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Dehydrogenation of amines in aryl-amine functionalized pincered 66A like nitrogen-donor redox non-innocent ligands *via* ligand reduction on Ni(II) template

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We have synthesized a series of new redox non-innocent azo aromatic pincer-like ligands: 2-(phenylazo)-6-(arylaminomethyl)pyridine (HL^{a-c}: HL^a = 2-(phenylazo)-6-(2,6-diisopropylphenylaminomethyl)pyridine, HL^b = 2-(phenylazo)-6-(2,6-dimethylphenylaminomethyl)pyridine, HL^c = 2-(phenylazo)-6-(phenylaminomethyl)pyridine), in which one side arm is an arylaminomethyl moiety and the other arm is a 2-phenylazo moiety. Nickel(II) complexes, 1-3, of these ligands HLa-c were synthesized in good yield (approximately 70%) by the reaction of ligands : (NiCl₂.6H₂O) in 1:1 molar ratio in methanol. The amine donor in each of the ligands HL^{a-c} binds to the Ni(II) centre without deprotonation. In the solid state, complex 3 is a dimer; in solution it exists as monomer 3a. Reduction of acetonitrile solutions of each of the complexes 1, 2 and 3a, separately, with cobaltocene (1 equivalent), followed by exposure of the solution to air, resulted in the formation of new complexes 7, 8 and 9, respectively. Novel free ligands L^x and L^y have also been isolated, in addition to complexes 7 and 8, from the reaction of complexes 1 and 2, respectively. Complexes 7-9 and free ligands Lx and Ly have been formed via a dehydrogenation reaction of the arylaminomethyl side arm. The mechanism of the reaction was thoroughly investigated using a series of studies, including cyclic voltammetry, EPR, UV-Vis spectral studies and density functional theory (DFT) calculations. The results of these studies suggest a mechanism initiated by ligand reduction followed by dioxygen activation. A Cl⁻/l⁻ scrambling experiment revealed that dissociation of the chloride ligand(s) was associated with oneelectron reduction of the ligand (azo moiety) in each of the complexes 1, 2 and 3a. The dissociated chloride ligand(s) were reassociated with the metal following the dehydrogenation reaction to yield the final products. All of the newly synthesized compounds were fully characterized using a variety of physicochemical techniques. Single-crystal X-ray structures of the representative compounds were determined to confirm the identities of the synthesized molecules.

Introduction

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Chemical transformations by transition metal complexes containing redox non-innocent ligand(s) have attracted considerable research interest in recent times.^{1,2} Research activity in this area is to be welcomed, as this type of ligand is expected to expand the scope of utilizing redox-inert metals in catalysis and because cheaper firstrow transition metal complexes can be utilized in various chemical transformations, etc.^{2c,3} For example, Chirik *et al.*, as well as others, have shown that Fe and Co complexes containing bis(imino) pyridine based ligands are very efficient at catalysing many novel chemical transformations involving solely the imine-based redox process.^{2a,3} Contemporarily, worldwide, many research groups have also been involved in exploring other transition metal complexes containing such redox non-innocent ligand(s) in various kind of chemical transformations.^{2c,4-8} Numerous potentially redox noninnocent azo aromatic nitrogen-donor ligands and their transition metal complexes are also known.9-12 Some of these complexes are reported to be active in chemical transformations involving azobased redox events.9b-d Herein, we report a new group of

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arylaminomethyl group-functionalized pincer-like redox noninnocent azo aromatic ligands **HL**^{a-c} and their dehydrogenative imine formation reaction (Scheme **1a**) on a nickel(II) template *via* ligand reduction (azo reduction).



Scheme 1. (a) Ni complexes of the ligands (HL^{a-c}) and their chemical transformation; (b) similar reported ligands and their complexes.

The synthesized azo aromatic pincer-like ligands HL^{a-c} in their respective nickel complexes, **1–3** (Scheme **1a**), possess structures in which the 6-arylaminomethyl side arm acts as a σ -donor moiety to the metal (reduced by two protons and two electrons compared to

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the phenylazo moiety), whereas the 2-phenylazopyridine part acts as both a σ -donor and a π -acceptor moiety.^{10a,13,14} Compared to the ligands HL^{a-c} in their corresponding complexes, 1, 2 and 3, the related reported pincer nitrogen donors in their complexes A and B (Scheme **1b**) have extended π -conjugation in the coordinating backbone of the ligands, allowing these to act only as σ -donor- and π -acceptor-type ligands.^{2a,3,8,9b-d} Complexes containing such pincer/pincer-like non-innocent ligands have been found to show reactivity in various kinds of chemical transformations.^{2a,3,8,9b-d,15-17} Recently, Rohde and co-workers have reported interesting ligandcentred reactivity with dioxygen in the pincer Ni(II) complex containing a one-electron reduced redox non-innocent bis(imino)pyridine radical ligand.¹⁸ As azo aromatic ligands are known for their redox non-innocence,9-12 we were interested to explore the reactivity of complexes 1, 2 and 3 upon reduction in air. The dimeric complex 3 in the solid state was converted to its monomer 3a in acetonitrile solution. It was found that reduction of the acetonitrile solutions of each of the complexes 1, 2 and 3a by cobaltocene (1 equivalent) led to ligand reduction (N=N bond), which, subsequently, in the presence of air promoted dehydrogenation of the arylaminomethyl side arm to yield complexes 7, 8 and 9, respectively. The novel free ligands L^x and L^y were also isolated, in addition to complexes 7 and 8, from the reaction of complexes 1 and 2, respectively (Scheme 1a).

The dehydrogenation reaction of coordinated amines^{19–25} in the presence of air has been reported by Curtis *et al.*²⁶ and is still under active investigation.^{25,27,28} Notably, in all of these cases,^{19–25} first, metal oxidation leads to the formation of the complex in a higher oxidation state, accompanied by a superoxide radical anion (Scheme **2**), which then undergoes a base-promoted dehydrogenation reaction to yield the final imine complex.^{19–28} In contrast, our experiment has shown that the ligand can also initiate such an oxidation reaction without changing the oxidation state of the metal. As far as we are aware, the involvement of a ligand-based redox process in the dehydrogenation of amines has not been reported in the literature (Scheme **2**).



Scheme 2. Reported reaction vs. our experiments

Results and discussion

(A) The ligands (HL^{a-c}) and their nickel complexes

(i) Synthesis

Our work began with the synthesis of the light ds H2 \approx (38 Show f a Scheme **3**. This involved preparation of compound **A** by the reaction of nitrosobenzene and 6-methyl-2-aminopyridine in alkaline conditions following the literature procedure,²⁹ followed by bromination of the methyl group in **A** using *N*-bromosuccinimide and azobisisobutyronitrile (AIBN) in CCl₄ solvent to isolate compound **B** and, finally, substitution of the bromide of the bromomethyl group of **B** with the corresponding aromatic amine. The ligands **HL**^{a-c} were isolated in approximately 70% yield.



Compounds A and B and ligands HLa-c were characterized satisfactorily by positive ion ESI-MS, IR and NMR spectral analysis (Figures S1-S15). The characterization data are available in the experimental section. The infra-red (IR) spectra of the ligands HLa-c showed strong absorption bands in the range 1430–1507 cm⁻¹, which were assigned to the N=N bond stretching frequency.¹⁰ In the positive ion ESI-MS spectra, the ligands HL^a, HL^b and HL^c showed intense peaks at m/z = 373.24, 317.17 and 288.14 amu, respectively, corresponding to the [MH]+ ion, where M represents the ligand. Their simulated spectra matched precisely with their corresponding experimental spectra (Figures S13-S15). The NMR spectra also fully corroborated the identity of the ligands HLa-c. For example, in the ¹H NMR, the ligand HL^a (Figure S5) showed a doublet signal for 12H at 1.28 ppm, which was assigned to the methyl groups of the isopropyl moieties. A multiplet signal for 2H at 3.45 ppm was assigned to the tertiary C–H protons of the isopropyl groups, and a singlet signal at 4.42 ppm was assigned to the protons of the CH₂ group attached to the pyridine ring. Thus, it is evident that the 2,6-diisopropylaniline moiety is indeed present in the ligand HL^a. In the aromatic region of the spectrum, we found signals for 11 protons that matched exactly with the number of aromatic protons expected in the ligand HL^a. The signal for the N-H proton was observed at 4.01 ppm.

