Synthesis, spectroscopic studies and crystal structures of $\text{Re}^{I}(\text{CO})_{3}(\text{NN})\text{Cl}$ complexes with *N*,*N*'-bis(substituted benzylidene)ethane-1,2-diamine Schiff base ligands

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Abstract Four new Re(I) tricarbonyl-diimine complexes were prepared by reaction of Re(CO)₅Cl with N,N'bis(substituted benzylidene)ethane-1,2-diamine Schiff base ligands. These compounds were characterized by physicochemical methods, and their crystal structures were established by X-ray diffraction. The coordination geometry at the Re atom is that of a distorted octahedron, with three carbonyl ligands in the facial geometry.

Introduction

The photochemistry and photophysics of diimine-Re(I)-tricarbonyl complexes are well established [1–3]. Their photochemical properties have been utilized for the electrocatalytic and photocatalytic CO₂ reduction to CO [4, 5]. Control or modulation of the absorption and/or emission energy can provide a very important tool to modify the catalytic behavior

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Department of Chemistry, Science and Research Campus, Islamic Azad University, Poonak, Tehran, Iran e-mail: zsrkk@yahoo.com

D. Milić (⊠) · D. Matković-Čalogović Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia e-mail: dmilic@chem.pmf.hr of these complexes. The lowest energy excited state of these complexes is generally long-lived metal-to-ligand charge transfer (MLCT). Because of the powerful reductive and/or oxidative properties in the MLCT state, such complexes can be find application as photosensitizers, e.g., in solar cells [6, 7]. Several $[\text{Re}(\text{CO})_3(\text{L})\text{X}]^{0/+}$ complexes, where L is α -diimine and X is a halide, bridging ligand or some other monodentate ligand, have been used as electroluminescent materials in OLED-type devices [8–10]. Modification in the diimine or axial ligands of these complexes has been used to tune their spectroscopic, photophysical, photochemical and electrochemical properties [11, 12].

In this research, synthesis, characterization and crystal structures of four tricarbonylrhenium(I) complexes, [Re(CO)₃-(4-mbzen)Cl], [Re(CO)₃(2-mbzen)Cl], [Re(CO)₃(4-m'bzen)-Cl] and [Re(CO)₃(3-bbzen)Cl] in which 4-mbzen = N,N'-bis(4-methoxybenzylidene)ethane-1,2-diamine, 2-mbzen = N,N'-bis(2-methoxybenzylidene)ethane-1,2-diamine, 4-m'bzen = N,N'-bis(4-methylbenzylidene)ethane-1,2-diamine and 3-bbzen = N,N'-bis(3-bromobenzylidene)ethane-1,2-diamine, are reported.

Experimental

Materials and methods

Organic reagents used for synthesis of the compounds were obtained from Merck and used as received. The solvents were dried before use with the appropriate drying reagents. IR spectra in KBr pellets were recorded on an IR Prestige-21 Shimadzu FTIR instrument. ¹H NMR spectra were performed on a Bruker Avance DRX500 (500 MHz) spectrometer using DMSO- d_6 and CDCl₃ as solvent and TMS as the internal reference. UV–Vis spectra were measured on a

Shimadzu UV-160 spectrophotometer in dichloromethane solution. Cyclic voltammograms were recorded on a threeelectrode cell containing Ag/AgNO₃ (in CH₃CN) reference electrode, a Pt wire counter electrode and a glassy carbon working electrode. The complexes were at 2×10^{-4} M concentration in deaerated CH₂Cl₂ containing 0.2 M Bu₄NClO₄ (TBAP) as a supporting electrolyte. The scans were recorded at 100 mV/s.

