DOI: 10.1002/ejic.200900312

1,8-Naphthyridine Revisited: Applications in Dimetal Chemistry

Jitendra K. Bera,*[a] Nabanita Sadhukhan,[a] and Moumita Majumdar[a]

Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Keywords: Dimetals / Organometallics / Iridium / Self-assembly / N ligands

The diverse applications of functionalized 1,8-naphthyridine (NP) ligands is the focus of this microreview. Simpler synthetic routes and the pliant nature of NP-R steered us towards their utilization in dimetal chemistry. The ongoing research on NP chemistry in our laboratory is highlighted. The topics include the comprehensive study of the ligand disposition around the quadruply bonded Mo_2 core, modulation of the metal–metal distance by axial donors in paddlewheel complexes, facile cyclometalation and C–C bond formation at axial sites of the diruthenium(I) core, building metallosupramolecular architectures, and the formation of novel unsupported iridium(II) dimer aided by redox-active NP-R ligands.

Introduction

The pharmacological and medicinal applications of 1,8-naphthyridine (NP) derivatives have shaped, and continue to influence, the growth of NP chemistry.[1] Nalidixic acid (Scheme 1) was the first NP derivative approved as an antibacterial drug. Further modifications have led to a new set of potent biologically active compounds. Beginning in 1970, NP has been regularly used as ligands in the field of coordination chemistry. A host of mononuclear transition metal and lanthanide complexes have been reported.[2] Monodentate binding of the N8 atom and bidentate-chelate binding utilizing the N1 and N8 atoms are the coordination modes in these compounds (Scheme 2). The κN_8 mode of binding is prevalent for NP having an appendage at 2-position. Eight-coordinate transition-metal complexes of stoichiometry $[M(NP)_4]^{2+}$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pd) have been reported, which were characterized by structural and spectroscopic studies.[3] The NP ligand, resembling two edge-fused pyridine rings, has a constrained "bite" distance (2.2 Å)[4] that is attributed to high-coordi-

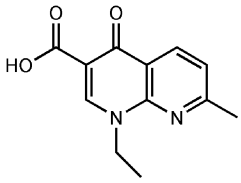
[a] Department of Chemistry,
Indian Institute of Technology Kanpur,
Kanpur 208016, India
Fax: +91-512-259-7436
E-mail: jbera@iitk.ac.in

Jitendra K. Bera received his MSc from the University of Kalyani in 1993 and his PhD from the Indian Institute of Science in 1999. After postdoctoral studies at Purdue University and Texas A&M University, he joined the faculty at IIT Kanpur in 2003, where he is presently an Associate Professor. His current research interests are centered on bimetallic complexes and their utility as catalysts for new, selective, and widely applicable organic transformations.

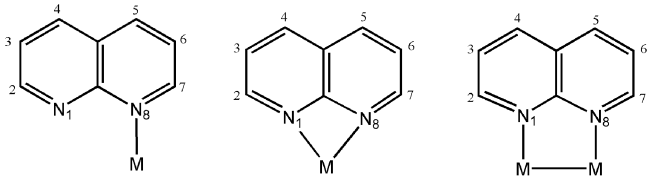
Nabanita Sadhukhan (left) obtained her MSc from the University of Kalyani in 2002. Currently, she is pursuing her PhD at the Indian Institute of Technology Kanpur. Her research interests include the supramolecular and organometallic chemistry of ferrocene–naphthyridine hybrid ligands.

Moumita Majumdar (right) obtained her MSc from the University of Calcutta in 2004. Currently, she is pursuing her PhD at the Indian Institute of Technology Kanpur. Her research interests include ligand-centered electrochemistry and organometallic chemistry on a dimetal platform.

nate architectures. However, the nature of the ancillary ligand, size of the metal ion, and solvent system play vital roles in defining the topology of the products, thus allowing investigation of dynamic processes involving metal site exchange between N1 and N8 atoms in solution.[5]



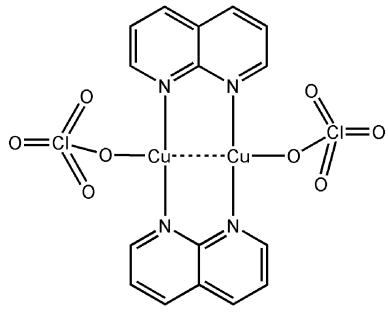
Scheme 1. Line drawing of nalidixic acid.



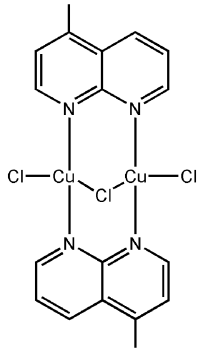
Scheme 2. Possible coordination modes of 1,8-naphthyridine.

The *syn* disposition of two N lone pairs in NP makes it an ideal choice to stabilize binuclear systems by μ-1κN1:2κN8 coordination (Scheme 2). Weakly interacting dimetal cores incorporating $Cu^{I}\cdots Cu^{I}$ (Scheme 3) and $Ag^{I}\cdots Ag^{I}$ interactions have been stabilized by NP.[6] Dirhodium(I) complexes $[Rh_2(NP)_2(diene)][ClO_4]_2$ {dienes are: nbd(norborna-2,5-diene) and cod (1,5-cyclooctadiene)} and the corresponding CO and/or PPh_3 substituted products have been isolated.[7] The binucleating behavior of NP is observed in the chlorido-bridged copper complex $[Cu_2(\mu\text{-}Cl)_2Cl_2(NP)_2]$.[8] Gatteschi and co-workers reported mixed-valent dinuclear complexes of Ni and Cu accessed by the applications of NP. In the nickel complex $[Ni_2(NP)_4Br_2]$-$[B(C_6H_5)_4]$, the formal oxidation state of the metal is 1.5 with a metal–metal distance of 2.421(5) Å.[9] The binuclear mixed-valent complex $[Cu_2(\mu\text{-}Cl)Cl_2(4\text{-}Me\text{-}NP)_2]$ (Scheme 4) with a shorter Cu–Cu distance of 2.38 Å was obtained by the reaction of $CuCl_2$ with NP in alcoholic medium.[10] EPR experiments confirmed the class III type delocalization of the unpaired electron on two equivalent metal centers in Robin and Day's scale.

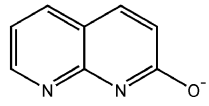
The ligands 1,8-naphthyridin-2-onate (ONP) (Scheme 5) and 1,8-naphthyridin-2,7-dionate (dONP) have been employed to stabilize a variety of di- and multinuclear compounds.[11] Oro and co-workers examined multiple coordination possibilities of ONP ligands.[12] The dinuclear complexes $[Rh_2(ONP)_2(CO)_4]$, $[Rh_2(Me_2\text{-}ONP)_2(cod)_2]$, and $[Rh_2(Me_2\text{-}ONP)_2(CO)_2(cod)]$ and the trinuclear complexes $[M_3(Me_2\text{-}ONP)_2(CO)_2(diene)_2]^{2+/1+}$ (M = Rh, Ir), $[Rh_2Ir(Me_2\text{-}ONP)_2(CO)_2(diene)_2]^{2+/1+}$, and $[Ir_2Rh(Me_2\text{-}ONP)_2(CO)_2(diene)_2]^{2+/1+}$ (dienes: cod and nbd) with BF_4^- or ClO_4^- anions have been reviewed.[13]



Scheme 3. Line drawing of Cu^{I} dimer $[Cu_2(NP)_2(ClO_4)_2]$.



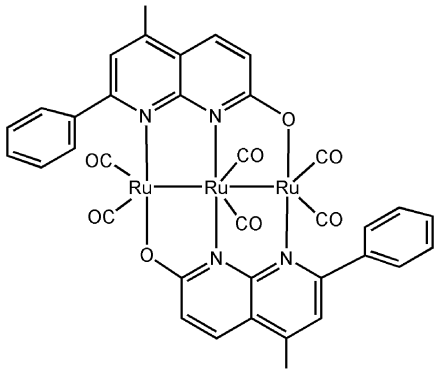
Scheme 4. Line drawing of $[Cu_2(\mu\text{-}Cl)Cl_2(4\text{-}Me\text{-}NP)_2]$.



Scheme 5. Line drawing of 1,8-naphthyridin-2-onate (ONP).

The diruthenium(II,II) *trans*-$[Ru_2(OAc)_2(5\text{-}Me\text{-}7\text{-}Ph\text{-}ONP)_2]$ was structurally characterized, which revealed N,N coordination of the NP core. On the contrary, the presence of an axial ligand in the diruthenium(II,III) complex *trans*-$[Ru_2(OAc)_2(5\text{-}Me\text{-}7\text{-}Ph\text{-}ONP)_2Cl]$ results in N,O coordination, as this leaves one axial site unencumbered for coordination of Cl^-. If the phenyl substituent at the 7-position is omitted, the N,N coordination is preferred as revealed in $Ru_2(5\text{-}Me\text{-}ONP)_4$. In the analogous complex $Ru_2(5\text{-}Me\text{-}7\text{-}Ph\text{-}ONP)_4$, the crowding of the adjacent phenyl substituents allows only three of the bridging ligands to adopt the N,O coordination mode, whereas the fourth one is N,N coordinated.[14]

Dipalladium(II) and diplatinum(II) complexes of the type *cis*-$[M_2L_2(bpy)_2]^{2+}$ (L = ONP, 7-Me-ONP),[15] dimolybdenum(II) complexes $[Mo_2(7\text{-}Me\text{-}ONP)_4]$, $[Mo_2(7\text{-}Me\text{-}SNP)_4]$ (SNP = 1,8-naphthyridine-2-thione), and the diruthenium(II) complex $[Ru_2(7\text{-}Me\text{-}ONP)_4]$ were synthesized.[16] A trinuclear complex $[Ru_3(5\text{-}Me\text{-}7\text{-}Ph\text{-}ONP)_2(CO)_6]$ (Scheme 6) consisting of a Ru^{I}–Ru^{0}–Ru^{I} chain was also prepared. The naphthyridines adopt a head-to-tail orientation and display a μ_3-1κO2:2κN1:3κN8 coordination mode with Ru–Ru bond lengths of 2.701(2) and 2.702(3) Å.[11]

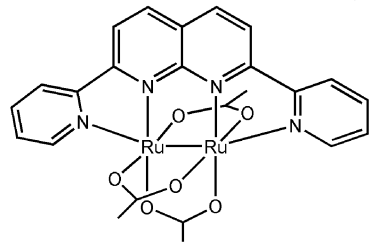


Scheme 6. Line drawing of $[Ru_3(5\text{-Me-7-Ph-ONP})_2(CO)_6]$.

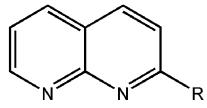
Trinuclear complexes *cis*-$[M_3(dONP)_2(bpy)_3]^{2+}$ (M = Pd, Pt)[15] and tetranuclear complex $[\{Mo_2(O_2C\text{-}t\text{Bu})_3\}_2(dONP)]$[17] have been prepared by employing 2,7-dione-NP (dONP) ligands.

The pliability of naphthyridine bite allows it to bridge a range of preformed dimetal cores, from singly bonded dirhodium(II) to quadruply bonded dimolybdenum(II) systems.[18] Kaska and co-workers isolated the dirhodium(II) complex $[Rh_2(NP)_4]Cl_4{\cdot}6H_2O$, obtained from the reaction of $Rh_2(OAc)_4$ with NP in aqueous HCl. Its structure, however, has not been verified by X-ray crystallography.[19] The crystal structure has been reported for the dimolybdenum(II) complex $[Mo_2(NP)_4(CH_3CN)_2][BF_4]_2$.[20] Incorporation of pyridyl donors at the 2- and 7-positions of NP results in crescent-shaped bpNP {2,7-bis(2-pyridyl)-1,8-naphthyridine}, which was employed in the synthesis of $[Rh_2(OAc)_3(bpNP)][PF_6]$,[21,22] $[Ru_2Cl_2(bpy)_2(bpNP)][PF_6]_2$, and $[Ru_2(OAc)_3(bpNP)][PF_6]$ (Scheme 7).[21] A Ru_2^{5+} species $[Ru_2(OAc)_3(dcNP)]$,[23] stabilized by dcNP (1,8-naphthyridine-2,7-dicarboxylate), has been structurally characterized. Attachment of a pyridyl group at the 2-position of NP allowed the incorporation of more than one NP-based ligand around a dimetal core. The first dirhodium(II) compound in this series $[Rh_2(pyNP)_3Cl_2][PF_6]_2$[24] {pyNP = [2-(2-pyridyl)-1,8-naphthyridine]} was reported by Ford and co-workers. Remarkable electrochemical behavior in a homologous series of $[M_2(OAc)_2(pyNP)_2]^{2+}$ complexes (M = Mo, Ru, Rh) was carried out by Dunbar and co-workers.[25] The neutral nitrogen donor ligands pyNP and tzNP {tzNP = 2-(2-thiazolyl)-1,8-naphthyridine} react readily with $[Re_2(CH_3CN)_{10}][BF_4]_4$ to provide *trans*-$[Re_2(CH_3CN)_4(pyNP)_2][BF_4]_4$ and *trans*-$[Re_2(CH_3CN)_4(tzNP)_2][BF_4]_4$, which were fully characterized by us recently.[26]

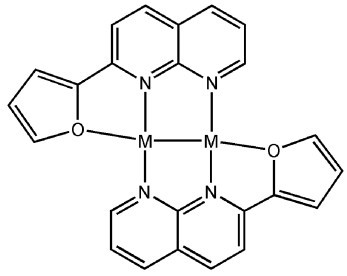
Despite the earlier success of NP-based ligands in the synthesis and structural elucidation of novel coordination compounds, their full prospect had not been recognized. In recent times, there has been resurgence in the wider applications of NP ligands, for example, in the field of bioinorganic chemistry,[27] supramolecular chemistry,[28] material chemistry,[29] and organometallics.[30] We have been engaged in examining the versatility of NP ligands in different areas of chemistry. The ligand employed in our work is designed to have covalent attachment at the 2-position; abbreviated as NP-R. (Scheme 8) The N–C–N moiety bridges a dimetal core by occupying equatorial positions and the appendage R simultaneously binds to an axial site of the dimetal core. Scheme 9 illustrates the coordination of two NP-R (R = pyridyl) units across a dimetal core. Such an NP-R ligand opens up the door to perform chemistry on the dimetal platform. Some of our achievements, namely, understanding the ligand disposition around a dimolybdenum(II) core, the effects of axial coordination on the metal–metal bond length, the C–H bond activation and C–C bond formation reactions on a $[Ru_2(CO)_4]^{2+}$ core, and the construction of metallosupramolecular architectures, are organized in the proceeding sections.