The synthesized ligands HL^{a-c} were reacted individually with hydrated Ni(II)Cl₂.6H₂O at a ratio of 1:1 metal:ligand in methanol to yield the corresponding nickel complexes, **1–3** (Scheme **4**). In a series of experiments, one equivalent of Ni(II)Cl₂.6H₂O was mixed with each of the ligands HL^{a-c} in methanol, upon which the reaction mixture immediately turned reddish-brown. Each mixture was refluxed for 1.5 h, and then the solvent was removed under reduced pressure. Extraction of the crude product using dichloromethane and its slow diffusion into hexane solvent resulted in the formation of reddish-brown crystals of complexes **1–3**, respectively, in approximately 70% yield. Further treatment of each of these synthesized complexes, **1**, **2** and **3**, with one equivalent of

pyridine resulted in complexes **4**, **5** and **6**, respectively, in approximately 85% yield (Scheme **4**).



Each of the complexes **1–6** was characterized convincingly (see below, Experimental section). Microanalytical CHN data matched exactly with the formulae of complexes **1–6**. In their IR spectra, these complexes showed the N=N stretching frequency¹⁰ in the range 1430–1490 cm⁻¹ and the N–H stretching frequency¹⁵ in the range 3200–3300 cm⁻¹. All of the complexes **1**, **2** and **4–6** are paramagnetic (two unpaired electrons), as evidenced by their room temperature magnetic susceptibility in the range μ_{eff} = 2.76–2.81 B.M. at 298 K. Compound **3** is dinuclear in the solid state; its room temperature magnetic susceptibility was found to be 4.33 B.M.

(ii) Crystal structure

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Ligand HL^c and complexes **1–3** and **6** were characterized by singlecrystal X-ray structure determination, for which suitable crystals of the compounds were grown by slow diffusion of dichloromethane solutions of the compounds into hexane. ORTEP representations of the structures of ligand HL^c and complexes **1**, **3** and **6** are shown in Figure **1**, and selected bond parameters are presented in Table **1**.

X-ray crystallographic analysis of ligand HL^c revealed that the phenylazo moiety combined with the spacer pyridine ring has a more planar structure than the arylaminomethyl moiety. A d_{N1-N2} value of 1.254(3) Å and a d_{C12-N4} value of 1.429(3) Å (Table 1) are indicative of the double- and single-bond characters, respectively, of these two bonds.

The coordination geometry of complex **1** is best described as a distorted trigonal bipyramid in which the ligand HL^a coordinates as a tridentate ligand, with the N_{azo} atom (N1) and N_{amine} atom (N4) occupying the apical positions and an N1–Ni–N4 angle of 154.82°. The other two coordination sites are occupied by the two terminal chloride ligands (Figure **1**).



Figure 1. ORTEP representations and atom numbering schemes for ligand HL^c (50%) and complexes 1, 3 and 6 at 50%, 30% and 50% probability levels, respectively.

The Ni–N bond lengths in complex **1** are in the range 1.950–2.200 Å, and are typical of metal–nitrogen bond lengths in complexes containing neutral nitrogen-donor ligands.^{30,31} A d_{N1–N2} value of 1.267(3) Å in complex **1** is indicative of an unreduced azo (N=N) bond.^{11,12,31–33} A d_{C12–N4} value of 1.490(3) Å clearly indicates the single-bond character of the CH₂–NH bond.^{15–17,34–37}

Whereas X-ray structure analysis of complex **2** showed qualitatively similar geometry to that of complex **1** (Figure **S16**), complex **3** crystallized as a dimer bridged by two chloride ligands, with each of the metal ions being hexacoordinated. Overall, complex **3** has C₂ crystallographic symmetry that makes one half of the molecule identical to the other half. The d_{N1-N2} and d_{C12-N4} values were almost equal to those of complex **1**, indicating unreduced azo and reduced C–N bonds in complex **3** as well.

X-ray structure determination of complex **6** showed that it crystallized as a mononuclear complex with a hexacoordinated geometry. A pyridine ligand coordinated *trans* to the **N3** donor atom of the pyridine moiety of ligand **HL**^c.

The structural parameters calculated from density functional theory (DFT) also closely matched with the crystallographically determined parameters. Selected experimental and DFT-calculated bond lengths and bond angles are given in Table 1. The optimized structure of ligands HL^a, HL^c and complexes 1, 3 and 6 are shown in Figures **S17–21**.

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Table 1. Experimental and DFT-calculated bond lengths and angles of complexes 1, 3, 6 and ligand HL^c.

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Bonds and angles	Complex 1 Bond lengths (Å) and bond angles (°)		Complex 3 Bond lengths (Å) and bond angles (°)		Complex 6 Bond lengths (Å) and bond angles (°)		Ligand HL ^c Bond lengths (Å) and bond angles (°)									
									Experimental	DFT	Experimental	DFT	Experimental	DFT	Experimental	DFT
									N1-N2	1.267(3)	1.266	1.259(2)	1.262	1.265(2)	1.261	1.254(3)
	Ni1-N1	2.151(2)	2.253	2.232(2)	2.302	2.134(2)	2.248									
Ni1-N4	2.193(2)	2.255	2.213(2)	2.240	2.218(2)	2.255										
Ni1-N3	1.960(2)	2.018	1.979(1)	2.033	1.977(1)	2.021										
Ni1-N5					2.050(1)	2.138										
C12-N4	1.491(4)	1.485	1.471(3)	1.487	1.488(2)	1.481	1.429(3)	1.453								
Ni1-Cl1	2.238(7)	2.347	2.334(6)	2.387	2.396(6)	2.427										
Ni1-Cl2	2.277(8)	2.270	2.347(5)	2.422	2.431(6)	2.459										
N1-Ni1-N3	75.48(8)	74.28	74.31(6)	72.52	75.33(6)	73.756										
N1-Ni1-N4	154.82(8)	152.9	152.91(6)	151.08	155.04(6)	149.9										
N3-Ni1-N4	79.44(8)	78.62	78.82(6)	78.60	79.74(6)	77.482										
C12-N4-Ni1	110.1(2)	109.32	108.9(1)	106.18	109.0(1)	107.19										
N4-C12-C11	111.9(2)	113.3	112.4(2)	111.68	113.4(2)	111.24										
N3-C11-C12	116.0(2)	116.80	115.7(2)	118.83	116.5(2)	115.56										

(B) Dehydrogenation reactions

(i) Chemical reactions

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Recently, transition metal complexes containing pincer or pincer-like redox non-innocent ligands have been exploited for various kinds of reactions involving ligand-based redox processes.^{1–12} For example, Rohde and co-workers have reported the interesting reactivity of dioxygen with the oneelectron reduced bis(imino)pyridine pincer ligand in its Ni(II) complex.¹⁸ As azo aromatic ligands have been reported to be potentially redox non-innocent,^{9–12} we were interested to explore the reactivity of complexes **1–3** upon reduction in air. Though complex **3** is dinuclear in the solid state, it exists as monomer **3a** in solution [see below, Scheme **5b** and Section **B(iii)**]. As all of the chemical reactions were carried out in solution, complex **3a** instead of **3** was considered in this reaction.

Examination of the redox properties of complexes **1** and **3a** using cyclic voltammetry showed that there are indeed facile irreversible reductive waves for both complexes at approximately -0.3 V (Figure **2**). The DFT-calculated MOs of the representative ligand **HL**^a and its complex **1** (Figure **2**) showed that the LUMOs are localized on the azo pyridine moiety, indicating that the irreversible reductions observed at approximately -0.3 V in complexes **1** and **3a** might be due to azo pyridine reduction.

The corresponding reduction potential of the free ligand HL^a appeared at -1.149(65) V as a reversible cathodic wave (Figure 2).



Figure 2. Cyclic voltammogram of ligand HL^a and complexes 1 and 3 in acetonitrile (left) and molecular orbitals of HL^a and complex 1 (right).

Interestingly, in the EPR spectrum, the electrogenerated complex [1]⁻⁻ showed a sharp single line spectrum (Figure 3) at g = 1.998 in an argon atmosphere at 90 K, confirming that ligand-centred reduction is associated with the reduction of complex 1.

Upon one-electron reduction of complex **1**, a square planar Ni(II) complex with an S = $\frac{1}{2}$ ground state was formed *via* dissociation of one of the chloride ligands. Formation of a similar square planar Ni(II) complex with an S = $\frac{1}{2}$ ground state *via* dissociation of one of the chloride ligands has been reported by Rohde *et al.* for one-electron reduction of a trigonal bipyramidal bis(imino)pyridine Ni(II) complex.¹⁸



Figure 3. Transient EPR spectrum (X-band) upon one-electron reduction of complex 1 at 90 K in tetrahydrofuran.

As ligand reduction was observed in the EPR spectrum, we therefore planned for the reaction of complexes **1**, **2** and **3a** using a reductant. Reduction of acetonitrile solutions of each of complexes **1**, **2** and **3a**, separately, with cobaltocene (1 equivalent) and their subsequent exposure to air showed a clean dehydrogenation reaction of the arylaminomethyl side arm in all of these complexes (Scheme **5**).



