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Coordination ambivalence of the electroactive bis-chelate ligand bis(1-methyl-2-imidazolyl)glyoxal (BIG) in mononuclear and dinuclear complexes with $Re(CO)_3Cl$

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Bis(1-methyl-2-imidazolyl)glyoxal (BIG) is reversibly reduced to an EPR, IR and UV-VIS spectroelectrochemically detectable α-diketyl radical anion. As a ligand BIG can coordinate through the carbonyl oxygen centres O and O′ and through the imine nitrogen atoms N and N′ of the imidazolyl rings. For *fac*-(BIG)Re(CO)$_3$Cl metal coordination occurs *via* both imine nitrogen centres, leading to a non-planar seven-membered chelate ring with a free α-dicarbonyl moiety as evident from X-ray structural analysis. For dinuclear (μ-BIG)[*fac*-Re(CO)$_3$Cl]$_2$ three essentially different structural coordination alternatives A–C are possible in a bis-chelate situation: Separate N,N′- and O,O′-coordination with one seven-membered and one five-membered chelate ring (A), N,O′- and N′,O-coordination with two edge-sharing six-membered chelate rings (B), or N,O- and N′,O′-coordination with two five-membered chelate rings and free rotation around the C(O)–C′(O′) single bond. Spectroscopic, electrochemical and spectroelectrochemical results obtained for the mono- and di-nuclear complexes suggest the π-conjugated structure alternative B for (μ-BIG)[*fac*-Re(CO)$_3$Cl]$_2$.

Introduction

Chelating ligands containing two or more imidazolyl donor functions have frequently been used for the modeling of active sites in metalloproteins.[1–3] One such ligand system is BIK = bis(1-methyl-2-imidazolyl)ketone[1] and its reduced derivatives.[2] Inserting a potentially π-conjugating keto group into BIK we have recently described the synthesis and structure of the potentially bis-chelating BIG = bis(1-methyl-2-imidazolyl)-glyoxal and of its organo-rhodium and -iridium complexes (Fig. 1).[4] With "hard" rhodium(III) and iridium(III) centres coordination occurs through the more basic imine nitrogen atoms of the 1-methyl-2-imidazolyl groups, leading to puckered seven-membered chelate rings. The free ligand BIG, on the other hand, adopts a structure with two perpendicular 1-methyl-2-imidazolylcarbonyl halves in the solid state.[4]

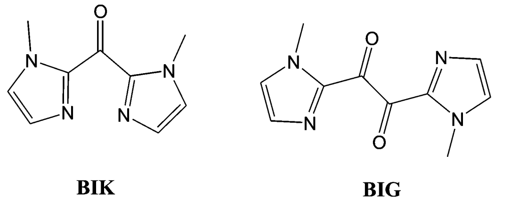

Fig. 1 Molecular formulae of BIK and BIG.

In this work we address the question whether the more electron-rich[5] organometallic complex fragment Re(CO)$_3$Cl also prefers this N,N′-coordination mode and whether dinuclear complexes can be formed and characterised. Three structural alternatives are possible for dinuclear (μ-BIG)[*fac*-Re(CO)$_3$Cl]$_2$, apart from the relative positioning (*syn*/*anti*, "*cis*/*trans*") of the chloride ligands (Fig. 2):[6] Separate N,N′- and O,O′-coordination with one seven-membered and one five-membered chelate ring (A), N,O′ and N′,O-coordination with two edge-sharing six-membered chelate rings (B), and N,O- and N′,O′-coordination with two five-membered chelate rings which would imply free rotation around the C(O)–C′(O′) single bond (C). Spectroscopic, electrochemical and spectro-electrochemical (IR, UV-VIS, EPR) results were obtained for the mono- and di-nuclear rhenium(I) complexes and for the free ligand BIG; the mononuclear (BIG)Re(CO)$_3$Cl could be structurally characterised.

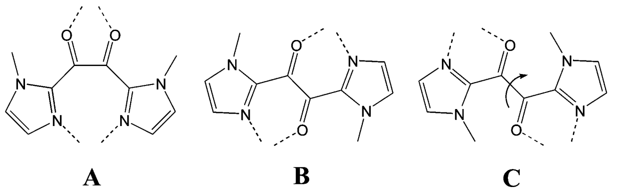

Fig. 2 Alternative structures for bis-chelate complexes of BIG.

