

Synthesis and Characterization of Novel $\text{Re}(\text{BIAN})(\text{CO})_3\text{Cl}$ Derivatives Including the First Example of a Water-soluble Tricarbonyl Rhenium(I) Complex with Bis(imino)acenaphthene Ligands

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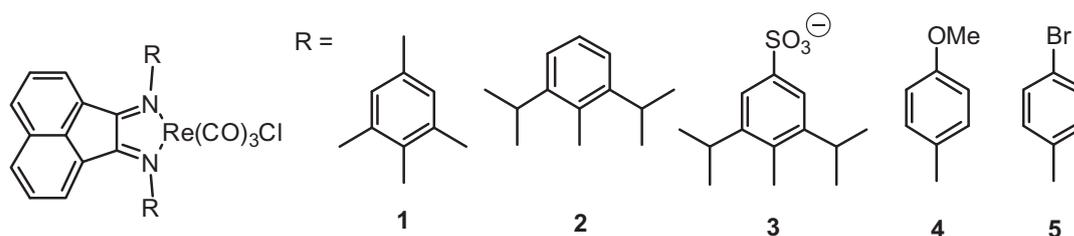
A series of rhenium(I) carbonyl chloride complexes carrying bis(imino)acenaphthene (BIAN) molecules as π -acceptor ligands was prepared and characterized by various spectroscopic techniques. Among the novel compounds described, the remarkable example of a deeply colored water-soluble rhenium carbonyl derivative is presented. The crystal structures of this family of BIAN compounds are also reported, which confirm the position of the chloro ligand at the tricarbonyl rhenium(I) center. In the case of BIAN ligands carrying bulky substituents in the *ortho*-position of the arylimino subunits, evidence has been found for an exchange of the halide ligand in solution, which is considered to be of major relevance for catalytic applications. Implications of our results for the fields of photocatalytic CO_2 reduction and the controlled release of the gas transmitter CO in aqueous solution are briefly discussed.

Key words: Rhenium, Carbonyl Complexes, Water Solubility, BIAN Ligands, Crystal Structures

Introduction

Tricarbonyl rhenium(I) complexes of the type *fac*- $\text{Re}(1,2\text{-diimine})(\text{CO})_3\text{Cl}$ carrying polypyridyls such as *o*-phenanthroline or 2,2'-bipyridine as diimine ligands have been extensively studied for many years due to their exceptionally rich photophysical and photocatalytic properties [1–5]. These compounds are characterized by the presence of low-lying excited states with significant metal-to-ligand charge transfer (MLCT) character, which can participate in bimolecular elec-

tron transfer processes. In order to shift the charge transfer absorption bands of such systems to longer wavelengths [6, 7], we introduced new derivatives with strong π -acceptor moieties such as $\text{Re}(\text{BIAN})(\text{CO})_3\text{Cl}$ complexes [7], where aryl-substituted derivatives of BIAN = bis(imino)acenaphthene instead of polypyridyls are coordinated to the tricarbonyl rhenium moiety as bidentate *N*-donor chelates. This turned the 1,2-diimine metal complexes into attractive photosensitizers for solar energy conversion in advanced photocatalytic systems and solar cell devices [8, 9].



Scheme 1.

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Here, the synthesis and characterization of novel Re(BIAN)(CO)₃Cl complexes **1–3** are reported (Scheme 1), together with the first molecular structures of such compounds. Moreover, the important class of *fac*-Re(1,2-diimine)(CO)₃Cl complexes has been successfully expanded to include also a water-soluble organometallic rhenium(I) derivative [10–12], which is a highly desirable feature for many biomedical and catalytic applications such as cell imaging, light-controlled release of carbon monoxide (PhotoCORMs), and homogeneous photocatalytic CO₂ reduction.

Results and Discussion

Synthesis and characterization

The title compounds were readily obtained by stirring the corresponding BIAN ligands with rhenium pentacarbonyl chloride under reflux in toluene. In the course of this reaction, deep-red products formed, indicating low-lying charge transfer absorption bands characteristic for the successful metallation process [7].

Typical UV/Vis spectra of the isolated compounds are displayed in Fig. 1. The main absorption maxima of all five complexes are summarized in Table 1.

