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Design and synthesis of multidentate ligands via metal promoted C–N bond formation processes and their coordination chemistry

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Abstract. This presentation reports some novel examples of organic ring amination reactions via metal mediation. The organic transformations are highly regioselective and can be controlled by the proper selection of the mediator complex. The two isomeric organic ligands viz. HL^1 and HL^2 were isolated in their pure states by the removal of the metal ions. These were fully characterized. The ligand HL^1 has low *pKa*, 8·5. Upon deprotonation, it behaves as a potential *bis* chelating N,N,N-donors. The coordination chemistry of the HL^1 ligand involving some 3*d*-metal ions is described. Two unusual low-spin complexes of manganese(II) and iron(III) are reported. The ferric complex displayed a rhombic EPR while, the corresponding manganese compound showed a complex pattern due to hyperfine coupling. All the complexes displayed large number of redox responses. A brief mention about the future projection of this work is noted.

Keywords. Metal promoted reactions; aromatic ring amination; new *bis* chelating N,N,N-donors; transition metal chemistry.

1. Introduction

Chemical transformation[1–5] of organic substrates, coordinated to transition metal ions, are important as these provide facile synthesis of many novel molecules that are otherwise difficult or even impossible to synthesize by conventional synthetic procedures. In these reactions, the metal ion acts as mediator, which in fact forms the basis of homogeneous catalysis. We have been interested[6–11] in transition metal promoted transformations in the context of design and synthesis of new organic ligands and to study their coordination chemistry. In this presentation we wish to discuss some of our recent results[12–16] on aromatic ring amination reaction of coordinated 2-(phenylazo)pyridine (pap). Amination of an aromatic ring belongs to a reaction[17–20] class of fundamental importance in chemistry in connection with carbon–nitrogen bond formation processes. Most of the results described herein are published.

2. Results and discussion

2.1 *The chemical reaction*s

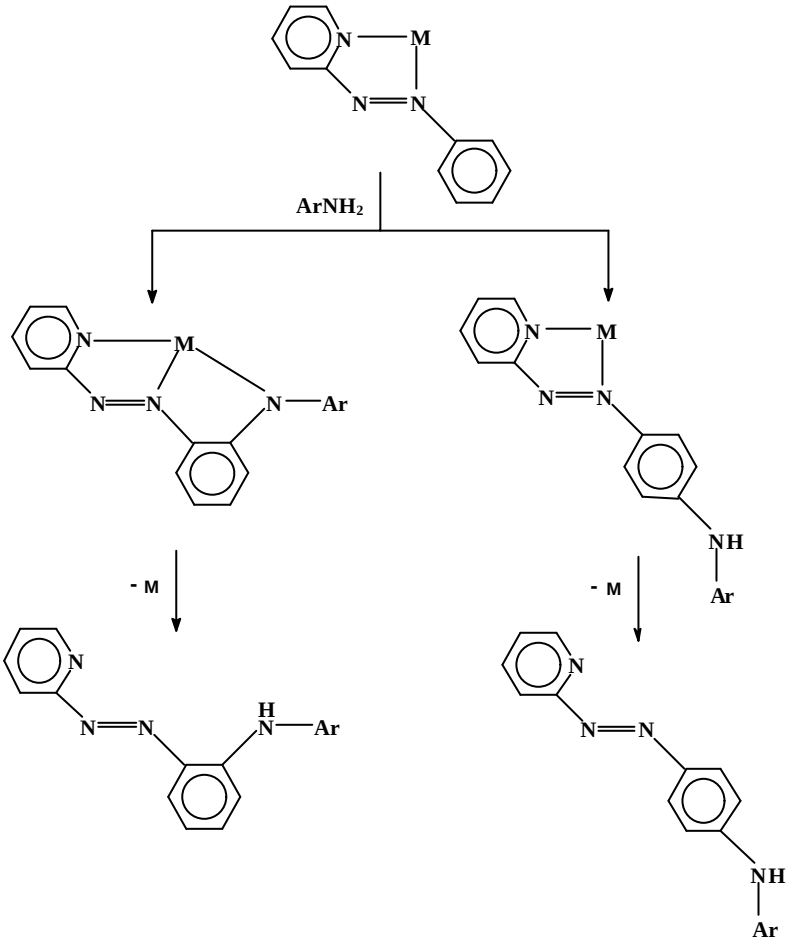
The aromatic ring amination reactions[6] of coordinated 2-(phenylazo)pyridine (pap) ligand are shown in the following scheme (scheme 1).