Scheme 7. Line drawing of monocationic unit of $[Ru_2(OAc)_3(bpNP)][PF_6]$.



Scheme 8. Line drawing of NP-R.



Scheme 9. Bridging modes of two NP-R (R = furyl) across a M_2 unit.

cis/*trans* Disposition of NP-R on a Dimolybdenum(II) Core[31,32]

Quadruply bonded Mo_2 units are reputed to be stabilized by NP through their dinuclear bridging mode of coordination.[16] The NP ligands in these complexes exhibit different spatial orientations leading to *cis*/*trans* isomers. For example, reaction of the potentially tetradentate PNNP ligand 2,7-bis(diphenylphosphanyl)-1,8-naphthyridine (dpnapy) with *cis*-$[Mo_2(OAc)_2(CH_3CN)_6][BF_4]_2$ afforded two isomeric dimolybdenum(II) complexes, *cis*-$[Mo_2(O_2CCH_3)_2(dpnapy\text{-}N,P)_2][BF_4]_2$ and *trans*-$[Mo_2(O_2CCH_3)_2(dpnapy\text{-}$

N,*N*′)$_2$] in 63 and 5% yields, respectively.[33] The *trans* arrangement of two dpnapy ligands, bridging through two N atoms on a dimetal core, is disfavored over the *cis* arrangement (N,P coordination) owing to steric repulsion between two uncoordinated phosphane groups. The rationales behind preferential formation of either *cis* or *trans* stereoisomers in dimolybdenum(II) chemistry has been lucidly discussed in a recent work of Cotton, Murillo, and coworkers.[34] In this work, dimolybdenum(II) mixed-ligand complexes comprising danif (*N*,*N*′-di-*p*-anisylformamidinate), acetate, and acetonitrile molecules are reported towards directed synthesis of building blocks for the construction of supramolecular assemblies. The structure of a given product is rationalized on the basis of the interplay of kinetic and thermodynamic stabilities.

The substitutional lability of dimolybdenum(II) carboxylates has been examined in detail.[35] The *cis*/*trans* isomerization in "$Mo_2(OAc)_2(L)_2$" complexes is said to involve acetate migration through axial coordination. It is therefore argued that the axial ligands would have a deterministic effect on the product configuration. A set of NP-R ligands allowed us to study the role of axial donors in the ligand isomerization processes of quadruply bonded dimolybdenum(II) compounds.[31] Reactions of *cis*-$[Mo_2(OAc)_2(CH_3CN)_6][BF_4]_2$ with NP-R {2-(2-R)-1,8-naphthyridine; R = pyridyl (pyNP), thiazolyl (tzNP), furyl (fuNP), thienyl (thNP) and 2,3-dimethyl-1,8-naphthyridine (Me_2NP)} lead to a series of *cis* and *trans* complexes. The NP-R ligands with stronger pyridyl and thiazolyl donors result in *cis* isomers *cis*-$[Mo_2(pyNP)_2(OAc)_2][BF_4]_2$ and *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$ (Figure 1a), whereas weaker furyl and thienyl appendages lead to *trans*-$[Mo_2(fuNP)_2(OAc)_2][BF_4]_2$ and *trans*-$[Mo_2(thNP)_2(OAc)_2][BF_4]_2$. The use of Me_2NP led to a *trans* structure $[Mo_2(Me_2NP)_2(OAc)_2][BF_4]_2$ (Figure 1b), in which Me_2NP ligands are arranged in a head-to-head fashion and a tetrafluoroborate anion occupies one of the axial sites. Molecular structures of these complexes were established by X-ray crystallography. The N–C–N unit of the NP fragment bridges two molybdenum centers, and the site *trans* to Mo–Mo quadruple bond is occupied by donor atoms of the appendage at the 2-position (Scheme 9). Thus, two tridentate ligands occupy four equatorial and two axial sites of the dimolybdenum unit. The remaining four sites of the paddlewheel arrangement are occupied by two bridging acetate groups.

Compounds *cis*-$[Mo_2(pyNP)_2(OAc)_2][BF_4]_2$ and *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$were also obtained from the reaction of $Mo_2(OAc)_4$ with appropriate NP-R in the presence of an excess of two equivalents of [*n*Bu_4N][BF_4]. Protonation of *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$ with triflic acid in acetonitrile leads to the replacement of bridging acetates by acetonitriles to yield *cis*-$[Mo_2(tzNP)_2(CH_3CN)_4][OTf]_4$ (Scheme 10). The reagents HBF_4·Et_2O and Me_3OBF_4 produce identical tetracationic species $[Mo_2(tzNP)_2(CH_3CN)_4]^{4+}$, but single crystals suitable for X-ray studies were obtained only with triflates as the counterions. Treatment of triflic acid with *trans*-$[Mo_2(fuNP)_2(OAc)_2][BF_4]_2$ readily produces *cis*-$[Mo_2(fuNP)_2(CH_3CN)_4][OTf]_4$. Reaction of

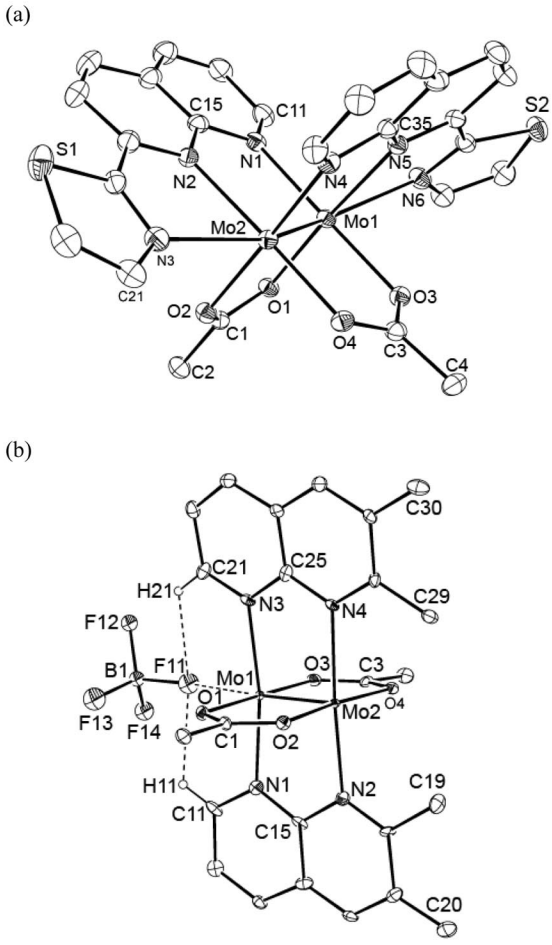
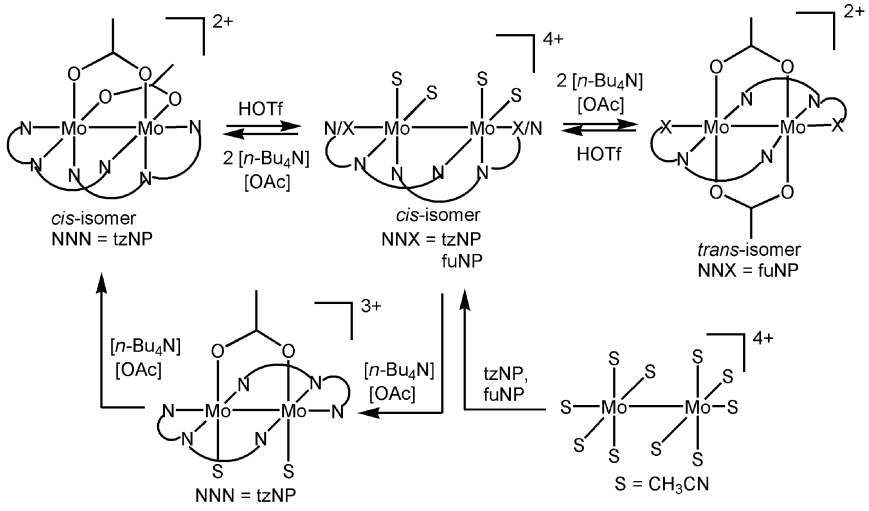


Figure 1. (a). ORTEP diagrams of the dicationic unit of *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$ and (b) the cationic unit of *trans*-$[Mo_2(Me_2NP)_2(OAc)_2(BF_4)][BF_4]$.

$[Mo_2(CH_3CN)_{10}][OTf]_4$ with corresponding NP-R provided *cis*-$[Mo_2(tzNP)_2(CH_3CN)_4][OTf]_4$ and *cis*-$[Mo_2(fuNP)_2(CH_3CN)_4][OTf]_4$. Only *cis* isomers are obtained when acetonitrile acts as the ancillary ligands, irrespective of the geometry of the initial precursors and the identity of NP-R.

The addition of two equivalents of [*n*Bu_4N][OAc] to *cis*-$[Mo_2(tzNP)_2(CH_3CN)_4][BF_4]_4$ provides the bis(acetate) compound *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$. In contrast, the addition of acetate ligands to *cis*-$[Mo_2(fuNP)_2(CH_3CN)_4][BF_4]_4$ results in *trans*-$[Mo_2(fuNP)_2(OAc)_2][BF_4]_2$. Stepwise addition of acetates to *cis*-$[Mo_2(tzNP)_2(CH_3CN)_4][BF_4]_4$ leads to *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$ through the intermediacy of *trans*-$[Mo_2(tzNP)_2(OAc)(CH_3CN)_2][BF_4]_3$, which contains one acetate and two acetonitrile units (Scheme 10), and was isolated in a high yield of 65%. X-ray crystallography reveals the *trans* configuration in the solid state, although NMR spectroscopic results show the presence of *cis* and *trans* isomers in a ratio of 1:1.3.

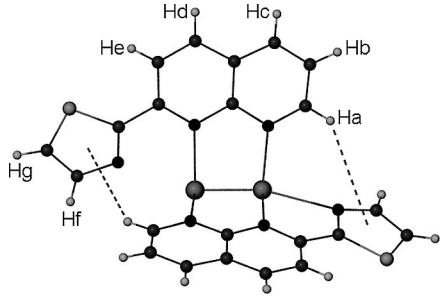
The ^{1}H NMR spectra in multiply bonded paddlewheel compounds reveal interesting features allowing one to distinguish between *cis* and *trans* isomers in solution. Protons residing in the equatorial region are observed downfield and those in the axial region are observed upfield from their



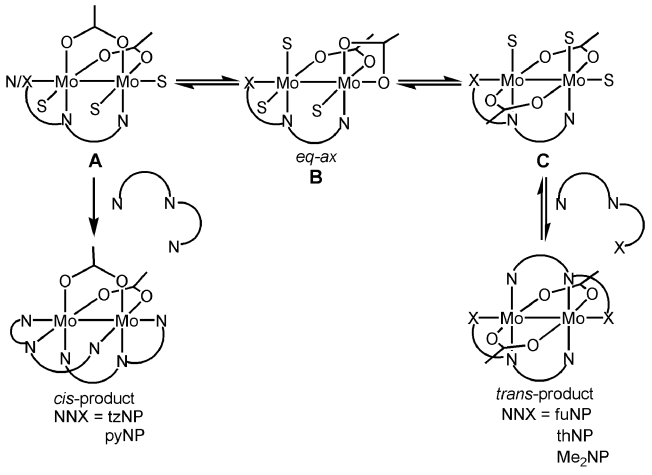
Scheme 10. Synthetic protocols for $[Mo_2(NP\text{-}R)_2(OAc)_n(CH_3CN)_{4-2n}]^{(4-n)+}$.

free form, which is attributed to the diamagnetic anisotropy of the Mo–Mo quadruple bond.[18,36] To cite an example, in *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$, the b–e proton signals are shifted downfield in the range 0.28–0.93 ppm with respect to the free ligand, whereas the Hf proton of the thiazolyl appendage experiences an upfield shift of 0.45 ppm (Scheme 11). Incidentally, the Hg proton exhibits a marginal upfield shift of 0.06 ppm being away from the dimetal core. The most unusual signal is noticed for Ha, which is shifted upfield by 1.28 ppm. Such a large shift cannot be attributed solely to the diamagnetic anisotropic field around the Mo–Mo quadruple bond. Following a hint from the earlier work of Ford,[19] it is recognized that the Ha proton of the NP core in *cis*-'$[Mo_2(NP\text{-}R)_2]$' is positioned above the R ring of the second NP-R unit. For *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$, the estimated Ha–X distances are 3.110 and 3.633 Å, where X is the centroid of the thiazolyl ring (Scheme 11). The shielding caused by the appendage ring current and Mo–Mo quadruple bond electrons result in large upfield shifts of the Ha protons. In contrast, for the *trans*-'$[Mo_2(NP\text{-}R)_2]$' complex, the *trans* arrangement of NP-R does not allow the ring current of R to affect Ha. The result is a normal upfield shift of $\Delta\delta$ = 0.08 ppm for Ha in *trans*-$[Mo_2(funNP)_2(OAc)_2][BF_4]_2$. Thus, the magnitude of upfield chemical shift difference of the Ha proton with respect to the free ligand is diagnostic for *cis*/*trans* isomers in solution. It is concluded on the basis of numerous '$Mo_2(NP\text{-}R)_2$' examples that a chemical shift difference $\Delta\delta$ of the Ha proton around 0.1 ppm is characteristic for *trans* geometry, whereas a corresponding value greater than 1 ppm signifies a *cis* orientation of the ligands.