Synthesis of the Schiff bases and complexes

N,N'-bis(4-methoxybenzylidene)ethane-1,2-diamine (4-mbzen)

Ethylendiamine (0.2 mL, 3 mmol) was added to a stirred solution of 4-methoxybenzaldehyde (6 mmol, 0.75 mL) in CH₂Cl₂ (15 mL). The mixture was stirred for 3 h at room temperature, then the precipitate was filtered off, and the yellow solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): v_{max} 1,639 (C=N). ¹H NMR (CDCl₃, δ /ppm): 3.62 (s, 6H, 2-(OCH₃)); 3.72 (s, 4H, -CH₂-CH₂-); 6.69–6.71 (d, 4H, aromatic hydrogens); 7.43–7.45 (d, 4H, aromatic hydrogens); 8.01 (s, 2H, iminic hydrogens).

N,N'-bis(2-methoxybenzylidene)ethane-1,2-diamine (2-mbzen)

This Schiff base was prepared by a procedure similar to 4mbzen using 2-methoxybenzaldehyde (0.82 g). The yellow solid was recrystallized from ethanol.

FTIR (KBr, cm⁻¹): v_{max} 1,634 (C=N). ¹H NMR (CDCl₃, δ/ppm): 3.61 (s, 6H, 2-(OCH₃)); 3.77 (s, 4H, -CH₂-CH₂-); 6.67-7.74 (m, 8H, aromatic hydrogens); 8.52 (s, 2H, iminic hydrogens).

N,N'-bis(4-methylbenzylidene)ethane-1,2-diamine (4-m'bzen)

This Schiff base was synthesized according to the procedure for 4-mbzen using 4-methylbenzaldehyde (0.7 mL). The yellow solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): v_{max} 1,639 (C=N). ¹H NMR (CDCl₃, δ /ppm): 2.17 (s, 6H, 2-(CH₃)); 3.75 (s, 4H, -CH₂-CH₂-); 6.98–7.00 (d, 4H, aromatic hydrogens); 7.38–7.40 (d, 4H, aromatic hydrogens); 8.05 (s, 2H, iminic hydrogens).

N,N'-bis(3-bromobenzylidene)ethane-1,2-diamine (3-bbzen)

The procedure was similar to that for 4-mbzen, except that 3-bromobenzaldehyde (0.7 mL) was used. The yellow solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): v_{max} 1,643 (C=N). ¹H NMR (CDCl₃, δ /ppm): 3.76 (s, 4H,

-CH₂-CH₂-); 7.04-7.69 (m, 8H, aromatic hydrogens); 8.01 (s, 2H, iminic hydrogens).

$[Re(CO)_3(4-mbzen)Cl]$ (1)

A mixture of Re(CO)₅Cl (0.2 g, 0.55 mmol) and 4-mbzen (0.16 g) in degassed CH₂Cl₂/toluene (30 mL, 1:2 V/V) was heated at reflux for 3 h. The solution was concentrated to half volume, and *n*-hexane was added to precipitate a yellow crude material of complex **1**. The product was recrystallized from CH₂Cl₂/toluene to give pale yellow crystals. FTIR (cm⁻¹): v_{max} 2,016, 1,884 (broad) (CO); 1,630 (C=N). ¹H NMR (DMSO-*d*₆, δ /ppm): 3.84 (s, 6H, 2-(OCH₃)); 4.04–4.07 and 4.16–4.20 (two sets of multiples, 4H, –CH₂–CH₂–); 7.09–7.11 (d, 4H, aromatic hydrogens); 7.98–8.00 (d, 4H, aromatic hydrogens); 9.06 (s, 2H, iminic hydrogens).

$[Re(CO)_3(2-mbzen)Cl]$ (2)

This complex was synthesized by a procedure similar to **1** using 2-mbzen (0.16 g). FTIR (cm⁻¹): v_{max} 2,013, 1,902 and 1,889 (CO); 1,630 (C=N). ¹H NMR (DMSO-*d*₆, δ /ppm): 3.89 (s, 6H, 2-(OCH₃)); 4.06–4.10 and 4.26–4.30 (two sets of multiples, 4H, –CH₂–CH₂–); 7.06–7.09 (t, 2H, aromatic hydrogens); 7.15–7.16 (d, 2H, aromatic hydrogens); 7.52–7.56 (m, 2H, aromatic hydrogens); 7.99–8.00 (d, 2H, aromatic hydrogens); 9.10 (s, 2H, iminic hydrogens).

