S. C.; Waring, R. H. In Ullmanns Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2000.
131. Kondo, K.; Ogawa, H.; Shinohara, T.; Kurimura, M.; Tanada, Y.; Kan, K.; Yamashita, H.; Nakamura, S.; Hirano, T.; Yamamura, Y.; Mori, T.; Tominaga, M.; Itai, A. Novel Design of Nonpeptide AVP V2 Receptor Agonists: Structural Requirements for an Agonist Having 1-(4-Aminobenzoyl)-2,3,4,5-tetrahydro-1H-1- benzazepine as a Template. J. Med. Chem. 2000, 43, 4388−4397. (b) Tafesh, A. M.; Weiguny. A Review of the Selective Catalytic Reduction of Aromatic Nitro Compounds into Aromatic Amines, Isocyanates, Carbamates, and Ureas Using CO. Chem. Rev. 1996, 96, 2035−2052.
132. Downing, R. S.; Kunkeler, P. J.; Van Bekkum, H. Catalytic syntheses of aromatic amines. Catal. Today 1997, 37, 121−136. (b) Vaidya, M. J.; Kulkarni, S. M.; Chaudhari, R. V. Synthesis of pAminophenol by Catalytic Hydrogenation of p-Nitrophenol. Org. Process Res. Dev. 2003, 7, 202−208.
133. Kadam, H. K.; Tilve, S. G. Advancement in methodologies for reduction of nitroarenes. RSC Adv. 2015, 5, 83391−83407. (b) Corma, A.; Serna, P. Chemoselective hydrogenation of nitro compounds with supported gold catalysts. Science 2006, 313, 332− 334. (c) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. Reduction of Nitro Compounds Using 3d-Non-Noble Metal Catalysts. Chem. Rev. 2019, 119, 2611−2680. (d) Verma, P. K.; Bala, M.; Thakur, K.; Sharma, U.; Kumar, N.; Singh, B. Iron and Palladium(II) Phthalocyanines as Recyclable Catalysts for Reduction of Nitroarenes. Catal. Lett. 2014, 144, 1258−1267.
134. Sorribes, I.; Wienhofer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. Chemoselective Transfer Hydrogenation to Nitroarenes Mediated by Cubane-Type Mo3S4 Cluster Catalysts. Angew. Chem., Int. Ed. 2012, 51, 7794−7798. (b) Yu, L.; Zhang, Q.; Li, S. S.; Huang, J.; Liu, Y. M.; He, H. Y.; Cao, Y. Gold-Catalyzed Reductive Transformation of Nitro Compounds Using Formic Acid: Mild, Efficient, and Versatile. ChemSusChem 2015, 8, 3029−3035. (c) Wienhofer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective IronCatalyzed Transfer Hydrogenation of Nitroarenes without Base. J. Am. Chem. Soc. 2011, 133, 12875−12879. (d) Lin, X.; Wu, M.; Wu, D.; Kuga, S.; Endo, T.; Huang, Y. Platinum nanoparticles using wood nanomaterials: eco-friendly synthesis, shape control and catalytic activity for p-nitrophenol reduction. Green Chem. 2011, 13, 283−287.
135. Yadav, S.; Kumar, S.; Gupta, R. Cobalt complexes of pyrrolecarboxamide ligands as catalysts in nitro reduction reactions: Influence of electronic substituents on catalysis and mechanistic insights. Inorg. Chem. Front. 2017, 4, 324−335. (b) Srivastava, S.; Dagur, M. S.; Ali, A.; Gupta, R. Trinuclear {Co2+−M3+−Co2+} complexes catalyse reduction of nitro compounds. Dalton Trans. 2015, 44, 17453−17461. (c) Kumar, S.; Gupta, R. Cobalt Complexes Catalyze Reduction of Nitro Compounds: Mechanistic Studies. ChemistrySelect. 2017, 2, 8197−8206.
136. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination compounds: Part A: Theory and Applications in Inorganic Chemistry; John Wiley & Sons, Inc.: 6th ed., 2008. (b) Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination compounds: Part B: Theory and Applications in Inorganic Chemistry; John Wiley & Sons, Inc.: 6th ed., 2008.
137. Jia, W. G.; Ling, S.; Zhang, H. N.; Sheng, E. H.; Lee, R. Half-Sandwich Ruthenium Phenolate−Oxazoline Complexes: Experimental and Theoretical Studies in Catalytic Transfer Hydrogenation of Nitroarene. Organometallics 2018, 37, 40−47. (b) Yang, D.; Tang, Y.; Song, H.; Wang, B. o-Aryloxide-N-heterocyclic Carbenes: Efficient Synthesis of the Proligands and Their p-Cymene Ruthenium Complexes. Organometallics 2015, 34, 2012−2017.

138. Del Bene, J. E.; Perera, S. A.; Bartlett, R. J. Hydrogen Bond Types, Binding Energies, and 1 H NMR Chemical Shifts. J. Phys. Chem. A 1999, 103, 8121−8124.
139. Yang, W. W.; Wang, L.; Zhong, Y. W.; Yao, J. Tridentate Cyclometalated Ruthenium(II) Complexes of "Click" Ligand 1,3- Di(1,2,3-triazol-4-yl)benzene. Organometallics 2011, 30, 2236−2240. (b) Ji, Z.; Huang, S. D.; Guadalupe, A. R. Synthesis, X-ray structures, spectroscopic and electrochemical properties of ruthenium(II) complexes containing 2,2-bipyrimidine. Inorg. Chim. Acta 2000, 305, 127−134. (c) Choi, M. Y.; Chan, M. C. W.; Zhang, S.; Cheung, K. K.; Che, M.; Wong, K. Y. MLCT and LMCT Transitions in Acetylide Complexes. Structural, Spectroscopic, and Redox Properties of Ruthenium(II) and -(III) Bis(σ-arylacetylide) Complexes Supported by a Tetradentate Macrocyclic Tertiary Amine Ligand. Organometallics 1999, 18, 2074−2080.
140. Bhalla, R.; Boxwell, C. J.; Duckett, S. B.; Dyson, P. J.; Humphrey, D. G.; Steed, J. W.; Suman, P. Chemical, Electrochemical and Structural Aspects of the Ruthenium Complexes Ru(η-arene)- Cl_2(P) (Where Arene = Benzene, [2.2]Paracyclophane and P = Trphenylphosphine, rac[2.2]Paracyclophanylphosphine). Organometallics 2002, 21, 924−928. (b) Kumar, P.; Singh, A. K.; Pandey, R.; Li, P.-Z.; Singh, S. K.; Xu, Q.; Pandey, D. S. Synthesis, characterization and reactivity of arene ruthenium compounds based on 2,2- dipyridylamine and di-2-pyridylbenzylamine and their applications in catalytic hydrogen transfer of ketones. J. Organomet. Chem. 2010, 695, 2205−2212. (c) Cheisson, T.; Mazaud, L.; Auffrant, A. Ruthenium complexes featuring cooperative phosphine−pyridine− iminophosphorane (PNN) ligands: synthesis, reactivity and catalytic activity. Dalton Trans 2018, 47, 14521−14530. (d) Bhadbhade, M. M.; Field, L. D.; Gilbert-Wilson, R.; Guest, R. W.; Jensen, P. Ruthenium Hydride Complexes of the Hindered Phosphine Ligand Tris(3-diisopropylphosphinopropyl)phosphine. Inorg. Chem. 2011, 50, 6220−6228. (e) Tsai, Y. W.; Chen, Y. F.; Li, Y. J.; Chen, K. H.; Lin, C. H.; Huang, J. H. Structural Determination of Ruthenium Complexes Containing Bi-Dentate Pyrrole-Ketone Ligands. Molecules 2018, 23, 159−169.