The isolation of *trans*-$[Mo_2(funNP)_2(OAc)_2][BF_4]_2$, *trans*-$[Mo_2(thNP)_2(OAc)_2][BF_4]_2$, and *trans*-$[Mo_2(Me_2NP)_2(OAc)_2][BF_4]_2$ from *cis*-$[Mo_2(OAc)_2(CH_3CN)_6][BF_4]_2$ precursor suggests geometry conversion during replacement of acetonitrile by the ligands. We proposed a possible sequence of steps in the substitution and isomerization process, as depicted in Scheme 12. The *trans* effect exerted by these ligands is proportional to their basicity, and the trend is NP-R > acetate > acetonitrile. The acetate group *trans* to the NP ligand in **A** is activated, which leads to the cleavage of one of the Mo–O bonds. The acetate ligand rearranges from a μ-bridging mode to a chelating eq–ax disposition of O atoms as shown in **B**. Precedence for this step exists as discussed in several reports including several well-characterized dimetal intermediates involving eq–ax acetate.[37] In a subsequent step, the acetate anion displaces the labile CH_3CN molecules thereby completing the geometry conversion (**C**). The second NNX replaces the acetonitrile ligands in the product-formation step, leading to the *trans* derivatives. The pyNP and tzNP ligands with strong axial donor rapidly replace three acetonitrile molecules in **A**, and the result is the formation of *cis* products. For any ligands to enter or leave the M_2 coordination sphere, the axial sites are the most probable pathway.[38] It is likely that stronger pyridyl/thiazolyl donors replace the axial acetonitrile ligands in **A** first, and subsequently the NP core displaces the equatorial acetonitrile ligands to bridge the dimolybdenum unit. In case of weak appendages such as furyl or thienyl, the acetate migration prevails over the axial coordination of fuNP/thNP, the result of which is conversion into the *trans* isomer.



Scheme 11. Representation of the *cis*-$[Mo_2(tzNP)_2]$ unit depicting the position of the Ha proton above the thiazolyl ring.



Scheme 12. Proposed pathway leading to *cis* or *trans* isomers of $[Mo_2(OAc)_2(NP\text{-}R)_2]^{2+}$.

Effects of Axial Coordination on the Metal–Metal Bond in Paddlewheel Complexes[39,40]

The extent to which the metal–metal distances in paddlewheel $M_2(O_2CR)_4{\cdot}X_2$ complexes are influenced by the identity of M, the nature of the R group, and the closeness of X has been discussed in numerous reports.[18,41] The Cr–Cr quadruple bond is certainly the most sensitive to the inductive character of the R group, and much more to axial ligation. Earlier studies showed that the donation of ligand electron density to σ*/π* of a Cr–Cr quadruple bond causes major lengthening of the Cr–Cr distance.[42] Although the effect is less dramatic, several computational and experimental studies on metal–metal singly bonded $Rh_2(O_2CR)_4{\cdot}X_2$ are aimed at assessing the influence of axial ligands on the metal–metal distances and on excited-state properties.[43]

A limited set of donors, for example, water, triphenylphosphane, methanol, THF, acetonitrile, are the most commonly used axial ligands. We initiated a study to understand the effects of axial coordination on metal–metal distances by systematically varying the nature and strength of axial donors. A set of NP-R ligands allowed the placement of different R groups at axial sites of the dimetal core. The tridentate bridged-chelate binding mode of NP-R to a dimetal core is described in the preceding section (Scheme 9). The axial donors considered are pyridyl, thiazolyl, furyl, thienyl, and pyrrolyl groups, reflecting their varied donor strengths. It should be noted that axial donors in our work are not exogenous,[42,43] rather they are constrained to the NP units.

In a series of *cis*/*trans*-$[Mo_2(NP\text{-}R)_2(OAc)_2][BF_4]_2$ complexes, the Mo–Mo distances vary with axial donors R.[31] For R = pyridyl and thiazolyl, the Mo–Mo distances are 2.124(1) and 2.115(1) Å, respectively. For relatively weaker furyl and thienyl donors, the Mo–Mo distances are comparatively shorter [2.087(1) and 2.078(3) Å]. The Mo–Mo distance in $[Mo_2(Me_2NP)_2(OAc)_2][BF_4]_2$ is 2.081(1) Å and contains a weakly coordinated axial tetrafluoroborate anion (See Figure 1b). The quadruply bonded Mo–Mo distances are also dependent on the nature and number of bridging ligands. A significant lengthening of the Mo–Mo distance is noted when bridging acetate groups are replaced by acetonitrile groups. The compound $[Mo_2(tzNP)_2(OAc)(CH_3CN)_2][BF_4]_3$ contains one bridging acetate and two acetonitrile groups, and the observed Mo–Mo distance 2.147(1) Å is of intermediate length between *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$ [2.115(1) Å] and *cis*-$[Mo_2(tzNP)_2(CH_3CN)_4][BF_4]_4$ [2.168(1) Å].

Further, we synthesized a series of NP-R complexes incorporating a metal–metal singly bonded $[Ru_2(CO)_4]^{2+}$ core. Reactions of $[Ru_2(CO)_4(CH_3CN)_6][X]_2$ (X = CF_3SO_3, BF_4, ClO_4) with two equivalents of 3-MeNP (3-methyl-1,8-naphthyridine), fuNP, pyNP, tzNP in acetonitrile provided $[Ru_2(CO)_4(NP\text{-}R)_2][X]_2$ and with prNP {2-(2-pyrrolyl)-1,8-naphthyridine} gave $[Ru_2(CO)_4(NP\text{-}R)_2]$ (Figure 2).[39] Isolation of these five complexes allowed us to investigate the variation in the Ru–Ru distances with axial donors. The general structure description of these complexes is similar to dimolybdenum(II) complexes described earlier. The N–C–N unit of the NP fragment bridges two ruthenium centers, and the site *trans* to the Ru–Ru bond is occupied by donor atoms of the respective appendages. In $[Ru_2(CO)_4(3\text{-}MeNP)_2][OTf]_2$, exogenous triflate groups occupy the axial sites. The presence of carbonyl ligands enforces the *cis* configuration in all complexes.

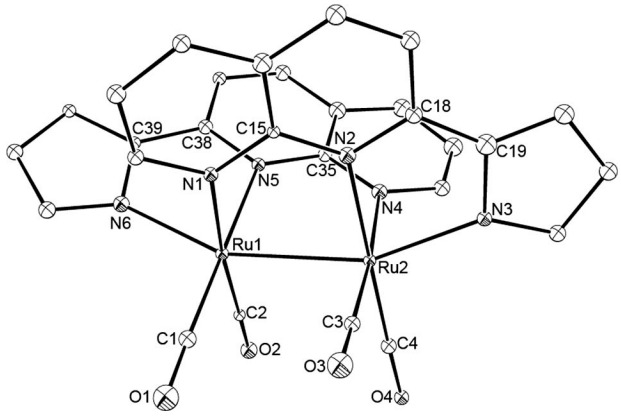
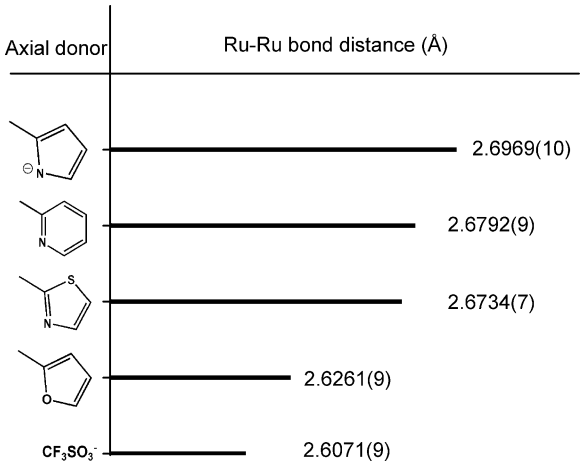


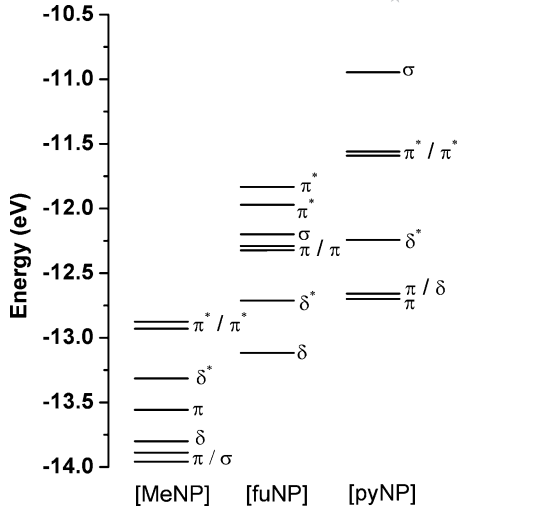
Figure 2. ORTEP diagram of $[Ru_2(prNP)_2(CO)_4]$.

A gradual, albeit small, increase in the Ru–Ru distances is measured by varying axial donors of increasing strengths. The longest Ru–Ru distance of 2.6969(10) Å is observed for pyrrolyl donors at axial sites, and the shortest distance of 2.6071(9) Å is observed when triflate groups are coordinated axially. The Ru–Ru distance [2.6261(9) Å] in the fuNP complex is longer than in $[Ru_2(3\text{-}MeNP)_2(CO)_4(OTf)_2]$. The axial donors in the tzNP and pyNP complexes exhibit comparable donor ability having Ru–Ru distances of 2.6734(7) and 2.6792(9) Å, respectively (Scheme 13).

The Ru–Ru distances are governed by the bridging ligands. The bridging NP ligand constrains the dimetal to a shorter separation than they would prefer otherwise. The unbridged $[Ru_2(CO)_4(bpy)_2(MeCN)_2][PF_6]_2$ exhibits a long



Scheme 13. Variation of Ru–Ru distances with axial donor R in $[Ru_2(CO)_4(NP\text{-}R)_2]^{2+}$.

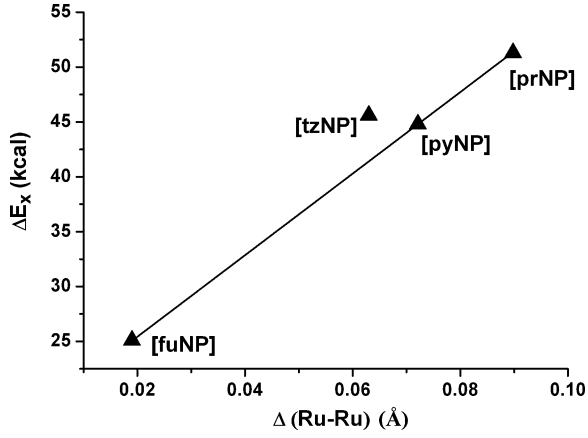


Scheme 14. Energy level of [Ru–Ru] bond orbital in [MeNP], [FuNP], and [PyNP].

Ru–Ru distance of 2.83 Å.[44] Similarly, the Ru–Ru separation in $[Ru_2(CO)_4(CH_3CN)_4(PPh_3)_2][PF_6]_2$ is the longest [2.8731(8) Å], for which PPh_3 ligands are axially bound.[45]

The response of the Ru–Ru bond orbital to axial ligands has been examined. Closed-shell single-point DFT calculations of dicationic $[Ru_2(3\text{-}MeNP)_2(CO)_4]^{2+}$ [MeNP], $[Ru_2(funNP)_2(CO)_4]^{2+}$ [funNP], $[Ru_2(tzNP)_2(CO)_4]^{2+}$ [tzNP], $[Ru_2(pyNP)_2(CO)_4]^{2+}$ [pyNP], and neutral $[Ru_2(prNP)_2(CO)_4]$ [prNP] were performed by using atomic coordinates available from X-ray structures. The energy levels of the Ru–Ru bond orbitals in [3-MeNP], [fuNP], and [pyNP] are shown in Scheme 14. The Ru–Ru σ orbital is elevated in energy because of its interaction with the axial lone pairs. In [3-MeNP], the lowest-energy metal–metal bond orbital is the Ru–Ru σ orbital. The Ru–Ru σ orbital in [fuNP] is elevated in energy because of interaction with O lone pairs of the furyl appendages, and it lies below the pair of π* orbitals. The extent of destabilization in the case of axial pyridyl donors in [pyNP] is significantly greater resulting in the Ru–Ru σ orbital being the HOMO. Similarly for thiazolyl and pyrrolyl donors in [tzNP] and [prNP], the HOMOs are predominantly Ru–Ru σ-type orbitals.

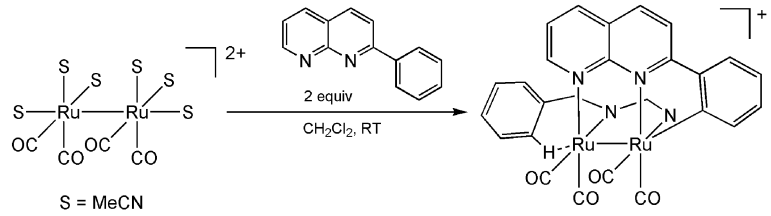
The shift of Ru–Ru σ bonding electrons to higher energy results in the weakening of the Ru–Ru bond. The degree of destabilization depends on the nature of the axial ligands: the stronger the ligand, the higher the elevation of Ru–Ru σ orbital and the longer the Ru–Ru distance. To get a fair estimation of the degree of destabilization of the Ru–Ru σ orbital, we reasoned that orbitals of δ symmetry are least perturbed by axial ligation. Therefore, quantitative estimation of the extent of destabilization of the Ru–Ru σ orbital is obtained by subtracting the difference in energy of Ru–Ru σ orbital between a particular species and [3-MeNP] from the difference in energy of the corresponding δ* orbital. The calculated values illustrate the comparative donor strength of the axial appendages. The increment in the Ru–Ru distance holds a linear relationship with the degree of destabilization of the Ru–Ru σ orbital (Scheme 15). The axial thiazolyl appendage presumably involves π-donation to the Ru_2 unit, thereby causing a small deviation from linearity.[46] In conclusion, the lengthening of Ru–Ru distances with respect to the axial donors follows along the direction pyrrolyl > pyridyl ≈ thiazolyl > furyl > triflate, and the trend correlates well with the computed destabilization of the Ru–Ru σ orbitals. Further, our study reveals that the weakening of M–M and M–L(ax) bonds works in synergism. The M–L(ax) distances are longer in quadruply bonded Mo_2 complexes in comparison to singly bonded Ru_2 systems. A closer axial approach of ligands is observed in the latter systems. The axial ligands weaken the M–M bond, which in turn weakens the M–L(ax) bonds.[47]



Scheme 15. Plot of comparative axial-donor strength vs. Ru–Ru distance.