The Re(BIAN)(CO)₃Cl complexes **1–3**, all carrying *ortho*-substituents at the arylimino groups of the BIAN ligand, display a more or less pronounced shoulder in their broad visible absorption band (Fig. 1), which had not been observed in the parent phenyl-BIAN compound and its *para*-substituted derivatives [7] such as **4** or **5** (Table 1).

This behavior is also observed in non-coordinating solvents like dichloromethane. Depending on the solvent used, however, the intensity ratio of the two absorption peaks in the charge transfer region may

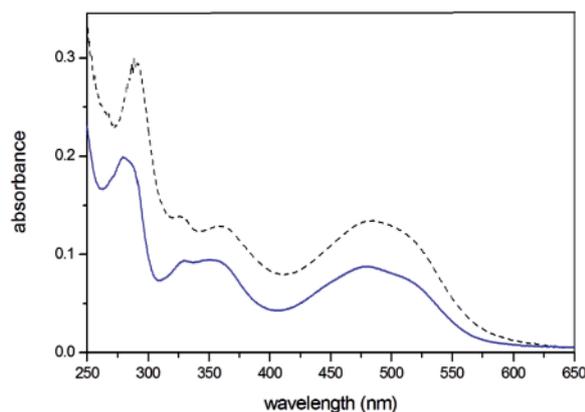


Fig. 1. Electronic absorption spectra of compound **1** in acetonitrile (dashed line) and compound **3** in aqueous solution (solid line) at $c = 1.7 \times 10^{-5}$ M and $c = 1.4 \times 10^{-5}$ M, respectively (1-cm cell).

vary. Furthermore, the bands in the visible region of all rhenium complexes undergo a bathochromic shift with decreasing solvent polarity. This negative solvatochromism is directly related to the charge transfer character of the corresponding electronic transitions. The solvatochromic shifts usually become smaller with an increasing π -acceptor strength of the diimine ligand and as a consequence of stronger mixing between metal $d\pi$ and ligand π^* orbitals. A less pronounced solvatochromic behavior than for the corresponding polypyridyl systems like 2,2'-bipyridine has been reported for BIAN derivatives, which could be attributed to an increased mixing between rhenium and ligand orbitals in the latter case [7]. Nevertheless, the charge transfer character of the chromophoric bands in the visible spectral region of Re(BIAN)(CO)₃Cl complexes is expected to dominate the excited state properties. This is also illustrated by quantum-chemical calculations, which indicate that the frontier orbital transitions are occurring mainly from the tricarbonyl rhenium(I) chlo-

Table 1. UV/Vis spectroscopic data of the substituted Re(BIAN)(CO)₃Cl derivatives **1–3**^a, **4**^b and **5**^b in acetonitrile solution unless otherwise noted and at 298 K.

Compound	λ_{\max} (in nm)	ϵ (in L mol ⁻¹ cm ⁻¹) in parentheses				
1	225 (77500)	291 (18300)	326 (8600)	368 (8000)	483 (8400)	522 sh ^c
2	228 (49400)	289 (9600)	330 (5100)	368 (4500)	489 (5000)	519 sh
3	228	293	328	368	488 sh	518
3 ^d	228 (56700)	278 (14200)	328 (6500)	353 (7200)	481 (6200)	516 sh
4	223 (51200)	285 (13500)	–	370 (7200)	451 (6600)	–
5	223 (65400)	288 (14800)	323 (8400)	350 (8600)	481 (5600)	–

^a This work; ^b data from ref. [7]; ^c sh: shoulder; ^d data obtained in H₂O.

ride moiety to the π^* orbitals of the BIAN acceptor ligands (Fig. 2).

The identity of the isolated compounds was further confirmed by ¹H NMR spectroscopy in CDCl₃ or D₂O solution (see Experimental Section), and by positive ion electrospray mass spectroscopy of samples in acetonitrile. Interestingly, the ESI-MS spectra of complexes **1** and **2** exclusively showed molecular ions of cationic solvent adducts of the type [Re(BIAN)(CH₃CN)(CO)₃]⁺ clearly resulting from a loss of the chloro ligand. A similar behavior is absent in the mass spectra of the *para*-substituted bis(arylimino)acenaphthene complexes [7], where such a facile substitution of the rhenium-bound chloro ligand by acetonitrile requires photochemical activation [13]. These results might indicate that the rhenium tricarbonyl chloride fragment of

Re(BIAN)(CO)₃Cl complexes has an increased preference for chloride exchange in the presence of bulky *ortho*-substituents at the BIAN ligand, which is consistent with the assumption of a dissociative substitution mechanism. It should be noted that the intermediate formation of a coordinatively unsaturated rhenium center is of considerable interest for potential applications of such compounds as novel catalysts for CO₂ reduction [5, 14]. In the case of the sulfonated compound **3**, the ESI-MS spectrum measured with samples in water/acetonitrile displayed the undecomposed molecular ion [MH]⁺ of the corresponding sodium salt.