*For correspondence

The ligand pap, upon coordination, is activated which resulted in the amination reaction. We wish to note here that these chemical transformations do not occur with the free pap ligand. Two positional isomers (viz. *ortho*- and *para*-) of the aminated pap ligands were isolated by the removal of the respective metal ions. The ligand HL^1, upon deprotonation, can act as a monoanionic tridentate N,N,N-donor. The *p*-aminated product, HL^2, on the otherhand, binds as a neutral bidentate N,N-donor. The fusion reaction, pap $\rightarrow$ HL^1 (HL^2) is associated with loss of H_2 ($2H^+ + 2e^-$), which presumably occurs via aerial oxidation.

2.2 *Site selectivity*

It has been observed that the *o*-fusion of an aromatic amine to coordinated pap ligand is more favourable in the case of labile mediator complex, while *p*-amination is preferred

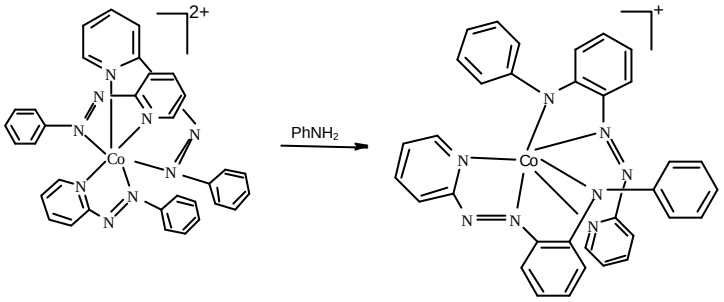


Scheme 1.

with an inert metal complex mediator. For example, the brown complex[21], $[Co(pap)_3]^{2+}$ reacts smoothly with neat $ArNH_2$ on a steam bath to produce an intense green product which on work up and subsequent crystallization gives crystalline compound (**1**) as the major product (yield >80%) (scheme 2).

The formation of the green cobalt(III) (**1**) compound was authenticated by its single crystal X-ray structure analysis. Its redox and spectral properties are reported[24]. In this reaction, one of the three coordinated pap ligands, is eliminated from the starting $[Co(pap)_3]^{2+}$ and rest two pap ligands got aminated at the *o*-carbon of the pendant phenyl ring to result in *bis* chelated complex, **1**. There are two similar extended N,N,N tridentate ligands in **1** which are formed due to oxidative fusion of $ArNH_2$ at the *o*-carbons of the pendant phenyl rings of two coordinated pap ligands. During this process the cobalt ion has undergone one step oxidation to cobalt(III) ion.

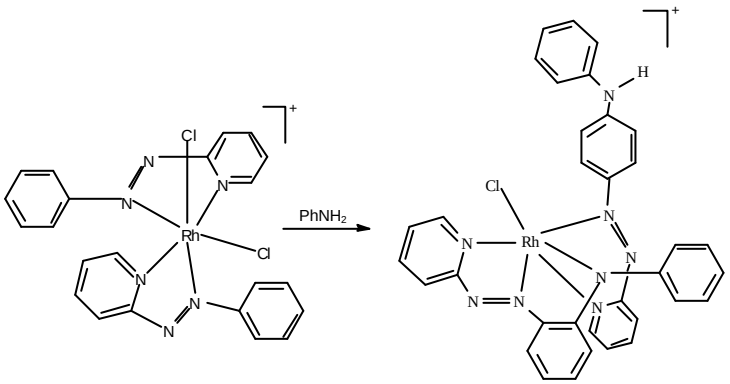
In contrast, a similar reaction using $[RhCl_2(pap)_2]^+$ as the mediator complex[22] produced an intense blue product **2**. X-ray structural analysis has revealed[12] that two types of fusion of $ArNH_2$ with the two pap ligands have occurred (scheme 3).