141. Kumar, P.; Gupta, R. The wonderful world of pyridine-2,6- dicarboxamide based scaffolds. Dalton Trans. 2016, 45, 18769− 18783.
142. Steiner, T. Hydrogen-Bond Distances to Halide Ions in Organic and Organometallic Crystal Structures: Up-to-date Database Study. Acta Crystallogr., Sect. B: Struct. Sci. 1998, B54, 456−463. (b) Desiraju, G. R.; Steiner, T. The weak hydrogen bond: in structural chemistry and biology; Oxford University Press, 1999. (c) Serebryanskaya, T. V.; Novikov, A. S.; Gushchin, P. V.; Haukka, M.; Asfin, R. E.; Tolstoy, P. M.; Kukushkin, V. Y. Identification and H(D)-bond energies of C−H(D)···Cl interactions in chloride−haloalkane clusters: a combined X-ray crystallographic, spectroscopic, and theoretical study. Phys. Chem. Chem. Phys. 2016, 18, 14104−14112.
143. Bolger, J. A.; Ferguson, G.; James, J. P.; Long, C.; McArdle, P.; Vos, J. G. Synthesis, characterisation and variable-temperature nuclear magnetic resonance of bis(bipyridine)ruthenium complexes containing dihydrazone ligands. J. Chem. Soc., Dalton Trans. 1993, 1577−1583. (b) Corral, E.; Hotze, A. C. G.; Magistrato, A.; Reedijk, J. Interaction between the DNA Model Base 9-Ethylguanine and a Group of Ruthenium Polypyridyl Complexes: Kinetics and Conformational Temperature Dependence. Inorg. Chem. 2007, 46, 6715− 6722. (c) Velders, A. H.; Massera, C.; Ugozzoli, F.; Biagini-Cingi, M.; Manotti-Lanfredi, A. M.; Haasnoot, J. G.; Reedijk, J. A Simple Example of the Fluxional Behaviour of Ruthenium-Coordinated C2- Symmetric Monodentate Ligands−Synthesis, 1 H NMR Spectroscopic Study, and Crystal Structure of cis-[Ru(bpy)2(4Pic)2](PF6)2. Eur. J. Inorg. Chem. 2002, 2002, 193−198. (d) Gilbert-Wilson, R.; Field, L. D.; Bhadbhade, M. Ruthenium Hydrides Containing the Superhindered Polydentate Polyphosphine Ligand P(CH2CH2P t Bu2)3. Inorg. Chem. 2014, 53, 12469−12479. (e) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. Exchange Couplings between a Hydride and a Stretched Dihydrogen Ligand in Ruthenium Complexes J. J. Am. Chem. Soc. 1998, 120, 4228−4229.

144. Lever, A. B. P. Electrochemical Parametrization of Metal Complex Redox Potentials, Using the Ruthenium(III)/Ruthenium- (II) Couple To Generate a Ligand Electrochemical Series. Inorg. Chem. 1990, 29, 1271−1285. (b) Vijayan, P.; Yadav, S.; Yadav, S.; Gupta, R. Ruthenium(II) complexes of pyridine-carboxamide ligands bearing appended benzothiazole/benzimidazole rings: Structural diversity and catalysis. Inorg. Chim. Acta 2020, 502, 119285− 119296. (c) Hathcock, D.; Morris, J.; Madden, J.; Slattery, S. J. Ligand Substituent Effects on Ruthenium (III/II) Redox Properties: An Advanced Inorganic Laboratory Experiment. Chem. Educ. 1997, 2, 1−8.
145. Nakamura, G.; Okamura, M.; Yoshida, M.; Suzuki, T.; Takagi, H. D.; Kondo, M.; Masaoka, S. Electrochemical Behavior of Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand. Inorg. Chem. 2014, 53, 7214−7226. (b) Matsuo, Y.; Nakamura, E. Ruthenium(II) Complexes of Pentamethylated [60]Fullerene. Alkyl, Alkynyl, Chloro, Isocyanide, and Phosphine Complexes. Organometallics 2003, 22, 2554−2563.