The Re(CO)₃ moiety of the new rhenium complexes was characterized with FTIR spectroscopy. In all cases, the occurrence of three CO stretching vibrations in the region between 2020 and 1880 cm⁻¹ is consistent with a facial (*fac*) arrangement of the three carbonyl ligands as expected. Accordingly, the BIAN ligands function as bidentate ligands, resulting in regular pseudooctahedral *d*⁶ complexes of the *fac*-Re(1,2-diimine)(CO)₃Cl family. In the water-soluble compound **3**, a characteristic strong peak at 1192 cm⁻¹ which is absent in the other complexes is assigned as the symmetrical SO stretching vibration of the sulfonato groups. The experimental FTIR spectra of the rhenium carbonyl complexes are in good agreement with the theoretical spectra obtained from DFT calculations (Fig. 3).

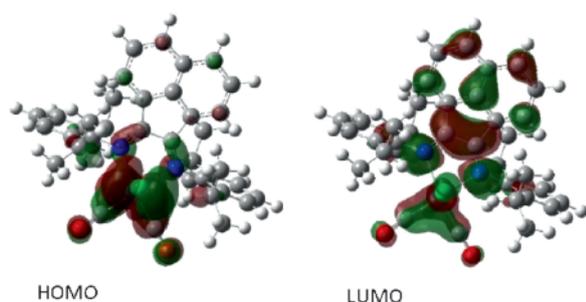


Fig. 2 (color online). Contour plots of the highest occupied (left) and the lowest unoccupied molecular orbitals of complex **2** (from DFT calculations at the B3LYP/6-31G(d,p)/Lan2DZ(Re) level).

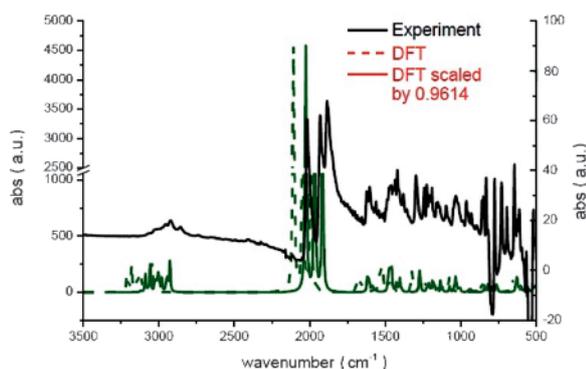


Fig. 3 (color online). Comparison of experimental and DFT-calculated IR spectra of complex **1**. All vibrational frequencies were scaled down with the recommended correction factor [15].

Crystal and molecular structures

Slow diffusion of diethyl ether into dichloromethane solutions of complexes **1**, **2**, **4**, and **5** afforded brownish-red crystals suitable for X-ray diffraction. Compounds **2**, **4** and **5** crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$ molecules in the unit cell. Complex **1** crystallizes as the toluene solvate in the orthorhombic space group $Pna2_1$ with $Z = 4$. The BIAN ligand acts as a bidentate chelate ligand, and the Re–N distances are in the range of 2.157–2.208 Å (Fig. 4). The bite angle of the BIAN ligand is between 75 and 76°. The Re atom exists in a distorted octahedral environment within a facial arrangement of three carbonyl groups, the two nitrogen atoms of the BIAN ligand and the chloride atom. In all complexes the Re–Cl bond lengths are almost identical (2.46–2.47 Å). Further structural data and details of the structure determinations are summarized in Tables 2 and 3, respectively.