$[Re(CO)_{3}(4-m'bzen)Cl]$ (3)

This complex was synthesized by a procedure similar to **1** using 4-m'bzen (0.15 g). FTIR (cm⁻¹): v_{max} 2,019, 1,915 and 1,865 (CO); 1,632 (C=N). ¹H NMR (DMSO-*d*₆, δ /ppm): 4.05–4.09 and 4.21–4.25 (two sets of multiples, 4H, –CH₂–CH₂–); 7.35–7.36 (d, 4H, aromatic hydrogens); 7.83–7.84 (d, 4H, aromatic hydrogens); 9.13 (s, 2H, iminic hydrogens).

$[Re(CO)_3(3-bbzen)Cl]$ (4)

The procedure was similar to that for **1**, except that 3-bbzen (0.22 g) was used. FTIR (cm⁻¹): v_{max} 2,023 and 1,894 (broad) (CO); 1,634 (C=N). ¹H NMR (DMSO-*d*₆, δ /ppm): 4.09–4.13 and 4.24–4.28 (two sets of multiples, 4H, –CH₂–CH₂–); 7.49–7.52 (t, 2H, aromatic hydrogens); 7.75–7.79 (m, 4H, aromatic hydrogens); 8.18 (s, 2H, aromatic hydrogens); 9.18 (s, 2H, iminic hydrogens).

Crystal structure determinations

Crystals suitable for X-ray crystallography were grown by slow evaporation of complexes dissolved in CH_2Cl_2 and

Table 1 Crystal	data and	structure refinement	parameters for	or complexes	1–4
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Complex	1	2	3	4
Empirical formula	C21H20ClN2O5Re	C21H20ClN2O5Re	C ₂₁ H ₂₀ ClN ₂ O ₃ Re	C ₁₉ H ₁₄ Br ₂ ClN ₂ O ₃ Re
Formula mass	602.04	602.04	570.04	699.79
Crystal size (mm ³)	$0.54\times0.28\times0.05$	$0.44\times0.15\times0.08$	$0.50\times0.28\times0.06$	$0.38 \times 0.35 \times 0.07$
Color	Pale yellow	Pale yellow	Pale yellow	Yellow
Crystal system	Triclinic	Orthorombic	Monoclinic	Monoclinic
Space group	$P \bar{1}$	Pnma	$P2_1/n$	$P2_1$
θ_{\max} (°)	32.2	32.1	30.0	32.1
a (Å)	7.1355(1)	14.5786(13)	10.985(2)	7.2544(1)
b (Å)	9.6395(2)	165,115(13)	10.551(2)	13.9627(2)
<i>c</i> (Å)	16.6392(4)	9.21652(18)	17.802(2)	11.0109(2)
α (°)	106.759(2)	90	90	90
β (°)	93.201(2)	90	94.194(5)	104.938(2)
γ (°)	95.755(2)	90	90	90
$V(\text{\AA}^3)$	1,086.03(4)	2,218.6(3)	2,057.8(6)	1,056.78(3)
Ζ	2	4	4	2
$D_{\text{calc}} (\text{Mg/m}^3)$	1.841	1.803	1.840	2.199
$\mu (\mathrm{mm}^{-1})$	5.75	5.652	6.07	9.68
F(000)	584	1,168	1,104	656
Index ranges	$-10 \le h \le 10$	$-21 \le h \le 18$	$-15 \le h \le 15$	$-10 \le h \le 10$
	$-14 \le k \le 14$	$-24 \le k \le 24$	$-14 \le k \le 14$	$-20 \le k \le 20$
	$-24 \leq l \leq 24$	$-13 \le l \le 13$	$-25 \leq l \leq 24$	$-16 \le l \le 16$
No. of measured reflections	31,371	16,090	26,513	15,296
No. of independent reflections/ R_{int}	7,132/0.020	3,773/0.031	5,989/0.033	6,675/0.023
No. of observed reflections with $I > 2\sigma(I)$	6,128	2,275	4,650	5,327
No. of parameters	273	162	265	253
Goodness-of-fit (GOF)	1.10	0.86	1.08	0.89
R_1 (observed data)	0.0230	0.0258	0.0299	0.0261
wR_2 (all data) ^a	0.0503	0.0531	0.0859	0.0499