Results and discussion

Synthesis and crystal structure

The complexes (BIG)Re(CO)$_3$Cl and (μ-BIG)[*fac*-Re(CO)$_3$Cl]$_2$ were obtained from reactions between the free ligand and the appropriate amount of Re(CO)$_5$Cl in toluene. The blue–green dinuclear complex is more labile in coordinating solvents such as acetone or acetonitrile, both complexes are susceptible to hydrolysis.[4] The ^{1}H-NMR spectra in CD$_2$Cl$_2$ show only one isomer with equivalent imidazolyl groups for (μ-BIG)-[Re(CO)$_3$Cl]$_2$; otherwise there are only small coordination shifts (Table 1).

Single crystals suitable for X-ray diffraction were obtained for orange-coloured (BIG)Re(CO)$_3$Cl through evaporation of a solution in acetone. The relevant data are summarised in Table 2, Fig. 3 illustrates the molecular structure.

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Table 1 ^{1}H-NMR data (δ) of BIG and its complexes

	BIG	(BIG)Re(CO)$_3$Cl	(μ-BIG)[Re(CO)$_3$Cl]$_2$
Solvent	DMSO-d$_6$	CD$_2$Cl$_2$	CD$_2$Cl$_2$
N–C*H*$_3$	4.04 (s, 6H)	3.86 (s, 6H)	3.86 (s, 6H)
C*H*	7.17 (s, 2H)	7.09 (d, 2H, J = 1.4 Hz)	7.63 (d, 2H, J = 1.4 Hz)
	7.67 (s, 2H)	7.55 (d, 2H, J = 1.4 Hz)	7.82 (d, 2H, J = 1.4 Hz)

Table 2 Selected bond distances (Å) and angles (°) for (BIG)Re(CO)$_3$Cl

Re(1)–C(1)	1.919(8)	C(1A)–C(11A)	1.476(9)
Re(1)–C(2)	1.917(7)	N(2B)–C(1B)	1.347(8)
Re(1)–C(3)	1.918(7)	C(1B)–C(11B)	1.487(9)
Re(1)–N(2B)	2.179(6)	O(11B)–C(11B)	1.218(8)
Re(1)–N(2A)	2.192(6)	O(11A)–C(11A)	1.219(8)
Re(1)–Cl(1)	2.4770(17)	C(11B)–C(11A)	1.563(9)
N(2A)–C(1A)	1.337(9)		
C(2)–Re(1)–C(3)	87.1(3)	AC(3)–Re(1)–Cl(1)	96.6(2)
C(2)–Re(1)–C(1)	90.6(3)	C(1)–Re(1)–Cl(1)	174.9(2)
C(3)–Re(1)–C(1)	88.1(3)	N(2B)–Re(1)–Cl(1)	84.09(15)
C(2)–Re(1)–N(2B)	94.1(3)	N(2A)–Re(1)–Cl(1)	85.42(16)
C(3)–Re(1)–N(2B)	178.6(3)	C(1A)–N(2A)–Re(1)	130.3(4)
C(1)–Re(1)–N(2B)	91.2(3)	N(2A)–C(1A)–C(11A)	128.6(6)
C(2)–Re(1)–N(2A)	176.7(3)	C(1B)–N(2B)–Re(1)	131.4(4)
C(3)–Re(1)–N(2A)	94.6(3)	N(2B)–C(1B)–C(11B)	128.7(5)
C(1)–Re(1)–N(2A)	92.3(3)	C(1B)–C(11B)–C(11A)	126.3(5)
N(2B)–Re(1)–N(2A)	84.3(2)	C(1A)–C(11A)–C(11B)	121.8(6)
C(2)–Re(1)–Cl(1)	91.6(2)		

