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Metal-Promoted Aromatic Ring Amination Reactions following Carbon−Nitrogen Bond Formation. Proof of Amine Coordination for *ortho* Amination

Amrita Saha,[†] Amit K. Ghosh,[†] Partha Majumdar,[†] Kedar N. Mitra,[†]
Sujit Mondal,[†] Kajal K. Rajak,[†] Larry R. Falvello,[‡] and Sreebrata Goswami*,[†]

*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India, and Departamento de Quimica Inorganica, Universidad de Zaragoza,
50009 Zaragoza, Spain*

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Summary: The present report exemplifies two novel aromatic ring amination reactions via metal mediation. A rationale with respect to site selection for the above amination reactions, based on relative labilities of the coordinated coligands, has been established.

Metal-mediated reactions which result in addition of $[NR]^{2-}$ fragments belong to a reaction class of fundamental importance in chemistry in connection with carbon−nitrogen bond formation processes.[1] In this respect, transition-metal imido complexes are implicated as reactive intermediates[2] in bringing about the above transformations. Herein we wish to report our results on aromatic ring amination of a pendant aryl ring of coordinated 2-(phenylazo)pyridine (pap). These reactions do not occur with free pap ligand. Upon coordination, both *o*- and *p*-C−H of the pendant phenyl group of the diaza ligand are activated. As a result, amination processes occurring at both *ortho* and *para* positions were observed (Scheme 1). By the use of two suitable metal complexes of completely different nature, it has been possible for us to show that labilities of coligands in the metal complexes play an important role for the *ortho*-fusion process. Two sets of reactions of $ArNH_2$ occurring at a labile complex, $[Co(pap)_3](ClO_4)_2$, and an inert complex, $[RhCl_2(pap)_2]ClO_4$, have been used for this purpose. It may be relevant to mention here that amination of an aromatic ring[3] by the activation of a C−H bond is still relatively rare but is synthetically a useful reaction.

The brown complex[4] $Co(pap)_3^{2+}$ reacts smoothly with neat $ArNH_2$ on a steam bath to produce an intense green mixture which on workup and subsequent crystallization gives[5] the crystalline green compound **1** as the major product (yield >80%).

$$\mathrm{Co(pap)_3}^{2+} \xrightarrow{\mathrm{ArNH_2}} \underset{\mathbf{1a-c}}{\mathrm{Co(pap\text{-}}o\text{-}\mathrm{am)_2}^{+}} \qquad \text{(i)}$$

$ArNH_2$ = aniline (**1a**),
p-toluidine (**1b**), *p*-anisidine (**1c**)

These diamagnetic cobalt(III) compounds are 1:1 electrolytes in acetonitrile and show highly resolved ^1H NMR spectra. The ^1H NMR spectra of the cobalt complexes are in complete agreement with the crystal structure of a representative example (vide infra). Notably, each kind of proton of the coordinated anionic ligand pap-*o*-am$^-$ gave rise to one signal. Thus, the two ligands in **1** are magnetically equivalent, indicating the presence of a 2-fold symmetry axis. The product from this unusual reaction was finally confirmed on the basis of the X-ray structure determination[6] of a representative complex, **1a**. The structural analysis of **1a** indeed authenticated the fusion of $ArNH_2$ at a position *ortho* to the aza group of pap (Figure 1). We refer to this as pap-*o*-am. There are two such extended ligands in **1a**, each of which acts as a N,N,N-tridentate donor with the deprotonation of the amino nitrogens (N(4) and N(8)). The geometry of the cationic complex is meridional, and the bond distances indicate the presence of backbone conjugation in the anionic pap-*o*-am$^-$ ligand. Thus, the aza nitrogen to phenyl carbon distances as well as the

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* To whom correspondence should be addressed. E-mail: icsg@mahendra.iacs.res.in. Fax: 91-33-473-2805.

[†] Indian Association for the Cultivation of Science.

[‡] Universidad de Zaragoza.

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(5) A mixture of $[Co(pap)_3](ClO_4)_2$ (0.2 g) and $ArNH_2$ (2.0 g) was heated on a steam bath for 1 h. The cooled green mixture was throughly washed with diethyl ether, and crystallization of the crude product from a CH_2Cl_2/C_6H_{14} mixture yielded **1** (80−85%) as green crystals. Physical data for a representative sample of **1a** are as follows. Anal. Calcd for $C_{34}H_{26}N_8ClO_4Co$: C, 57.92; H, 3.69; N, 15.30. Found: C, 57.35; H, 3.86; N, 15.45. UV/vis (CH_3CN): λ_{max} (ϵ) 787 sh (12 930), 712 sh (12 500), 405 (22 450), 308 sh (30 000), 246 nm (59 600). IR (KBr): ν(N=N) 1590, ν(C−N) 1250, $\nu(ClO_4^-)$ 1100, 625 cm^{-1}.

