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The BIAN ligand 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene:

An electron sponge or a "normal" α-diimine ligand ?

Isabell Löw, ^a Martina Bubrin, ^a Alexa Paretzki, ^a Jan Fiedler, ^b Stanislav Záliš, ^b Wolfgang Kaim^a

^a Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

^b J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

ABSTRACT

The compounds [*fac*-Re(CO)₃Cl(L)] and [M(CO)₄(L)], M = Cr, Mo, W and L = 1,2-bis[(2,6diisopropylphenyl)imino]acenaphthene, have been studied electrochemically and spectroelectrochemically (IR, UV-vis-NIR, EPR). The neutral rhenium complex contains an isopropyl-shielded chloride ligand; its reversible oxidation was shown to involve a largely metal-based HOMO. One electron could be added reversibly to the diimine-based LUMO of all complexes, as evident from EPR spectroscopy. However, there was no evidence for the reversible acquisition of more than one electron by L in these complexes, ruling out an electron reservoir functionality with multielectron reactivity. DFT and TD-DFT calculations were performed for the [Re(CO)₃Cl(L)]ⁿ redox series (n = +, 0, -).

Keywords:

^{*} Corresponding author.

E-mail: kaim@iac.uni-stuttgart.de.

BIAN diimine ligand

Carbonylmetal complexes

Electron transfer

Rhenium complexes

Spectroelectrochemistry

Research highlights

• Combined (IR, UV-vis-NIR, EPR) spectroelectrochemical study of complexes

 $[Re(CO)_3Cl(L)]$ and $[M(CO)_5(L)]$, M = Cr, Mo, W

- Reversible electrochemical oxidation of [Re(CO)₃Cl(L)]
- Mostly irreversible reduction despite two low lying orbitals of different character
- No special electron reservoir behavior detected.

1. Introduction

Electrocatalyzed reduction of CO₂ holds great promise in the current attempts to limit this end product of combustion in the atmosphere and to provide a new source for non-fossil hydrocarbons. As with all multielectron transfer processes [1], the challenges for such a mechanism are formidable. Based preferentially on renewable energy, the result would be an environmentally benign recycling of carbon dioxide. An established homogeneous scheme for such a purpose could involve *fac*-[Re(CO)₃Cl(bpy)] and related α -diimine complexes as catalyst precursors, which are known to promote the formation of CO from CO₂ [2-4]. Over the years, mechanistic studies [5-6] have revealed the two-electron reduced state [Re(CO)₃(bpy[•])]⁻ as crucial intermediate [2-4], reacting with CO₂ instead of proton electrophiles. Although further conversion to formate, formaldehyde or methanol would be highly desirable, heterodinuclear systems such as [L_nM(µ-BL)Re(CO)₃Cl] with M = hydride-

activating Rh or Ir and a redox-active bridging ligand BL have proven inadequate [7]. Redoxactive ligands capable of storing more than two electron equivalents might represent a solution to this problem, and an inspection of the α -diimine literature has thus led to the class of 1,2-diiminoacenaphthenes [8].

As a special sub-group of the α -diimine class of potentially non-innocent chelate ligands [9,10], the N,N'-diorgano-acenaphthoquinonediimines, especially the 1,2-bis(arylimino)acenaphthenes (BIANs), have been employed in catalysis and in other studies of transition and main group metals [11-16]. In contrast to the simple α -diimines RN=CH-CH=NR (R-DAB) with their *s*-trans conformation in the non-coordinated state, the preformed *s*-*cis* structure of the metal binding imine functions in the BIAN ligands provides a particularly attractive template for chelate coordination [11].



Furthermore, in 2003 Fedushkin et al. reported that 1,2-bis[(2,6diisopropylphenyl)imino]acenaphthene (L) is capable of stepwise accepting four electrons in the presence of charge compensating Na⁺ ions [13a]. The presence of two low-lying unoccupied molecular orbitals, $\pi^*(\alpha$ -diimine) (5b₂) and $\pi^*(naphthalene)$ (4a₂), in BIAN systems has prompted the notion that the first two electrons are being added to the α -diimine part while two further electrons are delocalized over the whole multiply cation-coordinated π system [12,13]. It was thus speculated as to how many electrons this ligand can accept from

coordinated metals, instigating further research on the main group metal coordination chemistry of N,N'-diorgano-acenaphthoquinonediimines [12].



