

Examples of Reductive Azo Cleavage and Oxidative Azo Bond Formation on $\text{Re}_2(\text{CO})_{10}$ Template: Isolation and Characterization of Re(III) Complexes of New Azo-Aromatic Ligands

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S Supporting Information

ABSTRACT: A new example of simultaneous reductive azo bond cleavage and oxidative azo bond formation in an azo-aromatic ligand is introduced. The chemical transformation is achieved by the reaction of $\text{Re}_2(\text{CO})_{10}$ with the ligand 2-[(2-N-Arylamino)phenylazo]pyridine (HL^1). A new and unexpected mononuclear rhenium complex $[\text{Re}(\text{L}^1)(\text{L}^3)]$ (**1**) was isolated from the above reaction. The new azo-aromatic ligand, H_2L^3 ($\text{H}_2\text{L}^3 = 2, 2'$ -dianilinoazobenzene) is formed in situ from HL^1 .

A similar reaction of $\text{Re}_2(\text{CO})_{10}$ and a closely related azo-ligand, 2,4-ditert-butyl-6-(pyridin-2-ylazo)-phenol (HL^2), resulted in a seven coordinated compound $[\text{Re}(\text{L}^2)\{(\text{L}^4)^{\bullet-}\}_2]$ (**2**; $\text{HL}^4 = 2$ -amino-4,6-ditert-butyl-phenol) *via* reductive cleavage of the azo bond. The complexes have been characterized by using a host of physical methods: X-ray crystallography, nuclear magnetic resonance (NMR), cyclic voltammetry, ultraviolet–visible (UV–vis), electron paramagnetic resonance (EPR) spectroscopy, and density functional theory (DFT). The experimental structures are well reproduced by density functional theory calculations and support the overall electronic structures of the above compounds. Complex **1** is a closed shell singlet, while complex **2** exemplifies a singlet diradical complex where the two partially oxidized aminophenoleto ligands are coupled to each other, yielding the observed diamagnetic ground state. Complexes **1** and **2** showed two successive one-electron redox responses. EPR spectral studies in corroboration with DFT results indicated that all of the redox processes occur at the ligand center without affecting the trivalent state of the metal ion.

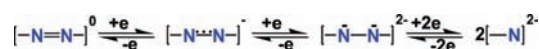


INTRODUCTION

Metathesis reactions¹ in unsaturated organic molecules constitute an important class of chemical reactions that occur with simultaneous bond cleavage and bond formation processes. Accordingly, metathesis in olefins has gained widespread use in research and industry for making products ranging from medicines and polymers to enhanced fuels.^{1,2} In comparison, such a reaction in azo compounds is not known. Diazo compounds, in general, and azo-aromatics, in particular, are high-value chemicals widely used in industry as organic dyes, indicators, pigments, food additives, radical reaction initiators, and therapeutic agents.³

In recent times, we have been in search⁴ of synthetic protocols suitable for the isolation of transition metal complexes of azo-anion radical ligands. In this respect, zerovalent metal carbonyl complexes were found^{4a–c} to be useful precursors where the electron-rich metal center acts as a possible electron pool. Following this synthetic protocol, we have been successful in isolation of stable complexes of azo-anion radical ligands. The ligands containing azo functions are known to undergo reduction^{4–6} chemically or electrochemically at rather accessible potentials to form stable azo-anion radicals (-1) or dianionic hydrazido (-2) species. The further addition of two more electrons to a hydrazido function leads to the rupture⁷ of the N–N bond (Scheme 1).

Scheme 1. Electron Transfer Series

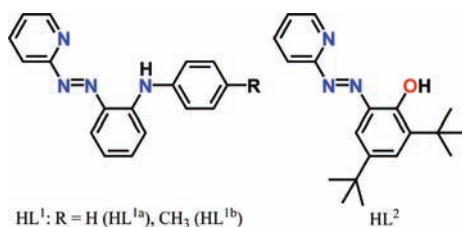


With this available knowledge, we set out to explore the chemical reactions of $\text{Re}_2(\text{CO})_{10}$ with the two extended tridentate azoaromatic ligands, HL^1 and HL^2 (Scheme 2), that are known to undergo facile reduction and produce stable azo-anion radical complexes.⁴ In practice, the reference chemical reaction with HL^1 produced a Re complex $[\text{Re}(\text{L}^1)(\text{L}^3)]$ (**1**) of a newly formed azoaromatic ligand H_2L^3 (Schemes 3 and 4). The formation of H_2L^3 from HL^1 is noteworthy and proceeds *via* simultaneous azo bond cleavage and N–N bond fusion reactions. However, a similar reaction with HL^2 (Scheme 3) and $\text{Re}_2(\text{CO})_{10}$ led only to the reductive cleavage of the azo function with the formation of a complex of a 2-aminophenol derivative, $[\text{Re}(\text{L}^2)\{(\text{L}^4)^{\bullet-}\}_2]$ (**2**; Scheme 4). Notably, metal mediated azo bond cleavage⁷ leading to the imido complexes has long been

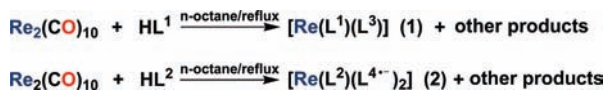
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Scheme 2. Ligands: Reactants



Scheme 3. Reactions



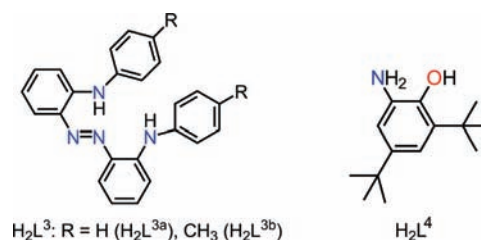
known in the literature, but unification of metal-imido fragments to azo arene *via* N–N coupling reactions is scarce.⁸ And these two reactions occurring together in a single chemical reaction, as happened here, is nonexistent in the literature.