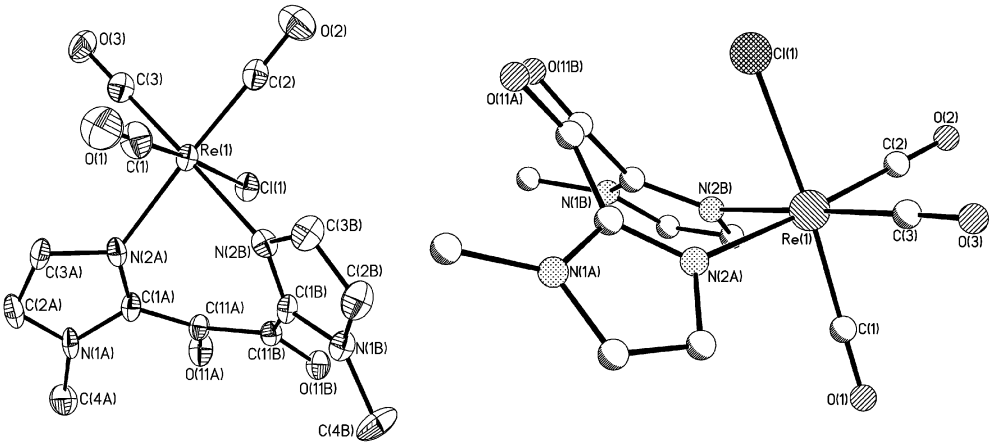

Fig. 3 Molecular structure of (BIG)Re(CO)$_3$Cl in the crystal: top and side views.

The structure of the *fac*-(BIG)Re(CO)$_3$Cl molecule confirms the N,N′-coordination of the metal centre as was previously found for [(BIG)RhCl(C$_5$Me$_5$)]$^+$.[4] A seven-membered chelate ring results which adopts a pronounced boat conformation. The chloride ligand is situated at the bowhead pointing inward. In contrast to the situation in the free ligand with orthogonal molecular halves[4] the primarily electroactive α-diketo function is essentially co-planar in this arrangement. The strong acceptor site thus formed through metal coordination is known to be susceptible to nucleophilic attack *e.g.* from hydroxide.[4]

Before discussing the coordination mode in (μ-BIG)-[Re(CO)$_3$Cl]$_2$ (which did not give crystals suitable for X-ray diffraction) we first present comprehensive spectroelectrochemical studies of the ligand BIG, the mononuclear compound and the dinuclear complex.

Electrochemistry and spectroelectrochemistry

The free ligand BIG, which adopts a non-conjugated (perpendicular) conformation in the solid state,[4] is reduced quasi-reversibly at −1.74 V *vs.* ferrocene/ferrocenium in CH$_3$CN/0.1 mol dm^{-3} Bu$_4$NPF$_6$ (Table 3). The rather negative value is similar to that of other α-diketones.[7] The quasi-reversibility of the wave (ΔE_{pp} = 120 mV) suggests planarisation on reduction due to the increasing bond order of the C(O)–C′(O′) bond; analysis of the EPR spectrum of BIG$^{\bullet-}$ yields hyperfine coupling constants which are in general agreement with π spin populations as calculated by the Hückel method for a planar π system (*cf.* below).

Table 3 Electrochemical data from cyclic voltammetry[a]

	BIG	(BIG)Re(CO)$_3$Cl	(μ-BIG)[Re(CO)$_3$Cl]$_2$
Solvent[b]	CH$_3$CN	CH$_2$Cl$_2$	CH$_2$Cl$_2$
$E_{1/2}$ (ox)	n.o.	0.97	n.o.
$E_{1/2}$ (red1)	−1.74	−0.95	−0.14
$E_{1/2}$ (red2)	n.o.	−1.69 (irr)	−0.93
E_{pc} (red3)	n.o.	−2.12 (irr)	−2.08 (irr)

[a] Potentials in V *vs.* [Fe(C$_5$H$_5$)$_2$]$^{+/0}$, scan rate 100 mV s^{-1}. [b] 0.1 mol dm^{-3} Bu$_4$NPF$_6$.