$[Co^{II}(pap)_3]^{2+}$ Brown

$[Co^{III}(pap\text{-}o\text{-}am)_2]^+$ Green, **1**

Scheme 2.



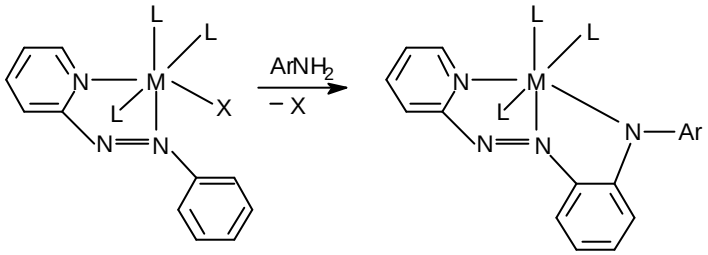
$[RhCl_2(pap)_2]^+$ Brown

$[Rh(pap\text{-}o\text{-}am)(pap\text{-}p\text{-}amH)]^+$ Blue, **2**

Scheme 3.

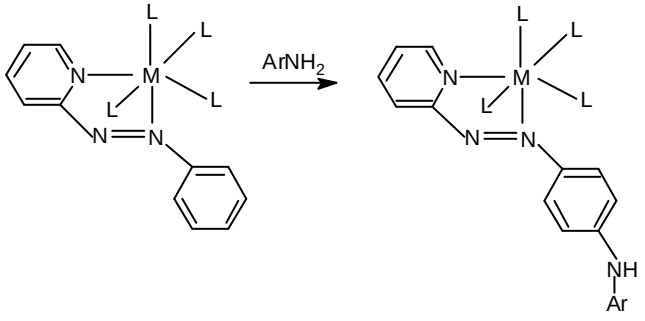
In the complex **2**, one of the extended ligands is neutral, viz. [pap-p-amH], which has the $ArNH_2$ fragment fused to pap at the *p*-position of the phenyl group of pap. This binds as a bidentate donor and chelates to rhodium via the pyridine and the aza nitrogen. The second ligand $[pap\text{-}o\text{-}am]^-$ acts as a monoanionic ligand as noted in the reaction of $[Co(pap)_3]^{2+}$ with $ArNH_2$.

The site selectivity of the amination reactions described in the above two schemes, 2 and 3, is different and presumably depends on the mediator complex. The starting cobalt complex, $[Co(pap)_3]^{2+}$ is labile and dissociates[21] one pap ligand easily. The dihalo rhodium complex, $[RhCl_2(pap)_2]^+$, in contrast, is substitutionally inert[22]. It is known that a substitution reaction at this cationic rhodium complex, even under the most forceful conditions, results only in monosubtituted complex, $[RhCl_2(N)(pap)_2]^{n+}$ (N = nucleophile, $n = 1, 2$). In the case of $[Co(pap)_3]^{2+}$ mediator, one bidentate pap ligand is eliminated from the trischelate creating two vacant sites. Coordiantion of two $ArNH_2$ residues at the vacant sites followed by oxidative fusion at the *o*-carbon of the pendant phenyl rings of coordinated pap ligands are the two most plausible steps for the reaction. Upon coordination, $ArNH_2$ residues come in proximity to the *o*-C–H of the pendant phenyl group of pap for *o*-fusion. We note here that only one of the two coordinated chloride ligands was eliminated during the reaction of $[RhCl_2(pap)_2]^+$ and $ArNH_2$. As a result only one of the two pap ligands was aminated at *o*- and the second ligand was aminated at the *p*-carbon as a second choice (scheme 4).



Labile complex
(X is a labile ligand)

o-amination



Inert complex

p-amination

Scheme 4.