RESULTS AND DISCUSSION

Syntheses and Characterization. The ligand, HL¹, offers three very different kinds of coordination atoms, namely, a pyridyl-N, a reducible azo function containing N, and a diarylamido-N (N, after deprotonation), whereas the ligand HL² is very similar to the previous one where the secondary amide-N is replaced by a phenolate group (Scheme 2). Pyridyl-N and azo-N are π accepting, whereas deprotonated amido-N and phenolate-O ligands are strongly donating.

The reactions of Re₂(CO)₁₀ (0.15 mmol) with HL¹ (0.60 mmol) in boiling *n*-octane produced new reddish pink [Re(L¹)(L³)] complexes (1a and 1b) in 45 and 43% yield, respectively (Scheme 3). While selecting Re(0)-carbonyl as the starting compound, it was anticipated that the substitution of CO ligands by [L¹][−] with concomitant internal electron transfer from the electron-rich metal Re(0) to the reducible azo aromatic ligand [L¹][−] would produce the metal radical complex directly.^{4a–c} However, the reference reaction produced a totally unexpected product. The compound, isolated from the reaction mixture, contained an undissociated tridentate ligand [L¹][−] and a new dianionic azo-aromatic ligand [L³]^{2−} coordinated in a tridentate fashion. Formation of the new ligand [H₂L³] is noteworthy, which involves simultaneous reductive azo bond cleavage and N–N bond formation. These results immediately prompted us to explore a similar reaction of Re₂(CO)₁₀ with another extended azo-aromatic ligand. We purposefully chose HL² for carrying out the reaction, as its conjugate base offers a nearly similar coordination environment like [L¹][−]. The reaction of HL² and Re₂(CO)₁₀, under identical reaction conditions, however, formed a seven coordinated mixed ligand complex [Re(L²){(L^{4−})^{•−}}₂] (2) in nearly 60% yield (Schemes 3 and 4). In this compound, two partially oxidized (semiquinone) aminophenolato ligands (L^{4−}) are coordinated along with an undissociated [L²][−] ligand. 2-Aminophenolato ligands are formed *in situ* *via* the reductive cleavage of the parent [L²][−] ligand. The above chemical reactions also produced several low-yield byproducts, as seen on a preparative TLC plate,

Scheme 4. Ligands: Products



which could not be purified so far. It may be worth noting that seven coordinated complexes of Re are rare.⁹

The complexes, 1 and 2, gave satisfactory elemental analyses (*cf.*, Experimental Section). Electrospray mass spectra of the complexes corroborate their formulation as [Re(L¹)(L³)] (1) and [Re(L²)(L^{4−})₂] (2), respectively. For example, each of the complexes 1a and 2 showed an intense peak due to the respective molecular ion [1a-H]⁺ and [2-H]⁺ at *m/z* 822 and 936 amu, respectively. Notably, the experimental spectral features of the complexes corroborate very well with their simulated isotopic pattern for the given formulation. Representative spectra of 1a and 2 along with their simulations are in the Supporting Information, Figures S1 and S2.

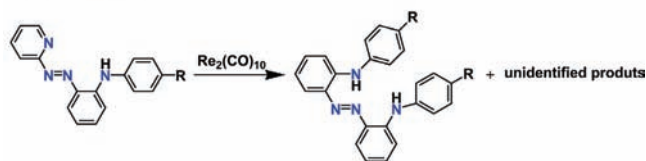
Complexes 1 and 2 possess *S* = 0 ground states, as determined by magnetic susceptibility measurements at room temperature. They display sharp ¹H NMR signals in the normal range¹⁰ for diamagnetic compounds. The ¹H NMR spectra of the representative complexes are submitted as Supporting Information, Figures S3–S5. Notably, the protons in the mixed ligand complexes 1 and 2 are unique and displayed a very large number of resonances. There has been serious overlap of resonances of the aromatic region, and it was not possible to assign them. However, complex 1b showed three methyl proton resonances at δ 1.99, 2.19, and 2.32 ppm. The two imine N–H protons of 2 appeared at δ 8.98 and 9.32 ppm, respectively, which disappeared on D₂O shake.

Rationale for the Transformation HL¹→H₂L³. The reaction of Re₂(CO)₁₀ with HL¹ exemplifies an unprecedented chemical reaction wherein a dianionic tridentate N,N,N donor (H₂L³) is formed *via* simultaneous four electron reductive cleavage and oxidative recombination of the aryl imides. The conversion HL¹→H₂L³ occurs within the coordination sphere, and the overall reaction is a multiple electron transfer process where the electron-rich dimetallic Re₂(CO)₁₀ serves as an electron pool.

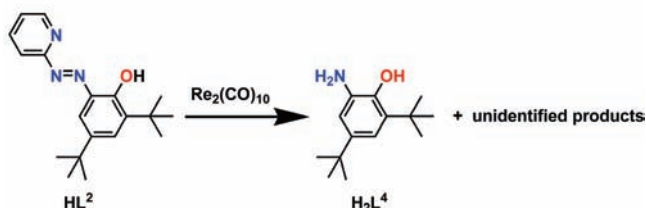
The mechanisms of these chemical reactions are not resolved as yet. However, a few reactions have been planned, and the results along with related literature have been used to make a reasonable assessment of the reference reaction. It has been argued^{7a,11} before that both reductive azo cleavage as well as oxidation of the coordinated organo-imides to a diazo function are facilitated by the dimetallic mediators. For example, an oxidative N–N bond formation reaction in a Ta complex has been achieved recently in a bridging imido dimer.⁸ For comparison, in the present case, the zero-valent Re₂ complex has mediated the two opposite redox processes, reductive bond cleavage as well as oxidative azo bond fusion, simultaneously. It is worth noting here that the reactions of the monomeric Re(CO)₅Cl with HL¹ under identical conditions failed to bring