(BIG)Re(CO)$_3$Cl is reduced reversibly at a 0.79 V less negative potential than BIG, and the dinuclear (μ-BIG)-[Re(CO)$_3$Cl]$_2$ exhibits even more facile reduction by about the same amount of 0.81 V (Table 3). This latter result and the absolute value of $E_{1/2}$(red1) = −0.14 V point to a highly conjugated π system in (μ-BIG)[Re(CO)$_3$Cl]$_2$, the π* MO of BIG being considerably stabilised through twofold coordination of σ-electrophilic Re(CO)$_3$Cl. Similar effects were observed with 2,2′-azobispyridine as bridging π acceptor ligand for Re(CO)$_3$Cl.[6]

Fig. 4 and Table 3 show that (BIG)Re(CO)$_3$Cl is further

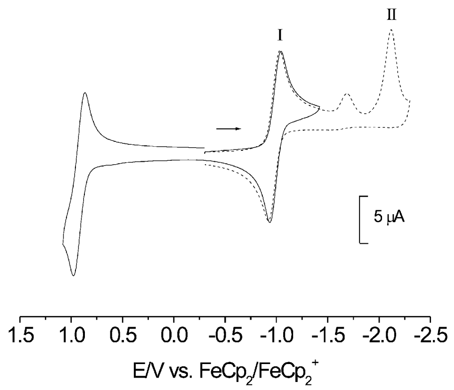

Fig. 4 Cyclic voltammograms of (BIG)Re(CO)$_3$Cl in CH$_2$Cl$_2$/0.1 mol dm^{-3} Bu$_4$NPF$_6$.

reduced irreversibly due to the typical chloride dissociation[6,8,9] but oxidised reversibly to a rhenium(II) containing monocation.[8] In contrast, (μ-BIG)[Re(CO)$_3$Cl]$_2$ exhibits a well-separated reversible *second* reduction but no oxidation in the accessible potential range (Fig. 5) — a consequence of stabilised metal d orbitals due to partial O coordination (*cf.* below).

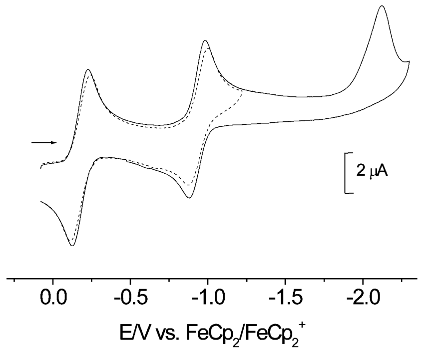

Fig. 5 Cyclic voltammograms of (μ-BIG)[Re(CO)$_3$Cl]$_2$ in CH$_2$Cl$_2$/0.1 mol dm^{-3} Bu$_4$NPF$_6$.

Ligand and metal carbonyl stretching bands in the infrared region can be conveniently monitored during electron transfer processes through spectroelectrochemistry using an optically transparent thin-layer electrolytic (OTTLE) cell.[10] Figs. 6 and 7 show the results for the reduction of the rhenium complexes, Table 4 summarises all data.

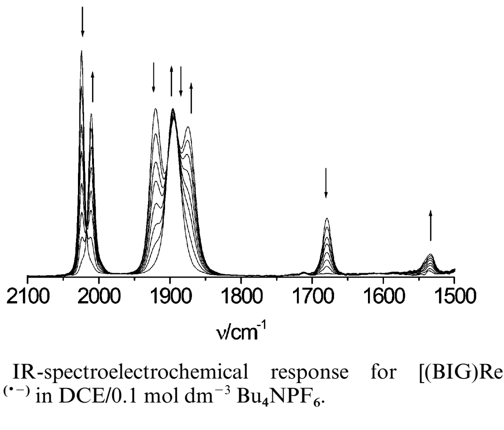

Fig. 6 IR-spectroelectrochemical response for [(BIG)Re(CO)$_3$Cl]$^{(0)}$ $\longrightarrow$ $^{(\bullet -)}$ in DCE/0.1 mol dm^{-3} Bu$_4$NPF$_6$.