To establish the proposition on the regioselectivity of the amination reaction of the above type, we have performed another reaction using $[Fe(pap)_3]^{2+}$ as the mediator metal complex. It is known[23] from the literature that $[Fe(pap)_3]^{2+}$ is more inert than $[Co(pap)_3]^{2+}$. The iron complex reacted smoothly with $ArNH_2$ over a steam bath to produce an intense blue iron compound. It decomposes readily in solution and gives inconsistent elemental analysis results. However, the transformed organic ligand was isolated by the decomposition of the iron complex and by the removal of the metal ion (scheme 5).

Two other inert metal complexes viz. $[Ru(pap)_3]^{2+}$ and $[CrCl_2(pap)_2]$, which are known to be unusually inert, also react with $ArNH_2$ smoothly to produce metal complexes of *p*-aminated ligands. The results of these reactions will be published in due course.

2.3 *Coordination chemistry of HL^1*

The ligand HL^1 can be deprotonated easily[24] (scheme 6). The *pKa* is low, 8·5 and its conjugate base $[L^1]^-$ binds as an anionic *bis* chelating N,N,N-donor.

Notably, the 2-(phenylazo)pyridine part of $[L^1]^-$ is soft while the coordinating nitrogen of $[NAr]^-$ is a hard base. Thus combination of the soft and hard donor characters of different sites of $[L^1]^-$ is anticipated to stabilize transition metal ions in different oxidation states. The 2:1 reaction of HL^1 with the metal chloride salts of Mn(II), Co(II), Ni(II) and Fe(III) afforded $[M(L^1)_2]^{n+}$ [$n = 0$ for Mn(II), Co(II), Ni(II) and $n = 1$ for M = Fe(III)] in excellent yields (80–85%). NMR spectra of the ligand HL^1 and the diamagnetic complex, $[Co(L^1)_2]^+$ are shown in figure 1 for comparison.

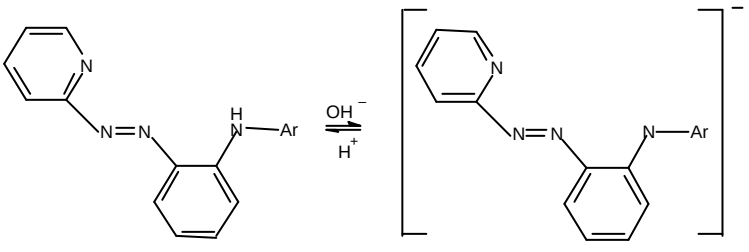
$$[Co(pap)_3]^{2+} \xrightarrow[O_2]{ArNH_2} [Co^{III}(L^1)_2]^+ \xrightarrow[(NH_4)_2Sx]{N_2H_4} [HL^1] + CoS + \text{other products},$$

Brown (labile complex); Green

$$[Fe(pap)_3]^{2+} \xrightarrow[O_2]{ArNH_2} [Fe^{II}(HL^2)_3]^{2+} \xrightarrow{\text{aq. } NH_3} [HL^2] + Fe_2O_3.nH_2O + \text{other products}.$$

Blue (inert complex); (intermediate complex)

Scheme 5.



pKa = 8·5

Scheme 6.