Scheme 5. Summary of Ligand Transformations

-N=N- metathesis:



-N=N- bond cleavage:



C-N bond cleavage:

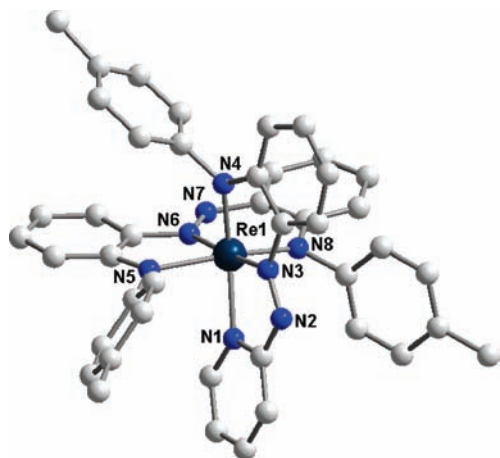
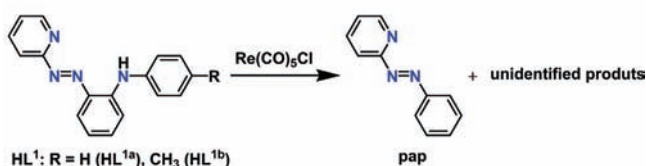


Figure 1. Molecular view of 1b. Hydrogen atoms are omitted for clarity.

about similar transformation. The latter reaction produced [Re(pap)(CO)₃Cl] (**3**) (pap = 2-(phenylazo)pyridine, N[^]N) as the only isolable product (cf. Experimental Section).¹² The formation of pap from HL¹ *via* deamination^{4c} has been observed previously in several other reactions. The three-dimensional X-ray structure (ORTEP) of compound **3** is submitted as Supporting Information Figure S6. In contrast, a similar reaction of HL² with Re₂(CO)₁₀ stopped after the cleavage of the azo bond, producing amino phenol from HL². We wish to note here that the two coordinated nitrogen atoms of the two amino phenolato ligands in compound **2** are disposed in *trans* orientations, which is not a favorable geometry for an interligand recombination reaction for N–N bond formation. Moreover, the reactions of closely related bidentate azo-aromatic ligands,

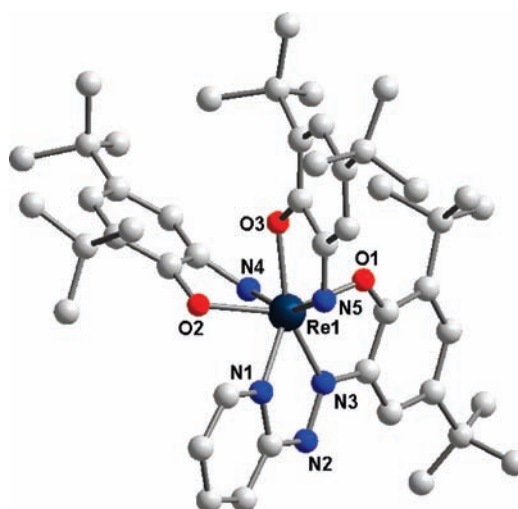


Figure 2. Molecular view of 2. Hydrogen atoms are omitted for clarity.

like pap or 4-aryl substituted pap (N[^]N) (L⁵) with Re₂(CO)₁₀ (see Experimental Section) under identical reaction conditions, underwent substitution and electron transfer, producing a diradical complex, [Re^{II}(N[^]N^{•-})₂(CO)₂].^{4a} To exclude the possibility of the formation of H₂L³ *via* multiple oxidative bond fusion of aromatic mono amine, produced *via* deamination of HL¹, a reaction with the –Me substituted ligand HL^{1b} (Scheme 2) was carried out. Interestingly, the product obtained from this reaction contains the new ligand H₂L^{3b}, which is symmetrical about the azo function. All of these observations taken together suggest that HL¹→H₂L³ conversion occurs *via* a sort of overall azo bond metathesis. However, the other metathesis product could not be identified so far. The observed ligand transformations in the present work are summarized in Scheme 5.

X-Ray Crystal Structure. The complexes **1b** and **2** form good quality crystals, whose structures have been solved by single-crystal X-ray diffraction studies. Molecular views of the compounds **1b** and **2** are displayed in Figures 1 and 2, respectively. Crystallographic data and selected experimental as well as DFT computed structural parameters are listed in Tables 1–3; ORTEPs are submitted as Supporting Information (Figures S7 and S8).

The X-ray structure of **1b** indeed confirmed the formation of H₂L³ from HL¹. Complex **1b** is hexa-coordinated and is meridional. The two deprotonated ligands, [L^{1b}]⁻ and [L^{3b}]²⁻, coordinate the central rhenium ion in an N₆-fashion using pairs of pyridyl-N, azo-N, and amido-N (deprotonated secondary amine) atoms. The chelate bite angle of N(pyridyl)–Re–N(azo) (73.57(5)°) is smaller than the average of N(azo)–Re–N(amide) (81.83(6)°).¹⁰ The crystal structure of compound **2**, on the other hand, is hepta-coordinated.⁹ An anionic tridentate ligand [L²]⁻ and two bidentate amino phenolato ligands (HL⁴)⁻ complete the coordination environment about the central Re atom. The ligand [HL⁴]⁻ is formed *via* reductive cleavage of the azo bond in HL². Its coordination geometry is distorted pentagonal bipyramidal, and the rhenium atom sits in a basal plane formed by O1, O2, O3, N1, and N3 atoms. The axial positions are occupied by N4 and N5 atoms (N4–Re1–N5 angle is 160°) (Figure 2) of the two [HL⁴]⁻ ligands. Notably, the two nitrogen atoms of the amino phenolate ligands are disposed *trans* to each other. We wish to note here that the average *d*_(N–N) lengths of