(6) X-ray structure of **1a**: X-ray-quality crystals (0.4 × 0.4 × 0.4 mm) of **1a** were obtained by slow diffusion of a chloroform solution of the complex into hexane. Cell parameters were obtained by least-squares fits of 30 machine-centered reflections. Data were collected ($3 \leq 2\theta \leq 43°$) on a Nicolet R3m/V diffractometer (295 K) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by the Patterson heavy-atom method using the SHELXTL-plus program package on a Micro VAXII computer. Refinement was done by the full matrix method. Crystal and refinement data: $C_{34}H_{26}ClCoN_8O_4$, triclinic, $P\bar{1}$, a = 9.106(4) Å, b = 10.360(3) Å, c = 17.356(6) Å, α = 104.04(3)°, β = 91.34(3)°, γ = 93.74(3)°, V = 1583.7(10) Å^3, Z = 2, with 433 parameters refined on 4158 data with $I > 2\sigma(I)$, R1 = 0.0397 and wR2 = 0.0903, GOF = 1.026.

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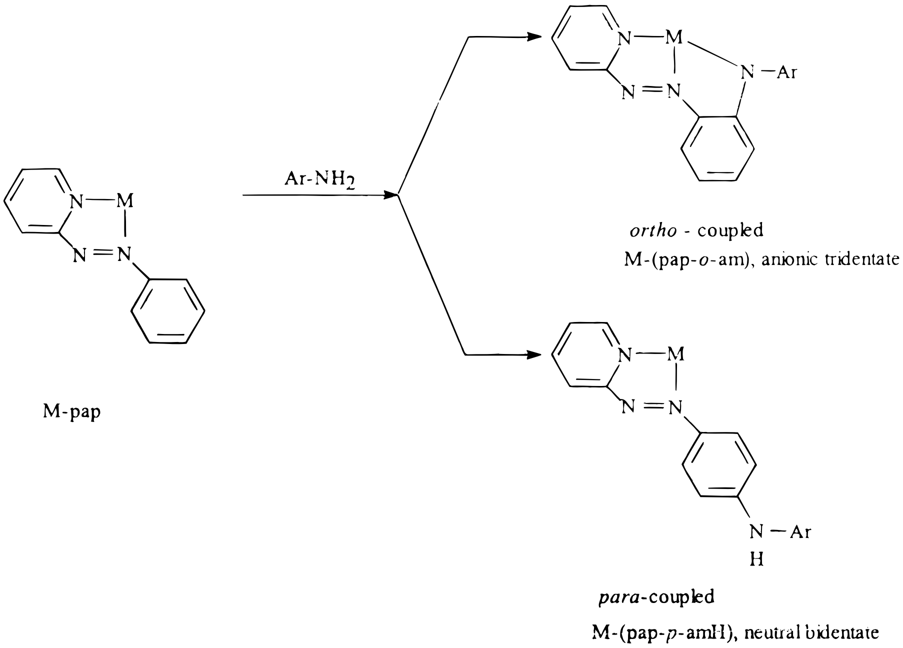
Scheme 1



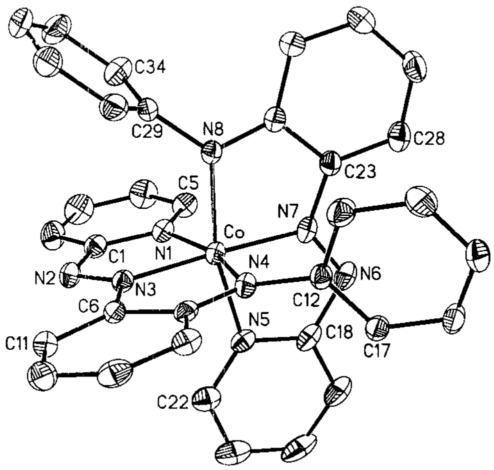


Figure 1. ORTEP plot and atom-numbering scheme for $[Co(pap\text{-}o\text{-}am)_2]^+$ (**1a**) in $[Co(pap\text{-}o\text{-}am)_2]ClO_4$. Hydrogen atoms are omitted for clarity.