146. Singh, S. K.; Chandra, M.; Pandey, D. S.; Puerta, M. C.; Valerga, P. Helices of ruthenium complexes involving pyridyl−azine ligands: synthesis, spectral and structural aspects Redox catalysis. J. Organomet. Chem. 2004, 689, 3612−3620. (b) Valerga, P; Puerta, M.C; Pandey, D.S Synthetic, spectral, electrochemical and structural aspects of some Ru(II) arene complexes with some novel bridging ligands. J. Organomet. Chem. 2002, 648, 27−32. (c) Lahuerta, P.; Latorre, J.; Soto, J.; Mugnier, Y. Electrochemical studies on organometallic compounds□xx. Electrogeneration of an unusual organometallic derivative of ruthenium(I). Polyhedron 1989, 8, 2803− 2807.
147. Brown, H. C.; Mead, E. J.; Rao, B. C. S. Study of solvents for sodiumborohydride and the effect of solvent and the metal ion on borohydride reductions. J. Am. Chem. Soc. 1955, 77, 6209−6213.
148. Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. Suppression of Unwanted Heterogeneous Platinum(0)- Catalyzed Reactions by Poisoning with Mercury(0) in Systems Involving Competing Homogeneous Reactions of Soluble Organoplatinum Compounds: Thermal Decomposition of Bis- (triethylphosphine)-3,3,4,4-tetramet hylplatinacyclopentane. Organometallics 1985, 4, 1819−1830. (b) Bayram, E.; Finke, R. G. Quantitative 1,10-Phenanthroline Catalyst-Poisoning Kinetic Studies of Rh(0) Nanoparticle and Rh4 Cluster Benzene Hydrogenation Catalysts: Estimates of the Poison Kassociation Binding Constants, of the Equivalents of Poison Bound and of the Number of Catalytically Active Sites for Each Catalyst. ACS Catal. 2012, 2, 1967−1975. (c) Tseng, K. N. T.; Rizzi, A. N.; Szymczak, N. K. Oxidant-Free Conversion of Primary Amines to Nitriles. J. Am. Chem. Soc. 2013, 135, 16352−16355.
149. Rai, R. K.; Mahata, A.; Mukhopadhyay, S.; Gupta, S.; Li, P. Z.; Nguyen, K. T.; Zhao, Y.; Pathak, B.; Singh, S. K. Room-Temperature Chemoselective Reduction of Nitro Groups Using Non-noble Metal Nanocatalysts in Water. Inorg. Chem. 2014, 53, 2904−2909.
150. Corbett, M. D.; Chipko, B. R. Synthesis and Antibiotic Properties of Chloramphenicol Reduction Products. Antimicrob. Agents Chemother. 1978, 13, 193−198. (b) Balbi, H. J. Chloramphenicol: A Review. Pediatrics in Review 2004, 25, 284−288. (c) Yunis, A. A. CHLORAMPHENICOL: Relation of Structure to Activity and Toxicity. Annu. Rev. Pharmacol. Toxicol. 1988, 28, 83−100. (d) Rahal, J. J.; Simberkoff, M. S. Bactericidal and bacteriostatic action of chloramphenicol against memingeal pathogens. Antimicrob. Agents Chemother. 1979, 16, 13−18.
151. Touaibia, M.; Jean-Francois, J.; Doiron, J. Caffeic Acid, A¸ Versatile Pharmacophore: An Overview. Mini-Rev. Med. Chem. 2011, 11, 695−713.
152. Alfonso, I.; Burguete, M. I.; Galindo, F.; Luis, S. V.; Vigara, L. Molecular Rotors as Simple Models to Study Amide NH-Aromatic Interactions and Their Role in the Folding of Peptide-like Structures. J. Org. Chem. 2007, 72, 7947−7956. (b) Imai, Y. N.; Inoue, Y.; Nakanishi, I.; Kitaura, K. Amide−π Interactions Between Formamide and Benzene. J. Comput. Chem. 2009,

30, 2267−2276. (c) Goyal, H.; Pachisia, S.; Gupta, R. Systematic Design of a Low-Molecular-Weight Gelator and Its Application in the Sensing and Retention of Residual Antibiotics Cryst. Cryst. Growth Des. 2020, 20, 6117−6128.