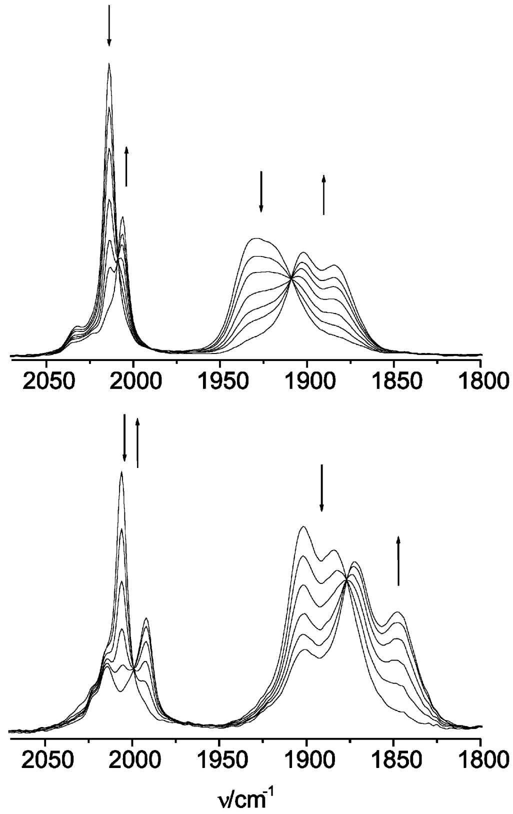

Fig. 7 IR-spectroelectrochemical responses for {(μ-BIG)[Re(CO)$_3$Cl]$_2$}$^{(0)}$ $\longrightarrow$ $^{(\bullet -)}$ (top) and {(μ-BIG)[Re(CO)$_3$Cl]$_2$}$^{(\bullet -)}$ $\longrightarrow$ $^{(2-)}$ in DCE/0.1 mol dm^{-3} Bu$_4$NPF$_6$.

The ligand carbonyl band at about 1675 cm^{-1} is shifted considerably to lower wavenumbers on reduction of (BIG)-Re(CO)$_3$Cl (Fig. 6) and of free BIG, indicating α-semidione formation; on the other hand, metal-based oxidation of the mononuclear complex produces only a slight high-energy shift (Table 4). The absence of such an intense band in the infrared spectrum signifies inversion symmetry for the dinuclear complex (structures B or C), structure A can also be ruled out from the appearance of only one set of metal carbonyl stretching bands: three separated bands are expected for a *fac* arrangement with three different donor atoms (Cl, N and O).[8,9] Reduction and oxidation (for (BIG)Re(CO)$_3$Cl), or first and second reduction in the case of the dinuclear complex, cause about the same shifts in the expected directions:[8,9] a high-energy shift for oxidation and a low-energy shift for reduction.

OTTLE cell spectroelectrochemistry could also be performed for the electronic absorptions in the uv and visible regions. Fig. 8

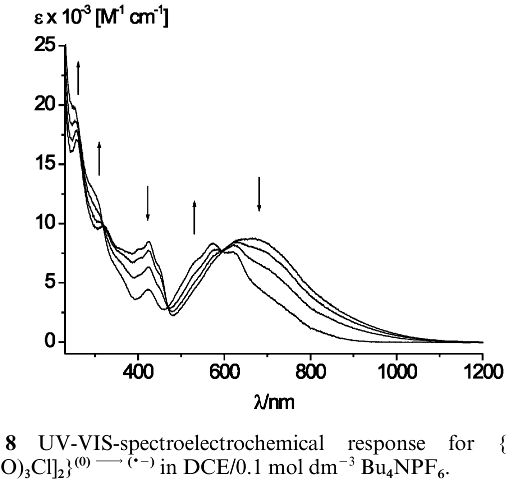

Fig. 8 UV-VIS-spectroelectrochemical response for {(μ-BIG)[Re(CO)$_3$Cl]$_2$}$^{(0)}$ $\longrightarrow$ $^{(\bullet -)}$ in DCE/0.1 mol dm^{-3} Bu$_4$NPF$_6$.

Table 4 Spectroelectrochemical data from IR, UV-VIS and EPR spectroscopy

	n	BIG^n	$[(BIG)Re(CO)_3Cl]^n$	$\{(\mu\text{-}BIG)[Re(CO)_3Cl]_2\}^n$
IR				
Solvent		CH_2Cl_2	DCE	DCE
ν_{CO}/cm^{-1}	0	1675	1677; 2026, 1925, 1894,	2014, 1933, 1925
	+1	n.o.	1692; 2038, 1933, 1916	n.o.
	−1	1404, 1384	1533; 2011, 1896, 1875	2006, 1902, 1885
	−2	n.o.	n.o.	1992, 1872, 1848
UV-VIS				
Solvent		CH_3CN	DCE	DCE
λ_{max} (ε)/nm (dm^3 mol^{-1} cm^{-1})	0	297 (27000)	403 (3400), 310sh, 269 (8800)	697 (8400), 450sh, 423 (8300), 399sh, 326 (8400)
	+1	n.o.	425sh, 317 (8000)	n.o.
	−1	457 (2700), 300sh	463 (3250), 323 (5200)	720sh, 623 (7550), 572 (8300), 529sh, 430 (4300), 350sh, 293sh
	−2	n.o.	n.o.	446 (6750), 345sh
EPR [a]				
Solvent		THF	THF	THF
g_{iso}		2.0054 $a(^{14}N) = 0.087$ (4N) $a(^1H) = 0.087$ (6H) $a(^1H) = 0.019$ (2H) $a(^1H) = 0.174$ (2H)	2.0050 $a(^{185,187}Re) = 0.28$	2.0077 [b] $g_1 = 2.025$ [c] $g_2 = 2.013$ $g_3 = 1.995$