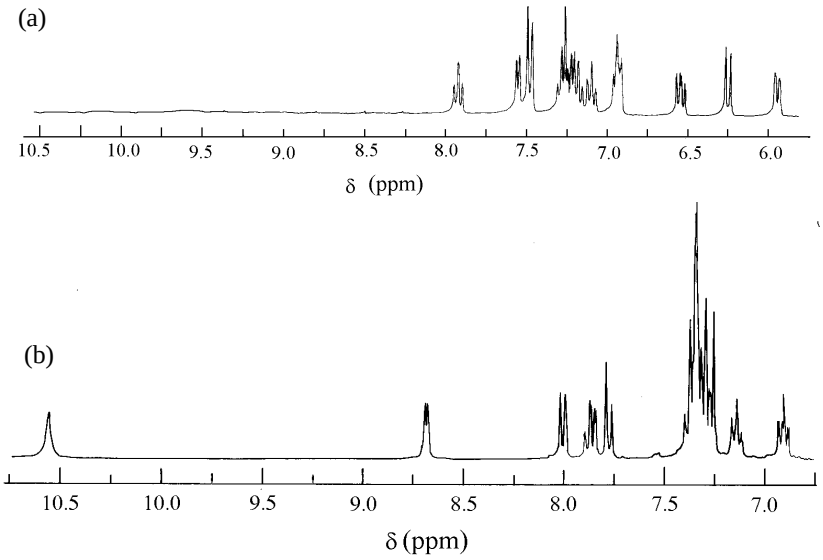


Figure 1. ^{1}H NMR spectra of (**a**) $[Co(L^1)_2]^+$ and (**b**) HL^1 in $CDCl_3$.

The brown ferric complex $[Fe(L^1)_2]^+$ undergoes reduction at an anodic poential (0·16V vs SCE) which allowed us to isolate the corresponding ferrous complex $[Fe(L^1)_2]$ from its ferric congener in almost quantitative yield. The colour of $[Fe(L^1)_2]$ is pink and it is diamagnetic (t_{2g}^6). Interestingly, the Mn(II), Fe(II) as well as Fe(III) complexes were obtained in their low spin states. The low spin states of the above metal ions are generally uncommon entities [25–26] due to their very high spin-pairing energy. The room temperature magnetic moments of the Mn(II) and Fe(III) complexes lie in the range 1·65–1·70 m_B, indicating the low spin states. Both of them are EPR active. The spectrum of $[Fe(L^1)_2]^+$, in frozen dichloromethane-toluene solution, displayed a rhombic spectrum with $g_1 = 2·11$, $g_2 = 2·08$ and $g_3 = 1·93$. However, the three *g*-components of the rhombic spectrum of $[Mn(L^1)_2]^+$ further splits due to hyperfine coupling to give complex spectral feature characteristic of the low spin state of the Mn(II) complexes. Two representative spectra of $[M(L^1)_2]^{n+}$ (M = Fe(III), $n = 1$ and M = Mn(II), $n = 0$) are shown in figure 2.

Each of the above complexes displayed multiple redox responses. Representative voltammograms are shown in figure 3.

Low potential anodic responses are assigned to metal redox processes, while the cathodic responses are due to ligand reductions. In order to study the spectra of the parent as well as stable members of the redox series, spectroelectrochemical studies have been made on all the above complexes using an OTTLE cell.

3. Conclusion and future plan

We have presented metal-promoted regioselective aromatic ring amination of a coordinated diaza ligand together with the coordination chemistry of the transformed ligand involving some 3*d*-metal ions. We have demonstrated that the site selectivity for this amination reactions can be controlled by the proper selection of the mediator metal complex. The relative coordination modes of the tridentate $[L^1]^-$ ligands are different in

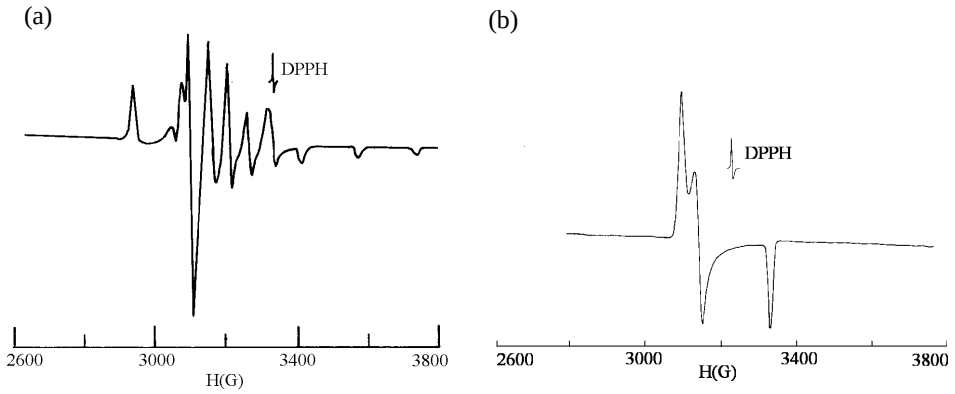


Figure 2. EPR spectra of (**a**) $[Mn(L^1)_2]$ and (**b**) $[Fe(L^1)_2]^+$ in frozen dichloromethane-toluene solution at 77 K (DPPH = diphenylpicrylhydrazyl).