In the case of the reaction of complex **1**, the free ligand L^x was isolated as the major product (60% yield), and complex **7** was isolated as the minor product (35% yield, Scheme **5a**). In the reaction of complex **2**, the isolated free ligand L^y was the minor product (25% yield), and complex **8** was the major product (65% yield, Scheme **5a**). For the reaction of complex **3a**, almost

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quantitative conversion to complex **9** containing rite owns observed, and no free ligand L^z was found **(Scheme Sb)** DT00466A

It is to be noted here that, in a separate chemical reaction, when the acetonitrile solutions of complexes 1 and 2 were treated with excess metallic Zn powder (3 equivalents) in air, complexes 7 and 8, respectively, were isolated in almost quantitative yield. No free imine ligands L^x and L^y were observed (Scheme 6). Zn powder is a mild reducing agent.^{9c,d} Thus, it reduced complexes 1 and 2 to [1].- and [2].-, respectively. Subsequently, these reduced complexes [1]. and [2]. underwent aerial dehydrogenation to yield complexes 7 and 8, respectively. We also found that the yield of complex 7 increased to approximately 75% when excess anhydrous ZnCl₂ (5 equivalents) was added to a solution of complex 1 reacting with cobaltocene (1 equivalent) in air (Scheme 6). The yield of complex 7 was found to be comparatively low, approximately 55%, when KCl (5 equivalents) was added instead of anhydrous ZnCl₂ in another separate reaction of complex 1 with cobaltocene (1 equivalent). We added anhydrous ZnCl₂ and KCl in these two separate chemical reactions to increase the concentration of chloride ligand in the reaction medium. An increase in the yield of complex 7 with increasing concentration of chloride ligand indicates that the dissociated chloride ligand(s) again reassociated with the metal following the dehydrogenation reaction to yield the final products (see below, Mechanistic investigations).



Our efforts to isolate the deprotonated complexes of **1** and **3a** by the reaction of **1** and **3a** with NaOtBu in acetonitrile were unsuccessful. The reaction of **1** with NaOtBu (1 equivalent) resulted in the complete decomposition of **1** (Scheme **S22**). In comparison, the identical reaction with **3a** yielded complex **9** (Scheme **S22**), along with the free ligand, **HL**^c. It is known that NaOtBu can act as a reductant,^{38,39} in addition to its strong basic nature. Thus, it may participate partly in reducing the ligand in **3a** to facilitate the dehydrogenation reaction.

The microanalytical CHN data matched exactly with the formulations of the nickel complexes, **7–9**, (see below, Experimental section). In the IR spectra, complexes **7–9** showed the N=N stretching frequency at around 1450 cm⁻¹ and the C=N stretching frequency at around 1575 cm⁻¹. Compounds **7** and **8** are paramagnetic (two unpaired electrons), as evidenced by

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their room temperature magnetic susceptibility, μ_{eff} = 2.78 and 2.80 B.M at 298 K, respectively. Compound **9** is dinuclear, and its room temperature magnetic susceptibility was found to be 4.54 B.M.

The isolated new ligands L^x and L^y were also characterized satisfactorily by positive ion ESI-MS, NMR and IR spectral studies (Figures S23–S28). In the IR spectra, the ligands L^x and L^y showed strong absorption bands at 1456 and 1472 cm⁻¹, respectively, assigned to the N=N bond stretching frequency.¹⁰ Strong absorption bands at 1589 and 1597 cm⁻¹ for ligands L^x and L^y, respectively, were assigned to the HC=N stretching frequency.³¹ In the positive ion ESI-MS, ligands L^x and L^y showed molecular ion peaks at m/z = 371.22 and 315.16 amu, respectively, due to the [MH]⁺ ion, where M represents the ligand (Figures S27-S28). Their simulated spectra matched exactly with their corresponding experimental spectra. The identities of the ligands were further clearly established by their NMR spectra (Figures S23-S26). For example, in the ¹H NMR spectra, ligand L^x showed a doublet signal for 12H at 1.19 ppm, which was assigned to the methyl group of the isopropyl moieties. A multiplet signal for 2H at 3.01 ppm was assigned to the tertiary C-H proton of the isopropyl groups, and the singlet signal at 8.51 ppm was assigned to the imine C–H proton. In the aromatic region of the spectrum, we found signals for 11 protons that matched exactly with the number of aromatic protons expected for ligand L^x.

(ii) Crystal structure

Final authentication of the dehydrogenation products came from the X-ray crystallographic structure determination of complexes **7–9** and ligand L^x. These molecular structures have confirmed the chemical reactions depicted in Schemes **5** and **7**. ORTEP plots of complexes **7**, **9** and ligand L^x are shown in Figure **4**, and ORTEP plot of complex **8** can be found in the supporting information file (Figure **S29**). Suitable crossels to support the determination of complexes, **7–9** and ligand L^x were grown by slow diffusion of a dichloromethane solution of the compounds into hexane.

X-ray structural analysis of compounds 7 and 8 showed a trigonal bipyramidal geometry, with Nazo (N1) and Nimine (N4) occupying the apical positions; complex 9 is a dimer bridged by two chloride ligands, with each metal centre having distorted octahedral geometry. Complex 9 has C₂ crystallographic symmetry; thus, one half of the molecule is identical to the other half. As complex 8 is structurally qualitatively similar to complex **7**, only complex **7** is discussed below. The d_{C12-N4} values for complexes **7** and **9** were 1.281(4) and 1.280(4) Å, respectively (Table 2), which were assigned to the CH=N bond.²⁶ Similarly, the d_{N1-N2} values for complexes **7** and **9** were 1.266(4) and 1.264(4) Å, respectively (Table 2), clearly indicating the unreduced state of the N=N bond. Thus, the coordinated ligands L^x and L^z in complexes 7 and 9, respectively, have one side arm containing an azo chromophore and the other side arm containing an imine chromophore. The corresponding d_{C12-N4} and d_{N1-N2} values for the free ligand L^x were 1.266(2) and 1.241(2) Å, respectively. Slight elongation of these two bonds in complexes 7 and 9 compared to the free ligand may be due to $d\pi(Ni)-\pi^*(ligand)$ back-bonding. A comparison of the overlaid structures of complexes 3 and 9 indeed showed a significant difference in geometry. The aminomethyl group (C12-N4) in complex 3 is significantly out of the plane, whereas it is in the plane of the molecule in complex 9 (Figure 5a).



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(b)

(a)

CI2

(c)

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Table 2. Experimental and DFT-calculated bond lengths and angles of complexes 7, 9 and ligand Lx.

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-	Complex 7	1	Complex 9		Ligand L×		
– Bonds and angles	Bond lengths (Å) and b	ond angles (°)	Bond lengths (Å) and bor	nd angles (°)	Bond lengths (Å) and bond angles (°)		
	Experimental	DFT	Experimental	DFT	Experimental	DFT	
N1N2	1.268 (3)	1.266	1.264(2)	1.264	1.241(2)	1.257	
Ni1-N1	2.214 (2)	2.292	2.310(17)	2.330			
Ni1-N4	2.166(2)	2.276	2.215(16)	2.243			
Ni1–N3	1.958 (2)	2.006	1.985(16)	2.032			
C12-N4	1.280(3)	1.282	1.280(3)	1.285	1.266(2)	1.275	
Ni1-Cl1	2.274(6)	2.856	2.325(6)	2.376			
Ni1-Cl2	2.248(6)	2.310	2.372(6)	2.416			
Ni1-Cl2'			2.440(6)	2.542			
N1-Ni1-N3	73.98(7)	72.956	72.68(6)	71.90			
N1-Ni1-N4	151.46(7)	149.63	149.48(6)	147.70			
N3-Ni1-N4	77.71(7)	76.80	77.06(6)	76.50			
C12-N4-Ni1	111.9(1)	109.517	110.66(14)	110.97			
N4-C12-C11	118.0(2)	119.63	118.80(19)	119.15			
N3-C11-C12	112.8(2)	114.529	113.85(18)	114.50			

DFT calculations were performed on the representative imine complexes **7** and **9** as well as ligand L^x. The DFT-calculated structural parameters closely matched the crystallographically determined parameters. Selected experimental and DFT-calculated bond lengths and bond angles are given in Table **2**. The optimized structures of ligand L^x and complexes **7** and **9** are shown in Figures **S30–S32** and the MOs of complexes **7–9** are shown in Figures **S33–S38**.

(iii) Comparison of structures 3 and 9 as solids and in solution

Even though both complexes **3** and **9** crystallized as chlorobridged dimers in the solid state, there are noticeable differences in the Ni(II)-bridging chloride bond lengths. The symmetry-generated pair of bonds, Ni1–Cl2', Ni1'–Cl2 are 2.614(5) Å and the Ni1–Cl2, Ni1'–Cl2' are 2.234(6) Å in complex **3** (Figure **5b**). The corresponding symmetry-generated pair of bond lengths in complex **9** are 2.440(6) and 2.372(6) Å, respectively (Figure **5c**). The Ni1–Cl2', Ni1'–Cl2 pair of bonds in complex **9** are significantly shorter than those in complex **3**, indicating stronger bridging of the Cl⁻ ligands in complex **9** compared to complex **3**. Thus, complex **3** exists as monomer **3a** (Scheme **5b**), whereas complex **9** retains its identity as a dimer in acetonitrile solution. This is also reflected in the spectral properties of the complexes in solution.