amine nitrogen of pap-*o*-am$^-$ bonds to the phenyl group of pap are shorter than a C−N single bond. The N−N aza distances in these anionic ligands are considerably longer than that observed[7] in $[papH]ClO_4$, in agreement with the notion of electron delocalization along the ligand backbone in the anionic pap-*o*-am$^-$. In this reaction two out of the three coordinated pap ligands in the starting compound, $Co(pap)_3^{2+}$, get aminated *ortho* to the aza nitrogen to result in the bis-chelated $[Co(pap\text{-}o\text{-}am)_2]^+$. During this process one bidentate ligand pap is eliminated from $Co(pap)_3^{2+}$, leaving behind two vacant coordination sites. Coordination of two Ar−NH_2 residues at the vacant sites followed by oxidative fusion[8] at the *ortho* carbon of the pendant phenyl ring of coordinated pap ligands are the two most plausible steps for this reaction. On coordination, $ArNH_2$ residues come in close proximity to the *o*-C−H of the pendant phenyl group of pap for *ortho* fusion. In this context, it is worthwhile to mention here that our recent work[9,10] on metal-promoted *ortho* dimerization of aromatic amines clearly demonstrated that these fusion reactions proceed via amine coordination to the metal center.

To establish the above proposition on the *ortho*-amination process, we performed another reaction using $RhCl_2(pap)_2^+$ as the starting compound.[11] Unlike $Co(pap)_3^{2+}$, which is very labile and loses one pap readily in solution, $RhCl_2(pap)_2^+$ is substitutionally inert. It is known that a substitution reaction[12] at this cationic rhodium complex, even under the most forceful conditions, results only in the monosubstituted complex $RhCl(N)(pap)_2^{n+}$ (N = nucleophile; $n = 1, 2$). Thus, if coordination to the metal center is a prerequisite for *ortho* amination, one would expect that *ortho* amination at best can occur at only one of the two coordinated pap ligands of $RhCl_2(pap)_2^+$.

The reaction of neat $ArNH_2$ with $RhCl_2(pap)_2^+$ produced[13] a deep blue mixture which on chromatographic purification yielded the ink blue crystalline compound **2** in ca. 65% yield.

$$\mathrm{RhCl_2(pap)_2^+} \xrightarrow{\mathrm{ArNH_2}} [\mathrm{RhCl(pap\text{-}}o\mathrm{\text{-}am)(pap\text{-}}p\mathrm{\text{-}amH)}]^+ \quad \text{(ii)}$$

2a−**c**

$ArNH_2$ = aniline (**2a**), *p*-toluidine (**2b**), *p*-anisidine (**2c**)

This compound is diamagnetic (Rh(III), $4d^6$) and showed a very complex ^1H NMR spectrum due to the presence

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[7] Majumdar, P.; Peng, S.-M.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 1569.

[8] The reactions under consideration do not occur in the absence of aerial oxygen. The overall transformation pap → papamH is a $2e^- + 2H^+$ transfer reaction.

[9] Mitra, K. N.; Majumdar, P.; Peng, S.-M.; Castiñeiras, A.; Goswami, S. *Chem. Commun.* **1997**, 1267.

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[11] Deb, A. K.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1989**, 1635.

[12] Majumdar, P.; Ghosh, A. K.; Goswami, S. Unpublished results.

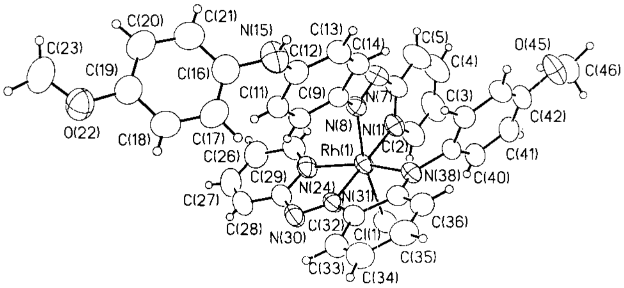

Figure 2. ORTEP plot and atom-numbering scheme for $[RhCl(pap\text{-}o\text{-}am)(pap\text{-}p\text{-}amH)]^+$ (**2c**) in $[RhCl(pap\text{-}o\text{-}am)(pap\text{-}p\text{-}amH)]ClO_4$.