C–H Bond Activation and C–C Bond Formation at Axial Site of the $[Ru_2(CO)_4]^{2+}$ Core[48,49]

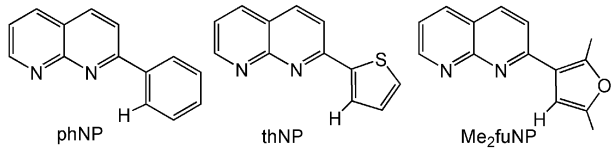
The successful applications of dirhodium(II) compounds in a variety of organic transformations prompted us to explore metal–metal bonded dimetal compounds in organometallic chemistry.[50] Enhanced reaction rate, selectivity



Scheme 16. Cyclometalation reaction at axial site of the diruthenium(I) unit.

and new types of reactions are expected to arise from the cooperation of two closely spaced metal components, referred as bimetallic synergic effect. Cyclometalation reactions of phosphane-based ligands at equatorial sites of dirhodium(II) unit have been reported at elevated temperature.[51] We focused our attention on the $[Ru\text{-}Ru]^{2+}$ core, which is isoelectronic with the dirhodium(II) core, having metal–metal valence configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^{*0}$, corresponding to a formal Ru–Ru single bond. Axial interaction of the $[Ru_2(CO)_4]^{2+}$ core with aryl C–H bond has been examined towards the synthesis of cyclometalated compounds, as shown in Scheme 16.

Following the same protocol employed earlier, different aryl C–H bonds are placed at axial sites of the $[Ru_2(CO)_4]^{2+}$ core by applying appropriate NP-R.[48] We describe herein reactions of three aryl appendages (Scheme 17). Reaction of phNP with $[Ru_2(CO)_4(CH_3CN)_6][BF_4]_2$ in dichloromethane and at room temperature resulted in the cyclometalated compound $[Ru_2(phNP)(C_6H_4\text{-}NP)(CO)_4][BF_4]$. The molecular structure (Figure 3) reveals that one of the phNP is orthometalated, whereas the second ligand is engaged in an agostic interaction. The cyclometalated phNP bridges the diruthenium (Ru1–Ru2) core via the NP unit and simultaneously Ru2 binds to the *ortho* carbon atom C20 of the phenyl fragment. The Ru1–Ru2 and Ru2–C20 distances are 2.692(1) and 2.074(5) Å, respectively, and the Ru1–Ru2–C20 angle is 160.5(1)°. The second phNP ligand bridges the diruthenium unit at equatorial sites and the *ortho* hydrogen of the phenyl appendage is located in the vicinity of Ru1. The metrical parameters of Ru1–H40 2.398 Å (calculated), Ru1–C40 2.786(5) Å, and Ru1–H40–C40 104.0(3)° are indicative of an agostic interaction.[52] The torsion angle (N4–C38–C39–C40) of 50.2(7)° between the phenyl and NP planes manifests the agostic configuration[53] of the C–H bond to the diruthenium unit. The corresponding value for the orthometalated phNP is 7.8(7)°. A doublet at 9.29 ppm in the ^1H NMR spectrum of the complex, representing a significant downfield shift as compared to the free ligand, is assigned for the agostic proton. The shift is in the opposite direction of what is normally observed for the hydrogen strongly bonded to a metal. Possible rationales for the downfield shift of the hydrogen lying at the axial site of the isoelectronic $[Rh_2]^{4+}$ have been offered by Thummel and coworkers.[54] We attribute the downfield shift of the agostic proton to the withdrawal of electron density from the C–H bond to the vacant Ru–Ru σ* orbital.



Scheme 17. NP-R ligands employed for C–H bond activation.

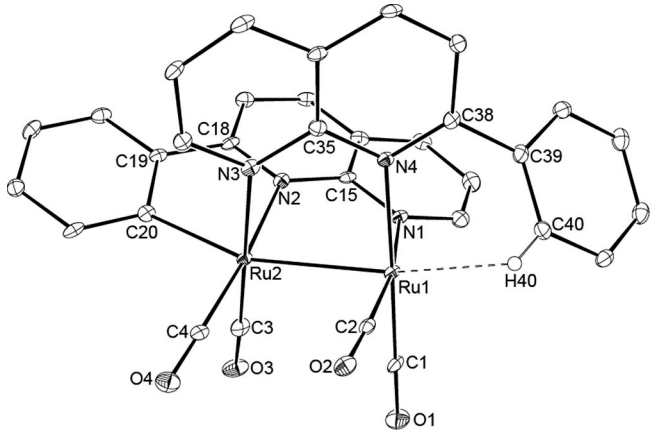
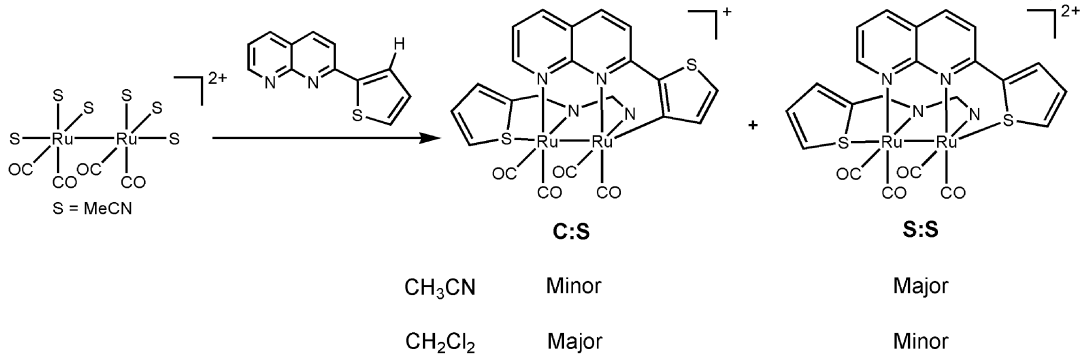


Figure 3. ORTEP diagram of the cationic unit $[Ru_2(phNP)(C_6H_4\text{-}NP)(CO)_4]^+$.

With Me_2fuNP, a similar agostic-cyclometalated compound $[Ru_2(Me_2fuNP)(C_4OMe_2\text{-}NP)(CO)_4][BF_4]$ was isolated, the key structural parameters of which are comparable to $[Ru_2(phNP)(C_6H_4\text{-}NP)(CO)_4][BF_4]$ described above. The agostic hydrogen in this compound is characterized by a doublet at 9.35 ppm.

Noncoordinating solvents are preferred over coordinating solvents for C–H bond activation. This is illustrated by the reaction of thNP with $[Ru_2(CO)_4(CH_3CN)_6][BF_4]_2$. In dichloromethane, the red cyclometalated compound $[Ru_2(thNP)(C_4H_2S\text{-}NP)(CO)_4][BF_4]$ is isolated as the major product, having C and S axial coordinations and henceforth described as (C:S). A small amount of the yellow compound $[Ru_2(thNP)_2(CO)_4][BF_4]_2$ having S,S coordination is also observed. This minor product is referred as (S:S) (Scheme 18). In acetonitrile, however, the latter (*S*:*S*) compound is obtained exclusively, with no trace of (C:S). Both compounds have been characterized structurally and spectroscopically.



Scheme 18. Reaction illustrating solvent dependent C–H bond activation.

Despite the success of the isoelectronic $[Ru_2(CO)_4]^{2+}$ core to cleave aryl C–H bonds at the axial site, the isoelectronic $[Rh_2]^{4+}$ does not display similar reactivity even at high temperature. Reaction of phNP with $Rh_2(OAc)_4$ in refluxing 1,2-dichloroethane and subsequent crystallization in dichloromethane resulted in the formation of the agostic compound $[Rh_2(OAc)_3(phNP)Cl]$ (Figure 4). The structural parameters [Rh2–H20 2.462 Å, Rh2–C20 2.822(3) Å, Rh2–H20–C20 102.4(2)°, and N2–C18–C19–C20 47.0(5)°] and a doublet at 11.38 ppm confirms the agostic configuration of the *ortho* hydrogen.

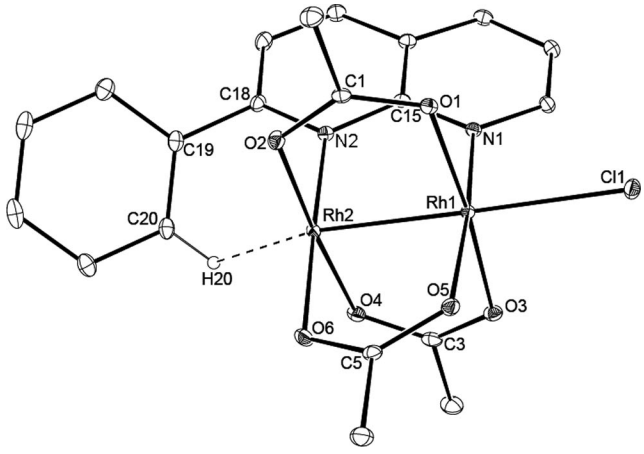
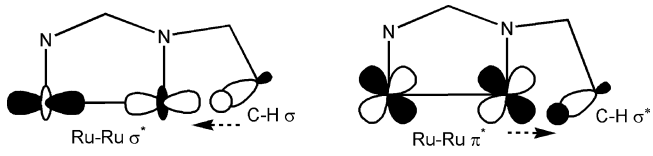


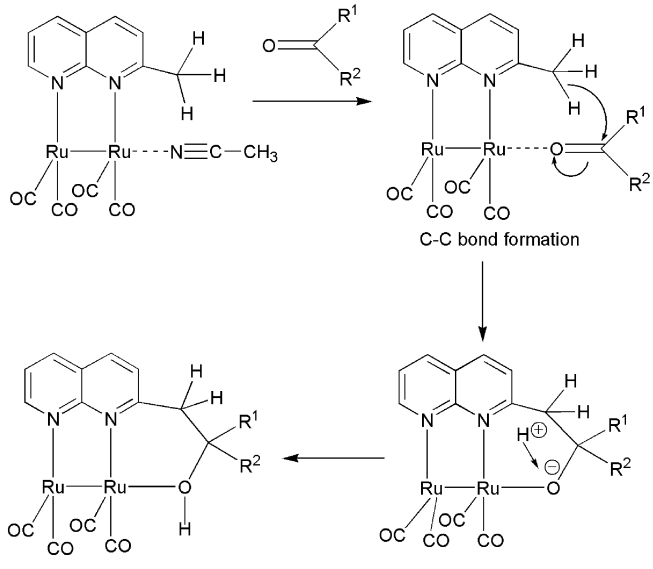
Figure 4. ORTEP diagram of the agostic compound $[Rh_2(phNP)(OAc)_3Cl]$.

A theoretical framework based on orbital interactions is offered to explain the proclivity of the $[Ru_2(CO)_4]^{2+}$ core to activate the C–H bond at room temperature. To understand the electronic structure of the $[Ru_2(CO)_4]^{2+}$ core, DFT calculations on $[Ru_2(3\text{-}MeNP)_2(CO)_4]^{2+}$ were carried out. The LUMO is a Ru–Ru σ* orbital resulting from the antibonding interaction of the two d_{z^2} orbitals. The HOMO and HOMO-1 are closely spaced Ru–Ru π* orbitals originating from out-of-phase d_{xz}–d_{xz} and d_{yz}–d_{yz} interactions. The C–H bond at site *trans* to the Ru–Ru bond donates bonding electron pair to the Ru–Ru σ* LUMO, and the back-donation occurs from the filled Ru–Ru π* to C–H σ* orbital, as depicted in Scheme 19. The combination of these two interactions results in facile C–H bond cleavage.



Scheme 19. Orbital interaction between $[Ru\text{-}Ru]^{2+}$ and C–H bond.

In addition to C–H bond activation, C–C bond forming reaction is achieved at the axial site of the $[Ru_2(CO)_4]^{2+}$ core. Aldol-like addition of ketone to 2-methyl-1,8-naphthyridine, anchored on a $[Ru_2(CO)_4]^{2+}$ core, afforded the C–C-coupled compounds at room temperature as shown in Scheme 20. The NP ligands used in this study are 2-methyl-1,8-naphthyridine, 2,3-dimethyl-1,8-naphthyridine, and the ketones employed are acetone and ethyl methyl ketone. Several diruthenium(I) compounds of general formula $[Ru_2(CO)_4(L)_2][X]_2$ (L is the C–C coupled naphthyridyl alcohol, X = BF_4 or OTf) are structurally characterized and their solution behavior has been analyzed in a recent publication.[49]



Scheme 20. Reaction pathway leading to C–C coupled product formation.

1,8-Naphthyrid-2-yl-ferrocene (FcNP) and 1,1′-Bis(1,8-naphthyrid-2-yl)ferrocene ($FcNP_2$)[55–57]

Covalent attachment of different R groups to NP at the 2-position provided tools in our arsenal to tackle fundamental problems in dimetal chemistry as described in the preceding sections. Naphthyridine ligands are redox-active, in particular, the substitution at 2-position with thiazolyl or pyridyl group makes them accessible for two electron reductions. Two such ligands wrapped around a dimetal unit (Mo_2, Ru_2, Rh_2) display fascinating electrochemistry. The cyclic voltammogram of $[Mo_2(OAc)_2(tzNP)_2][BF_4]_2$ exhibits four reversible reduction couples which are ligand-centered and located at $E_{1/2}^{(1)}$ = –0.35(65) V, $E_{1/2}^{(2)}$ = –0.53(65) V, $E_{1/2}^{(3)}$ = –1.21(76) V, and $E_{1/2}^{(4)}$ = –1.46(68) V (Figure 5).[31] This is indicative of electron delocalization in the mixed-valent intermediates. The corresponding comproportionation constant values reflect the stability of the intervalent species.[25] Covalent attachment of one or two ferrocene to NP provides FcNP and $FcNP_2$, comprising oxidizing and reducing centers. The cyclic voltammogram of FcNP, for example, exhibits an irreversible oxidation at Ep,a = +0.85 V (vs. Ag/AgCl) with a reduction wave at Ep,c = +0.50 V. The redox behavior and conformational flexibility of Fc-NP conjugates play important roles in providing access to novel molecular and supramolecular compounds.