In the case of the water-soluble complex **3**, crystallization of the deprotonated form from methanol/diethyl ether yielded small crystals of acceptable qual-

ity. Two different kinds of crystals could be isolated, one species containing water and the other methanol as crystal solvent. The refinement of the hydrate

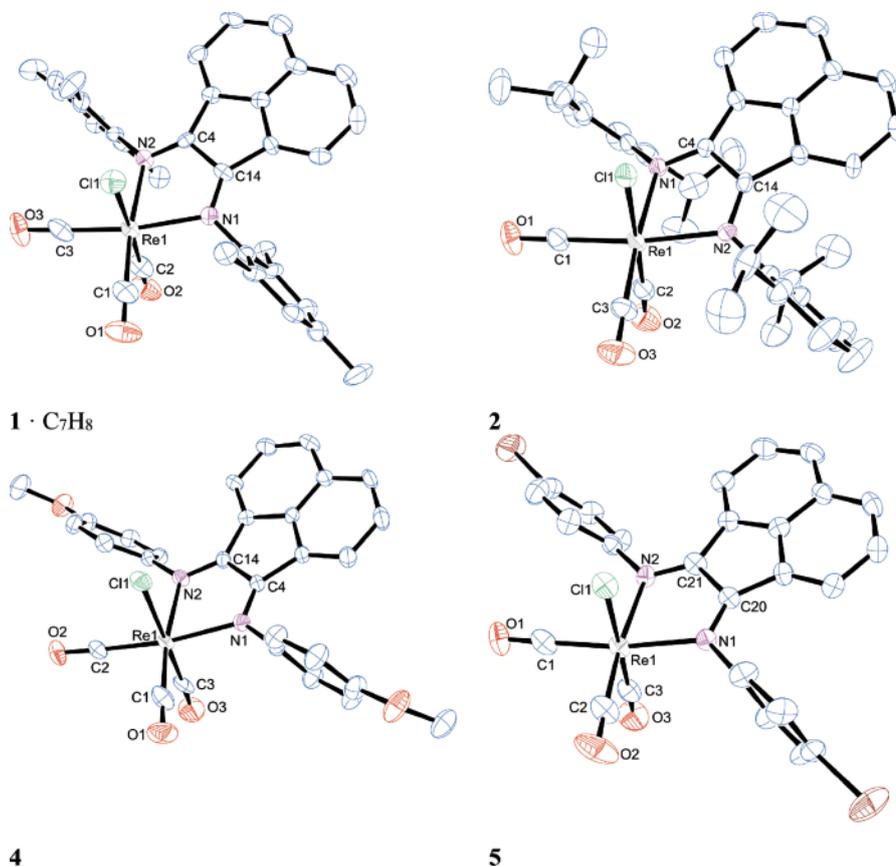


Fig. 4 (color online). Molecular structures of complexes **1** · C₇H₈, **2**, **4**, and **5** (ORTEP; displacement ellipsoids at the 50% probability level; H atoms and solvent molecules are omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (deg) of complexes **1** · C₇H₈, **2**, **3** · (MeOH)₃, **4**, and **5**.

Bond lengths	1 · C ₇ H ₈	2	3 · (MeOH) ₃	4	5
Re1–N1/Re1–N2	2.18(1) 2.18(1)	2.187(4) 2.180(4)	2.18(1) 2.19(2)	2.157(4) 2.208(4)	2.161(4) 2.176(4)
Re1–Cl1	2.462(2)	2.479(2)	2.47(1)	2.463(1)	2.473(1)
Re–CO (<i>trans</i> to Cl)	1.91(1)	1.913(7)	1.93(3)	1.93(1)	1.90(1)
Re–CO (<i>trans</i> to N)	1.92(1) 1.92(1)	1.92(1) 1.93(1)	1.86(3) 1.99(3)	1.93(1) 1.93(1)	1.92(1) 1.91(1)
Angles					
N1–Re1–N2	75.8(2)	76.2(2)	75(1)	75.2(2)	74.8(1)
Cl1–Re1–CO (<i>trans</i>)	176.2(2)	178.5(2)	177(1)	178.0(2)	179.1(1)
N–Re–CO (<i>trans</i>)	171.2(3) 171.4(3)	173.1(2) 172.3(2)	172(1) 173(1)	171.9(2) 169.6(2)	171.7(2) 170.3(2)

Table 3. Crystal structure data for **1** · C₇H₈, **2**, **3** · (MeOH)₃, **4**, and **5**.