^a $w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0264P)^2]$ for **2**, $w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 2.4507P]$ for **3** and $w = 1/[\sigma^2(F_o^2) + (0.027P)^2]$ for **4**, where $P = (F_o^2 + 2F_o^2)/3$

toluene (2:1). Crystallographic data are summarized in Table 1. X-ray intensity data were collected on an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at temperature of 295(2) K. The data reduction, including the analytical numeric absorption correction [13], was performed using the CrysAlis software package [14]. The structures were solved by direct methods (SHELXS-97) [15] and refined by full-matrix least-squares method on F^2 (SHELXL-97) [15]. The non-hydrogen atoms were refined anisotropically. In complexes 2 and 3, the restraints on geometrical and displacement parameters were applied for the disordered structural fragments. All of the hydrogen atoms were positioned geometrically and refined with the riding model approximation, with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$. All calculations were carried out using the WinGX package of the crystallographic programs [16] and PLATON [17]. For the molecular graphics, the program ORTEP-3 [18] was used.

Results and discussion

General characterization

The complexes 1–4 were prepared by a substitution reaction between equimolar amounts of the diimine ligand and Re(CO)₅Cl, as shown in Scheme 1. The obtained complexes are stable in air, either as solid or in solution, and were characterized by the usual spectroscopic techniques. The metal centers have an almost ideal octahedral coordination sphere with a facial arrangement of three carbonyl groups. The typical *fac*-tricarbonyl unit in these complexes is evidenced by the CO stretching frequencies as detected in the IR spectra and is confirmed by the X-ray crystal structures. The IR spectra of the complexes show two or one (broad) lower energy and sharp intense bands in the carbonyl range of 1,865–2,023 cm⁻¹ [19, 20]. The electron donor substituents shift the CO and CN stretching bands to



Scheme 1 Preparation of the characterized Re(I) tricarbonyl-diimine complexes

lower frequencies. The π -donor character of the chlorine atom increases the Re-CO back-bonding, which decreases the energy of v(CO) [20]. The NMR spectra and peak assignments are presented in the experimental section. The ¹H NMR spectra of the free Schiff bases show the -CH₂-CH₂- groups as singlets, but these signals appear as two sets of multiplets in the complexes indicating that these protons are not equivalent. All signals in the ¹H NMR spectra of the complexes are shifted to the low-field region with respect to the free ligands as a result of ligand coordination. The electronic absorption spectroscopic data of the ligands and complexes in CH₂Cl₂ are included in Table 2. In general, the electronic absorption spectra of rhenium(I) diimine complexes show intense high-energy absorption bands at ca. 230-300 nm and low-energy absorption bands at above 350 nm [21, 22]. The highenergy absorption bands, which are also found in the free diimine ligands, are assigned as $\pi \to \pi^*$ transitions of diimine ligands, while the low-energy absorption bands are tentatively assigned as the $d\pi$ (Re) $\rightarrow \pi^*$ (diimine) metalto-ligand charge transfer (MLCT) transitions. The MLCT transitions of the complexes in DMSO solution (1×10^{-3}) M) appear at 368, 361, 363 and 361 nm for 1, 2, 3 and 4, respectively. Thus, with increase in polarity of the solvent, negative solvatochromism (blue shift) is observed. This hypsochromic shift of the MLCT absorption bands is explained by assuming that the transfer of the charge in the MLCT excited state occurs anti-parallel to the ground state dipole moment [23] (the excited state has a lower dipole moment than the ground state). The higher transition energy in more polar solvent (DMSO) may thus be attributed to the ground state stabilization prevailing with respect to the excited state stabilization during the transition [24]. The electrochemical behavior of the prepared complexes was examined by means of cyclic voltammetry in CH₂Cl₂ (Fig. 1). The electrochemical waves are quasireversible couples with E_a values of 1.11, 1.12, 1.10 and 1.2 V versus Ag/AgNO₃ (in CH₃CN), for complexes 1, 2, 3 and 4, respectively. These couples can be attributed to oxidation of the rhenium center, commonly observed in the