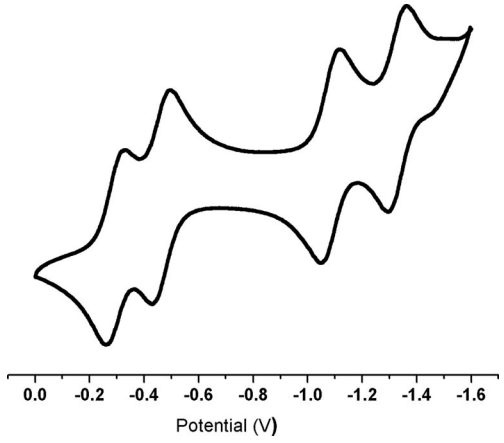


Figure 5. Cyclic voltammogram of *cis*-$[Mo_2(tzNP)_2(OAc)_2][BF_4]_2$.

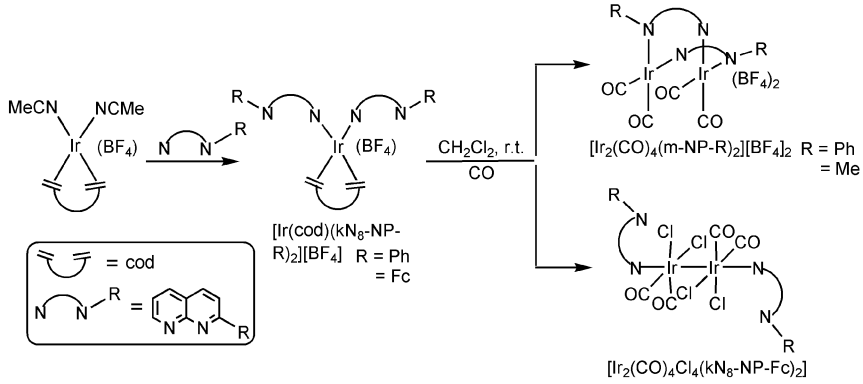
Diiridium Chemistry[55]

NP-R ligands have been employed successfully in diiridium chemistry. Reactions of $[Ir(cod)(MeCN)_2][BF_4]$ with NP-R afford $[Ir(cod)(NP\text{-}R)_2][BF_4]$ (Scheme 21). X-ray structures of compounds for R = Ph and Fc revealed 8-N coordination of two NP ligands. When cod is replaced by carbon monoxide, a diiridium(I) compound $[Ir_2(CO)_4(NP\text{-}R)_2][BF_4]_2$ (R = Me) is isolated, the structure of which has been confirmed by X-ray crystallography. The molecular structure consists of a diiridium core with two *cis* MeNP ligands, arranged in a head-to-tail fashion, bridging metal centers (Figure 6). Each iridium atom is additionally bonded to two carbonyls. The Ir···Ir non-bonding distances 2.8151(7) and 2.8051(7) Å, noted for two independent molecules in the asymmetric unit, are similar to those found in weakly interacting d^8–d^8 systems.[58] Two Ir^I ions held in close proximity by neutral N-donor ligands is a rare example although diiridium(I) compounds incorporating anionic bridging ligands are abundant in literature.[59]

Most intriguingly, substitution of cod from $[Ir(cod)(FcNP)_2][BF_4]$ by CO in dichloromethane affords a novel diiridium(II) compound $[Ir_2Cl_4(CO)_4(FcNP)_2]$, featuring an unsupported Ir–Ir bond.[55] The X-ray structure reveals a dimer of '$[IrCl_2(CO)_2]$' (Figure 7). The molecule has an imposed C_2 axis across the unsupported Ir–Ir bond. The geometry about the iridium centers is near-octahedral with two *cis* CO and two *cis* chlorides bonded to each iridium atom. The remaining sites are satisfied by axial FcNP and the second iridium. The Ir1–Cl1 and Ir1–Cl2 distances are 2.378(2) and 2.386(3) Å; Ir1–C1 and Ir1–C2 distances are 1.871(11) and 1.892(10) Å, respectively. The axial NP-Fc forms a linear N1–Ir1–Ir1–N1 axis as reflected in the N1–Ir1–Ir1 bond angle 178.8(2)°. The Ir1–N1 distance is 2.183(7) Å. Iridium atoms and coordinating atoms around its equatorial sites are arranged in a plane; the largest deviation from the best plane is less than 0.01 Å. The staggered geometry of the dimer is exhibited in the Cl1–Ir1–Ir1–Cl1 twist angle of 48.5(1)°.

The unsupported Ir–Ir distance of 2.7121(8) Å is shorter than that found in association dimers of Ir^I and longer than the corresponding distances in bridged diiridium(II) compounds. The NP-bridged $Ir^I\cdots Ir^I$ distance in $[Ir_2(CO)_4(MeNP)_2][BF_4]_2$ is 0.1 Å longer than the unsupported Ir^{II}–Ir^{II} distance in $[Ir_2Cl_4(CO)_4(FcNP)_2]$, strongly suggesting a single bond between metals in the latter compound.

Unsupported diiridium(II) compounds are distinguished by their rarity. Only five examples of Ir^{II} dimers, including two reported recently, are known.[60] Tedious and unconventional methods have been adopted in the synthesis of unsupported diiridium(II) compounds. However, FcNP provides an easy access to a diiridium(II) compound. The role of FcNP in providing the unsupported diiridium(II) compound $[Ir_2Cl_4(CO)_4(FcNP)_2]$ is examined critically. A tentative pathway detailing the product formation is depicted in Scheme 22. Initially, incorporation of two chlorides occurs through reduction of dichloromethanes across a diiridium(I) compound $[Ir_2(CO)_4(FcNP)_2][BF_4]_2$, generated in situ by displacement of cod by carbon monoxides in $[Ir(cod)(FcNP)_2][BF_4]$. The result is the dicationic $[Cl–Ir^{II}–Ir^{II}–Cl]$. The byproduct of this reaction, 1,2-dichloroethane, has been identified by a GC technique. Subsequently, the $[Cl–Ir^{II}–Ir^{II}–Cl]^{2+}$ species undergoes reduction, generating the $[Cl–Ir^I\cdots Ir^I–Cl]$ core. The FcNP, present in excess of two equivalents per diiridium, is the reducing agent. The dicationic $[Cl–Ir^{II}–Ir^{II}–Cl]$ core is a stronger oxidant compared to its neutral diiridium(II) analogues involving anionic bridges and therefore reduced by FcNP (Ep,a = 0.85 V vs. Ag/AgCl) yielding neutral $[Cl–Ir^I\cdots Ir^I–Cl]$. The oxidized product $[FcNP]^+$ proved to be elusive for identification. Attempts to identify the oxidized species invariably led to the isolation of protonated salt



Scheme 21. Synthesis of NP-R bridged diiridium(I) and unsupported diiridium(II) compounds.

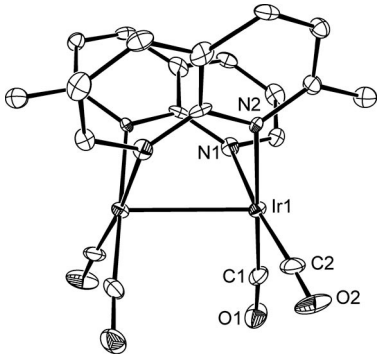
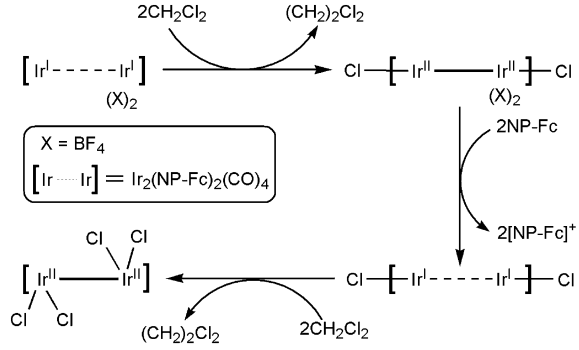


Figure 6. ORTEP view of dicationic $[Ir_2(CO)_4(\mu\text{-MeNP})_2]^{2+}$ unit.



Scheme 22. Pathway leading to unsupported $Ir_2Cl_4(CO)_4$ core.

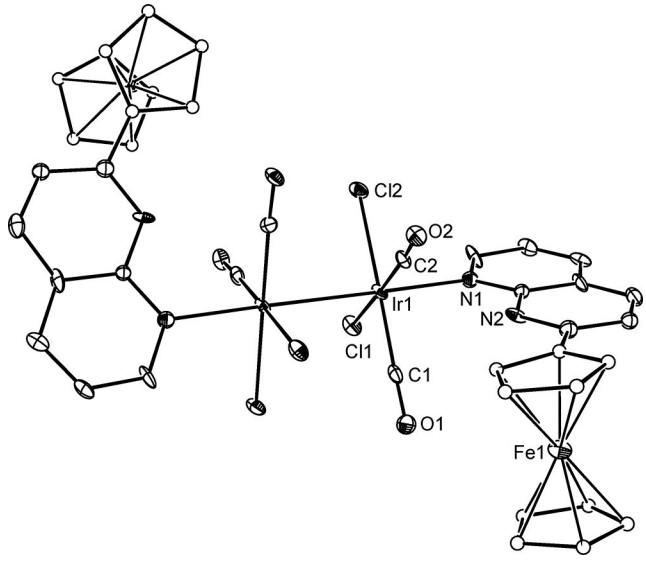


Figure 7. ORTEP view of $[Ir(Cl)_2(CO)_2(\kappa^1\text{-FcNP})]_2$.

$[HFcNP]^+[BF_4]^-$. Subsequent activation of dichloromethanes results in oxidative additions of two more chlorides across the diiridium(I) core that proceeds with concomitant growth of an Ir^{II}–Ir^{II} single bond. Incorporation of four chlorides, in addition to four carbonyls present at the diiridium core, leads to migration of FcNP to an axial position, resulting in the unsupported iridium(II) dimer $[Ir_2Cl_4(CO)_4(FcNP)_2]$.

Mixed-Metal Assemblies[56,57]

FcNP has been employed to synthesize a host of mixed-metal assemblies.[56] Reactions of appropriate salts of Fe^{II}, Cu^{II}, Zn^{II}, and Cd^{II} with FcNP provide $[FeCl_2(\kappa N_8\text{-FcNP})_2]$, $[Cu(\kappa N_8\text{-FcNP})_2(NO_3)_2]$, $[Zn(\kappa N_8\text{-FcNP})_4][OTf]_2$, and $[Cd(\kappa N_8\text{-FcNP})_2(\kappa^2 N_1,N_8\text{-FcNP})_2][BF_4]_2$. The bridged dirhodium(II) compound $[Rh_2(\mu\text{-FcNP})_2(\mu\text{-}O_2CCH_3)_2(H_2O)][OTf]_2$ is isolated when $[Rh_2(\mu\text{-}O_2CCH_3)_2(CH_3CN)_6]^{2+}$ is employed as a precursor. The coordination environment of metal ions in these compounds deviates considerably from their ideal geometry. For cases where direct comparison is possible, it is observed that the composition and structures of FcNP complexes are different from the corresponding NP compounds. Although 1,8-naphthyridine is widely known to bridge a variety of metal ions, the κN_8 mode of coordination through the distal nitrogen atom of FcNP appears to be most prevalent. Representative dicationic unit $[Zn(\kappa N_8\text{-FcNP})_4]$ in complex $[Zn(\kappa N_8\text{-FcNP})_4][OTf]_2$ is presented in Figure 8a. In complex $[Cd(\kappa N_8\text{-FcNP})_2(\kappa^2 N_1,N_8\text{-FcNP})_2][BF_4]_2$, two FcNP ligands chelate to Cd^{II} in $\kappa_2 N^1,N^8$ modes as well (Figure 8b). The bridging mode of FcNP is noted for a preformed dimetal precursor, as in $[Rh_2(\mu\text{-FcNP})_2(\mu\text{-}O_2CCH_3)_2(H_2O)][OTf]_2$ (Figure 8c). ESI-MS studies reveal that the identity of each complex, as revealed in the solid-state structure, is retained in solution.

Introduction of a NP unit to each Cp ring in ferrocene provides $FcNP_2$.[61] The coordination versatility of NP and

conformational flexibility of Fc are attributed to the formation of novel metallomacrocycles upon complexation with transition metal ions.[56,57] $PdCl_2$ forms a neutral chelate complex $[PdCl_2(FcNP_2)]$ in which the Pd atom links two NP units of $FcNP_2$ through distal N atoms in *trans* geometry. The geometry at Pd is square planar. The plane constructed by the Pd and the coordinating atoms (within 0.067 Å) is near orthogonal to the NP planes, the interplanar angle being 78.46°.

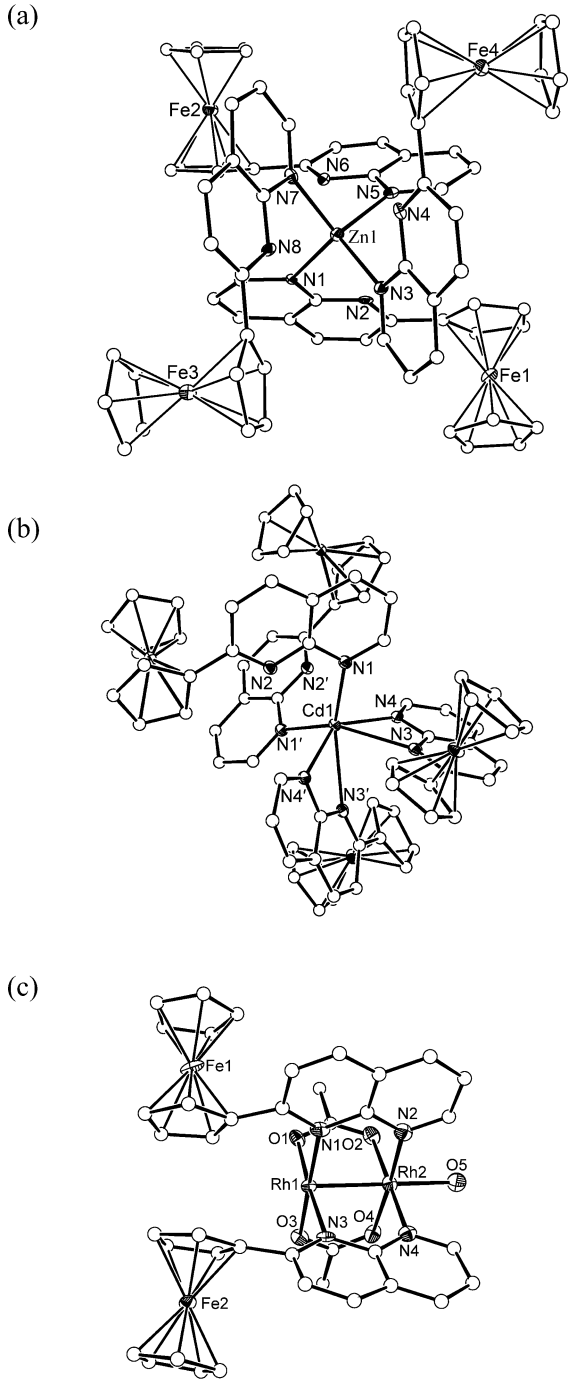


Figure 8. ORTEP diagram of the dicationic units: (a) $[Zn(FcNP)_4]$, (b) $[Cd(FcNP)_4]$ and (c) $[Rh_2(FcNP)_2(OAc)_2(H_2O)]$.