[a] Coupling constants a in mT. [b] Peak-to-peak line width 1.0 mT. [c] At 110 K in frozen solution.

shows a representative example, Table 4 contains the spectral data.

Formation of the non-coordinated α-semidione $BIG^{\bullet-}$ results in the appearance of a broad band in the visible region, assigned to a SOMO ⟶ LUMO transition as observed for other α-semidione radicals.[11] The rhenium(I) complexes of π accepting BIG are distinguished by metal-to-ligand charge transfer (MLCT, d ⟶ π*) bands in the visible region (Table 4). The unusually intense long-wavelength band at 697 nm of $(\mu\text{-}BIG)[Re(CO)_3Cl]_2$ (Fig. 8) agrees with the strongly shifted reduction potential and confirms a high degree of π conjugation in the BIG bridge.

On reduction or oxidation of the complexes, the orginal MLCT bands typically shift to higher energies and new bands involving the singly occupied MOs emerge. Exact assignments require open-shell excited-state calculations which shall be pursued.

The stability of the one-electron reduced states of BIG and its complexes has allowed us to study these paramagnetic species by EPR. The oxidized form of the mononuclear compound with rhenium-centred spin did not reveal EPR signals as was noted previously in related instances.[8]

Reduction of BIG by potassium metal in THF produces a partially resolved EPR spectrum (Fig. 9) which could be tentatively interpreted with the help of Hückel MO spin population calculations (Fig. 10).[12]

Because of spin density concentration in the α-semidione moiety the coupling constants from ^1H and ^{14}N nuclei are generally small (< 0.2 mT). A hyperfine splitting from the four nitrogen atoms and the two methyl groups of the order of 0.087 mT was extracted, in addition to 0.019 mT and 0.174 mT splittings from the imidazolyl ring protons 2 and 3, respectively (Fig. 10). The weak O donors should thus become much better coordination atoms on reduction, stabilizing the chelate radical complexes.

In fact, both complexes exhibit EPR signals at ambient temperatures with isotropic g factors not far from $g(\text{electron}) = 2.0023$. The mononuclear $[(BIG)Re(CO)_3Cl]^{\bullet-}$ exhibits a small $^{185,187}Re$ coupling of 0.28 mT ($I = 5/2$ for both isotopes, 100% combined natural abundance). Such a value is unusually small when compared to other species $(L^{\bullet-})Re(CO)_3Cl$.[6,8] The negligible metal contribution is also evident from the marginal g shift relative to $BIG^{\bullet-}$ and from the absence of detectable g anisotropy in frozen solution at 110 K. The origin of this effect lies in the crystallographically established binding of $Re(CO)_3Cl$ not at the spin-bearing oxygen atoms but at the imine nitrogen centres with their only marginal spin population.

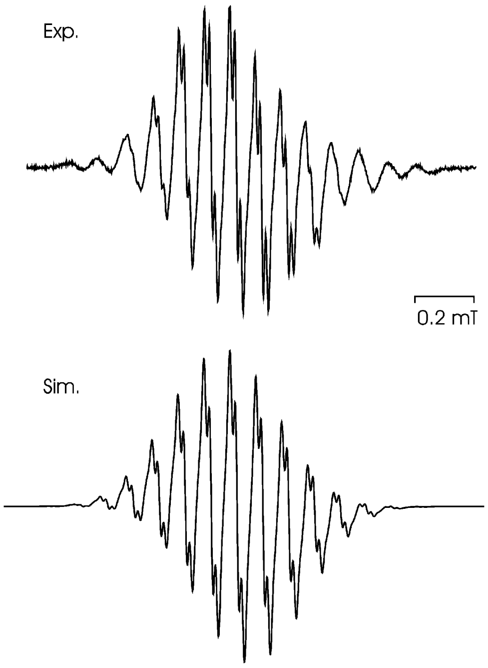

Fig. 9 EPR spectrum of $BIG^{\bullet-}$ in THF (top) with simulation.