153. Nitro-substituted phenols were used for the substrate binding studies due to their signature absorption spectral features and their ability to form H-bonds either through −NO2 or via −OH group.
154. Pandey, S.; Kumar, P.; Gupta, R. Polymerization led selective detection and removal of Zn2+ and Cd2+ ions: Isolation of Zn- and Cd- MOFs and reversibility studies. Dalton Trans. 2018, 47, 14686−14695. (b) Kumar, P.; Kumar, V.; Gupta, R. Arene-based fluorescent probes for the selective detection of iron. RSC Adv. 2015, 5, 97874−97882. (c) Kumar, P.; Kumar, V.; Gupta, R. Selective fluorescent turn-off sensing of Pd2+ ion: applications as paper strips, polystyrene films, and in cell imaging. RSC Adv. 2017, 7, 7734−7741.
155. Bansal, D.; Gupta, R. Chemosensors containing appended benzothiazole group(s): selective binding of Cu2+and Zn2+ ions by two related receptors. Dalton Trans. 2016, 45, 502−507. (b) Kumar, V.; Kumar, P.; Gupta, R. Fluorescent detection of multiple ions by two related chemosensors: structural elucidations and logic gate applications. RSC Adv. 2017, 7, 23127−23135.
156. Thordarson, P. Determining association constants from titration experiments in supramolecular chemistry. Chem. Soc. Rev. 2011, 40, 1305−1323. (b) Hibberta, D. B.; Thordarson, P. The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis. Chem. Commun. 2016, 52, 12792− 12805.
157. Bordwell, F. G. Equilibrium acidities in dimethyl sulfoxide solution. Acc. Chem. Res. 1988, 21, 456−463. (b) Reusch, W. Virtual Textbook of Organic Chemistry, 1999.
158. Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 1: non-covalent interactions as a tool for building and modifying homogeneous catalysts. Chem. Soc. Rev. 2014, 43, 1660−1733. (b) Addala, A.; Geiger, D. K.; Setifi, Z.; Setifi, F. Hydrogen bonding and π-π interactions in the cocrystal salt [Fe(bpe)2(H2O)4](TCEP)2.2(bpe) [bpe is trans-1,2-bis(pyridin4-yl)ethene and TCEP is 1,1,3,3-tetracyano-2-ethoxypropenide]. Acta Crystallogr., Sect. C: Struct. Chem. 2019, C75, 348−353.
159. Wu, D.; Deng, K.; Zeng, Q.; Wang, C. Selective Effect of Guest Molecule Length and Hydrogen Bonding on the Supramolecular Host Structure. J. Phys. Chem. B 2005, 109, 22296−22300.
160. Viswamitra, M. A.; Radhakrishnan, R.; Bandekar, J.; Desiraju, G. R. Evidence for O-H···C and N-H···C Hydrogen Bonding in Crystalline Alkynes, Alkenes, and Aromatics. J. Am. Chem. Soc. 1993, 115, 4868−4869. (b) Janiak, C.; Scharmann, T. G. Supramolecular C-H···O, C-H···N and C-H···Cl interactions in metal compounds with multi-topic poly(pyrazolyl)borate ligands. Polyhedron 2003, 22, 1123−1133.
161. Dyson, R. M.; Hazenkamp, M.; Kaufmann, K.; Maeder, M.; Studer, M.; Zilian, A. J. Modern tools for reaction monitoring: hard and soft modelling of ‘non-ideal’, on-line acquired spectra. J. Chemom. 2000, 14, 737−750. (b) Leipzig, B. Ü ber stufenweist des nitrobenzols mit begrenztem kathodenpotential. Z. Elektrochem. Angew. Phys. Chem. 1898, 22, 506−514.