A tetrameric compound $[ZnCl_2(FcNP_2)]_4$ is obtained from the reaction of $FcNP_2$ and $ZnCl_2$. Each discrete unit of $[ZnCl_2(FcNP_2)]_4$ consists of alternating $ZnCl_2$ and $FcNP_2$ units (Figure 9). The overall structure of metallomacrocycle consists of a Zn_4 square of dimension 9.584(2) Å spanned by $FcNP_2$ units. The Fc units are alternatively above and below the plane of the Zn_4 square, forming a Fe_4 tetrahedron consisting of four isosceles triangles with Fe···Fe distances of 9.271(3) and 7.844(2) Å. Each Fe atom is connected to two neighboring Zn atoms by Cp-NP units with Fe···Zn distances of 5.995(2) and 6.261(2) Å.

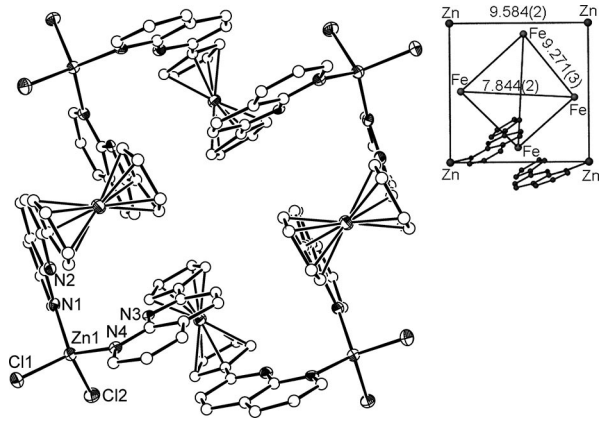
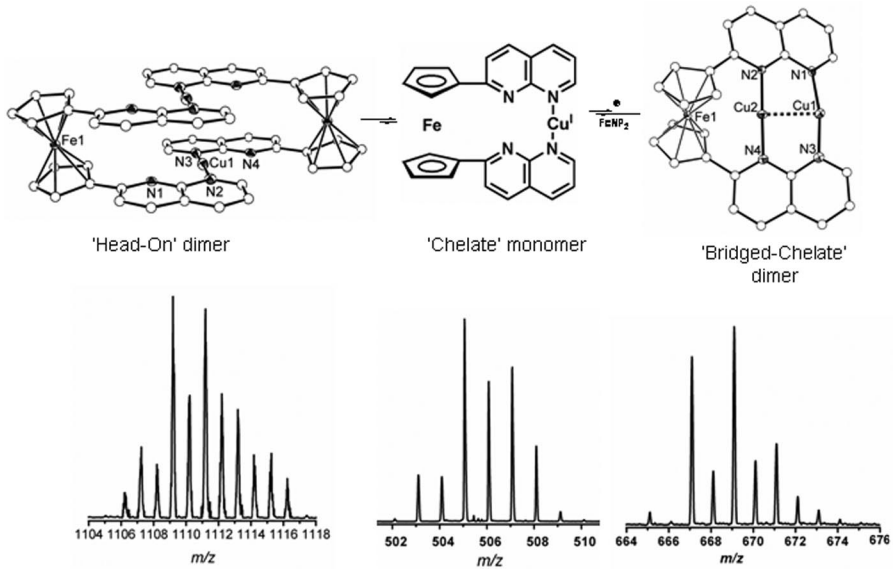


Figure 9. ORTEP diagram of $[ZnCl_2(FcNP)_2]_4$ and the skeletal arrangement of Zn_4Fe_4 shown in inset.

Discrete rectangular-shaped metallomacrocycles of formula $[M_2(FcNP_2)_2][X]_2$ (M = Cu, X = ClO_4; M = Ag, X = OTf) are obtained by the treatment of appropriate salts of Cu^I and Ag^I with $FcNP_2$ in 1:1 ratios. Molecular structures reveal a head-on arrangement of two $FcNP_2$ linked by the metal ions. In $[Cu_2(FcNP_2)_2][ClO_4]_2$, each copper atom is coordinated to distal nitrogen atoms of two $FcNP_2$ in a quasi-linear environment with Cu–N distances of 1.889(3) and 1.898(3) Å and N2–Cu1–N3 angle of 176.47(13)° (see 'head-on' dimer in Scheme 23). In contrast, the Ag atom in $[Ag_2(FcNP_2)_2][OTf]_2$ was found to be disordered over two positions, separated by 0.696 Å with occupancies of 0.62 (Ag1) and 0.38 (Ag1′), located at the pocket created by two NP units from two $FcNP_2$, leading to a metallomacrocycle that is smaller in width [Fe···Fe 9.127(1) Å] in comparison to "$[\{Cu(FcNP_2)\}_2]^{2+}$" [Fe···Fe 11.104(3) Å].

The reaction of two equivalents of Cu^I with $FcNP_2$ results in the bridged-chelate complex $[Cu_2(FcNP_2)(OClO_3)][ClO_4]$ in quantitative yield, the structure of which is established from X-ray crystallography. The NP appendages in $FcNP_2$ bridge two copper atoms in *trans* geometry, as shown in Figure 10. The coordination geometry for two metals can be described as linear two-coordinate: one is bonded to proximal nitrogen atoms, and the second one is bonded to distal nitrogen atoms of NP units. The inner copper makes an N4–Cu2–N2 angle of 178.01(15)° with shorter Cu–N distances [Cu2–N4 1.875(4) Å, Cu2–N2 1.879(3) Å]. In contrast, the geometry of the outer copper



Scheme 23. Interconversion reactions among metallomacrocycles and the corresponding ESI-MS spectrum.

deviates considerably from linearity, as reflected in the N1–Cu1–N3 angle [168.7(2)°], involving longer Cu–N distances [Cu1–N1 1.943(4) Å and Cu1–N3 1.946(4) Å]. One of the perchlorate anions is located in the vicinity of Cu1. The μ-$\kappa^2N_1,N_8:\kappa^2N_1',N_8'$ coordination of $FcNP_2$ forces two copper atoms to acquire a Cu···Cu distance of 2.466(1) Å which is significantly shorter than the corresponding distances 2.506(2) and 2.533(2) Å reported for the dicopper(I) complex bridged by two independent naphthyridine ligands.[6d,6e] The short Cu···Cu separation in $[Cu_2(FcNP_2)(OClO_3)][ClO_4]$ is primarily attributed to ligand architecture, although the presence of metallophilic interactions has been supported and refuted as well for similar dicopper(I) complexes.[62]

It is remarkable that $FcNP_2$ provides access to two topologically different structures obtained by employing Cu^I and $FcNP_2$ in different ratios. The "head-on" dimer is obtained from 1:1 metal-to-ligand assembly, and the "bridged-chelate" complex is the isolated product when a metal-to-ligand ratio of 2:1 is employed. Both complexes are identified in their corresponding mass spectrum along with a ubiquitous signal at m/z = 505, attributed to $[Cu(FcNP_2)]^+$. It is proposed that $[Cu_2(FcNP_2)_2]^{2+}$ exists in equilibrium with the monomeric 1:1 species $[Cu(FcNP_2)]^+$, for which a "chelate" structure, depicted in Scheme 23 is proposed. We and others have synthesized similar chelate compounds with Fc*Py_2 {1,1′-bis(2-pyridyl)octamethylferrocene}[63] and $FcQu_2$ {1,1′-bis(quinolin-2-yl)ferrocene}.[64]

The addition of two equivalents of $[Cu(CH_3CN)_4][ClO_4]$ to an acetonitrile/nitromethane solution of $[Cu_2(FcNP_2)_2][ClO_4]_2$ and the recording of the mass spectrum revealed a mixture of the "head-on" dimer (m/z = 1109), "chelate" monomer (m/z = 505), and "bridged chelate" dimer (m/z = 669) compounds. The ratio of the "head-on" dimer and "bridged-chelate" dimer was found to be 1:1, even when the reaction was allowed for a prolonged period. In contrast,

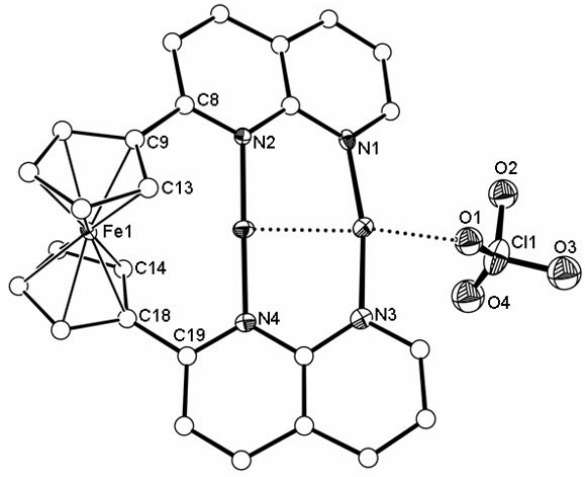


Figure 10. ORTEP diagram of cationic unit of $[Cu_2(FcNP)_2(OClO_3)][ClO_4]$.

the "bridged-chelate" complex converts fully to "head-on" dimer on treatment with $FcNP_2$. The parent signal at m/z = 669 for the "bridged-chelate" dimer vanishes, and a new signal at m/z = 1159 for the "head-on" dimer appears. It is concluded from ESI-MS experiments that both 1:1 and 2:1 Cu^I-$FcNP_2$ complexes exist predominantly as the monomer $[Cu(FcNP_2)]^+$ in solution. The equilibrium is shifted toward the "bridged-chelate" dimer on addition of Cu^I to the 1:1 complex, whereas the 2:1 dimer transforms to the 1:1 complex completely on addition of $FcNP_2$. The "head-on" or the "bridged-chelate" dimer is the isolated product in the solid state depending on the metal-to-ligand ratio. Despite the chelate complex $[Cu(FcNP_2)]^+$ being the major species in solution, we have been unsuccessful in isolating it in our study, and either $[Cu_2(FcNP_2)_2][ClO_4]_2$ or $[Cu_2(FcNP_2)(ClO_4)_2]$ was obtained in quantitative amount by crystallization.

Other Major Activities and Further Prospects

In addition to our activities involving the NP-R ligands, several prominent groups utilize NP based ligands in their respective field of interest. Lippard and co-workers have employed NP-based dinucleating ligands to model dinuclear active sites in metalloenzymes.[27] The N atoms of NP are exploited by the group of Zimmerman as H-bond donors for bimolecular recognition of urea and related compounds.[65] Making use of this H-bonded complexation, several supramolecular polymer blends have been prepared.[66] Ruthenium(II)-NP complexes have been used as catalyst for electrochemical reduction of CO_2 by Tanaka and co-workers.[67] The reduced NP ligand provides the electrons required for the reduction of CO_2. Water decomposition catalyzed by a family of dinuclear Ru^{II} complexes involving NP-based ligands has been studied by Thummel and co-workers.[68] Suitably tailored NP ligand and their complexation with Ru^{II} provided a set of ligands, which are excellent photosensitizers.[69] These results illustrate the versatility of NP based ligand in diverse applications. We and others have developed synthetic protocols for different NP derivatives giving promise for future applications.[70] The NP-based ligands have assumed a central role in our present activity on cooperative bimetallic catalysis. The flexibility and adaptability of the NP core ensure that the integrity of the dimetal core is intact during the course of the reaction thereby proving valuable mechanistic insights into organometallic reactions. We plan to report these new findings in near future.

Acknowledgments

J. K. B. thanks Prof. V. Chandrasekhar for his insightful comments on this manuscript. The contribution of Dr. S. K. Patra to this chemistry is acknowledged. This work was financially supported by the Department of Science and Technology (DST), India through the grant of a Ramanna fellowship. M. M. and N. S. thank the Council of Scientific and Industrial Research (CSIR), India for fellowships.