Fig. 1 Cyclic voltammograms of $[\text{Re}(\text{CO})_3(2\text{-mbzen})\text{Cl}]$ (*a*), $[\text{Re}(\text{CO})_3(4\text{-mbzen})\text{Cl}]$ (*b*), $[\text{Re}(\text{CO})_3(3\text{-bbzen})\text{Cl}]$ (*c*) and $[\text{Re}(\text{CO})_3(4\text{-mbzen})\text{Cl}]$ (*d*) in CH₂Cl₂ at 298 K (scan rate = 100 mV/s, $c = 2 \times 10^{-4}$ M)

electrochemical studies of other related rhenium-containing complexes [11]. The nature of the diimine ligand affects the oxidation potential values. The electron-withdrawing substituent on the ligand leads to a stabilization of the Re(I) center. Hence, the abstraction of the electron from the metal center occurs at more positive potentials for complex **4** when compared with the other complexes. In the cyclic voltammetry scans, peak to peak separation (ΔE_p) of 93, 101 and 85 mV was observed for complexes **1**, **2** and **3**, respectively.

X-ray structural study of the complexes

The metal center has an almost ideal octahedral coordination sphere with a facial arrangement of three carbonyl groups in the synthesized complexes 1-4 (Figs. 2, 3, 4, 5). The octahedral coordination is completed by a Cl atom and two N atoms from the diimine Schiff base ligands. Selected bond lengths and angles of the four complexes are summarized in Table 3. In the crystal structures of 1, 3 and 4, there is one complex molecule in the asymmetric unit, whereas in 2, there is only half since it lies on the

Table 2Electronic absorptionspectral data of the ligands andcomplexes 1-4 in CH_2Cl_2

Compound	Concentration (M)	λ_{\max} (nm) [ε] (M ⁻¹ cm ⁻¹)
4-mbzen	8×10^{-5}	256 [23,737]
2-mbzen	8×10^{-5}	246 [20,425], 303 [12,750]
4-m'bzen	8×10^{-5}	246 [23,087]
3-bbzen	8×10^{-5}	244 [21,137], 289 [3,950]
Complex 1	4×10^{-5}	235 [17,875], 286 [29,550], 377 [1,926] ^a
Complex 2	4×10^{-5}	235 [19,225], 261 [24,250], 293 [17,150], 368 [1,793] ^a
Complex 3	4×10^{-5}	236 [15,175], 263 [29,250], 371 [1,832] ^a
Complex 4	4×10^{-5}	237 [19,975], 254 [25,550], 374 [1,858] ^a

^a
$$c = 1 \times 10^{-3} \text{ M}$$



Fig. 2 The molecular structure of complex 1, showing 30% probability displacement ellipsoids and the atomic numbering



Fig. 3 The molecular structure of complex **2**, showing 20% probability displacement ellipsoids and the atomic numbering. The methylene groups, as well as the axially disposed carbonyl and chloro ligands are disordered over two sites (see text for details). Symmetry code: (*i*) x, 1/2 - y, z



Fig. 4 The molecular structure of complex 3, showing 30% probability displacement ellipsoids and the atomic numbering. The axially disposed carbonyl and chloro ligands are disordered over two sites with occupancies of 0.803(4) and 0.197(4) (denoted by A and B, respectively)



Fig. 5 The molecular structure of complex 4, showing 30% probability displacement ellipsoids and the atomic numbering

crystallographic mirror plane. The methylene groups in **2** are disordered over two positions with a site occupancy factor fixed at 50% (due to the crystallographic symmetry; Fig. 3). The axially disposed chloro and carbonyl ligands are also disordered over two positions (denoted by A and B for the major and minor components, respectively; Fig. 3) with the refined site occupancy factors of 0.778(7) and 0.222(7). Similarly, the axially disposed chloro and carbonyl ligands in complex **3** are disordered over two positions (denoted by A and B for the major and minor components, respectively; Fig. 4) with a refined site occupancy ratio of 0.803(4)/0.197(4). In the presence of sufficient anomalous scattering effect, it was possible to determine the absolute structure of complex **4** [Flack parameter = -0.024(6)] [25].