162. Engert, J. M.; Slenczka, A.; Kensy, U.; Dick, B. Visible and Near UV Absorption Spectrum of Nitrosobenzene Isolated in Solid Argon: Maximum Entropy Analysis, Homogeneous Line Width of S2, and Semiempirical Electronic Structure Calculations. J. Phys. Chem. 1996, 100, 11883−11892.
163. Loos, P.; Alex, H.; Hassfeld, J.; Lovis, K.; Platzek, J.; Steinfeldt, N.; HÜ bne, S. Selective Hydrogenation of Halogenated Nitroaromatics to Haloanilines in Batch and Flow. Org. Process Res. Dev. 2016, 20, 452−464. (b) Pietrowski, M. Recent Developments in Heterogeneous Selective Hydrogenation of Halogenated Nitroaromatic Compounds to Halogenated Anilines. Curr. Org. Synth. 2012, 9, 470−487.

164. Cantillo, D.; Moghaddam, M. M.; Kappe, C. O. Hydrazinemediated Reduction of Nitro and Azide Functionalities Catalyzed by Highly Active and Reusable Magnetic Iron Oxide Nanocrystals. J. Org. Chem. 2013, 78, 4530−4542. (b) Larsen, J. W.; Freund, M.; Kim, K. Y.; Sidovar, M.; Stuart, J. L. Mechanism of the carbon catalyzed reduction of nitrobenzene by hydrazine. Carbon 2000, 38, 655−661.
165. Huang, J.; Chen, J.; Gao, H.; Chen, L. Kinetic Aspects for the Reduction of CO2 and CS2 with Mixed-Ligand Ruthenium(II) Hydride Complexes Containing Phosphine and Bipyridine. Inorg. Chem. 2014, 53, 9570−9580. (b) Rodriguez, V.; Donnadieu, B.; SaboEtienne, S.; Chaudret, B. Hydride and Dihydrogen Ruthenium Complexes of the Tripyrrolylphosphine Ligand. Organometallics 1998, 17, 3809−3814. (c) Al-Ibadi, M. A. M.; Duckett, S. B.; McGrady, J. E. Characterisation of tri-ruthenium dihydride complexes through the computation of NMR parameters. Dalton Trans. 2012, 41, 4618− 4625.
166. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals; Pergamon Press: Oxford, UK, 1980.
167. Kumar, S.; Kishan, R.; Gupta, R. Convenient Route for the Synthesis of Ortho-, Meta-, and Para-Substituted Diphenylphosphinoamine. Indian Patent No. 309321, 2019.
168. Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. (η6 -Hexamethylbenzene)ruthenium Complexes. Inorg. Synth. 1982, 21, 74−78. (b) Bennett, M. A.; Smith, A. K. Arene Ruthenium(II) Complexes formed by Dehydrogenation of Cyclohexadienes with Ruthenium(III) Trichlorides. J. Chem. Soc., Dalton Trans. 1974, 233− 241.
169. Swayer, D. T.; Roberts, J. L. Experimental Electrochemistry for Chemists; Wiley: New York, 1974.
170. Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. Chem. Rev. 1996, 96, 877−910.
171. CrysAlisPro, v 1.171.33.49b; Oxford Diffraction Ltd., 2009.
172. SMART & SAINT Software Reference manuals, Version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.
173. Sheldrick, G. M. SADABS, A software for empirical absorption correction, Ver. 2.05; University of Göttingen: Göttingen, Germany, 2002.
174. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. Completion and Refinement of Crystal Structures with SIR92. J. Appl. Crystallogr. 1993, 26, 343−350.
175. Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, A64, 112−122.
176. Farrugia, L. J. WinGX - A multipurpose crystallographic tool, v1.70; Department of Chemistry, University of Glasgow, 2003.
177. Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: The Netherlands, 2002. (72) Ritchie, D. W. Hex; Inria, 2012. http://hex.loria.fr/.