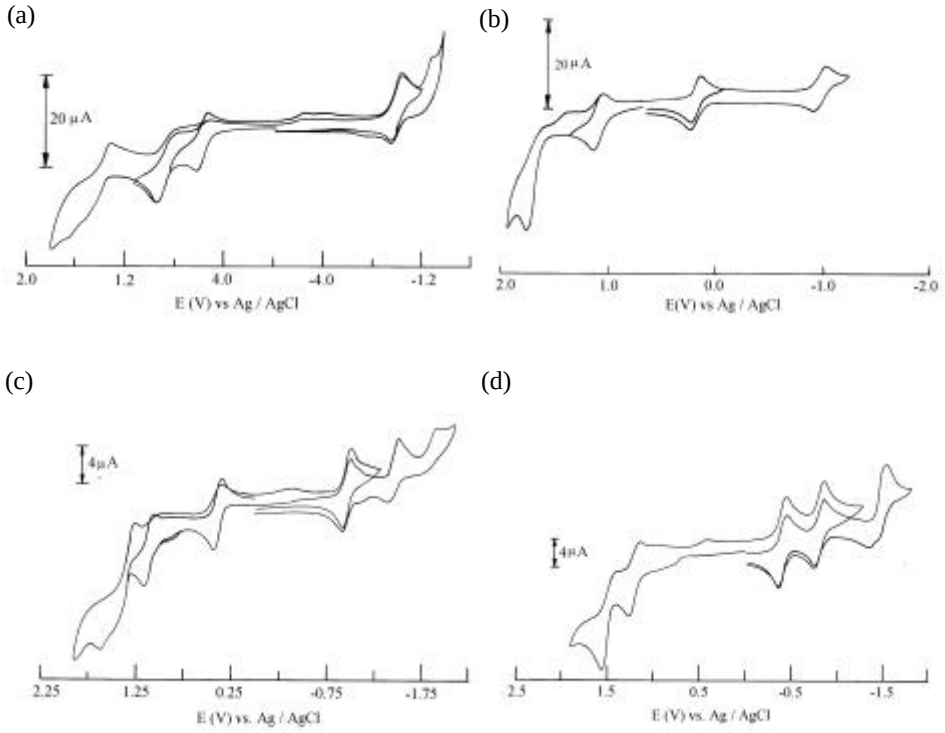


Figure 3. Segmented cyclic voltammograms (scan rate 50 mVs^{-1}) of a 10^{-3} (M) solution in acetonitrile (0·1 M NEt_4ClO_4) at 298 K at a platinum working electrode of (**a**) $[Ni(L^1)_2]$; (**b**) $[Fe(L^1)_2]^+$; (**c**) $[Mn(L^1)_2]$ and (**d**) $[Co(L^1)_2]^+$.

the metal complexes of 4*d*- and 5*d*-elements. Moreover, the heavier transition metal ions appear to promote an otherwise unreactive C(phenyl)-N(amine) single bond cleavage processes leading to deamination [27] of the ligands.

In an attempt to design and synthesize multidentate polynucleating ligands using the above synthetic strategy, different aromatic amines with additional binding sites are being explored. In this respect the use of two positional isomers of amino pyridine needs special mention. It is anticipated that fusion of these amines to 2-(phenylazo)pyridine might lead to the synthesis of suitable bridging ligands for the development of polymetallic systems . Preliminary results in this area are encouraging.