[1] a) M. Dinakaran, P. Senthilkumar, P. Yogeeswari, D. Sriram, *Biomed. Pharmaco.* **2009**, *63*, 11; b) S. K. Srivastava, M. Jaggi, A. T. Singh, A. Madan, N. Rani, M. Vishnoi, S. K. Agarwal, R. Mukherjee, A. C. Burman, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6660; c) S. K. Srivastava, M. Jaggi, A. T. Singh, A. Madan, N. Rani, M. Vishnoi, S. K. Agarwal, R. Mukherjee, A. C. Burman, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6660; d) M. Atanasova, S. Ilieva, B. Galabov, *Eur. J. Med. Chem.* **2007**, *42*, 1184; e) D. Sriram, P. Senthilkumar, M. Dinakaran, P. Yogeeswari, A. China, V. Nagaraja, *J. Med. Chem.* **2007**, *50*, 6232;D. Sriram, P. Senthilkumar, M. Dinakaran, P. Yogeeswari, A. China, V. Nagaraja, *Medicinal Chemistry* **2007**, *3*, 6232; f) V. P. Litvinov, *Adv. Heterocycl. Chem.* **2006**, *91*, 189 and references cited therein; g) Y. Tsuzuki, K. Tomita, Y. Sato, S. Kashimoto, K. Chiba, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3189; h) Y. Tsuzuki, K. Tomita, K.-i. Shibamori, Y. Sato, S. Kashimoto, K. Chiba, *J. Med. Chem.* **2004**, *47*, 2097; i) R. F. Clark, S. Wang, Z. Ma, M. Weitzberg, C. Motter, M. Tufano, R. Wagner, Y.-G. Gu, P. J. Dandliker, C. G. Lerner, L. E. Chovan, Y. Cai, C. L. Black-Schaefer, L. Lynch, D. Kalvin, A. M. Nilius, S. D. Pratt, N. Soni, T. Zhang, X. Zhang, B. A. Beutel, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3299; j) K. Tomita, Y. Tsuzuki, K. Shibamori, M. Tashima, F. Kajikawa, Y. Sato, S. Kashimoto, K. Chiba, K. Hino, *J. Med. Chem.* **2002**, *45*, 5564; k) K. Tomita, Y. Tsuzuki, K.-i. Shibamori, M. Tashima, F. Kajikawa, Y. Sato, S. Kashimoto, K. Chiba, K. Hino, *J. Med. Chem.* **2002**, *45*, 5564; l) J. T. Leonard, R. Gangadhar, S. K. Gnanasam, S. Ramachandran, M. Saravanan, S. K. Sridhar, *Biol. Pharm. Bull.* **2002**, *25*, 798; m) D. Bouzard, P. Di Cesare, M. Essiz, J. P. Jacquet, B. Ledoussal, P. Remuzon, R. E. Kessler, J. Fung-Tomc, *J. Med. Chem.* **1992**, *35*, 518; n) P. Remuzon, D. Bouzard, C. Guiol, J. P. Jacquet, *J. Med. Chem.* **1992**, *35*, 2898.

[2] a) A. Emad, K. Emerson, *Inorg. Chem.* **1972**, *11*, 2288; b) C. Mealli, L. Sacconi, *Acta Crystallogr., Sect. B* **1977**, *33*, 710; c) D. Hendricker, R. J. Foster, *Inorg. Chem.* **1973**, *12*, 349; d) G. W. Bushnell, K. R. Dixon, M. A. Khan, *Can. J. Chem.* **1978**, *56*, 450; e) E. L. Enwall, K. Emeson, *Acta Crystallogr., Sect. B* **1979**, *35*, 2562; f) M. A. Cavanaugh, V. M. Cappo, C. J. Alexander, M. L. Good, *Inorg. Chem.* **1976**, *15*, 2615; g) U. Monkowius, Y. N. Svartsov, T. Fischer, M. Zabel, H. Yersin, *Inorg. Chem. Commun.* **2007**, *10*, 1473; h) R. J. Foster, D. G. Hendricker, *Inorg. Chim. Acta* **1972**, *6*, 371; i) R. J. Foster, R. L. Bodner, D. G. Hendricker, *J. Inorg. Nucl. Chem.* **1972**, *34*, 3795; j) R. Bodner, D. G. Hendricker, *Inorg. Chem.* **1970**, *9*, 1255.

[3] a) D. G. Hendricker, R. L. Bodner, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 187; b) A. Clearfied, P. Singh, I. Bernal, *J. Chem. Soc. D* **1970**, 389; c) P. Sing, A. Clearfield, I. Bernal, *J. Coord. Chem.* **1971**, *1*, 29; d) R. J. Foster, D. G. Hendricker, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 421; e) J. M. Epstein, J. C. Dewan, D. L. Kepert, A. H. White, *J. Chem. Soc., Dalton Trans.* **1974**, 1949; f) R. L. Bonder, D. G. Hendricker, *Inorg. Chem.* **1973**, *12*, 33.

[4] a) P. Singh, A. Clearfield, I. Bernal, *J. Coord. Chem.* **1971**, *1*, 29; b) J. C. Dewan, D. L. Kepert, A. H. White, *J. Chem. Soc., Dalton Trans.* **1975**, 490.

[5] a) H. Schmidbaur, K. C. Dash, *J. Am. Chem. Soc.* **1973**, *95*, 4855; b) K. Dixon, *Inorg. Chem.* **1977**, *16*, 2618; c) K. R. Dixon, D. T. Eadie, S. R. Stobart, *Inorg. Chem.* **1982**, *21*, 4318; d) C.-L. Yao, L.-P. Korp, J. L. Bear, *Inorg. Chem.* **1988**, *27*, 4385; e) M. Munakata, S.-G. Yan, M. Maekawa, M. Akiyama, S. Kitagawa, *J. Chem. Soc., Dalton Trans.* **1997**, 4257; f) H. Nakajima, H. Nagao, K. Tanaka, *J. Chem. Soc., Dalton Trans.* **1996**, 1405.

[6] a) A. Emad, K. Emerson, *Inorg. Chem.* **1972**, *11*, 2288; b) W. P. Griffith, T. Y. Koh, A. J. P. White, D. J. Williams, *Polyhedron* **1995**, *14*, 2019; c) T. Tsuda, S. Ohba, M. Takahashi, M. Ito, *Acta Crystallogr., Sect. C* **1989**, *45*, 887; d) M. Maekawa, M. Munakata, S. Kitagawa, T. Kuroda-Sowa, Y. Suenaga, M. Yamamoto, *Inorg. Chim. Acta* **1998**, *271*, 129; e) M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi, H. Masuda, *Inorg. Chim. Acta* **1990**, *167*, 181.

[7] a) A. Tiripicchio, M. T. Camellini, R. Uson, L. A. Oro, M. A. Ciriano, F. Viguri, *J. Chem. Soc., Dalton Trans.* **1984**, 125; b) J. A. Cabeza, L. A. Oro, A. Tiripicchio, M. T. Camellini, *J. Chem. Soc., Dalton Trans.* **1988**, 1437.

[8] a) C. Mealli, F. Zanobini, *J. Chem. Soc., Chem. Commun.* **1982**, 97; b) H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, *Inorg. Chem.* **2007**, *46*, 10032; c) W. R. Tikkanen, C. Kruger, K. D. Bomben, W. L. Jolly, W. C. Kaska, P. C. Ford, *Inorg. Chem.* **1984**, *23*, 3633.

[9] a) D. Gatteschi, C. Mealli, L. Sacconi, *J. Am. Chem. Soc.* **1973**, *95*, 2736; b) L. Sacconi, C. Mealli, D. Gatteschi, *Inorg. Chem.* **1974**, *13*, 1985; c) A. Bencini, E. Berti, A. Caneschi, D. Gatteschi, E. Giannasi, I. Invernizzi, *Chem. Eur. J.* **2002**, *8*, 3660.

[10] D. Gatteschi, C. Mealli, L. Sacconi, *Inorg. Chem.* **1976**, *15*, 2774.

[11] M. Mintert, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1995**, 2663.

[12] L. A. Oro, M. A. Ciriano, J. J. Perez-Torrente, B. E. Villaroye, *Coord. Chem. Rev.* **1999**, *193–195*, 941.

[13] a) B. Eva Villarroya, L. A. Oro, F. J. Lahoz, A. J. Edwards, M. A. Ciriano, P. J. Alonso, A. Tiripicchio, M. T. Camellini, *Inorg. Chim. Acta* **1996**, *250*, 241; b) A. M. M. Lanfredi, A. Tiripicchio, R. Uson, L. A. Oro, M. A. Ciriano, B. E. Villaroya, *Inorg. Chim. Acta* **1984**, *88*, L9; c) A. Tiripicchio, F. J. Lahoz, L. A. Oro, M. A. Ciriano, B. E. Villaroya, *Inorg. Chim. Acta* **1986**, *111*, L1.

[14] M. Mintert, W. S. Sheldrick, *Inorg. Chim. Acta* **1995**, *236*, 13.

[15] B. Oskui, M. Mintert, W. S. Sheldrick, *Inorg. Chim. Acta* **1999**, *287*, 72.

[16] W. S. Sheldrick, M. Mintert, *Inorg. Chim. Acta* **1994**, *219*, 23.

[17] R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1991**, *113*, 8709.

[18] F. A. Cotton, C. A. Murillo, R. A. Walton in *Multiple Bonds between Metal Atoms*, 3rd ed., Springer, New York, **2005**.

[19] W. R. Tikkanen, E. Binamira-Soriaga, W. C. Kaska, P. C. Ford, *Inorg. Chem.* **1984**, *23*, 141.

[20] A. Dossing, S. Larsen, A. van Lelieveld, R. M. Bruun, *Acta Chim. Scandinavica* **1999**, *53*, 230.

[21] a) W. R. Tikkanen, E. Binamira-Soriaga, W. C. Kaska, P. C. Ford, *Inorg. Chem.* **1983**, *22*, 1147; b) R. P. Thummel, F. Lefoulon, D. Williamson, M. Chavan, *Inorg. Chem.* **1986**, *25*, 1675.

[22] E. Binamira-Soriaga, N. L. Keder, W. C. Kaska, *Inorg. Chem.* **1990**, *29*, 3167.

[23] J.-P. Collin, A. Jouaiti, J.-P. Sauvage, W. C. Kaska, M. A. McLoughlin, N. L. Keder, W. T. A. Harrison, G. D. Stucky, *Inorg. Chem.* **1990**, *29*, 2238.

[24] A. T. Baker, W. R. Tikkanen, W. C. Kaska, P. C. Ford, *Inorg. Chem.* **1984**, *23*, 3254.

[25] a) C. S. Campos-Fernández, L. M. Thomson, J. R. Galan-Mascaros, X. Ouyang, K. R. Dunbar, *Inorg. Chem.* **2002**, *41*, 1523; b) C. S. Campos-Fernández, X. Ouyang, K. R. Dunbar, *Inorg. Chem.* **2000**, *39*, 2432.

[26] J. K. Bera, E. J. Schelter, S. K. Patra, J. Bacsa, K. R. Dunbar, *Dalton Trans.* **2006**, 4011.

[27] a) J. Kuzelka, J. R. Farrell, S. J. Lippard, *Inorg. Chem.* **2003**, *42*, 8652; b) J. Kuzelka, S. Mukhopadhyay, B. Spingler, S. Lippard, *Inorg. Chem.* **2003**, *42*, 6447; c) C. He, J. L. Dubios, B. Hedman, K. O. Hodgson, S. J. Lippard, *Angew. Chem. Int. Ed.* **2001**, *40*, 1484; d) C. He, S. J. Lippard, *Inorg. Chem.* **2001**, *40*, 1414; e) C. He, S. J. Lippard, *J. Am. Chem. Soc.* **2000**, *122*, 184; f) C. He, A. M. Barrios, D. Lee, J. Kuzelka, R. M. Davydov, S. J. Lippard, *J. Am. Chem. Soc.* **2000**, *122*, 12683; g) C. He, S. J. Lippard, *Inorg. Chem.* **2000**, *39*, 5225; h) C. He, V. Goméz, B. Spingler, S. J. Lippard, *Inorg. Chem.* **2000**, *39*, 4188; i) N. V. Kaminskaia, C. He, S. J. Lippard, *Inorg. Chem.* **2000**, *39*, 3365; j) D. D. LeCloux, R. Davydov, S. J. Lippard, *Inorg. Chem.* **1998**, *37*, 6814.

[28] a) J. L. Katz, B. J. Geller, P. D. Foster, *Chem. Commun.* **2007**, 1026; b) H. C. Ong, S. C. Zimmerman, *Org. Lett.* **2006**, *8*, 1589; c) T. Park, E. M. Todd, S. Nakashima, S. C. Zimmerman, *J. Am. Chem. Soc.* **2005**, *127*, 18133; d) S. C. Zimmermann, Y. Wang, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1998**, *120*, 2172; e) L. Xing, U. Zeiner, T. C. Sutherland, L. A. Cuccia, *Chem. Commun.* **2005**, 5751; f) K. Ghosh, T. Sen, R. Fröhlich, *Tetrahedron Lett.* **2007**, *48*, 2935; g) I. Alkorta, J. Elguero, S. Goswami, R. Mukhergee, *J. Chem. Soc. Perkin Trans. 2* **2002**, 894; h) S. Goswami, K. Ghosh, R. Mukhergee, *Tetrahedron* **2001**, *57*, 4987; i) M. Mazik, H. Cavga, *Eur. J. Org. Chem.* **2007**, 3633; j) M. Mazik, W. Sicking, *Chem. Eur. J.* **2001**, *7*, 664; k) K. Nakatani, S. Horie, I. Saito, *J. Am. Chem. Soc.* **2003**, *125*, 8972; l) K. Nakatani, S. Sando, H. Kumasawa, J. Kikuchi, I. Saito, *J. Am. Chem. Soc.* **2001**, *123*, 2172; m) K. Nakatani, S. Sando, I. Saito, *J. Am. Chem. Soc.* **2000**, *122*, 2172; n) T. W. Bell, A. B. Khasanov, M. G. B. Drew, *J. Am. Chem. Soc.* **2002**, *124*, 14092; o) S.-H. Lu, S. Selvi, J.-M. Fang, *J. Org. Chem.* **2007**, *72*, 117; p) J.-M. Fang, S. Selvi, J.-H. Liao, Z. Slanina, C.-T. Chen, P.-T. Chou, *J. Am. Chem. Soc.* **2004**, *126*, 3559; q) H. Ohkawa, G. B. W. L. Ligthart, R. Sijbesma, E. W. Meijer, *Macromolecules* **2007**, *40*, 1453; r) G. B. W. L. Ligthart, H. Ohkawa, R. P. Sijbesma, E. W. Meijer, *J. Am. Chem. Soc.* **2005**, *127*, 810; s) T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.* **2006**, *128*, 13986; t) E. Goto, M. Usuki, H. Takenaka, K. Sakai, T. Tanase, *Organometallics* **2004**, *23*, 6042; u) V. J. Catalano, B. L. Bennett, R. L. Yson, B. C. Noll, *J. Am. Chem. Soc.* **2002**, *124*, 10056; v) V. J. Catalano, H. M. Kar, B. L. Bennett, *Inorg. Chem.* **2000**, *39*, 121–127; w) R.-H. Uang, C.-K. Chan, S.-M. Peng, C.-M. Che, *J. Chem. Soc., Chem. Commun.* **1994**, 2561; x) M.-M. Yu, Z.-X. Li, L.-H. Wei, D.-H. Wei, M.-S. Tang, *Org. Lett.* **2008**, *10*, 5115; y) Y. Zhou, Y. Xiao, X. Qian, *Tetrahedron Lett.* **2008**, *49*, 3380; z) A. Petitjean, L. A. Cuccia, M. Schmutz, J.-M. Lehn, *J. Org. Chem.* **2008**, *73*, 2481.