The UV-Vis spectrum of the free ligand HL^a showed a weak absorption at 452 nm ($\varepsilon = 614 \text{ M}^{-1} \text{ cm}^{-1}$) and a high intensity absorption at 317 nm ($\varepsilon = 18739 \text{ M}^{-1} \text{ cm}^{-1}$). In complex **1**, the low-energy absorption at 452 nm of ligand HL^a disappeared, and the high-energy transition at 317 nm red-shifted to 353 nm ($\varepsilon = 15141 \text{ M}^{-1} \text{ cm}^{-1}$). Even though complex **3** is dimeric in the solid state, it showed a spectrum similar to that of the mononuclear complex **1** in solution. Spectra of HL^a and complexes **1** and **3** are shown in Figure **S39**. Even in the variable temperature UV-Vis spectral studies in acetonitrile solution, none of its spectral features changed significantly. In cyclic voltammetry, both the amine complexes **1** and **3** showed similar voltammograms (Figure **2**, see above). Thus, it is concluded that the solid-state form of the binuclear complex **3** is converted to its mononuclear analogue **3a** in solution.

In comparison, the dinuclear azo imine complex **9** has a completely different spectrum in acetonitrile solution compared to the monomeric complex **7**. While the mononuclear complex **7** showed only one intense absorption at 358 nm, dimer **9** showed two prominent absorption peaks at 365 and 300 nm (Figure **S39**). In the variable temperature UV-Vis spectral study, interestingly, it showed a slight shift of the equilibrium towards the mononuclear form, as identified by the appearance of a new peak at 320 nm, accompanied by the disappearance of the peaks at 365 and 300 nm (Figure **6**). Notably, on cooling the solution, the original spectrum of complex **9** was regenerated very slowly.



The dimeric structure of complex **9** in acetonitrile solution was further probed by means of cyclic voltammetry. The mononuclear complex **7** showed one irreversible reduction at -0.25 V, whereas complex **9** showed two reversible reductions at -0.28(70) and -0.53(75) V. These two successive reductions are associated with the reduction of the two azo pyridine moieties in complex **9**. Representative voltammograms of complexes **7** and **9** are shown in the supporting information file (Figure **S40**).

(iv) Mechanistic investigations

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We carried out further experimental investigations in order to gain insight into the mechanisms of the chemical transformations that these ligands and complexes undergo. To confirm the fact that the chloride ligand(s) indeed dissociated from complexes 1, 2 and 3a upon one-electron reduction, and that the dissociated chloride ligand(s) again reassociated with the metal following the dehydrogenation reaction to yield the respective final products 7, 8 and 9, we studied the halide scrambling reaction by adding potassium iodide (KI) to the reaction. The representative complex 3a was used in this study (Scheme 7). Complex 3a was reduced by cobaltocene (1 equivalent) to generate complex [3a].-. Subsequently, 1 equivalent of solid KI was added, and the solution was stirred for 1 h. The mixture was then exposed to air for the dehydrogenation reaction to occur. Following crystallization of the crude products, complex 11 was isolated as the major product (45% yield), and complex 10 was isolated as the minor product (20% yield, Scheme 7). Analysis of the X-ray structures of complexes 10 and 11 showed that complex 10 is mononuclear (Figures S41), containing two iodide ligands with trigonal bipyramidal geometry, whereas complex 11 is a dimer bridged by two chloride ligands, and each of the metal atoms has distorted octahedral geometry. In addition to ligand L^z and the bridging chlorides, sixth coordination site in each of the metal atoms has occupied by a mixture of terminal iodide and chloride ligands with occupancy of approximately 0.69 iodide and 0.31 chloride. An ORTEP of the compound 11 is

shown in Figure 7. Identification of the iodide ligands in the complex 10 as well as both iodide and define the figure 4.1 indeed confirms the Cl⁻/l⁻ exchange reaction, as shown in Scheme 7. When excess KI (5 equivalents) was added, complex 10 was isolated as the sole product (Scheme 7). Notably, complex 3a/9 without reduction by cobaltocene (1 equivalent) did not result in any Cl⁻/l⁻ exchange product over the same timescale (Scheme 7).







Figure 7. An ORTEP of the complex 11 at 50% probability level

The reduced complex **[3a]**⁻⁻ was unreactive in an inert atmosphere, even on heating the solution. Complexes **1**, **2** and **3a** were inert towards (2,2,6,6-tetramethylpiperidin-1yl)oxyl (TEMPO'), O2⁻⁻ and Ph₃CCl (Scheme **8**). It was also observed that reaction of TEMPO'/O2⁻⁻ with the oneelectron reduced partners **[1]**⁻⁻, **[2]**⁻⁻ and **[3a]**⁻⁻ of complexes **1**, **2** and **3a**, respectively, in an inert atmosphere did not result in any dehydrogenation products; instead, the respective unreduced complexes **1**, **2** and **3a** were isolated as the major products, along with some minor unidentified compounds. However, exposure of each of the reduced complexes **[1]**⁻⁻, **[2]**⁻⁻ and **[3a]**⁻⁻ in acetonitrile solution to air Published on 16 April 2020. Downloaded by Université de Paris on 4/20/2020 12:21:47 PM

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led to dehydrogenation of the arylaminomethyl side arm, indicating involvement of the putative reactive intermediate 'A' (Scheme 8) in this reaction.^{22c}



To confirm the reaction of aerial oxygen with the oneelectron reduced complexes [1].-, [2].- and [3a].-, the chemical transformation of one of them, [3a].-, in air was monitored by time-dependent UV-Vis spectral studies, and the spectral changes are shown in Figure 8. Complex [3a].showed three prominent transitions at 331, 430 and 595 nm in the absence of air. Upon exposure of a solution of [3a].- to air, the peaks at 430 and 595 nm disappeared and the peak at 331 nm increased in intensity. Notably, the spectrum of the solution showed only one transition at 331 nm that was very similar to the spectrum of the mononuclear dehydrogenated complex 7. Significantly, the isolated complex 9, the end product of the reaction of [3a]. in air, is a binuclear complex (see above, Crystal structure). Thus, it is proposed that, initially, the mononuclear complex 12 was formed in the dehydrogenation reaction (Scheme 5b), which then dimerized slowly to form the comparatively more stable binuclear complex 9. Notably, the reflux of an acetonitrile solution of complex 9 with Zn powder resulted in a significant quantity of mononuclear complex 12, as evidenced by the increase in intensity of the band at 322 nm in the UV-Vis spectrum (Figure S42). Following 6 h of reflux, crystallization of the crude mixture resulted in two different types of crystals. Their characterization by Xray structure determination confirmed the formation of the mononuclear complex 12 (Figure S43).



Figure 8. Time-dependent UV-Vis spectrum of complex $[\mathbf{3a}]^-$ in acetonitrile upon exposure to air

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Generally, during the oxidation of the aminomethyl mojety to the imine moiety in the metal complexed, 1the loop dinated superoxide radical anion first abstracts a hydrogen atom to form a complex containing the methylamino radical ligand and a peroxide ligand.¹⁹⁻²⁸ Then, the peroxide ligand is either released as H_2O_2 from this intermediate complex following the abstraction of a proton^{19–21,23–28} or it participates further in the oxidation of the methylamino radical moiety, resulting in a hydroxo complex containing an imine ligand.^{22c} Following significant efforts on our part, we were unable to identify any trace of H_2O_2 . It was found that $Zn(OH)_2$ was generated from the reaction of complex 1 with metallic Zn powder (Scheme 6), even when dry air was used. Formation of Zn(OH)₂ was confirmed by the IR spectrum of the crude product following extraction of complex 7. A broad stretching frequency at 3465 cm⁻¹ characteristic of the Zn–OH moiety was observed (Figure S44). Similarly, in the reaction of complex 3a with 1 equivalent of cobaltocene, cobaltocenium hydroxide, [Cp2Co]OH, was isolated as the by-product (Scheme 5b). A broad stretching frequency at 3287 cm⁻¹ in the IR spectrum characteristic of [Cp₂Co]OH was observed⁴⁰ (Figure **S45**). The electron count showed that, in general, this reaction is a three-electron oxidation starting from the one-electron reduced complexes [1]-, [2]- and [3a]-. Formation of a hydroxo complex by three-electron transfer in oxygen in a similar dehydrogenation reaction has been reported.^{22c} Moreover, multiple-electron transfer to dioxygen resulting in O-O bond cleavage and formation of a hydroxo complex in other chemical reactions have also been reported.⁴¹