Table 1. Crystallographic Data for **1b**, **2**, and **3**

	1b	2	3
empirical formula	C ₄₄ H ₃₇ N ₈ Re	C ₄₇ H ₆₆ N ₅ O ₃ Re	C ₁₄ H ₉ ClN ₃ O ₃ Re
molecular mass	864	963.27	488.90
temp (K)	150 K	150 K	150 K
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.7491(3)	10.579(6)	12.4199(19)
<i>b</i> (Å)	19.0490(6)	12.786(7)	9.0921(14)
<i>c</i> (Å)	21.1424(6)	18.829(11)	13.818(2)
α (deg)	90	94.595(14)	90
β (deg)	100.0780(10)	92.864(16)	102.650(5)
γ (deg)	90	102.871(14)	90
<i>V</i> (Å ³)	3865.8(2)	2469(2)	1522.5(4)
<i>Z</i>	4	2	4
<i>D</i> _{calcd} (g/cm ³)	1.630	1.296	2.133
cryst dimens (mm)	0.08 × 0.16 × 0.18	0.15 × 0.17 × 0.19	0.08 × 0.16 × 0.18
θ range for data collection (deg)	1.5–28.6	1.1–24.7	2.0–24.3
GOF	1.01	1.03	1.01
reflns collected	43806	26869	16378
unique reflns	9605	8364	2484
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0338 w <i>R</i> 2 = 0.0714	<i>R</i> 1 = 0.0599 w <i>R</i> 2 = 0.1668	<i>R</i> 1 = 0.0322 w <i>R</i> 2 = 0.0702

Table 2. Summary of Selected Experimental and Calculated Bond Lengths (Å) of Complexes **1b**, [**1b**]⁺, and [**1b**]²⁺

bonds	1b		[1b] ⁺	[1b] ²⁺
	X-ray	theoretical	theoretical	theoretical
Re1–N(1)	2.076(3)	2.101	2.109	2.120
Re1–N(3)	1.972(3)	1.990	2.020	2.073
Re1–N(4)	1.957(3)	2.012	1.992	1.976
Re1–N(5)	1.977(3)	2.008	2.038	2.116
Re1–N(7)	2.037(3)	2.077	2.062	2.047
Re1–N(8)	2.081(3)	2.131	2.100	2.028
N(2)–N(3)	1.336(5)	1.322	1.306	1.286
N(6)–N(7)	1.330(5)	1.296	1.304	1.316
C(35)–N(8)	1.402(5)	1.400	1.382	1.343

the azoaromatic ligands in both the compounds **1b** and **2** are elongated (for **1b**, 1.333(5); **2**, 1.347(11)Å) compared to the uncoordinated ligand salt,¹³ [HL^{1a}]ClO₄ (1.246(5)Å). The elongation of the –N=N– chromophores in these complexes is due to extensive Re(*d* π)-ligand(π^*) back-bonding,^{10,14} which has been supported by DFT studies. However, the two aminophenolates in complex **2** are partially oxidized: the C–N and C–O lengths are in agreement with the bond lengths in its semiquinone oxidation state.¹⁵ Ambiguities of oxidation states in the above coordinated azo-aromatics have been finally sorted out by their DFT analysis (cf. below).

The metal–nitrogen bonds in these complexes are unexceptional, lying in the range 1.95–2.07 Å. The bonds from Re to the neutral 2-pyridyl-N atoms are distinctly longer than those to the anilido or azo nitrogen atoms.^{10,14} The effects of the –N=N– bond elongation due to back bonding are also reflected by the lowering of vibrational frequencies of $\nu_{\text{N=N}}$ as compared to the

Table 3. Summary of Selected Experimental and Calculated Bond Lengths (Å) of Complexes **2**, [**2**]⁺, and [**2**]²⁺

bonds	2		[2] ⁺	[2] ²⁺
	X-ray	theoretical	theoretical	theoretical
Re1–O1	2.016(6)	2.069	2.063	2.024
Re1–O2	1.976(6)	2.081	2.118	2.132
Re1–O3	2.047(6)	2.035	2.091	2.113
Re1–N1	2.066(8)	2.098	2.131	2.159
Re1–N3	2.020(8)	2.047	2.087	2.121
Re1–N4	1.990(7)	2.035	2.087	2.077
Re1–N5	1.971(8)	2.019	2.052	2.076
C25–O2	1.350(12)	1.325	1.301	1.291
N2–N3	1.347(11)	1.325	1.312	1.301
C20–N4	1.353(11)	1.365	1.340	1.326
C20–C25	1.378(14)	1.428	1.445	1.469
C21–C22	1.392(16)	1.386	1.375	1.372
C23–C24	1.389(16)	1.392	1.379	1.374
C39–O3	1.332(11)	1.337	1.309	1.298
C34–N5	1.361(12)	1.364	1.347	1.327
C34–C39	1.435(12)	1.418	1.441	1.464
C35–C36	1.366(14)	1.388	1.377	1.371
C37–C38	1.409(13)	1.394	1.374	1.371

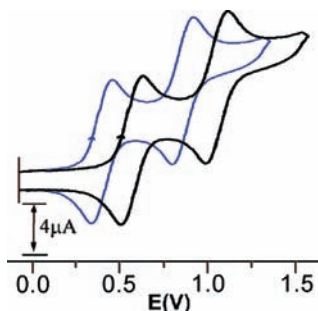
uncoordinated HL¹/HL². For example, the $\nu_{\text{N=N}}$ band in free ligands appears near 1380 cm^{−1}, whereas it is lowered considerably in the coordinated states and appeared at 1285 and 1260 cm^{−1} in the complexes **1a** and **2**, respectively.^{13,16}