Compound	1 · C ₇ H ₈	2	3 · (MeOH) ₃	4	5
Empirical formula	C ₄₀ H ₃₆ ClN ₂ O ₃ Re	C ₃₉ H ₄₀ ClN ₂ O ₃ Re	C ₄₂ H ₄₇ ClN ₂ Na ₂ O ₁₂ ReS ₂	C ₂₉ H ₂₀ ClN ₂ O ₅ Re	C ₂₇ H ₁₄ Br ₂ ClN ₂ O ₃ Re
Molecular weight, g mol ⁻¹	814.36	806.38	1103.57	698.12	795.87
Size, mm ³	0.50 × 0.25 × 0.11	0.63 × 0.42 × 0.32	0.49 × 0.09 × 0.09	0.44 × 0.25 × 0.12	0.41 × 0.30 × 0.20
Crystal system	orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	19.765(2)	10.2350(5)	10.267(1)	9.0947(8)	8.874(1)
<i>b</i> , Å	19.578(2)	11.9736(6)	19.738(4)	11.522(1)	11.691(1)
<i>c</i> , Å	8.9218(8)	18.6448(8)	25.678(4)	12.922(1)	12.970(2)
α , deg	90	80.064(2)	90	71.144(3)	72.246(4)
β , deg	90	87.707(2)	95.643(5)	89.949(3)	87.428(4)
γ , deg	90	65.500(2)	90	83.113(3)	79.243(4)
<i>V</i> , Å ³	3452.3(6)	2046.7(2)	5178(2)	1271.2(2)	1258.8(3)
$\rho_{\text{calcd.}}$, g cm ⁻³	1.57	1.31	1.41	1.82	2.10
<i>Z</i>	4	2	4	2	2
$\mu(\text{MoK}\alpha)$, mm ⁻¹	3.6	3.1	2.6	4.9	8.1
<i>T</i> , K	200	200	200	200	205
θ_{max} , deg	22.9	25.0	17.5	25.1	25.1
Measured reflections	21700	7186	21633	15775	24495
Independent reflections	3969	7186	3183	4455	4424
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3130	6653	2843	4157	3913
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.47/0.69	0.25/0.44	0.37/0.80	0.33/0.59	0.14/0.29
Restraints/refined param.	1/431	0/423	0/537	0/345	0/325
<i>R</i> 1 [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.028	0.040	0.063	0.037	0.027
<i>wR</i> 2 (<i>F</i> ²)	0.052	0.097	0.166	0.095	0.067
Flack parameter <i>x</i>	-0.011(9)	–	–	–	–
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.48 / -0.37	3.22 / -1.33	2.53 / -0.59	2.72 / -2.37	1.11 / -1.11
CCDC number	973347	973348	973350	973351	973352

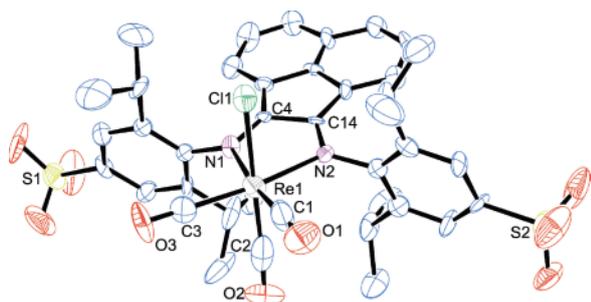


Fig. 5 (color online). Molecular structure of the dianion in crystals of the sodium salt of **3** · (MeOH)₃. (ORTEP; displacement ellipsoids at the 50% probability level; H atoms, sodium atoms, and methanol molecules are omitted for clarity).

3 · (H₂O)_{*x*} was complicated by an ill-defined amount of water molecules, and the final structure is of poor quality indicating some serious crystallographic problems which could not be solved sufficiently. For completeness, these data are presented in the Supporting Information only and are not further discussed here (see note at the end of the paper for availability).