Based on these observations, it is proposed that dissociation of the chloride ligand(s) was indeed associated with oneelectron reduction of the complexes. Following the dehydrogenation reaction, the dissociated chloride ligand(s) were again reassociated with the metal to yield the final dehydrogenated complexes (Schemes 5 and 7). The oneelectron reduced intermediate complexes [1]-, [2] - and [3a]activated dioxygen to facilitate the dehydrogenation reaction, and the superoxide radical anion generated from complexes [1] -, [2] - and [3a] - participated in the reaction while remaining coordinated to the metal (Scheme 8).22c This active putative coordinated superoxide radical anion picked up a hydrogen atom from the NH position of the ligands,^{22c} forming a Ni(II) peroxo complex (Scheme 9). The metal-coordinated peroxide participated further in the oxidation of the amino radical ligand, leading to the formation of a Ni(II) hydroxo complex and a free hydroxyl radical^{22c} (Scheme 9). This Ni(II) hydroxo intermediate, upon exchange of its hydroxide ligand with the dissociated chloride ligand, generated the final dehydrogenated complexes (Scheme 9). Furthermore, as the hydroxyl radical is a highly reactive species, it might have decomposed the intermediate hydroxo complex to liberate free ligands L^x and L^y in the reaction of complexes 1 and 2, respectively, with cobaltocene (Scheme 9). Oxidation of the metal complexes by the hydroxyl radical has been reported in the literature.42 Notably, metal-promoted amine oxidation in transition metal complexes has been studied for quite some time, 19-28 and is still under active investigation.^{25,27,28} In all of these examples, metal oxidation initiates the reaction. However, such reactions, where ligand

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reduction promotes dehydrogenation of the amine to an imine has not been reported in the literature.



Scheme 9. Plausible reaction pathways

Conclusions

In conclusion, a series of redox non-innocent azo aromatic pincer-like ligands: 2-(phenylazo)-6-(arylphenylaminomethyl)pyridine (HLa-c) have been synthesized in which the aminomethyl group is reduced by two electrons and two protons from its iminopyridine congener, whereas the 2-phenylazo fragment is oxidized by two electrons and two protons from its hydrazo congener. In their nickel(II) complexes, 1-3, the aryl aminomethyl moiety binds the Ni(II) centre without deprotonation. In the solid state, complex 3 is a dimer, while it exists as monomer 3a in solution. In all of these three complexes, 1, 2 and 3a, the aryl aminomethyl moiety undergoes a dehydrogenative imine formation reaction in air via the reduction of the azo pyridine moiety in the same ligand to yield the new complexes 7, 8 and 9, respectively. In addition, free ligands L^x and L^y have also been isolated from the reaction of complexes 1 and 2, respectively. The reaction mechanism was investigated thoroughly by cyclic voltammetry, EPR, UV-Vis spectroscopic studies, Cl⁻/l⁻ exchange reaction, as well as DFT calculations. Though transition metal mediated oxidative dehydrogenative imine formation reactions have been the subject of continuous study for quite some time, to date, only metal oxidation has been found to initiate the dehydrogenation reaction. As far as we are aware, such a dehydrogenation reaction via ligand reduction has not been reported in the literature. Moreover, this reaction has resulted in a new type of pincer-like ligand, L^x and L^y, in which one side arm has a redox non-innocent azo chromophore, while another side arm has a redox non-innocent imine chromophore.³ Our efforts to explore

Experimental

Materials and reagents

All reagents were of analytical grade purity, commercially available, and used without further purification. The solvents used were purified and dried using standard procedures. Tetrabutylammonium perchlorate was prepared and recrystallised as reported earlier^{12b}. Perchlorate salts are potential explosives and should be handled with care.

Instrumentation and methods

Cyclic voltammetry was conducted in 0.1 M Bu₄NClO₄ solutions by using a three-electrode configuration (Pt working electrode, Pt counter electrode, and Ag/AgCl reference electrode) and PCcontrolled PAR model 273A electrochemistry system. A PerkinElmer model 2400 elemental analyser was used to obtain microanalytical data (C, H, and N). The ESI mass spectra of the samples were recorded on a maxis impact UHR spectrometer (Bruker Daltonics) and Q-Tof micro (WATERS) mass spectrometer. ¹H and ¹³C NMR spectra were recorded using 400 MHz JEOL and Bruker 500 MHz spectrometers, respectively. Chemical shifts were reported as δ -values relative to the internal reference of tetramethylsilane (TMS) and solvent peak for ¹H NMR and ¹³C NMR, respectively. IR spectroscopic data were recorded using the PerkinElmer Spectrum RX I spectrometer with KBr pellets. UV-vis spectra were obtained using a Cary 8454 UV-vis spectrophotometer. Spectroscopic grade solvents were used for spectroscopic and electrochemical studies. X-band EPR spectra were recorded using a Bruker Biospin EMX^{micro} spectrometer. Room-temperature magnetic moment was measured using the Gouy balance (Sherwood Scientific, Cambridge, UK).

Synthesis of the Compound A

Compound **A** was synthesised using the procedure reported in the literature.²⁹ To the warm solution of 50% sodium hydroxide (50 mL), 6-methyl-2-aminopyridine (2 g) was added. The resulting solution was then gently heated, and benzene (5 mL) was added to it. Nitrosobenzene (2.5 g) was added for 10 min with stirring. The mixture was stirred at 70°C for 8 h. The reaction mixture was extracted using benzene (2 × 100 mL) to obtain a solution that was heated with charcoal, filtered, and concentrated to 100 mL under a reduced pressure. The concentrate was purified using column chromatography with silica gel (100–200 mesh size) as a stationary phase and toluene as an eluent. The yield and characterisation data of the resultant compound A are as follows: Yield: 70%, ESI-MS: m/z 198 amu [MH]⁺,¹H NMR (400 MHz, CDCl₃): 8.02-8.00 (m, 2H); 7.74 (t, 1H, J= 7.64 Hz); 7.57 (d, 1H, J = 7.9 Hz); 7.51-7.49 (m, 3H); 7.25 (d, 1H, J= 7.1 Hz); 2.68 (s, 3H); ¹³C NMR (400MHz,CDCl₃): 162.96(C); 158.80(C-H); 152.51(C-H); 138.62(C-H); 132.22(C-H); 129.26(C); 125.18(C-H); 123.78(C-H); 110.95 (C-H); 24.60 (CH₃); IR: 1421 cm⁻¹ (N=N); UV-vis: λ , 321 nm; (ϵ = 19649 M⁻¹ cm⁻¹).

Synthesis of the Compound B

A total of 700 mg (3.55 mmol) of compound **A** was dissolved in 15 mL of carbon tetrachloride in a 100 mL RB flux. A catalytic amount of AIBN and 0.812 g (4.61 mmol) of N-

bromosuccinamide were added to it, and the mixture was refluxed for 12 h. The crude mass obtained from the evaporation of carbon tetrachloride was dissolved in a minimum volume of dichloromethane, and the product was isolated using column chromatography with stationary-phase silica gel (100–200 mesh size) and toluene as the eluent. The yield and characterisation data are as follows: Yield: 60%, ESI-MS: m/z 276 amu [MBr⁷⁹],278 amu [MBr⁸¹], ¹H NMR(400MHz,d₆-DMSO): 8.08 (t, 1H, J=7.8Hz); 7.99-7.96 (m, 2H); 7.75 (d, 1H, J=7.64Hz); 7.67-7.64 (m, 4H); 4.83 (s, 2H); ¹³C NMR (400MHz,CDCl₃): 162.95 (C); 157.09 (C); 152.42 (C-H); 139.64 (C-H); 132.66 (C-H); 129.39 (C); 125.34 (C-H); 123.93 (C-H); 112.61 (C-H); 33.41 (CH₂); IR: 1417 cm⁻¹(N=N); UV-vis: λ , 319 nm; (ϵ = 18595 M⁻¹ cm⁻¹).