Cyclic Voltammetry and EPR. Cyclic voltammograms of **1a**, **1b**, and **2** were recorded in CH₂Cl₂ solutions containing 0.1 M TBAP at 25 °C. The potentials are referenced to the saturated

Table 4. Electrochemical Data^a

compound	oxidation $E_{1/2}$, ^b V (ΔE_p , mV)
[Re(L ^{1a})(L ^{3a})] (1a)	0.43 (80), 0.82 (70)
[Re(L ^{1b})(L ^{3b})] (1b)	0.41 (75), 0.79 (80)
[Re(L ²)(L ^{4*-}) ₂] (2)	0.53 (75), 0.10 (80)

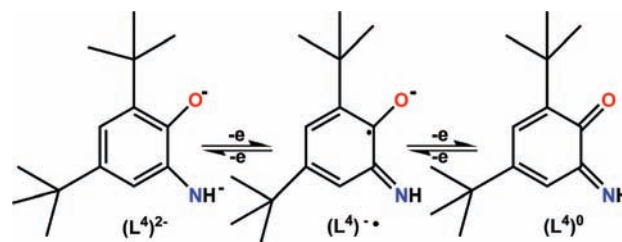
^a Conditions: solvent, dichloromethane; supporting electrolyte, NBu₄ClO₄ (0.1M); working electrode, platinum for oxidation and reduction processes; reference electrode, Ag/AgCl; solute concentration, ca. 10⁻³(M); scan rate, 50 mVs⁻¹. ^b $E_{1/2} = 1/2(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$ in mV (E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential).

Figure 3. Cyclic voltammogram of **1** and **2** in CH₂Cl₂.

Ag/AgCl electrode. The results are summarized in Table 4, and the voltammograms (for **1a** and **2**) are displayed in Figure 3. Both complexes **1** and **2** showed two reversible anodic responses in the potential range 0.3–1.0 V. One-electron stoichiometry of the reversible redox processes was confirmed by exhaustive electrolyses of the representative compounds **1a** at 0.65 and 1.0 V and **2** at 0.7 and 1.2 V, respectively.

To have an insight into the nature of the electronic levels associated with the reversible redox processes, electrogenerated complexes were studied by EPR spectroscopy in CH₂Cl₂/0.1 M TBAP at 77 K. The one electron oxidized complexes [**1a**]⁺ and [**2**]⁺, generated by exhaustive electrolysis of [**1a**] and [**2**] at 0.65 and 0.7 V, respectively, displayed ligand-centered sharp single line spectra at $g = 2.006$ and $g = 2.003$, respectively, with peak to peak line widths of 308 mT to 343 mT, which indicate that each of the oxidized complexes undergoes ligand based oxidation, and consequently the unpaired spin is localized primarily on the coordinated ligand.^{4,15} The two electron oxidized dipositive compounds, [**1**]²⁺ and [**2**]²⁺, are, however, EPR silent, as expected. EPR spectra of all of the above one electron oxidized complexes are displayed in Figure S9 of the Supporting Information. These results are fully corroborated by density functional theory (DFT) calculations, which show that the highest occupied molecular orbitals (HOMO, HOMO–1) of the complexes **1b** and **2** are primarily ligand-centered (cf. below). Thus, one electron oxidation in these complexes is expected to occur from the ligand centers and produce monocationic ligand-centered radical complexes of Re(III), as observed experimentally.

The Electronic Structures and UV–Vis Spectra. Because of the redox noninnocent nature of the coordinated ligands, the assignment of electronic structures of these complexes is an important issue in view of different electronic structure possibilities^{4,15} (Schemes 1 and 6). In order to have a definite look into the electronic structures of these two complexes **1** and

Scheme 6. Different Electronic Possibilities of H₂L⁴

2, the geometries of the complexes **1b** and **2** in both singlet and triplet states were optimized, using density functional theory (B3LYP and SDD on Re; 6-31+G(d) on C, N, and O; 6-31G on H atoms—see Experimental Section). The agreement between the experimental structural parameters and that obtained through DFT calculations for **1b** and **2** were found to be excellent. Calculated selected bond lengths and angles are compared with experimental ones in Tables 2 and 3.

The most stable structure of **1b** proves to be a closed-shell singlet state, [Re^{III}(L^{1b})(L^{3b})], and all attempts to locate open-shell singlet [Re^V(L^{1b})^{•-}(L^{3b})^{•-}] configurations using the BS-DFT approach converged back to the closed-shell configuration. Complex **2**, on the other hand, on broken symmetry density functional theoretical calculations (BS ($S = 0$)), clearly shows that the two aminophenoleto ligands (L⁴) are open-shell, π -radical monoanions [(L⁴)^{•-}], as was shown computationally for the analogous systems.¹⁵ The sensitive bond distances associated with the coordinated L⁴ (C–O and C–N X-ray bond distances) and NBO calculated average Wiberg bond order (C–O, 1.138 (1.151 and 1.125) and C–N, 1.223 (1.229 and 1.219)) in complex **2** suggests its intermediate semiquinone [(L⁴)^{•-}] radical state leading to the valence configuration of [Re^{III}(L²)⁻{(L⁴)^{•-}}₂]. Notably, one of these two ligands remains in the spin-up manifold, while the second one is in the spin-down manifold, yielding the observed antiferromagnetically coupled diamagnetic singlet ($S = 0$) ground state. This notion is further confirmed by the Mulliken spin population analysis (Figure S10, Supporting Information) and is very similar to the results calculated for similar systems.¹⁵ The elongation of the azo-chromophores in both complexes **1** and **2** is due to substantial $d\pi(\text{Re}) \rightarrow \pi^*(\text{N}=\text{N})$ back bonding, which indeed is consistent with the substantially reduced Wiberg index for the N–N bonds (1.33 and 1.41 for **1b**, 1.29 for **2**) compared to the free-ligand value of 1.77.¹⁴