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Within our general interest in non-innocent ligand behavior [9a,10,17] and especially in those systems with two energetically close-lying but conjugatively connected π^* acceptor MOs located at *different* sites of ligand molecules we have previously investigated the systems of 1,10-phenanthroline (phen) [18], dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) [19], 2,3-bis(1-methylimidazol-2-yl)quinoxaline (bmiq) [20], and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4,4'-bptz) [21] (Scheme 1).



Scheme 1. Ligands with two different close-lying LUMOs [18-21].

It was thus shown that 4,4'-bptz has the tetrazine-localized orbital a_u occupied on the first electron uptake when $X = W(CO)_5$ complex fragments are coordinated to the terminal 4-pyridyl groups. However, a fully delocalized MO b_{1u} is populated on reduction when the pyridyl functions are quaternized (X = R⁺) [21].

Herein we describe a number of transition metal carbonyl complexes of 1,2-bis[(2,6diisopropylphenyl)imino]acenaphthene = L and their response to addition or removal of electrons in order to probe whether there is any evidence for exceptional and therefore useful multielectron reducibility caused by the presence of the BIAN ligand. The compounds are $[Re(CO)_3Cl(L)]$ and $[M(CO)_4(L)]$, M = Cr, Mo, W. In addition to photo- and electrocatalytic CO_2 reduction [3,13f] the rhenium compound has been investigated for its biochemically useful CO releasing properties [22], while the tetracarbonylmetal analogues can display similar electronic structures [23].

Metal carbonyl complex fragments were considered suitable for probing highly reduced forms of a coordinated ligand, if available, because the metals in a formally low oxidation state would not easily be reduced to the metallic state while they can be expected to facilitate the reduction of coordinated noninnocent ligands such as the α -diimines [24,25].

2. Results and Discussion

2.1 Synthesis and Stability

The complexes were obtained either by thermal reactions with precursors $[\text{Re}(\text{CO})_5\text{Cl}]$ or $\text{Mo}(\text{CO})_4(\text{nbd})$, nbd = 2,5-norbornadiene, or by irradiation of $\text{M}(\text{CO})_6$, M = Cr or W, in THF in the presence of L. The rhenium and molybdenum compounds have been obtained before, their crystal and molecular structures were reported [13e,f]. The complex $[\text{Cr}(\text{CO})_4(\text{L})]$ proved to be light-sensitive and generally labile so that measurements of this system were limited.

2.2 Crystal structure of [Re(CO)₃Cl(L)]

For a meaningful discussion of the molecular structure and the bond parameters we have obtained an improved single crystal diffraction analysis of $[Re(CO)_3Cl(L)]$, the data and illustrating figures are summarized in Tables S1 and S2 and in Figures 1A-C. DFT calculated bond lengths and angles for $[Re(CO)_3Cl(L)]$ are listed in Table S2. The comparison of calculated and measured bonding parameters shows that DFT-optimized structural parameters agree with the experimental structure.

The molecular structure of [Re(CO)₃Cl(L)] in the crystal contains a familiar [13f,26] motif, a *fac*-tricarbonylrhenium(I) group coordinated to the α -diimine chelate ligand and to the monodentate ligand, here chloride. The steric repulsion involving the *ortho*-positioned isopropyl groups causes the N-aryl rings to adopt a nearly orthogonal position relative to the BIAN π plane, however, there is a significant difference between the axial ligands Cl and CO_{ax}: The former lies shielded right between two isopropyl groups from two different aryl substituents (d(Cl---HCMe₂) 2.53 Å) whereas CO_{ax} has moved away from the isopropyl groups (Fig. 1C). Accordingly, the octahedral configuration is notably distorted with the N-Re-Cl angles rather small at about 83° whereas the N-Re-CO_{ax} angles have increased to about 96°. The "locked" configuration as illustrated (Fig. 1) is also evident from the inequivalence of the isopropyl groups in the ¹H NMR experiment (see Exp. Section and ref. [13f]), confirming restricted rotation at room temperature on the NMR time scale.

The bond lengths at the metal show little difference relative to corresponding analogues [26]. The bond parameters within the chelate ring indicate only minor π back donation from the low-valent rhenium to the good π acceptor L: The CN bonds at about 1.28 Å and especially the connecting C-C bond at 1.521(4) Å, a value very close to that in the free ligand [27], indicate [28] the absence of significant π back donation via metal-to-ligand charge transfer in the ground state.