Synthesis of Ligand, HL^a

In 10 mL of THF, 300 mg (1.09 mmol) of compound B was dissolved in a 100 mL round bottom flask. A total of 1.35 g (7.63 mmol) of 2, 6-diisopropyl aniline and 1 equivalent of dry sodium carbonate with respect to 2, 6-diisopropyl aniline was added and stirred at reflux temperature for 14 h. The crude mass, obtained after THF evaporation, was dissolved in a minimum volume of dichloromethane, and excess 2, 6-diisopropyl aniline was evaporated by heating overnight at 60°C-70°C. Subsequently, the crude mass was extracted using dichloromethane and loaded on a preparative silica gel TLC plate for purification. A solvent mixture of hexane: ethyl acetate (9:1) was used as an eluent to isolate ligand HL^a in its pure state. Its yield and characterization data are as follows: Yield: 70%, ESI-MS: m/z 373.24 amu [MH]⁺; ¹H NMR(400MHz,CDCl₃): 8.10 (d, 2H, J=7.6 Hz); 7.83 (t, 1H, J=8.4 Hz); 7.71 (d, 1H, J=7.6 Hz); 7.54 (m, 4H); 7.14 (m, 3H); 4.42 (s, 2H); 4.01 (br, s, 1H); 3.45 (m, 2H); 1.28 (d, 12H, J=6.8Hz);¹³C NMR (400MHz, d₆-DMSO): 162.12 (C); 159.68 (C); 151.88 (C); 143.19 (C-H); 142.44 (C); 139.27 (C-H); 132.49 (C); 129.65 (C-H); 123.84 (C-H); 123.53 (C-H); 123.31 (C-H); 122.97 (C-H); 112.00 (C-H); 56.05 (CH₂); 27.02 (C-H); 24.25 (CH₃); IR: 1430 cm⁻¹(N=N); 3316 cm⁻¹(2° NH); UV-vis: ε_{319 nm}, 18843 M⁻¹ cm⁻¹; $\epsilon_{444 \text{ nm}}$, 734 M⁻¹ cm⁻¹.

Synthesis of Ligand, HL^b

Ligand **HL**^b was synthesised following the procedure similar to that followed for **HL**^a synthesis. The yield and characterisation data of ligand **HL**^b are as follows: Yield: 71.4%, ESI-MS: m/z 317.17 amu [MH]⁺; ¹H NMR(400MHz,CDCl₃): 8.08-8.06 (m, 2H); 7.80 (t, 1H, J = 7.7 Hz); 7.67 (d, 1H, J = 7.9 Hz); 7.58-7.54 (m, 3H); 7.39 (d, 1H, J = 7.5 Hz); 7.01 (d, 2H, J = 7.5 Hz); 6.84 (t, 1H, J = 7.4 Hz); 4.46 (s, 2H); 2.34 (s, 6H);¹³C NMR (400MHz, d₆-DMSO): 162.4 (C); 160.4 (C); 151.8 (C); 148.2 (C-H); 139.3 (C-H); 132.4 (C); 129.6 (C-H); 128.9 (C-H); 122.9 (C-H); 119.9 (C-H); 116.0 (C-H); 112.2 (C-H); 111.3 (C-H); 48.6 (CH₂); IR: 1441 cm⁻¹(N=N); 3310 cm⁻¹(2° NH); UV-vis: ϵ_{315nm} , 18716 M⁻¹ cm⁻¹; ϵ_{454nm} , 811 M⁻¹ cm⁻¹

Synthesis of Ligand, HL^c

Ligand **HL**^c was synthesised following the procedure similar to that followed for **HL**^a synthesis. Its yield and characterisation data are as follows: Yield: 68.93%, ESI-MS: m/z 288.14 amu [MH]⁺; ¹H NMR(400MHz,CDCl₃):8.07-8.05 (m, 2H);7.84 (t, 1H, 7.9 Hz); 7.67 (d, 1H, 7.9 Hz); 7.57-7.53 (m, 3H); 7.50 (d, 1H, 7.5 Hz); 7.19 (t, 2H, 7.6 Hz); 6.75-6.69 (m, 3H); 4.64 (s, 2H); ¹³C NMR (400MHz, d₆-DMSO): 162.42 (C); 160.48 (C); 151.86 (C); 148.25 (C-H); 139.38 (C-H); 132.51 (C); 129.66 (C-H); 128.98 (C-H); 122.92 (C-H); 119.99 (C-H); 116.09 (C-H); 112.28 (C-H); 111.39 (C-H); 48.35 (CH₂); IR: 1507 cm⁻¹(N=N); 3385 cm⁻¹(2° NH); UV-vis: ϵ_{312nm} , 37247 M⁻¹ cm⁻¹; ϵ_{445nm} ,1922 M⁻¹ cm⁻¹

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Synthesis of Complex 1

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In 10 mL of methanol, 200 mg (0.53 mmol) of ligand **HL**^a was dissolved in a round bottom flask. In 5 mLof methanol, 191.12 mg (0.80 mmol) of NiCl₂.6H₂O was dissolved, and the resulting solution was then added dropwise to the ligand solution present in the round bottom flask. During addition, the colour of the reaction mixture immediately changed from red to reddishbrown. After 1.5 h of reflux, the solvent evaporated, and the crude mass thus obtained was dried under high vacuum. The product was then extracted with a dichloromethane solvent and layered with hexane for slow diffusion, and crystalline compound **1** was isolated. Its yield and characterisation data are as follows: Yield: 70%, Anal. Calcd. for C₂₄H₂₈Cl₂N₄Ni: C, 57.53; H, 5.43; N, 11.18; Found C, 57.51; H, 5.46; N, 11.11; IR: 1438 cm⁻¹(N=N); 3268 cm⁻¹ (2° NH); UV-vis: ε_{354nm} , 16209 M⁻¹ cm⁻¹.

Synthesis of Complex 2

Complex **2** was synthesised using the procedure similar to complex **1** synthesis. Its yield and characterisation data are as follows: Yield: 68.1%, Anal. Calcd. for $C_{20}H_{20}Cl_2N_4Ni_1$: C, 53.98; H, 4.30; N, 12.59; Found C, 53.92; H, 4.31; N, 12.56; IR: 1450 cm⁻¹(N=N); 3268 cm⁻¹ (2° NH); UV-vis: ϵ_{356nm} , 20035 M⁻¹ cm⁻¹.

Synthesis of Complex 3

Complex **3** was synthesised by following the procedure similar to that of complex **1** synthesis. Its yield and characterisation data are as follows: Yield: 72.1%, Anal. Calcd. for $C_{36}H_{32}Cl_4N_8Ni_2$: C, 51.73; H, 3.86; N, 13.41; Found C, 51.77; H, 3.81; N, 13.46; IR: 1492 cm⁻¹(N=N); 3205 cm⁻¹ (2° NH); UV-vis: ϵ_{350nm} , 41693 M⁻¹ cm⁻¹.

Synthesis of Complex 4

In 5 mL of dry acetonitrile, 30.4 mg (0.06 mmol) of complex **1** was dissolved. Subsequently, 1 equivalent (0.06 mmol) of pyridine was added to the complex solution. During addition, the colour of the reaction mixture immediately changed from reddish-brown to greenish-brown. After 3-h stirring at room temperature, the solvent was evaporated under the reduced pressure. Thus, the crude mass was obtained and dissolved in acetonitrile. The pure compound was isolated through ether diffusion into the acetonitrile solution of the crude product. Its yield and characterisation data are as follows: Yield: 83%, Anal. Calcd. for C₂₉H₃₃Cl₂N₅Ni: C, 59.93; H, 5.72; N, 12.05; Found C, 59.95; H, 5.70; N, 12.09; IR: 1432 cm⁻¹(N=N); 3285 cm⁻¹ (2° NH); UV-vis: $\epsilon_{352 nm}$, 36856 M⁻¹ cm⁻¹.

Synthesis of Complex 5

Complex **5** was synthesised by following the procedure similar to that of complex **4** synthesis. Yield: 85%, Anal. Calcd. for $C_{25}H_{25}Cl_2N_5Ni:$ C, 57.18; H, 4.80; N, 13.34; Found C, 57.13; H, 4.89; N, 13.33; IR: 1443 cm⁻¹(N=N); 3290 cm⁻¹(2° NH); UV-vis: ϵ_{358} nm, 22856 M⁻¹ cm⁻¹.