[29] a) G. Zhang, H.-W. Tseng, R. P. Thummel, *Inorg. Chem.* **2008**, *47*, 990; b) R. Zong, F. Naud, C. Segal, J. Burke, F. Wu, R. P. Thummel, *Inorg. Chem.* **2004**, *43*, 6195.

[30] a) T.-a. Koizumi, K. Tanaka, *Angew. Chem. Int. Ed.* **2005**, *44*, 5891; b) T. Tomon, T.-a. Koizumi, K. Tanaka, *Angew. Chem. Int. Ed.* **2005**, *44*, 2229; c) T. Tamon, D. Ooyama, T. Wada, K. Shiren, K. Tanaka, *Chem. Commun.* **2001**, 1100; d) X. Zhang, Z. Xi, A. Liu, W. Chen, *Organometallics* **2008**, *27*, 4401; e) J. Ye, S. Jin, W. Chen, H. Qiu, *Inorg. Chem. Commun.* **2008**, *11*, 404; f) S. A. Moya, J. Gajardo, J. C. Araya, J. J. Cornejo, V. Guerchais, H. L. Bozec, J. C. Bayón, A. J. Pardey, P. Aguirre, *Appl. Organomet. Chem.* **2008**, *22*, 471; g) S. A. Moya, R. Pastene, R. Sariego, R. Sartori, P. Aguirre, H. L. Bozec, *Polyhedron* **1996**, *15*, 1823; h) A. E. M. Boelrijik, T. X. Neenan, J. Reedijk, *J. Chem. Soc., Dalton Trans.* **1997**, 4561; i) A. E. M. Boelrijik, M. M. Van Velzen, T. X. Neenan, J. Reedijk, H. Kooijman, *Chem. Commun.* **1997**, 4561.

[31] M. Majumdar, S. K. Patra, M. Kannan, K. R. Dunbar, J. K. Bera, *Inorg. Chem.* **2008**, *47*, 2212.

[32] M. Majumdar, S. K. Patra, J. K. Bera, *Polyhedron* **2007**, *26*, 1597.

[33] T. Tanase, T. Igoshi, K. Kobayashi, Y. Yamamoto, *J. Chem. Res. (S)* **1998**, 538.

[34] F. A. Cotton, C. Y. Liu, C. A. Murillo, *Inorg. Chem.* **2004**, *43*, 2267.

[35] a) C. A. Crawford, J. Matonic, W. E. Streib, J. C. Huffman, K. R. Dunbar, G. Christou, *Inorg. Chem.* **1993**, *32*, 3125; b) R. H. Cayton, S. T. Chacon, M. H. Chisholm, K. Folting, *Polyhedron* **1993**, *12*, 415; c) H. T. Chifotides, K. R. Dunbar, *Acc. Chem. Res.* **2005**, *38*, 146; d) J. A. Howell, *Dalton Trans.* **2007**, 3798.

[36] F. A. Cotton, L. M. Daniels, P. Lei, C. A. Murillo, X. Wang, *Inorg. Chem.* **2001**, *40*, 2778.

[37] a) T. R. Webb, T. Y. Dong, *Inorg. Chem.* **1982**, *21*, 114; b) J. M. Casas, R. H. Cayton, M. H. Chisholm, *Inorg. Chem.* **1991**, *30*, 358.

[38] H. T. Chifotides, K. V. Catalan, K. R. Dunbar, *Inorg. Chem.* **2003**, *42*, 8739.

[39] S. K. Patra, N. Sadhukhan, J. K. Bera, *Inorg. Chem.* **2006**, *45*, 4007.

[40] S. K. Patra, M. Majumdar, J. K. Bera, *J. Organomet. Chem.* **2006**, *691*, 4779.

[41] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, **1993**.

[42] a) F. A. Cotton, L. M. Daniels, C. A. Murillo, I. Pascual, H. C. Zhou, *J. Am. Chem. Soc.* **1999**, *121*, 6856; b) F. A. Cotton, M. W. Extine, G. W. Rice, *Inorg. Chem.* **1978**, *17*, 176.

[43] a) P. M. Bradley, B. E. Bursten, T. Claudia, *Inorg. Chem.* **2001**, *40*, 1376; b) F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, S.-E. Stiriba, *Inorg. Chem.* **2000**, *39*, 1748; c) G. Aullón, S. Alvarez, *Inorg. Chem.* **1993**, *32*, 3712; d) R. J. H. Clark, A. J. Hempleman, *Inorg. Chem.* **1989**, *28*, 746; e) T. Sowa, T. Kawamura, T. Shida, T. Yonezawa, *Inorg. Chem.* **1983**, *22*, 56; f) H. Nakatsuji, J. Ushio, K. Kanda, Y. Onishi, T. Kawamura, T. Yonezawa, *Chem. Phys. Lett.* **1981**, *79*, 299; g) F. A. Cotton, T. R. Felthouse, *Inorg. Chem.* **1981**, *20*, 584; h) B. E. Bursten, F. A. Cotton, *Inorg. Chem.* **1981**, *20*, 3042; i) J. G. Norman, H. J.

Kolari, *J. Am. Chem. Soc.* **1978**, *100*, 791; j) L. Dubicki, R. L. Martin, *Inorg. Chem.* **1970**, *9*, 673.
[44] G. Cripps, A. Pellissier, S. Chardon-Noblat, A. Deronzier, R. Haines, *J. Organomet. Chem.* **2004**, *689*, 484.
[45] W. J. Klemperer, B. Zhong, *Inorg. Chem.* **1993**, *32*, 5821.
[46] F. A. Cotton, L. M. Daniels, C. A. Murillo, I. Pascual, H.-C. Zhou, *J. Am. Chem. Soc.* **1999**, *121*, 6856.
[47] J. G. Norman, H. J. Kolari, *J. Am. Chem. Soc.* **1978**, *100*, 791.
[48] S. K. Patra, J. K. Bera, *Organometallics* **2006**, *25*, 6054.
[49] S. K. Patra, J. K. Bera, *Organometallics* **2007**, *26*, 2598.
[50] a) M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919; b) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911.
[51] a) J. Lloret, K. Bieger, F. Estevan, P. Lahuerta, P. Hirva, J. Pérez-Prieto, M. Sanaú, *Organometallics* **2006**, *25*, 5113; b) J. Lloret, F. Estevan, P. Lahuerta, P. Hirva, J. Pérez-Prieto, M. Sanaú, *Organometallics* **2006**, *25*, 3156; c) K. Bieger, F. Estevan, P. Lahuerta, J. Lloret, J. Pérez-Prieto, M. Sanaú, N. Siguero, S. E. Stiriba, *Organometallics* **2003**, *22*, 1799; d) P. Lahuerta, J. Paya, M. A. Pellinghelli, A. Tiripicchio, *Inorg. Chem.* **1992**, *31*, 1224; e) D. F. Taber, S. C. Malcom, K. Bieger, P. Lahuerta, Z. N. da Rocha, M. Sanaú, S. E. Stiriba, J. Pérez-Prieto, M. A. Monge, *J. Am. Chem. Soc.* **1999**, *121*, 860–861; f) A. R. Chakravarty, F. A. Cotton, D. A. Tocher, J. H. Tocher, *Organometallics* **1985**, *4*, 8.
[52] a) M. J. Tenorio, K. Mereiter, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **2000**, *122*, 11230; b) W. Baratta, E. Herdtweck, P. Rigo, *Angew. Chem. Int. Ed.* **1999**, *38*, 1629; c) D. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter, T. Scheiring, *J. Am. Chem. Soc.* **1999**, *121*, 8087; d) R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789; e) M. Brookhart, M. L. H. Green, L. L. Wong, *Prog. Inorg. Chem.* **1988**, *36*, 1.
[53] A. J. Toner, S. Gründemann, E. Clot, H.-H. Limbach, B. Donndieu, S. Sabo-Etienne, B. Chaudret, *J. Am. Chem. Soc.* **2000**, *122*, 6777.
[54] R. P. Thummel, F. Lefoulon, D. Williamson, M. Chavan, *Inorg. Chem.* **1986**, *25*, 1675.
[55] S. K. Patra, S. M. W. Rahaman, M. Majumdar, A. Sinha, J. K. Bera, *Chem. Commun.* **2008**, 2511.
[56] N. Sadhukhan, S. K. Patra, K. Sana, J. K. Bera, *Organometallics* **2006**, *25*, 2914.
[57] N. Sadhukhan, J. K. Bera, *Inorg. Chem.* **2009**, *48*, 978.
[58] a) L. A. Oro, M. A. Ciriano, J. J. Pérez-Torrente, B. E. Villarroya, *Coord. Chem. Rev.* **1999**, *193–195*, 941; b) G. S. Rodman, K. R. Mann, *Inorg. Chem.* **1988**, *27*, 3338; c) G. S. Rodman, K. R. Mann, *Inorg. Chem.* **1985**, *24*, 3507; d) K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood, M. J. Zaworotko, *Organometallics* **1983**, *2*, 1447; e) K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, J. L. Atwood, M. J. Zaworotko, *J. Am. Chem. Soc.* **1982**, *104*, 920; f) A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko, J. L. Atwood, *J. Am. Chem. Soc.* **1982**, *104*, 922; g) J. L. Dempsey, A. J. Esswein, D. R. Manke, J. Rosenthal, J. D. Soper, D. G. Nocera, *Inorg. Chem.* **2005**, *44*, 6879 and references cited therein.
[59] a) C. Tejel, M. A. Ciriano, B. E. Villarroya, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem. Int. Ed.* **2003**, *42*, 530; b) R. D. Brost, G. W. Bushnell, D. G. Harrison, S. R. Stobart, *Inorg. Chem.* **2002**, *41*, 1412; c) M. V. Jiménez, E. Sola, M. A. Egea, A. Huet, A. C. Francisco, F. J. Lahoz, L. A. Oro, *Inorg. Chem.* **2000**, *39*, 4868; d) K. R. Dunbar, S. O. Majors, J.-S. Sun, *Inorg. Chim. Acta* **1995**, *229*, 373; e) N. Kanematsu, M. Ebihara, T. Kawamura, *J. Chem. Soc., Dalton Trans.* **1999**, 4413 and references cited therein.
[60] a) K. J. Del Rossi, B. B. Wayland, *J. Chem. Soc., Chem. Commun.* **1986**, 1653; b) H. Hückstädt, H. Homborh, *Z. Anorg. Allg. Chem.* **1997**, *623*, 369; c) P. G. Rasmussen, J. E. Anderson, O. H. Bailey, M. Tamres, J. C. Bayón, *J. Am. Chem. Soc.* **1985**, *107*, 279; d) H. Huang, A. L. Rheingold, R. P. Hughes, *Organometallics* **2009**, *28*, 1575; e) H.-P. Lee, Y.-F. Hsu, T.-R. Chen, J.-D. Chen, K. H.-C. Chen, J.-C. Wang, *Inorg. Chem.* **2009**, *48*, 1263.
[61] a) R. Pastene, H. L. Bozec, S. A. Moya, *Inorg. Chem. Commun.* **2000**, *3*, 376; b) F. Gelin, R. P. Thummel, *J. Org. Chem.* **1992**, *57*, 3780.
[62] a) C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips, K. H. Leung, *Angew. Chem. Int. Ed.* **2000**, *39*, 4084; b) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597; c) J.-M. Poblet, M. Benard, *Chem. Commun.* **1998**, 1179; d) P. Pyykkö, F. Mendizabal, *Inorg. Chem.* **1998**, *37*, 3018.
[63] a) U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, *Chem. Commun.* **1997**, 1723; b) B. Neumann, U. Siemeling, H.-G. Stammler, U. Vorfeld, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F. F. de Biani, P. J. Zanello, *J. Chem. Soc., Dalton Trans.* **1997**, 4705.
[64] J. K. Bera, unpublished work.
[65] a) J. R. Quinn, S. C. Zimmerman, J. E. D. el Bene, I. Shavitt, *J. Am. Chem. Soc.* **2007**, *129*, 934; b) H. C. Ong, S. C. Zimmerman, *Org. Lett.* **2006**, *8*, 1589; c) T. Park, E. M. Todd, S. Nakashima, S. C. Zimmerman, *J. Am. Chem. Soc.* **2005**, *127*, 18133; d) M. F. Mayer, S. Nakashima, S. C. Zimmerman, *Org. Lett.* **2005**, *7*, 3005.
[66] a) T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.* **2006**, *128*, 11582; b) T. Park, S. C. Zimmerman, S. Nakashima, *J. Am. Chem. Soc.* **2005**, *127*, 6520.
[67] a) T. Mizukawa, K. Tsuge, H. Nakajima, K. Tanaka, *Angew. Chem. Int. Ed.* **1999**, *38*, 362; b) K. Tanaka, T. Mizukawa, *Appl. Organomet. Chem.* **2000**, *14*, 863; c) T.-A. Koizumi, T. Tomon, K. Tanaka, *J. Organomet. Chem.* **2005**, *690*, 4272.
[68] a) Z. Deng, H.-W. Tseng, R. Zong, D. Wang, R. P. Thummel, *Inorg. Chem.* **2008**, *47*, 1835; b) R. Zong, R. P. Thummel, *J. Am. Chem. Soc.* **2005**, *127*, 12802.
[69] A. Kukrek, D. Wang, Y. Hou, R. Zong, R. P. Thummel, *Inorg. Chem.* **2006**, *45*, 10131.
[70] a) C. He, S. J. Lippard, *Tetrahedron* **2000**, *56*, 8245; b) C. J. Fahrni, A. Pfaltz, M. Neuburger, M. Zehnder, *Helv. Chim. Acta* **1998**, *81*, 507; c) R. Zong, D. Wang, R. Hammitt, R. P. Thummel, *J. Org. Chem.* **2006**, *71*, 167; d) C. F. H. Allen, *Chem. Rev.* **1950**, *47*, 275–305; e) P. S. Corbin, S. C. Zimmerman, P. A. Thiessen, N. A. Hawryluk, T. J. Murray, *J. Am. Chem. Soc.* **2001**, *123*, 10475.

Received: April 3, 2009
Published Online: July 15, 2009