The refinement of the methanol solvate **3** · (MeOH)₃ yielded structural data of acceptable quality (*P*2₁/*n*, *Z* = 4). In both crystals, the sulfonated BIAN acts as a bidentate ligand as for the other complexes, and the rhenium atom exists in a quasi-octahedral environment (Fig. 5). The oxygen atoms of both the sulfonate groups and the methanol molecule are coordinated to

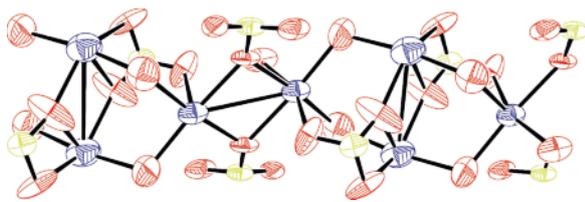


Fig. 6 (color online). Excerpt of the cell plot depicting the aggregation of the sodium ions (blue – sodium; red – oxygen; yellow – sulfur. ORTEP; displacement ellipsoids at the 50% probability level).

the sodium atoms in bridging modes forming infinite chains (Fig. 6).

Summary and Conclusion

We have synthesized and characterized a series of novel tricarbonyl rhenium(I) complexes carrying aryl-substituted bis(imino)acenaphthene (BIAN) ligands including the first water-soluble derivative of this class of organometallic compounds. Spectrometric evidence was found that a loss of the chloro ligand and the generation of a coordinatively unsaturated site at the rhenium center may be influenced by the substitution pattern in the aryl groups connected to the 1,2-diimine core of these complexes. The novel rhenium(I) complexes reported here, and in particular also the red-brown water-soluble carbonyl complex, display promising properties for potential applications as molecular catalysts for the reduction of carbon dioxide [5, 14] and as biocompatible pro-drugs for the controlled photochemical release of carbon monoxide (PhotoCORMs) [11]. Studies in these directions are currently underway in our group.

Experimental Section

Materials and instrumentation

All starting materials were commercially available and used as received without further purification. The bis(arylimino)acenaphthene ligands BIAN-R were prepared from acenaphthenequinone and the corresponding substituted anilines in analogy to literature methods [6, 16]. NMR spectra were recorded at room temperature in CDCl₃ or D₂O on a Bruker Digital Avance III (300 MHz) spectrometer. ¹H NMR shifts are reported in ppm relative to Si(CH₃)₄ and were referenced internally to the residual signal of the deuterated solvent. UV/Vis absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. FTIR spec-

tra in the 4000–400 cm⁻¹ range were recorded from the solid materials on a Shimadzu IR-Affinity-1 spectrometer equipped with a Specac Golden Gate single reflection diamond ATR accessory. Mass spectra were recorded on a Finnigan LCQDecaXPplus ion trap mass spectrometer with an ESI ion source.

Syntheses

For the preparation of compounds **1** and **2**, equimolar amounts of Re(CO)₅Cl and the corresponding bis(arylimino)acenaphthene ligand were refluxed in dry toluene for 30 min. Complete precipitation of the products was achieved upon cooling the reaction mixture to room temperature and slow addition of *n*-hexane. The deeply red-brownish precipitates were filtered off and dried *in vacuo*. Preparation of the water-soluble derivative **3** required a modified procedure, which is described in detail below. The synthesis of the rhenium carbonyl complexes **4** and **5** has already been reported elsewhere [7].

Re(2,4,6-Me₃C₆H₂-BIAN)(CO)₃Cl (**1**)

Reaction of Re(CO)₅Cl (0.05 g, 0.14 mmol) with Mes-BIAN (0.057 g, 0.14 mmol) yielded 85 mg (85%) of a brownish powder. – ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.98 (d, *J* = 8.17 Hz, 2H), 7.42 (t, *J* = 7.80 Hz, 2H), 7.06 (s, 2H), 6.95 (s, 2H), 6.67 (d, *J* = 7.2 Hz, 2H), 2.56 (s, 6H), 2.35 (s, 6H), 2.07 (s, 6H) ppm. – IR: ν(CO) = 2016, 1931, 1884 cm⁻¹. – MS (ESI, MeCN-H₂O): *m/z* (%) = 728.00 (100) [(Mes-BIAN)(CO)₃Re+MeCN]⁺, 687.27 (50) [(Mes-BIAN)(CO)₃Re]⁺. – UV/Vis (MeCN): λ_{max} = 225, 291, 326, 368, 483, 522(sh) nm.