The energies and compositions of the DFT calculated frontier orbitals for both complexes, [Re(L^{1b})(L^{3b})] (**1b**) and [Re^{III}(L²){(L⁴)^{•-}}₂] (**2**), are listed in the Supporting Information (Tables S1 and S2). For both complexes **1b** and **2**, the MO representations show the highest occupied MO (HOMO) to be formed by a combination of d metal orbitals and ligand orbitals with a major contribution from the ligand orbitals (**1b**: L^{1b}, 05%; Re, 09%; L^{3b}, 86% and **2**: L², 11%, Re, 04%; L⁴, 85%). Closely lying occupied HOMO–1 is again formed by a major contribution of ligand orbitals. The lowest lying unoccupied MOs (LUMOs) are, to a large extent, delocalized over the π system of the ligands; metal orbitals contribute to this orbital only by a very little amount (Tables S1 and S2, Supporting Information).

Geometry optimizations were also carried out on the one- and two-electron oxidized redox partners of **1b** and **2**. Optimized

Table 5. UV–Vis–NIR Spectral Transition of the Complexes **1** and **2**

compound	electronic spectra λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
$[\text{Re}(\text{L}^{1\text{a}})(\text{L}^{3\text{a}})]$ (1a)	555 (12170), 464 (10873), 390(12776), 334 (17940), 270(22403)
$[\text{Re}(\text{L}^{1\text{b}})(\text{L}^{3\text{b}})]$ (1b)	559 (9015), 468 (7785), 390 (9173), 337(14376), 270(18509)
$[\text{Re}(\text{L}^2)(\text{L}^{4\text{a}-})_2]$ (2)	935 (5598), 602 (8458), 490 (20901), 290(18093)

structural parameters and net spin densities for the computed ground states of the $[\mathbf{1b}]^+$, $[\mathbf{1b}]^{2+}$, $[\mathbf{2}]^+$, and $[\mathbf{2}]^{2+}$ are collected in Tables 2 and 3. The one electron oxidized monocationic complexes, $[\mathbf{1b}]^+$ and $[\mathbf{2}]^+$, have a doublet ground state, and the changes in net spin density indicate that the oxidation process is clearly ligand centered, although in the case of $[\mathbf{1b}]^+$, it is mainly localized on a single ligand ($\text{L}^{3\text{b}}$; $\text{Re} = 0.1857$, $\text{L}^{1\text{b}} = 0.0147$, $\text{L}^{3\text{b}} = 0.7996$; Figure S11, Supporting Information) while it is delocalized over the two aminophenolato ligands in $[\mathbf{2}]^+$ ($\text{Re} = -0.1523$, $\text{L}^2 = 0.0445$, and $\text{L}^{4\text{a}-} = 1.1078$; Figure S12, Supporting Information). The two electron oxidized complexes $[\mathbf{1b}]^{2+}$ and $[\mathbf{2}]^{2+}$ have closed-shell singlet state structures, which again is consistent with the ligand centered redox process.

Overall, the oxidation states of the metal and the two ligands in compounds **1b** and **2** may be described as $[\text{Re}^{\text{III}}(\text{L}^{1\text{b}})^-(\text{L}^{3\text{b}})^{2-}]$ (**1b**) and $[\text{Re}^{\text{III}}(\text{L}^2)\{(\text{L}^{4\text{a}-})^-\}_2]$ (**2**), respectively. The central $\text{Re}(\text{III})$ ion remains essentially invariant in the two redox processes $[\mathbf{1b}/\mathbf{2}]^{1+/2}$, with all redox events localized on the ligands, which is in line with the EPR data.

All of the compounds **1** and **2** are freely soluble in nonpolar solvents like dichloromethane and chloroform, and their electronic spectra were recorded in dichloromethane solution. The experimental spectral results are collected in Table 5, and the corresponding spectra are displayed in Figure S13 (Supporting Information). The low intensity tail observed in the experimental spectrum compares well with the calculated value for the HOMO→LUMO transition at around 900–950 nm. The two midintensity peaks with transition maxima close to 550 (for **1b**) and 600 nm (for **2**) can be readily assigned to HOMO–1/HOMO–2→LUMO transitions, which are computationally predicted to appear at 592 and 606 nm, respectively. Several possible transitions were found to lie between 250 and 400 nm, which are assigned as the intraligand (ligand(π)→ligand(π^*)) charge transfer transition.⁴

CONCLUSION

In conclusion, we have introduced an unprecedented type of multiple step redox process in Re-coordinated azoaromatic ligands. Attempts have been made to rationalize the formation of H_2L^3 from HL^1 . Considering the products of all of the above-noted reactions together, one may think of the most simplest pathway of four electron reductive azo cleavage followed by oxidation of one of the imide fragments, leading to a symmetrical azo-aromatic ligand $[\text{H}_2\text{L}^3]$. It is thus concluded that dimetallic electron-rich mediators can cleave and reform azo bond(s) only on multidentate azo-aromatics. The results have generated a scope of synthesizing otherwise inaccessible extended new azo-aromatic compounds by reactions of multimetal–carbonyls with

polydentate (tri and higher) azoaromatic substrates. Our studies in this area are in progress.