2.3 Cyclic voltammetry

All compounds described here exhibit an apparently reversible reduction (Figures 2,3 Table 1). A second reduction process has been noted for $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ [3] and $[\text{M}(\text{CO})_4(\text{L})]$ (Figs. S1,S2), however, this was found completely irreversible in each case. The anodic oxidation behaved reversibly for $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ and $[(\text{Cr}(\text{CO})_4(\text{L})]$ (Figures 2 and 3).

In comparison with complexes of *tert*-Bu-DAB [26], the reduction potential for the representative [Re(CO)₃Cl(L)] lies about 0.6 V more positive under comparable conditions, reflecting the lower lying LUMO. The large π system as well as the presence of electron-withdrawing aryl N-substituents are responsible for this shift.

The lability of such compounds on second reduction is caused by the dissociation of the chloride ligand which is essential for the function of such species in CO_2 reduction catalysis [4-6]. Ligand dissociation is also expected on two-electron acquisition by tetracarbonylmetal complexes in order to retain the 18 valence electron count.

Like in $[Re(CO)_3Cl(tert-Bu-DAB)]$ [26] the oxidation of $[Re(CO)_3Cl(L)]$ was observed to proceed reversibly in the cyclic voltammogram, the electron-withdrawing aryl N-substituents leading to about 0.3 V more positive potentials.

2.4 EPR Spectroscopy

Cathodic reduction of the carbonylmetal compounds *in situ* produced EPR spectra (Figures 4 and S3, Table 2) with isotropic g values generally near the free electron value of 2.0023 and splitting through two equivalent diimine ¹⁴N atoms. The magnitude and the strongest g deviation for the tungsten complex with the large spin-orbit coupling constant of the metal are as expected [29], confirming the formation of diimine radical anion ligands with very little spin density on the metals. Figure 5 depicts DFT calculated spin densities for oxidized and reduced forms of the rhenium complex. Spin densities calculated for the oxidized form are 0.730, 0.174, 0.083 and 0.013 for Re, Cl, CO and BIAN, respectively. In contrast, the spin density is localized at BIAN for the reduced complex (Figure 5). The ADF calculated EPR

parameters for $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]^{\bullet}$ reflect this spin density localization at the 5b₂ MO of BIAN. An isotropic *g* value of about 2.006 confirms the spin localization at the ligand, and a UKS calculation gave a hyperfine coupling constant a_{iso} (¹⁸⁵Re) of -35.2 G, in good agreement with the experimental value of 34.9 G for the sextet coupling from electron spin interaction with ^{185,187}Re (I = 5/2; Figure 5). This value agrees with parameters for similar cases [5,26], supporting the (α -diimine[•])/Re^I formulation.

While the chromium complex $[Cr(CO)_4(L)]$ proved rather labile under the conditions of anodic oxidation with no reliable EPR, IR or UV/VIS spectroelectrochemical information available, the rhenium compound failed to show an anodic EPR signal after reversible oxidation to $[Re(CO)_3Cl(L)]^+$, even at 4 K. Such EPR silence of rhenium(II) carbonyl species (cf. Figure 5) has been noted before [26], it is attributed to very rapid relaxation favored by large spin-orbit contributions from the heavy metal.

2.5 IR Spectroelectrochemistry

The neutral compounds $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ and $[\text{M}(\text{CO})_4(\text{L})]$ and show the expected [5,24-26] carbonyl stretching bands in the 2000 cm⁻¹ region (Figures 6 and 7, Tables 3 and 4). On oxidation of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ the bands shift significantly to higher energies, confirming a diminished π back donation on metal-based oxidation. The reversible oxidation (clean isosbestic points, 85% recovery on re-reduction) of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ produces the high-energy shifted bands with different intensity patterns for the neutral and the cationic forms (Figure 6). This variation has been noted before [26] and is attributed to a significant structure change during the metal-based oxidation (Figure 5).

Reduction of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ was observed to result in the expected [26] low-energy shifts but also in more than one kind of product, as illustrated by non-uniform band changes and poor isosbestic point behavior (Figure 6, Table 3). Careful inspection reveals a follow-up product with further low-energy shifted bands, resulting from the slow loss of chloride even

after the first reduction. Similar processes have been noted for the reduction of other complexes $[Re(CO)_3Cl(L)]$ [6]. The comparison of experimental and calculated CO stretching frequencies in Table 3 shows that calculations with PCM solvent correction reproduces the ground state IR spectrum as well as the shifts of CO stretching frequencies to higher values in the course of oxidation and to lower values for reduction.