of large numbers of unique protons. Fortunately, the product, **2c**, obtained from the reaction of *p*-anisidine with $RhCl_2(pap)_2^+$ formed crystals suitable for the determination[14] of its X-ray structure. In this case, unlike reaction (i), two types of fusion of $ArNH_2$ with the pap moiety have occurred to result in isomeric pap-amH ligands (Figure 2). In the present rhodium complex **2**, one of the extended ligands is neutral, namely that which contains N(1), N(8), and N(15). This ligand has the *p*-anisidine fragment fused to pap at the *para* position (relative to the aza fragment) of the phenyl group of pap; we shall refer to this as pap-*p*-amH. This ligand is bidentate and chelates to rhodium through the pyridine nitrogen N(1) and the aza nitrogen N(8). The amine nitrogen atom N(15) of this bears a hydrogen atom, which is in marked opposition to the corresponding pap-*o*-am$^-$, which binds as an anionic ligand. The second ligand, pap-*o*-am$^-$, acts as a monoanionic tridentate ligand which is similar to that observed in the $Co(pap)_3^{2+}$ and $ArNH_2$ reaction. The bidentate pap-*p*-amH and tridentate pap-*o*-am$^-$ along with one chloride complete a distorted-octahedral coordination environment about rhodium. Furthermore, comparison of bond distances in this molecule indicates the presence of more delocalization in the anionic pap-*o*-am$^-$ than that in the neutral pap-*p*-amH.

Thus, the above results have clearly demonstrated that an *ortho*-fusion process is favored in the case of a labile metal complex. It seems reasonable, since the coordination of an amine residue to the metal ion at the vacant site of the leaving ligand can bring it in close proximity to the *o*-C−H of the pendant phenyl group to promote *ortho* amination. In the absence of any such vacant site at the metal center, the *ortho* carbon is not approachable by $ArNH_2$ and fusion occurs at the *para* carbon as a second choice. Therefore, the site selectivity for this amination process can be controlled by the proper selection of metal complex.

Finally, we wish to note here that we have been successful in isolating both isomers of the aminated organic compounds, viz. pap-*o*-amH and pap-*p*-amH, as free ligands by the removal of the respective metal ions. The coordination chemistry of these pyridyl aza-amines appears to be rich and is currently under scrutiny.

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Supporting Information Available: Complete details on the X-ray analyses of **1a** and **2c**, including tables of bond distances and angles, atomic coordinates, anisotropic displacement parameters, and hydrogen atom coordinates, and figures giving representative ^1H NMR spectra for complexes **1a** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] A mixture of $[Rh(pap)_2Cl_2]ClO_4$ (0.2 g) and $ArNH_2$ (2.0 g) was heated on a steam bath for 1 h. The cooled green mixture was throughly washed with diethyl ether and was purified on a silica gel column. Finally, crystallization from a CH_2Cl_2/C_6H_{14} mixture yielded **2** (60−65%) as dark blue crystals. Physical data for a representative sample of **2a** are as follows. Anal. Calcd for $C_{34}H_{27}N_8Cl_2O_4Rh$: C, 51.97; H, 3.43; N, 14.26. Found: C, 51.79; H, 3.50; N, 13.96. UV/vis (CH_3CN): λ_{max} (ϵ) 801 sh (6180), 600 (25 500), 375 sh (13 800), 266 (63 400), 220 nm (96 000). IR (KBr): ν(N−H) 3500, ν(N=N) 1580, ν(C−N) 1300, $\nu(ClO_4^-)$ 1100, 620, ν(Rh−Cl) 340 cm^{-1}.

[14] X-ray structure of **2c**: geometric and intensity data on **2c** were gathered from a dark, block-shaped crystal ($0.49 \times 0.43 \times 0.36$ mm), obtained by slow diffusion of a dichloromethane solution into hexane, using a Nonius CAD-4 diffractometer. After the initial reflection search and indexing, axial photographs were taken for *a*, *b*, *c*, and [111] to verify the dimensions of the triclinic lattice. The scan parameters for data collection were based on two-dimensional ($\omega-\theta$) plots of 18 reflections. Absorption corrections were based on a full three-dimensional absorption model derived from 15 ψ-scans with bisecting-mode Eulerian angle χ between −31 and +44°. The structure was solved by direct methods and developed and refined in the usual alternating series of least-squares cycles and difference Fourier maps, which showed residual extrema at 0.75 and −0.50 e Å^{-3}. Crystal and refinement data: $C_{36}H_{31}Cl_2N_8O_6Rh$, triclinic, $P\bar{1}$, $a = 9.0138(5)$ Å, $b = 12.6198(10)$ Å, $c = 16.695(3)$ Å, $\alpha = 109.968(9)°$, $\beta = 100.865(9)°$, $\gamma = 93.809(7)°$, $V = 1735.2(4)$ Å^3, $Z = 2$, with 602 parameters refined on 6074 data with $F_o^2 \geq 2\sigma(F_o^2)$, R1 = 0.0370 and wR2 = 0.1035, GOF = 1.041.