Acknowledgements

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References

1. Black D St C 1987 *Comprehensive coordination chemistry* (eds) R D Gillard and J A McCleverty (London: Pergamon) vol 1, p. 415, vol. 6, p. 155
2. Hegedus L S 1998 *Coord. Chem. Rev*. **168** 49; Hegedus L S 1998 *Coord. Chem. Rev*. **175** 159
3. Braterm P S 1986 *Reactions of coordinated ligands* (New York: Plenum)
4. Sheldon R A and Kochi J K 1981 *Metal catalyzed oxidation of organic compounds* (New York: Academic Press)
5. Bandyopadhyay P, Bandyopadhyay D, Chakravorty A, Cotton F A, Falvello L R and Han S 1983 *J. Am. Chem. Soc.* **105** 6327; Lahiri G K, Goswami S, Falvello L R and Chakravorty A 1987 *Inorg. Chem*. **13** 1714
6. Mitra K N and Goswami S 1997 *Chem. Commun*. 49
7. Mitra K N and Goswami S 1997 *Inorg. Chem.* **36** 1322
8. Mitra K N, Majumdar P, Peng S-M, Castineiras A and Goswami S 1997 *Chem. Commun*. 1267
9. Mitra K N, Peng S-M and Goswami S 1998 *Chem. Commun*. 1685
10. Mitra K N, Chaudhury S, Castineiras A and Goswami S 1998 *J. Chem. Soc., Dalton Trans.* 2901
11. Majumdar P, Falvello L R, Thomas M and Goswami S 2001 *Chem. Eur. J*. **7** 5222
12. Saha A, Ghosh A K, Majumdar P, Mitra K N, Mondal S, Rajak K K, Falvello L R and Goswami S 1999 *Organometallics* **18** 3772
13. Mitra K N and Goswami S 1999 *Proc. Indian-Acad. Sci.* (*Chem. Sci.*) **111** 461
14. Ghosh A K, Majumdar P, Falvello L R, Mustafa G and Goswami S 1999 *Organometallics* **18** 5086
15. Ghosh A K, Mitra K N, Mustafa G and Goswami S 2000 *Eur. J. Inorg. Chem.* 1961
16. Saha A, Majumdar P, Peng S-M and Goswami S 2000 *Eur. J. Inorg. Chem.* 2631
17. Hartwig J F 1998 *Angew. Chem., Int. Ed. Engl*. **37** 2046
18. Bruncko M, Khoung T-A V and Sharpless K B 1996 *Angew. Chem., Int. Ed. Engl.* **35** 454
19. Gray S D, Thorman J L, Adamian V A, Kadish K M and Woo K L 1998 *Inorg. Chem.* **37** 1
20. Li Z, Quan R W and Jacobsen E N 1995 *J. Am. Chem. Soc*. **117** 5889
21. Mahapatra A K 1986 *Synthesis, structure and reactivities of transitions metal azo complexes*, Ph D thesis, Jadavpur University, Kolkata
22. Deb A K and Goswami S 1989 *J. Chem. Soc., Dalton Trans*. 1635
23. Raghavendra B S and Chakravorty A 1976 *Indian J. Chem.* **A14** 166
24. Saha A, Majumdar P and Goswami S 2000 *J. Chem. Soc., Dalton Trans*. 1703
25. Ganguly S, Karmakar S, Pal C K and Chakravorty A 1999 *Inorg. Chem*. **38** 5984; Knof U, Weyhermuller T, Wolter T and Weighardt K 1993 *J. Chem. Soc., Chem. Commun*. 726; Griffith W P 1975 *Coord. Chem. Rev*. **17** 177
26. Ray M, Ghosh D, Shirin Z and Mukherjee R 1997 *Inorg. Chem*. **36** 3568, and references therein; Karmakar S, Chaudhury S B and Chakravorty A 1994 *Inorg. Chem.* **33** 6148; Morice C, Maux P L and Simonneaux G 1998 *Inorg. Chem*. **37** 6100
27. Das C, Peng S-M, Lee G-H and Goswami S 2002 *New J. Chem.* **26** 0000