Synthesis of Complex 6

Complex **6** was synthesised following the procedure similar to that of complex **4** synthesis. For the reaction, two equivalents (0.18 mmol) of pyridine with respect to complex **3** were used. The yield and characterisation data of complex 6 are as follows: Yield: 87%, Anal. Calcd. for $C_{23}H_{21}Cl_2N_5Ni$: C, 55.69; H, 4.06; N,

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14.12; Found C, 55.62; H, 4.08; N, 14.10; IR: 1446 cm $^{-1}(N=N);$ 3224 cm $^{-1}$ (2° NH); UV-vis: $\epsilon_{351\,nm},$ 36856 M $^{-1}\,cm^{-1}.$

Synthesis of the Complex 7 and Ligand L^x

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In 10 mL of dry degassed acetonitrile, 100 mg (0.19 mmol) of compound 1 was dissolved in a 25-mL Schlenk tube. Subsequently, one equivalent of cobaltocene (37.6 mg, 0.19 mmol) was added under the inert atmosphere maintained with argon. The colour of the reaction mixture immediately changed from reddish-brown to deep brown. After 2.5 h of stirring at room temperature, the reaction mixture was exposed to air. The colour of the reaction mixture changed to light brown. The solution was then evaporated under the reduced pressure. The crude mass thus obtained was dissolved in dichloromethane and crystallised through a slow diffusion of the dichloromethane solution into hexane. After one week, a crop of block-shaped crystals was separated from the mixture. Moreover, a light green precipitate was deposited in the solution along with the crystals. The collected crystals were of complex 7. The solution phase was decanted in a 100-mL round bottom flask, and the precipitate was discarded. The solvent was evaporated under reduced pressure. The crude product obtained after solvent evaporation was extracted thrice using 5 mL of diethyl ether. The combined ether solution was filtered through a cellite pad, and the filtrate was collected. The solvent was evaporated under reduced pressure to obtain pure ligand Lx. Their yield and characterisation data are as follows:

Complex 7: Yield: 35%. Anal. Calcd. for $C_{24}H_{26}Cl_2N_4Ni$: C, 57.64; H, 5.24; N, 11.20; Found C, 57.62; H, 5.25; N, 11.17; IR: 1449 cm⁻¹ (N=N); 1573 cm⁻¹ (CH=N); UV-vis: $\epsilon_{359 \text{ nm}} = 16209 \text{ M}^{-1} \text{ cm}^{-1}$.

Ligand L*: Yield: 60%. ESI-MS: m/z 371.22 amu $[MH]^+$; ¹H NMR(400MHz,CDCl₃): 8.51(s,1H); 8.46(d,1H); 8.09-8.08(m,3H); 7.93(d,1H); 7.55(d,3H); 7.21-7.13(m,3H); 3.01(m,2H); 1.19(d,12H), ¹³C NMR (400MHz, CDCl₃): 163.30(C); 162.55(C); 154.36(C-H); 152.30(C); 148.20(C); 139.14(C-H); 137.21(C); 132.62(C-H), 129.30(C-H); 124.68(C-H); 123.83(C-H); 123.15(C-H); 122.66(C-H); 114.68(C-H); 28.06(C-H); 23.52(CH₃), IR: 1456 cm⁻¹(-N=N-); 1589 cm⁻¹(-CH=N-).

Synthesis of Complex 8 and Ligand L^{y}

Complex **8** and Ligand L^y were synthesised by following the procedure similar to that followed for complex **7** and ligand L^x syntheses. Their yield and characterisation data are as follows:

 $\begin{array}{l} \label{eq:complex 8: Yield: 65\%, Anal. Calcd. for $C_{20}H_{18}Cl_2N_4Ni: C,54.10;$\\ H,4.09; N, 12.62; Found C, 54.06; H, 4.01; N, 12.58; IR: 1465 cm^{-1}(N=N); 1589 cm^{-1} (CH=N); UV-vis: $\epsilon_{359 \ nm}, 19027 \ M^{-1} \ cm^{-1}. \end{array}$

Ligand L^y: Yield: 25%. ESI-MS: m/z 315.16 amu [MH]⁺, 337.14 amu [MNa]⁺; ¹H NMR(400MHz,CDCl₃): 8.54 (s,1H); 8.46(d,1H); 8.09-8.08(m.2H); 8.03(t,1H); 7.93(d,1H); 7.56-7.54(t,3H); 7.10(d,2H); 7.02-6.98(t,1H); 2.20(s,6H); ¹³C NMR (400MHz, CDCl₃): 162.85 (C); 154.21 (C); 152.11 (C-H); 149.89 (C); 138.90 (C-H); 132.41 (C-H); 129.10 (C-H); 128.07 (C-H); 126.69 (C); 124.12 (C-H); 123.62 (C-H); 132.33 (C-H); 114.82 (C-H); 18.22 (CH₃); IR: 1472 cm⁻¹(N=N); 1597 cm⁻¹(-CH=N-).

Synthesis of Complex 9

Complex **9** was synthesised by following the procedure similar to that of complex **7** synthesis. In this reaction, one equivalent of cobaltocene with respect to the complex **3a** (Scheme **5b**) was

utilised. No free ligand L^z emerged from the reaction mixture. The yield and characterisation data of complex 19 37 cost follows: Yield: 90%, Anal. Calcd. for C₃₆H₂₈Cl₄N₈Ni₂: C, 51.98; H, 3.39; N, 13.47; Found C, 51.91; H, 3.39; N, 13.46; IR: 1488 cm⁻¹(N=N); 1589 cm⁻¹ (CH=N); UV-vis: ε_{315} nm, 30548 M⁻¹ cm⁻¹; ε_{371} nm, 27214 M⁻¹ cm⁻¹.

After the crystallisation of complex **9**, the precipitate was characterised using IR spectroscopy. A broad stretching frequency obtained at 3287 cm⁻¹ was the characteristic of [Cp₂Co]OH (Figure **S30**).

Chloride/Iodide exchange reaction: Synthesis of Complex 10 and 11

In 10 mL of dry degassed acetonitrile, 42.3 mg (0.05 mmol) of complex 3 was dissolved in a 25-mL Schlenk tube under argon atmosphere in a Schlenk line. 19 mg (2 equivalent, 0.1 mmol) of solid cobaltocene was added to it maintaining the inert atmosphere. During addition, the colour of the solution immediately changed from brown to deep reddish-brown. The reaction mixture was stirred for 15 min. Afterwards, 8.4 mg of KI (1 equivalent) was added in acetonitrile. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was then exposed to air. The colour of the solution changed from deep brown to considerably light reddish-brown. The solvent was then evaporated, and the crude mass was dried under high vacuum. The product obtained was dissolved in dichloromethane and stored for the slow diffusion of hexane. After three days, a crop of block-shaped crystals was separated from the mixture as a minor product (complex **10**). The solution was decanted and evaporated under reduced pressure followed by crystallisation through the slow diffusion of hexane into the dichloromethane solution, which resulted in complex **11** formation in 5 days. Their isolated yield and characterisation data are as follows:

Complex **10**: Yield: 20%, Anal. Calcd. for $C_{18}H_{14}I_2N_4Ni$: C, 36.10; H, 2.36; N, 9.36; Found C, 36.08; H, 2.38; N, 9.31; IR: 1400 cm⁻¹(N=N); 1586 cm⁻¹ (CH=N); UV-vis: ϵ_{313} nm, 21497 M⁻¹ cm⁻¹; ϵ_{368} nm, 20725 M⁻¹ cm⁻¹.

Complex **11:** Yield: 45%, Anal. Calcd. for $C_{38}H_{32}CI_{6.64}I_{1.36}N_8Ni_2$: C,40.54; H, 2.86; N, 9.95; Found C, 40.68; H, 2.75; N, 10.01; IR: 1414 cm⁻¹(N=N); 1595 cm⁻¹ (CH=N); UV-vis: ϵ_{313} nm, 21497 M⁻¹ cm⁻¹; ϵ_{368} nm, 20725 M⁻¹ cm⁻¹.

When the identical reaction was conducted with excess KI (5 equivalents), only complex **10** was isolated.

Dehydrogenation reaction with metallic Zn-powder

In 10 mL of acetonitrile solution, 100 mg (0.199 mmol) of compound **1** was dissolved in a 25-mL round bottom flask. To the solution, 38.8 mg (3 equivalents) of Zn powder was added. The mixture was stirred for 2 h at room temperature. The solvent was then evaporated under reduced pressure and the crude product was extracted using dichloromethane. The dichloromethane extract was concentrated and layered with hexane in a 10-mL beaker for slow diffusion. After 7 days, compound **7** was isolated as crystals with a 95% yield.

The characterisation results of compound **7** obtained from UVvis spectrum and CHN analysis demonstrated that it was the same product that was obtained from the reaction of compound **1** with cobaltocene in air.

After the extraction of compound **7** from the crude reaction mixture by using dichloromethane, the residue present in the 25-mL round bottom flask was collected, and its IR spectrum was obtained, which showed a strong absorption at 3465 cm⁻¹

Furthermore, the same reaction was observed for compound 2.

Dehydrogenation reaction of the complex 1 with cobaltocene in the presence of excess anhydrous ZnCl_2

In 10 mL of dry degassed acetonitrile, 100 mg (0.19 mmol) of compound 1 was dissolved in the 25-mL Schlenk tube. Subsequently, one equivalent of cobaltocene (37.6 mg, 0.19 mmol) was added by maintaining the inert atmosphere with argon. After 2.5 h of stirring at room temperature, anhydrous ZnCl₂ (5 equivalents) was added and stirred for another 10 min. Afterwards, the reaction mixture was exposed to air and the solution was evaporated under the reduced pressure. The crude mass obtained was dissolved in dichloromethane and crystallised through the slow diffusion of the dichloromethane solution into hexane. After one week, a crop of block-shaped crystals was separated from the mixture. Moreover, light green precipitate deposited in the solution along with crystals. Crystals were collected as complex 7 with approximately 75% yield. The solution phase was decanted in a 100-mL round bottom flask. and the precipitate was discarded. The solvent was evaporated under reduced pressure. Thus, the crude product obtained after solvent evaporation was extracted thrice using 5 mL of diethyl ether. The combined ether solution was filtered through the cellite pad, and the filtrate was collected. The solvent was evaporated under the reduced pressure to obtain pure ligand L^x. Ligand L^x was isolated as a minor yield (10%).