The limited reductive lability in the present case may be compared with the complete irreversibility of even the first reduction of $[Re(CO)_3Cl(tert-Bu-DAB)]$ [26]. This slowdown is associated with the structurally established shielding of the chloride ligand in the *iso*-propyl---Cl---*iso*-propyl region (Figure 1). Although less detectable in conventional cyclic voltammetry (Figure 2), the slower time-scale of the OTTLE spectroelectrochemistrty experiment reveals this labilization which may become useful for CO₂ activation [3].

While the neutral tetracarbonylmetal complexes exhibit overlapping bands A_1/B_1 [25], the reduction reveals a splitting and thus the presence of all four IR active vibrations v(CO).

2.6 UV-vis-NIR Spectroelectrochemistry

In agreement with the frontier orbital characteristics derived from EPR (see above and Figures 5 and S4) the compounds exhibit moderately intense metal-to-ligand charge transfer (MLCT) absorptions [2-6,24-26] in the visible region (Table 5, Figures 8, 9 and S5). The energies (E_{max} in eV) at the long-wavelength band maxima match well with the difference Δ (ox-red) between the oxidation and reduction potentials, suggesting rather little inter- and intramolecular reorganization on excitation [25,29] to the 5b₂ LUMO. The structurally and ¹H NMR spectroscopically established rigidity is held responsible for the observation [3] of the apparently vibrationally structured MLCT absorption band of [Re(CO)₃Cl(L)] (Figures 8, 9). The higher MLCT transition energy for the rhenium compound [Re(CO)₃Cl(L)] is mainly due to stabilized HOMOs as confirmed by the high oxidation potential, while the series [M(CO)₄(L)], M = Cr, Mo, W, exhibits a well known trend [25], i.e. an increase in absorption

energy from the Cr via the Mo to the W analogue. A second MLCT absorption at higher energies involves a transition to the SLUMO (LUMO+1) of $4a_2$ character.

On oxidation of $[\text{Re}^{I}(\text{CO})_{3}\text{Cl}(\text{L})]$ to $[\text{Re}^{I}(\text{CO})_{3}\text{Cl}(\text{L})]^{+}$, a weak band occurs at 982 nm which is attributed to an intra-ligand transition. In all cases the reduction to the anion radical complexes $[\text{M}^{\circ}(\text{CO})_{4}(\text{L}^{\bullet})]^{-}$ and $[\text{Re}^{I}(\text{CO})_{3}\text{Cl}(\text{L}^{\bullet})]^{-}$ produced a weak near IR band at about 1200 nm with the MLCT absorption remaining largely unchanged. The NIR absorption is assigned to an intraligand transition of L^{\bullet} between the singly occupied α -diimine based MO (5b₂) and the naphthalene-delocalized MO (4a₃).

Although α -diimine compounds with the Re(CO)₃Cl complex fragment are typically emissive [24,31] we did not observe luminescence from [Re(CO)₃Cl(L)] at room temperature in the solid or in solution. Such a lack of luminescence had been observed and discussed before for related complexes [8].

The DFT calculated MO scheme with corresponding frontier molecular orbitals (FMO) of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ is depicted in Figures S4 and S6. Close lying HOMO and HOMO-1 orbitals are mainly formed by Re d_π orbitals with Cl and CO contributions. The LUMO is mainly composed from the π^* BIAN orbital (88%) with slight metal d_{xz} (4%) and CO contributions. The LUMO+1 has purely π^* BIAN character (4a₂) and is separated from the 5b₂ LUMO by 0.71 eV, a rather large energy gap. In the course of oxidation an electron is withdrawn from a metal based MO whereas the reduction introduces an electron preferably to a BIAN localized orbital. TD DFT calculated low lying excitations are listed for three oxidation states in Table

3. Conclusion

6.

In contrast to what may have been expected from an unreflected MO analysis there was no evidence in our experiments for the acquisition of more than two electrons [12] by carbonylmetal complexes of BIAN. Such excess reduction will require the presence of charge

compensating cations [13a-d], and neither $[M(CO)_5]$ fragments nor $[Re(CO)_3Cl]$ meet this requirement.