EXPERIMENTAL SECTION

Materials. $\text{Re}_2(\text{CO})_{10}$ is an Aldrich reagent. The ligands $\text{L}^{1(\text{a/b})}$ and L^2 were prepared by following the reported procedure.¹⁷ All other chemicals were of reagent grade and used as received. Solvents were purified and dried prior to use.

Instrumentation. ^1H NMR spectra were taken on a Bruker Advance DPX 300 spectrometer, and SiMe_4 was used as the internal standard. Infrared spectra were obtained using a Perkin-Elmer 783 spectrophotometer. Cyclic voltammetry was carried out in 0.1 M Bu_4NClO_4 solutions using a three-electrode configuration (platinum working electrode, Pt counter electrode, Ag/AgCl reference) and a PC-controlled PAR model 273A electrochemistry system. The $E_{1/2}$ for the ferrocenium–ferrocene couple under our experimental conditions was 0.39 V. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263). EPR spectra in the X band were recorded with a JEOL JES-FA200 spectrometer.

Syntheses. *Reaction of $\text{Re}_2(\text{CO})_{10}$ and $\text{HL}^{1(\text{a/b})}$: Synthesis of $[\text{Re}(\text{L}^{1\text{a}})(\text{L}^{3\text{a}})]$ (**1a**).* A total of 100 mg of $\text{Re}_2\text{CO}_{10}$ (0.15 mmol) and 165 mg of $\text{HL}^{1\text{a}}$ (0.60 mmol) were heated at reflux for 4 days in *n*-octane. The color of the solution changed from red to pink during this period. The solution was filtered, which on evaporation produced a dark mass. The crude product was then loaded onto a preparative silica TLC plate for purification. Toluene was used as the eluent. Complex **1a** was separated on a TLC plate as a pink band with several other minor overlapping products. It was recrystallized by slow diffusion of a dichloromethane solution of the compound into hexane. Its yields and characterization data are as follows. Yield: 45%. IR (KBr, cm^{-1}): 1585 [$\nu(\text{C}=\text{N})$], 1295 [$\text{L}^1\nu(\text{N}=\text{N})$], 1285 [$\text{L}^2\nu(\text{N}=\text{N})$]. ESI-MS, m/z : 822 [$\text{MH}]^+$. Anal. Calcd for $\text{C}_{41}\text{H}_{31}\text{N}_8\text{Re}$: C, 59.91; H, 3.80; N, 13.63. Found: C, 59.87; H, 3.82; N, 13.62. ^1H NMR (500 MHz, d_6 -DMSO, 300 K): δ 8.15 (d, 1H, J = 8.5), 7.62 (d, 1H, J = 8.0 Hz), 7.53 (t, 1H, J1 = 7.0, J2 = 8.0 Hz), 7.41 (t, 1H, J1 = 7, J2 = 8.5 Hz), 7.30–7.28 (m, 2H), 7.16 (d, 1H, J = 8.0 Hz), 7.10–7.02 (m, 6H), 6.92 (t, 1H, J1 = 7.5, J2 = 7.5 Hz), 6.77 (t, 1H, J1 = 7.5, J2 = 7.5 Hz), 6.73–6.69 (m, 7H Hz), 6.65–6.60 (m, 3H), 6.55 (d, 1H, J = 8.0 Hz), 6.50 (t, 1H, J1 = 7.5, J2 = 7.5 Hz), 6.46 (t, 1H, J1 = 7.5, J2 = 7.0 Hz), 6.39 (d, 1H, J = 7.5 Hz), 6.30 (t, 1H, J1 = 6.5, J2 = 6.5 Hz), 6.23 (d, 1H, J = 8.0 Hz).

*Synthesis of $[\text{Re}(\text{L}^{1\text{b}})(\text{L}^{3\text{b}})]$ (**1b**).* This was synthesized following the same procedure as described for **1a**. Its yield and characterization data are as follows. Yield: 42%. IR (KBr, cm^{-1}): 1585 [$\nu(\text{C}=\text{N})$], 1280 [$\text{L}^1\nu(\text{N}=\text{N})$], 1275 [$\text{L}^2\nu(\text{N}=\text{N})$]. ESI-MS, m/z : 864 [$\text{MH}]^+$. Anal. Calcd for $\text{C}_{44}\text{H}_{37}\text{N}_8\text{Re}$: C, 61.16; H, 4.32; N, 12.97. Found: C, 61.14; H, 4.34; N, 12.93. ^1H NMR (500 MHz, d_6 -DMSO, 300 K): δ 8.12 (d, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 8.0 Hz), 7.50–7.49 (m, 2H), 7.42 (t, 1H, J1 = 7.5, J2 = 8.0 Hz), 7.34 (d, 1H, J = 8.5 Hz), 7.28 (d, 1H, J = 6.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 7.08 (d, 1H, J = 8.0 Hz), 7.02 (t, 1H, J1 = 8.0, J2 = 8.5 Hz), 6.77 (d, 1H, J = 7.5 Hz), 6.73–6.67 (m, 6H), 6.60 (t, 1H, J1 = 7.5, J2 = 7.5), 6.53–6.49 (m, 5H), 6.43 (t, 1H, J1 = 7.5, J2 = 8 Hz), 6.27 (t, 1H, J1 = 6.5, J2 = 7.0), 6.21 (d, 1H, J = 6.0 Hz), 6.13 (d, 1H, J = 8.0 Hz).