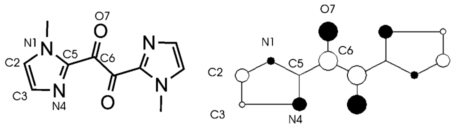

Fig. 10 Graphical representation of the SOMO of $BIG^{\bullet-}$ from Hückel MO calculations (parameters $h_{N1} = 1.50$, $h_{N4} = 0.50$, $h_O = 1.00$, $k_{C\text{–}N} = 0.80$, $k_{C\text{–}O} = k_{C\text{–}C} = 1.00$[12]).

Regardless of the structure alternative B or C, however, the dinuclear $\{(\mu\text{-}BIG)[Re(CO)_3Cl]_2\}^{\bullet-}$ must use imine-N and carbonyl-O donors as a metal–ligand interface[8] for interaction with rhenium(I). Consequently, a distinct g anisotropy could

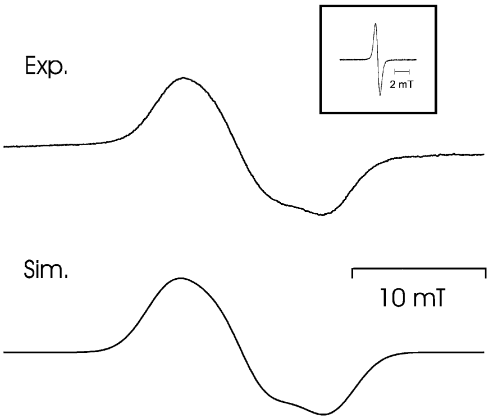

Fig. 11 EPR spectrum of $\{(\mu\text{-BIG})[\mathrm{Re(CO)_3Cl}]_2\}^{\bullet-}$ in THF at 110 K (top) with simulation. Insert: EPR spectrum at ambient temperature.

be observed in frozen solution (Fig. 11, Table 4), as measured and calculated similarly for dirhenium(I) complexes of azo-containing bridging radicals.[13] However, no ^{185,187}Re hyperfine coupling could be detected in frozen solution or at room temperature. This result is the more unusual as the rhenium isotopes have particularly high isotropic hyperfine coupling constants $a_o > 1000$ mT,[14] however, a similar observation has been reported previously for a dirhenium(I) complex of reduced 2,5-diacetylpyrazine, also with a N,O;N′,O′-donor atom set.[15]

As noted above, three structural alternatives A–C are conceivable for a bis-chelate coordination of two metal centres with the BIG ligand. Of these, alternative A would imply two very differently coordinated metal atoms, one centre strongly bound through the N,N′ imine atoms (*cf.* the mononuclear complex) and the other metal coordinated through the O,O′ keto oxygen atoms. Reduction centred at the α-dicarbonyl moiety would increase the otherwise weak metal–O bond. The unsymmetrical alternative A can be ruled out as there is only one set of carbonyl stretching bands observable for the neutral, the one-electron and the two-electron reduced forms of (μ-BIG)-[*fac*-Re(CO)$_3$Cl]$_2$. Also, the closer ^{1}H-NMR chemical shifts (Table 1) of the imidazole protons in the dinuclear complex would not agree with alternative A.

The symmetrical alternatives B and C are harder to distinguish experimentally: B would imply an approximately planar BIG ligand because of the edge-sharing of two equivalent, largely π-conjugated six-membered chelate rings (N,O′ and N′,O coordination). Together with the σ electron withdrawing and π electron donating capacity of two Re(CO)$_3$Cl moieties this should lead to a considerable narrowing of the HOMO–LUMO gap, resulting in very facile reduction and very low-energy MLCT absorptions. In contrast, the alternative structure C contains two five-membered chelate rings (N,O and N′,O′ coordination), connected by a C–C single bond in the neutral state. Facile rotation around this single bond is likely to produce two almost perpendicular molecular halves as the energy minimum conformation, as was observed for the free ligand BIG.[4] Repulsive interactions between N-methyl groups and carbonyl oxygen atoms would also contribute to a non-planar structure of C. However, such a conformation would not result in a particularly lowered LUMO and thus neither facile reduction nor low-energy MLCT absorption bands could be expected. The similarity of the position of the methyl protons in the NMR of the mono- and di-nuclear species also support the assignment of the structure to B upon consideration of the relationship of the methyl protons and the C=O group.