The electrochemical and spectroelectrochemical results presented in this study do therefore not support the notion that the BIAN ligands can act as special electron "reservoirs" or electron "sponges". The two acceptor MOs, α -diimine centered 5b₂ and the more naphthalene based 4a₂, are well separated in energy. An extended π system and the N-substitution with electron-accepting aryl groups produce a low-lying but not extremely stabilized [30] LUMO. Furthermore, the MO situation at the metal-ligand interface is not unusual, as evident from the fairly conventional metal and nitrogen hyperfine coupling in the EPR spectra of radical anion complexes. Summarizing, the BIAN ligands are good π acceptors but do not exhibit exceptional suitability for multielectron transfer reactivity, which would be required e.g. for CO₂ reduction beyond the CO [2-4] or formate stage.

4. Experimental Section

The following compounds were commercially available: Pentacarbonylchlororhenium (ABCR), hexacarbonylchromium (ABCR), hexacarbonyltungsten (Fluka), acenaphthylenequinone (ABCR), diisopropylamine (TCl).

The solvents were dried under argon atmosphere according to standard procedures. All reactions were carried out using standard Schlenk techniques. The chromatography columns contained silica gel 90 Dm (Merck).

4.1 Instrumentation.

EPR spectra in the X band were recorded with a Bruker System EMX. ¹H-NMR spectra were taken on a Bruker AC 250 spectrometer. IR spectra were obtained using a Nicolet 6700 FT-IR instrument; solid state IR measurements were performed with an ATR unit (smart orbit with diamond crystal). UV-Vis-NIR absorption spectra were recorded on J&M TIDAS and Shimadzu UV 3101 PC spectrophotometers. Cyclic voltammetry was carried out in 0.1 M Bu₄NPF₆ solutions using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^{+}) reference. couple served internal as Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell [31]. A two-electrode capillary served to generate intermediates for X band EPR studies [32].

4.2 Syntheses

Compounds $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$][3,8,13f] and $[\text{Mo}(\text{CO})_4(\text{L})]$ [13e] have been described earlier. $[\text{Cr}(\text{CO})_4(\text{L})]$. A solution of hexacarbonylchromium (100 mg, 0.46 mmol) and L (568.8 mg, 1.14 mmol) in THF (40 mL) was stirred for 8 h under UV irradiation. The solvent was

removed under reduced pressure and the resulting green thermo- and photolabile solid was run three times over a silica gel column (pentane/THF= 20/1). Yield 35 mg (12 %). Anal. Calcd for $C_{40}H_{40}CrN_2O_4$ (664.75 g/mol) × 0.2 C_5H_{12} × 0.3 THF: C, 72.26; H, 6.52; N, 3.99%. Found: C, 72.15; H, 6.52; N, 3.98%. ¹H-NMR (CDCl₃): δ [ppm] = 0.91 (d, 12H, *CH*₃-Ar, *J* = 6.9 Hz), 1.4 (d, 12H, *CH*₃-Ar, *J* = 6.9 Hz), 3.14 (sept, 4H, C-*H*, *J* = 7.3 Hz), 6.41 (d, 2H, Ar-*H*, *J* = 7.2 Hz), 7.34 (8 H, m, Ar-*H*), 7.81 (d, 2H, Ar-*H*, *J* = 8.4 Hz).

[W(CO)₄(L)]. A solution of hexacarbonyltungsten (80 mg, 0.15 mmol) and L (186.3 mg, 0.37 mmol) in THF (30 mL) was stirred for 3 h under UV irradiation. The solvent was removed under reduced pressure and the resulting green solid was purified using a silica gel column (pentane/ THF= 20/1). Yield 94 mg (80 %). Anal. Calcd for C₄₀H₄₀N₂O₄W (796.60 g/mol) × 0.1 C₃H₁₂ × 0.35 THF: C, 60.70; H, 5.35; N, 3.38%. Found: C, 60.20; H, 5.36; N, 3.38%. ¹H-NMR (CDCl₃): δ [ppm] = 0.87 (d, 12H, *CH*₃-Ar, *J* = 6.9 Hz), 1.38 (d, 12H, *CH*₃-Ar, *J* = 6.9 Hz), 3.12 (sept, 4H, C-*H*, *J* = 7.0 Hz), 6.33 (d, 2H, Ar-*H*, *J* = 7.2 Hz), 7.37 (8 H, m, Ar-*H*), 7.87 (d, 2H, Ar-*H*, *J* = 8.4 Hz).