Synthesis of Complex 12

In 10 mL of dry acetonitrile, 40.2 mg (0.048 mmol) of complex 9 was dissolved, and 15.7 mg (5 equivalents, 0.24 mmol) of zinc powder was added. During addition, the colour of the reaction mixture immediately changed from reddish-brownish to light green. The reaction mixture was then refluxed for 2.5 h, and the colour changed to deep brown. After solvent evaporation, the crude mass was dried under high vacuum. The product was then dissolved in dichloromethane and layered with hexane for slow diffusion. After one week, the crop of block-shaped and rodshaped crystals was separated. The structure of block-shaped crystals was determined using X-ray diffraction, and the crystals exhibited the mononuclear form. The characterisation data of complex 12 are as follows: Anal. Calcd. for $C_{18}H_{14}Cl_2N_4Ni$: C,51.98; H, 3.39; N, 13.47; Found C, 51.91; H, 3.31; N, 13.41; IR: 1442 cm⁻¹(N=N); 1586 cm⁻¹ (CH=N); UV-vis: ε_{357 nm}, 18985 M⁻¹ cm⁻¹.

X-ray Crystallography

For diffraction, the high-quality suitable single crystals of compounds **HL**^c, **L**^x, **1**, **2**, **6**, **7**, **8**, **11**, and **12** were coated with fomblin oil, fixed on a loop, and mounted on a goniometer under N₂ flow at a temperature of 100 K. The data were collected in a Agilent SuperNova, (Dual, Cu at zero, Eos) diffractometer by using either a monochromatic Mo K α source ($\lambda = 0.71073$ Å) or a monochromatic Cu K α source ($\lambda = 1.5406$ Å). Data reduction was performed with *CrysAlisPRO*, Agilent Technologies, Version 1.171.37.34. Single-crystal structures were refined using *Olex2*⁴³ software package, with the *Superflip*⁴⁴ or *ShelXT*⁴⁵ structure solution programme by using *Charge flipping* or intrinsic phasing method. All structures were

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refined using the ShelXL46 refinement package with leastsquares minimisation, in Olex2 refine43. The switzble high quality single crystals of complexes 3, 9, and 10 were mounted on the goniometer head by using loops and collected on a Bruker SMART APEX-II diffractometer equipped with graphitemonochromated Mo K α radiation (λ = 0.71073 Å) and were corrected for Lorentz polarisation effects. Data reduction was performed using Bruker SAINT software.47 Structures were investigated by employing the SheIXT programme package⁴⁵ and were refined using either ShelXL⁴⁶ with full-matrix least-squares method or Olex248. All hydrogen atoms were calculated and fixed using *ShelXL* after the hybridisation of all non-hydrogen atoms.⁴⁹ Refinement details and relevant explanations (wherever applicable) are included in the individual CIFs. Table 3 presents all crystallographic parameters for compounds HL^c, L^x, 1, 3, 6, 7, 9, and 11, and Table S1 presents those for compounds 2, 8, 10, and 12. Table 1 and 2 present the selected bond lengths and angles, respectively. All the data were deposited in www.ccdc.cam.ac.uk. The CCDC no. of the crystals reported here 1887721(**1**), 1887736(**2**), 1887737(**3**), 1887738(**6**). are 1887739(7), 1964891(**8**), 1887740(**9**), 1887741(10), 1887742(11), 1887743(12), 1887744(HL^c), and 1887745(L^x).

Computational Details

All computational calculations were performed in Gaussian 09 program package (revision A.02).⁵⁰ The complete geometry optimisation of ligands (HL^a, HL^c, and L^x) and nickel complexes (1, 3, 6, 7–9) was conducted using the density functional theory method at the RB3LYP and UB3LYP level of theory.⁵¹ The 6-31+G basis set was used for C, H, N, and Cl atoms, and the LANL2DZ basic set with effective core potential was used for Ni atoms.⁵²⁻⁵⁴ Vibrational frequency calculations were performed to ensure that the optimised geometries represented the local minima, and only positive Eigenvalues were obtained. An isosurface value of 0.04 was used for the visualisation of Kohn-Sham molecular orbitals.

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Conflicts of interest

There are no conflicts to declare.

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Table 3. Crystallographic Data of the ligand HL ^c , L ^x and complexes 1, 3, 6, 7, 9 and 11.								
Parameters	HLc	L×	1	3	6	7	9	11
CCDC no.	1887744	1887745	1887721	1887737	1887738	1887739	1887740	1887742
empirical formula	$C_{18}H_{16}N_4$	$C_{24} H_{26} N_4$	$C_{24}H_{28}Cl_2N_4Ni$	C ₃₆ H ₃₂ Cl ₄ N ₈ Ni ₂	C ₂₃ H ₂₁ Cl ₂ N ₅ Ni	$C_{24}H_{26}Cl_2N_4Ni$	C ₃₆ H ₂₈ Cl ₄ N ₈ Ni ₂	$C_{38}H_{32}CI_{6.64}I_{1.36}$ N ₈ Ni ₂
formula wt.	288.35	370.49	502.09	835.88	497.06	500.10	831.88	1126.11
crystal system	orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	Pna2 ₁	P -1	P-1	P 2 ₁ /n	P -1	P 2 ₁ /n	P 2 ₁ /n	P 2 ₁ /c
a (Å)	29.279(4)	8.6058(4)	9.4290(5)	9.6504(4)	9.1097(5)	19.0222(4)	12.3109(15)	10.4316(3)
<i>b</i> (Å)	10.4375(13)	10.9184(4)	10.4037(8)	14.5816(5)	10.1284(5)	12.3486(2)	9.8915(13)	15.7887(4)
<i>c</i> (Å)	4.6429(6)	11.7427(4)	12.8727(8)	12.5608(4)	12.2167(7)	20.4706(4)	15.806(2)	13.0106(3)
α (deg)	90.00	68.670(3)	107.115(7)	90.00	90.864(4)	90.00	90.00	90.00
<i>β</i> (deg)	90.00	83.291(4)	90.214(5)	98.294(2)	100.473(4)	90.436(<i>2</i>)	108.517(7)	100.576(2)
γ (deg)	90.00	89.451(3)	100.707(6)	90	101.390(4)	90.00	90.00	90.00
Cell Volume	1418.9(3)	1020.09(7)	1183.54(13)	1749.05(11)	1085.07(10)	4808.35(16)	1825.1(4)	2106.46(9)
R-factor	4.32	3.61	3.75	2.81	2.78	4.68	2.94	2.71
Z	4	2	2	2	2	8	2	2
Т (К)	100.00(10)	100.00(10)	100.00(10)	296.15(10)	100.00(10)	100.00 (10)	296.15(10)	100.03(11)
μ (mm ⁻¹)	0.654	0.562	1.064	1.423	1.162	3.345	1.363	13.134
$ ho_{calcd}$ (g cm ⁻³)	1.350	1.206	1.409	1.587	1.521	1.382	1.514	1.775
F (000)	608.0	396.0	524.0	856.0	512.0	2080.0	848.0	1114.0
2∂ range (deg)	6.04 to 132.6	8.14 to 132.22	3.32 to 54.24	4.3 to 55.26	4.1 to 52.74	6.32 to 132.72	3.68 to 55.76	8.62 to 132.42
Data/restraints/ parameters	2470/1/199	3526/0/257	4489/0/287	4056/0/290	4441/0/284	8387/0/567	4307/0/282	3692/0/257
$R_1, wR_2[l > 2\sigma(l)]$	0.0432, 0.1050	0.0361 <i>,</i> 0.0972	0.0375, 0.0811	0.0281,0.0609	0.0278,0.0620	0.0468, 0.1267	0.0294,0.0599	0.0271,0.0697
R_1 , wR_2 (all data)	0.0475, 0.1092	0.0383, 0.0991	0.0444 <i>,</i> 0.0862	0.0423,0.0663	0.0319,0.0648	0.0492 <i>,</i> 0.1297	0.0488,0.0672	0.0289,0.0707
GOF on F ²	1.072	1.055	1.041	1.047	1.057	1.039	1.030	1.066
largest difference in peak and hole (e Å ⁻³)	0.24/-0.23	0.43/ -0.23	0.49/ -0.37	0.35/-0.41	0.32/-0.33	0.66/ -0.64	0.31/-0.33	0.82,-0.64

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