*Reaction of $\text{Re}_2(\text{CO})_{10}$ and HL^2 : Synthesis of $[\text{Re}(\text{L}^2)\{(\text{L}^{4\text{a}-})^-\}_2]$ (**2**).* A total of 100 mg of $\text{Re}_2\text{CO}_{10}$ (0.15 mmol) and 190 mg of HL^2 (0.61 mmol) were heated at reflux for 96 h in *n*-octane. The color of the solution changed from orange to dull green during this period. The solution was filtered, which on evaporation produced a dark mass. The crude product was then loaded onto a preparative silica TLC plate for purification. Chloroform was used as the eluent. Complex **2** was separated on a TLC plate as a dull green band as a major product with some other minor overlapping products. It was recrystallized by slow evaporation of a methanol–dichloromethane solvent mixture of the

complex. Its yields and characterization data are as follows. Yield: 60%. IR (KBr, cm^{-1}): 1580 [$\nu(\text{C}=\text{N})$], 1260 [$\text{L}^1\nu(\text{N}=\text{N})$]. ESI-MS, m/z : 936 [MH^+]. Anal. Calcd for $\text{C}_{47}\text{H}_{66}\text{N}_5\text{O}_3\text{Re}$: C, 60.36; H, 7.11; N, 7.49. Found: C, 60.32; H, 7.15; N, 7.45. ^1H NMR (500 MHz, CDCl_3 , 300 K): δ 9.32 (s, 1H (N–H)), 8.98 (s, 1H (N–H)), 7.84 (s, 1H), 7.79–7.58 (m, 2H), 7.48 (t, 1H, $J_1 = 9$, $J_2 = 8.5$ Hz), 7.41 (t, 1H, $J_1 = 8.5$, $J_2 = 8.0$ Hz), 7.06 (s, 1H), 6.98 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H Hz), 6.66 (s, 1H Hz), 1.45–1.23 (s, 54H).

Reaction of $\text{Re}(\text{CO})_5\text{Cl}$ and HL^1 : Synthesis of $[\text{Re}(\text{pap})(\text{CO})_3\text{Cl}]$ (3). A total of 100 mg of $\text{Re}(\text{CO})_5\text{Cl}$ (0.27 mmol) and 150 mg of HL^1 (0.54 mmol) was heated at reflux for 3 days in *n*-octane. The color of the solution changed from red to deep blue during this period. The solution was filtered, which on evaporation produced a dark mass. Recrystallization of the crude product from dichloromethane/hexane solution produced complex 3. Its yield and characterization data are as follows. Yield: 75%. IR (KBr, cm^{-1}): 1580 [$\nu(\text{C}=\text{N})$], 1290 [$\text{L}^1\nu(\text{N}=\text{N})$], 1905 [$\nu(\text{C}=\text{O})$]. ESI-MS, m/z : 489 [MH^+]. Anal. Calcd for $\text{C}_{14}\text{H}_9\text{ClN}_3\text{O}_3\text{Re}$: C, 34.39; H, 1.86; N, 8.59. Found: C, 34.37; H, 1.89; N, 8.58.

Reaction of $\text{Re}_2(\text{CO})_{10}$ and HL^5 : Synthesis of $[\text{Re}(\text{L}^{5*})_2(\text{CO})_2]$ (4). A total of 100 mg of $\text{Re}_2\text{CO}_{10}$ (0.15 mmol) and 165 mg of HL^{1a} (0.61 mmol) were heated at reflux for 96 h in *n*-octane. The color of the solution changed from orange to deep blue during this period. The crude complex was crystallized from a hot *n*-octane solution of the reaction mixture. Its yield and characterization data are as follows. Yield: 75%. IR (KBr, cm^{-1}): 1195 [$\nu(\text{N}=\text{N})$]; 1875, 1940 [$\nu(\text{C}=\text{O})$]. ESI-MS, m/z : 791 [MH^+]. Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_8\text{O}_2\text{Re}$: C, 54.67; H, 3.57; N, 14.17. Found: C, 54.63; H, 3.60; N, 14.14.

EPR Spectral Studies. The one electron oxidized complexes $[1]^+$ and $[2]^+$, generated by exhaustive electrolysis of the respective complexes 1 and 2 at 0.65 and 0.7 V, respectively, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAP, were immediately dipped into liquid nitrogen, and the resulting frozen solutions were used for the EPR measurements at 77 K. The applied potential for the two electron oxidized complexes $[1]^{2+}$ and $[2]^{2+}$ are 1.0 and 1.2 V, respectively.

Crystallography. Crystallographic data for compounds 1b, 2, and 3 are collected in Table S-1 (Supporting Information). Suitable X-ray quality crystals of these are obtained as follows: 1b, by slow evaporation of a dichloromethane–hexane solvent mixture of the compound; 2, by slow evaporation of a methanol–dichloromethane solution of the compound; and 3, by slow evaporation of dichloromethane–hexane solution of the compound.

All data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz-polarization effects. 1b: A total of 43 806 reflections were collected, of which 9605 were unique ($R_{\text{int}} = 0.063$), satisfying the ($I > 2\sigma(I)$) criterion, and were used in subsequent analysis. 2: A total of 26 869 reflections were collected, of which 8364 were unique ($R_{\text{int}} = 0.057$). 3: A total of 16 378 reflections were collected, of which 2484 were unique ($R_{\text{int}} = 0.082$).

The structures were solved by employing the SHELXS-97 program package¹⁸ and were refined by full-matrix least-squares based on F^2 (SHELXL-97).¹⁹ All hydrogen atoms were added in calculated positions.

Computational Details. All calculations described in this paper were performed using density functional theory as implemented in the Gaussian 03 package.²⁰ Full geometry optimizations were performed without symmetry constraints. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and that there are only positive Eigen values. The hybrid B3LYP exchange-correlation functional was used in conjunction with the SDD basis set with effective core potential for the Re atom and the 6-31G(d) basis set for C, H, N, and O atoms. GaussSum²¹ was used to calculate the fractional contributions of various groups to each molecular orbital.

■ ASSOCIATED CONTENT

Supporting Information. Experimental and characterization details, X-ray crystallographic files in CIF format, and ORTEP and respective atom numbering schemes for 1–3 are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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