4.3 Crystallography

Single crystals of $[Re(CO)_{3}Cl(L)]$ were obtained from a dichloromethane solution at -18°C. X-ray diffraction (XRD) data were collected using a Bruker Kappa Apex2duo diffractometer. The structure was solved using the Patterson method with refinement by full-matrix least-squares techniques on F^{2} employing the program system SHELX-97 [35a]. The absorption corrections were done by the multiscan technique [35b]. Since the solvent molecules could not be located, the PLATON/SQEEZE procedure [35c] was used. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model.

4.4 Quantum chemical calculations

Electronic structures were calculated by the density functional theory (DFT) method using the Gaussian 09 [36] and ADF 2014.01 [37] program packages. The optimized geometries of the ground state of $[Re(CO)_3Cl(L)]$ and of its oxidized and reduced forms were calculated. The DFT calculations employed the Perdew, Burke, Ernzerhof [38,39] hybrid functional. For H, C, N, O and Cl atoms, either polarized triple- ζ basis sets 6-311g(d) [40] (geometry optimization) or cc-pvdz correlation-consistent polarized valence double- ζ basis sets [41] (calculations of spectral transitions) were used. The Re orbitals were described with quasirelativistic effective core pseudopotentials and a corresponding optimized set of basis functions [42,43]. Geometry optimizations were followed by vibrational analyses in order to characterize stationary states. The solvent was described by the polarizable continuum model (PCM) [44]. Low-lying excitation energies were calculated by time-dependent DFT (TD-DFT) at the optimized geometry.

Within the ADF program Slater type orbital (STO) basis sets of triple- ζ quality with two polarisation functions for Re, C, N, O and Cl atoms and double- ζ with one polarization function for H atom were employed. Inner shells were represented by the frozen core approximation (1s for C, N and O, 2p for Cl and 1s-4d for Re were kept frozen) within the calculation of the *g* tensor, core electrons were included in the calculation of the *A* tensor. Within ADF the PBE0 functional was used (ADF/PBE0). *A* and *g* tensors were obtained by first-order perturbation theory from a ZORA Hamiltonian in the presence of a time-independent magnetic field [45,46]. The *g* tensor was obtained from a spin-polarized wave function after incorporating the spin-orbit (SO) coupling.

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Appendix A. Supplementary material

.ine vers Supplementary data associated with this article can be found, in the online version, at

http://dx.doi.org/xxx.

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Table 1

Redox potentials $E_{1/2}$ (ΔE) of compounds from cyclic voltammetry.^a

| | $E_{_{1/2}}(\Delta E)$ | | ~ |
|--|------------------------|--------------|--------------|
| | oxidation | 1. reduction | 2. reduction |
| $[\operatorname{Re}(\operatorname{CO})_{3}\operatorname{Cl}(L)]^{b}$ | 1.17 (140) | -1.11 (140) | (-2.04) |
| $[Cr(CO)_4(L)]^c$ | 0.06 (90) | -1.56 (90) | -2.14 |
| $[Mo(CO)_4(L)]^c$ | (0.30) | -1.45 (110) | (-2.40) |
| $\left[W(CO)_4(L)\right]^c$ | (0.22) | -1.40 (70) | (-2.43) |

^a Potentials $E_{1/2}$ vs Fc^{+/o}, peak potential differences ΔE in mV/s. Peak potentials for irreversible processes in parentheses. Scan rate 100 mV/s, 0.1 M Bu₄NPF₆ as electrolyte.

 b In CH₂Cl₂ solution.

^e In DMF solution.

Table 2

EPR Data of reduced complexes at 298 K in CH₂Cl₂/0.1 M Bu₄NPF₆.

| | <i>g</i> ; <i>a</i> (G) |
|--|---|
| $[\operatorname{Re}(\operatorname{CO})_{3}\operatorname{Cl}(L)]^{\bullet}(\exp)$ | $2.0042; 6.10 (^{14}N), 34.9 (^{185,187}Re)$ |
| $[\operatorname{Re}(\operatorname{CO})_{3}\operatorname{Cl}(\operatorname{L})]^{\bullet}(\operatorname{calc})$ | 2.0060^{a} ; 5.00 (¹⁴ N), -35.2 (^{185,187} Re) ^b |
| $[Cr(CO)_4(L)]^{\bullet}$ | 2.0031; 6.5 (¹⁴ N), 3.5 (⁵³ Cr) |
| $[Mo(CO)_4(L)]^{\bullet}$ | 2.0044; 6.15 (¹⁴ N), 3.2 (^{95.97} Mo) |
| $[W(CO)_4(L)]^{\bullet}$ | 2.0069; 5.90 (¹⁴ N), 6.7 (¹⁸³ W) |
| | |

^aCalc.: $g_1 = 2.010, g_2 = 2.008, g_3 = 2.000.$

^b Calc.: *A*₁ = -38.2 G, *A*₂ = -37.5 G, *A*₃ = - 30.0 G.