Re(2,6-*i*Pr₂C₆H₃-BIAN)(CO)₃Cl (**2**)

Reaction of Re(CO)₅Cl (0.05 g, 0.14 mmol) with *i*Pr₂BIAN (0.07 g, 0.14 mmol) yielded 90 mg (82%) of a brownish powder. – ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.94 (d, *J* = 8.3 Hz, 2H), 7.2–7.4 (m, 8H), 6.47 (d, *J* = 7.2 Hz, 2H), 4.15 (m, 2H), 3.02 (m, 2H), 1.35 (d, *J* = 6.65 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.04 (d, *J* = 6.7 Hz, 6H), 0.46 (d, *J* = 6.8 Hz, 6H) ppm. – IR ν(CO) = 2016, 1931, 1902 cm⁻¹. – MS (ESI, MeCN-H₂O): *m/z* (%) = 812.00 (100) [(*i*Pr₂-BIAN)(CO)₃Re+MeCN]⁺, 771.33 (25) [(*i*Pr₂-BIAN)(CO)₃Re]⁺. – UV/Vis (MeCN): λ_{max} = 289, 330, 368, 489, 519 (sh) nm.

Re(2,6-*i*Pr₂-4-sodiumsulfonato-C₆H₂-BIAN)(CO)₃Cl (**3**)

The sodium salt of 2,6-diisopropyl sulfanilic acid (0.72 g, 2.6 mmol) and acenaphthenequinone (0.26 g, 1.43 mmol) were dissolved in 10 mL of dry methanol. Five drops of formic acid were added to this yellow solution. After stirring for 45 min at 70 °C, the color had changed to orange. The mixture was further stirred at 70 °C for 24 h. After cooling to

room temperature, methanol was evaporated, and the residue was dissolved in hot methanol and filtered. To initiate the precipitation of the product, a small amount of diethyl ether was added. The *i*Pr₂-sulfonato-BIAN ligand [17] was then isolated as a yellow solid and dried (0.62 g, yield: 60%).

A solution of *i*Pr₂-sulfonato-BIAN (0.049 g, 0.07 mmol) in 6 mL ethanol was added to a suspension of Re(CO)₅Cl (0.025 g, 0.07 mmol) in 3 mL toluene. The mixture was stirred under reflux for 1 h. After cooling the reaction mixture to room temperature and addition of *n*-hexane, the product was precipitated from solution as a red-brownish powder (0.06 g, 83%). – ¹H NMR (300 MHz, D₂O): δ = 8.17 (d, *J* = 8.35 Hz, 2H), 7.9 (s, 2H), 7.76 (s, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 2H), 3.95 (m, 2H), 2.93 (m, 2H), 1.31 (d, *J* = 6.5 Hz, 6H), 1.22 (d, *J* = 6.6 Hz, 6H), 0.98 (d, *J* = 6.65 Hz, 6H), 0.42 (d, *J* = 6.6 Hz, 6H) ppm. – IR: ν(CO) = 2019, 1935, 1902 cm⁻¹; ν(S–O) = 1192 cm⁻¹. – MS (ESI, MeCN–H₂O): *m/z* (%) = 1011.13 (100) [(*i*Pr₂-sulfonato-BIAN)(CO)₃Re+H]⁺. – UV/Vis (H₂O): λ_{max} = 228, 278, 328, 353, 481, 516 (sh) nm.

Crystal structure analyses

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer with MoK_α radiation (λ = 0.71073 Å). The structures were solved by Direct Methods (SHELXL-97) [18] and refined by full-matrix least-squares on *F*² (SHELXL-97) [19]. The H atoms were calculated geometrically, and a riding model was applied during the refinement process.

CCDC 973347–973352 contain the supplementary crystallographic data for this paper. These data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details

The GAUSSIAN09 program was used in the calculations [20]. Initial coordinates were taken from the corresponding X-ray molecular structure. All quantum-chemical calculations were carried out using a density functional theory (DFT) based method with hybrid B3LYP [21–23] functional. The 6-31G(d,p) basis [24–26] was used for calculations. For the complexed metal atom a LanL2DZ basis set [27–29] was applied. The obtained geometries were verified to correspond to real minima by establishing an absence of imaginary IR frequencies. The calculated vibrational frequencies were scaled down by a factor of 0.9614 to suit the experimental values [15].

Supporting information

Further spectroscopic and computational details as well as crystallographic data on **3** · (H₂O)_{*x*} (CCDC 973349) are given as Supporting Information available online (DOI: [10.5560/ZNB.2014-4016](https://doi.org/10.5560/ZNB.2014-4016)).

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