Summarising, we infer the structure in Fig. 12 for the dinuclear complex, based on its strongly stabilised π* LUMO. The ligand BIG may thus be added to the list of symmetrically bridging bis-chelate acceptor ligands[16] which are suitable for studying molecule-mediated metal–metal interaction.[17]

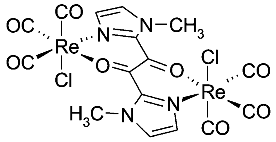

Fig. 12 Structure proposed for $\{(\mu\text{-BIG})[\mathrm{Re(CO)_3Cl}]_2\}^{\bullet-}$.

Experimental

Instrumentation

EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ^{1}H-NMR spectra were taken on a Bruker AC 250 spectrometer, infrared spectra were obtained using Perkin-Elmer Paragon 1000 PC and Philips 9800 FTIR instruments. UV-VIS/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at a 100 mV s^{-1} scan rate 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 couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[10] for UV-VIS and IR spectra, radicals for EPR measurement were generated through reduction with a K/[2.2.2] cryptand in THF under vacuum.

Synthesis of (BIG)Re(CO)$_3$Cl

A suspension of BIG[4] (57.8 mg, 0.264 mmol) and Re(CO)$_5$Cl (95.8 mg, 0.264 mmol) in 25 cm^3 toluene was stirred for 18 hours at 65 °C. The orange solid formed after cooling to ambient temperature was collected, washed with toluene and petrol ether (bp 60–80 °C) and dried under vacuum (87.0 mg, 63%). Found: C, 29.74; H, 1.72; N, 10.44%. $\mathrm{C_{13}H_{10}ClN_4O_5Re}$ (523.91) requires C, 29.80; H, 1.92; N, 10.70%.

Synthesis of (μ-BIG)[Re(CO)$_3$Cl]$_2$

A suspension of BIG (30.1 mg, 0.138 mmol) and Re(CO)$_5$Cl (100.0 mg, 0.276 mmol) in 30 cm^3 toluene was stirred for 44 hours at 65 °C. The greyish blue solid formed after cooling to −18 °C was collected and washed with petrol ether. Recrystallisation from dichloromethane and drying under vacuum yielded 79.6 mg (70%) of the product. Found: C, 23.12; H, 1.06; N, 6.59%. $\mathrm{C_{16}H_{10}Cl_2N_4O_8Re_2}$ (829.58) requires C, 23.17; H, 1.22; N, 6.76%.

Crystallography

An orange crystal of (BIG)Re(CO)$_3$Cl with dimensions 0.4 × 0.3 × 0.2 mm was obtained through slow evaporation from an acetone solution. X-Ray data of (BIG)Re(CO)$_3$Cl were collected at 173(2) K on a Siemens P3 diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), employing the ω–2Θ scan technique. The unit cell parameters were determined from 25 reflections measured by a random search routine. The intensity data were corrected for Lorentz polarisation and absorption effects. The structure was solved using direct methods. The non-hydrogen atoms were refined anisotropically.

Crystal data for (BIG)Re(CO)$_3$Cl. $\mathrm{C_{13}H_{10}ClN_4O_5Re}$, M = 523.90, monoclinic, a = 19.562(4), b = 15.552(3), c = 13.249(3) Å, β = 127.12(3)°, U = 3214.1(11) Å^3, T = 173 K, space group $C2/c$, Z = 8, μ(Mo-Kα) = 7.750 mm^{-1}, 4864 reflections measured, 4677 unique (R_{int} = 0.0523) which were used in all calculations. The final $wR(F^2)$ was 0.1408 (all data).

CCDC reference number 180999.

See http://www.rsc.org/suppdata/dt/b2/b202636h/ for crystallographic data in CIF or other electronic format.

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