Table 3

Experimental and G09/PBE0/PCM-CH₂Cl₂ calculated CO stretching frequencies of $[Re(CO)_{3}Cl(L)]^{n}$.

| Experin | nental (cn | n^{-1}) in | | | Calculat | $ed^{a}(cm^{-1})$ | | | |
|-----------------------------------|------------|---------------|-------------------|----------|----------|-------------------|----|-------|----------|
| CH ₂ Cl ₂ / | 0.1 M Bu | $_4$ NPF $_6$ | | | | | | | |
| n=0 | n= 1 | Δ | n= -1 | Δ | n=0 | n= 1 | Δ | n= -1 | Δ |
| | | | | | | | | | |
| 1904 | 2005 | 101 | 1859 ^b | -45 | 1909 | 1989 | 80 | 1865 | -44 |
| | | | | | | | | | |
| 1937 | 2039 | 102 | 1884 [°] | -53 | 1934 | 2018 | 84 | 1885 | -50 |
| | | | | | | | | | |
| 2025 | 2093 | 68 | 1995 ^ª | -30 | 2026 | 2089 | 63 | 1999 | -37 |
| | | | | | AV | | | | |

^a Scaling factor 0.961.

^b Follow-up species: 1841 cm⁻¹ (sh).

^c Follow-up species: 1853 cm⁻¹.

^d Follow-up species: 1961 cm⁻¹.

Table 4

IR Spectroelectrochemical data of complexes.^a

| n | $[Mo(CO)_{4}(L)]^{n}$ | $\left[W(CO)(L)\right]^{n}$ |
|----------|--|-----------------------------|
| | | |
| 0 | 2006, 1907, 1860 | 2000, 1898, 1863 |
| -1 | 1983, 1861, 1848sh, 1809 | 1974, 1845, 1840sh, 1806 |
| ' In DMF | $F/0.1 \text{ M Bu}_4\text{NPF}_6$, values $v(\text{CO})$ in cm ⁻¹ . | |
| | | |
| | | |
| | R | |
| 6 | 5 | |
| | | |

Table 5

UV/VIS/NIR Spectroelectrochemical data of complexes.^a

| complex | n = 0 | n = -1 | n = +1 |
|---|-------------------------|-------------|------------|
| [Re(CO) ₃ Cl(L)] ⁿ | 294 (5300) | 293 (5100) | 286 (6300) |
| | 330 (3050) | 327 (3400) | 345 (4800) |
| | 368 (2500) | 375 (3200) | 447 (2700) |
| | 496 (3100) | 498 (2800) | 960 (200) |
| | 517 (3050) ^d | 1150 (150) | |
| $[Cr(CO)_4(L)]^{\flat}$ | 328 (7380) | N/A | N/A |
| | 441 (2750) | | |
| | 670 (8530) ^e |) | |
| $\left[\operatorname{Mo}(\operatorname{CO})_4(\operatorname{L})\right]^{\operatorname{nb}}$ | 301 (14000) | 302 (19000) | N/A |
| | 330 (7500) | 361 (13000) | |
| | 392 (6300) | 415 (sh) | |
| 0 | 611 (14500) | 568 (5900) | |
| | | 1320 (930) | |
| $[W(CO)_4(L)]^{nc}$ | 301 (3500) | 300 (sh) | N/A |
| | 330 (1900) | 362 (2900) | |
| | 406 (1900) | 412 (sh) | |
| | | | |

613 (5700) 596 (1500)

1290 (190)

Acceleration

Table 6

TD-DFT (PBE0/PCM-CH₂Cl₂) Calculated lowest lying transitions of $[Re(CO)_{3}Cl(L)]^{n}$ with oscillator strengths larger than 0.005^{a} .

| | state | main contributing excitations | calc. transition | calc. | exp. abs. | molar |
|---|------------------|--|---------------------|-------|------------|----------------------------------|
| n | | (%) | energy ^b | osc. | maximum | extinction |
| | | | eV (nm) | str. | eV (nm) | M ⁻¹ cm ⁻¹ |
| | b ¹ A | 97 (HOMO-1 \rightarrow LUMO) | 2.44 (507) | 0.169 | 2.40(517) | 3050 |
| | | | | S | 2.50(496) | 3100 |
|) | c ¹ A | 84 (HOMO \rightarrow LUMO+1) | 3.20 (387) | 0.119 | 3.37(368) | 2500 |
| | d ¹ A | 91 (HOMO-8 \rightarrow LUMO) | 3.77 (329) | 0.046 | | |
| | e ¹ A | 76 (HOMO-10 \rightarrow LUMO) | 3.83 (324) | 0.123 | 3.76(330) | 3050 |
| | $f^{i}A$ | 14 (HOMO-6 \rightarrow LUMO+1) | 3.96 (313) | 0.158 | 4.22(294) | 5300 |
| | b ² A | $98(\alpha HOMO \rightarrow \alpha LUMO)$ | 1.15 (1073) | 0.018 | 1.08(1150) | 150 |
| | c ² A | 84 (β HOMO-1 $\rightarrow \beta$ LUMO) | 2.76 (449) | 0.050 | 2.49(498) | 2800 |
| 1 | d ² A | 81(α HOMO $\rightarrow \alpha$ LUMO+2) | 3.02 (410) | 0.066 | | |
| | e ² A | $79(\alpha HOMO-1 \rightarrow \alpha LUMO)$ | 3.29 (377) | 0.102 | 3.31(375) | 3200 |
| | $f^{2}A$ | $67(\alpha HOMO \rightarrow \alpha LUMO+5)$ | 3.36 (368) | 0.016 | | |



^a MOs involved in calculated transitions are depicted in Figures S6, S7, S8. ^b Wavelengths in

parentheses.









Fig. 1. Molecular structure of $[Re(CO)_{3}Cl(L)]$ in the crystal from various perspectives.



Fig. 2. Cyclic voltammogram of [Re(CO)₃Cl(L)] in CH₂Cl₂/0.1 M Bu₄NPF₆ at 100 mV/s.



Fig. 3. Cyclic voltammograms of $[Cr(CO)_4(L)]$ (top) and $[W(CO)_4(L)]$ (bottom) in DMF/0.1 M Bu₄NPF₆ at 100 mV/s.



Fig. 4. EPR spectrum of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]^{\bullet}$ in $\text{CH}_2\text{Cl}_2/0.1$ M Bu₄NPF₆ at 298 K (top) with simulation (bottom).



Fig. 5. DFT (PBE0/PCM-CH₂Cl₂) calculated spin density for $[Re(CO)_3Cl(L)]^n$ for n=1 and n=-1 from top to bottom, respectively.



Fig. 6. IR spectroelectrochemical response of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ on oxidation (top) and reduction (bottom) in CH₂Cl₂/0.1 M Bu₄NPF₆.



Fig. 7. IR spectroelectrochemical response of $[Mo(CO_4)(L)]$ on reduction in DMF/0.1 M Bu₄NPF₆.



Fig. 8. Spectroelectrochemical response for the oxidation of $[Re(CO)_3Cl(L)]$ in CH₂Cl₂/0.1 M Bu₄NPF₆ in the UV/VIS (top) and NIR region (bottom).



Fig. 9. Spectroelectrochemical response for the reduction of $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ in $\text{CH}_2\text{Cl}_2/0.1$ M Bu_4NPF_6 in the UV/VIS (top) and NIR region (bottom).



Fig. 10. α HOMO and α LUMO spin orbitals involved in the lowest lying excitation (calculated at 1073 nm) of [Re(CO)₃Cl(L)][•].

Graphical abstract

The BIAN ligand 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene: An electron sponge or a "normal" α-diimine ligand ?

Isabell Löw, Martina Bubrin, Alexa Paretzki, Jan Fiedler, Stanislav Záliš, Wolfgang Kaim*

Despite a capacity for multistep reduction there is no evidence for special multielectron transfer behavior of the BIAN ligand system in carbonylmetal complexes beyond the established two-electron process for CO_2/CO conversion.