The Re–C bond distances [1.897(4)-1.937(3) Å] are similar to those in the related complexes [26, 27]. Due to the π -donor character induced by the coordinated chloride ligand, the Re–C linkages *trans* to the Re–Cl linkages are slightly longer than those *trans* to the Re–N linkages. The C=N bond distance values in the complexes are slightly longer than those observed in free Schiff base ligands [28-30]. As commonly observed in previously characterized Re(I)-tricarbonyl diimine systems [31-33], the N–Re–N bond angles are found to be less than 90° as required by the steric requirements of chelating ligands. As can be seen in Table 3, the *trans* angles at the Re(I) site show a slight deviation from an ideal octahedral arrangement. No

Complex 1			
Re(1)-Cl(1)	2.4769(6)	N(1)-Re(1)-N(2)	78.11(8)
Re(1)–N(1)	2.192(2)	N(1)-Re(1)-C(2)	97.94(9)
Re(1)–N(2)	2.233(2)	N(2)-Re(1)-C(3)	100.32(10)
Re(1)-C(1)	1.937(3)	C(1)-Re(1)-C(2)	87.25(12)
Re(1)-C(2)	1.901(3)	C(1)-Re(1)-C(3)	90.42(11)
Re(1)-C(3)	1.922(2)	C(1)–Re(1)–Cl(1)	175.58(8)
Complex 2			
Re(1)-Cl(1A)	2.4412(19)	N(1)-Re(1)-N(1A)	77.12(9)
Re(1)-Cl(1B)	2.412(10)	N(1)-Re(1)-C(2)	99.55(11)
Re(1)–N(1)	2.209(2)	C(1A)-Re(1)-C(2)	89.7(3)
Re(1)-C(1A)	1.921(5)	C(1B)-Re(1)-C(2)	91.3(4)
Re(1)-C(1B)	1.933(6)	C(1A)-Re(1)-Cl(1A)	174.2(4)
Re(1)-C(2)	1.898(3)	C(1B)-Re(1)-Cl(1B)	177.1(9)
Complex 3			
Re(1)-Cl(1A)	2.4634(18)	N(1)-Re(1)-N(2)	77.41(13)
Re(1)-Cl(1B)	2.449(10)	N(1)-Re(1)-C(2)	97.52(17)
Re(1)–N(1)	2.218(3)	N(2)-Re(1)-C(3)	98.56(19)
Re(1)–N(2)	2.222(4)	C(1A)-Re(1)-C(2)	87.9(2)
Re(1)-C(1A)	1.935(7)	C(1A)-Re(1)-C(3)	88.3(3)
Re(1)-C(1B)	1.98(2)	C(1B)-Re(1)-C(2)	90.4(9)
Re(1)-C(2)	1.909(5)	C(1B)-Re(1)-C(3)	86.0(9)
Re(1)-C(3)	1.918(5)	C(1A)-Re(1)-Cl(1A)	177.6(2)
		C(1B)-Re(1)-Cl(1B)	175.8(9)
Complex 4			
Re(1)–Cl(1)	2.4884(11)	N(1)-Re(1)-N(2)	77.28(13)
Re(1)–N(1)	2.208(3)	N(1)-Re(1)-C(2)	97.66(16)
Re(1)–N(2)	2.206(4)	N(2)-Re(1)-C(3)	101.14(17)
Re(1)-C(1)	1.899(5)	C(1)-Re(1)-C(2)	91.5(2)
Re(1)-C(2)	1.909(5)	C(1)-Re(1)-Cl(3)	88.43(19)
Re(1)–C(3)	1.897(4)	C(1)–Re(1)–Cl(1)	175.40(16)

significant influence of the different substituents is seen on the bonds and angles in the complexes. Their influence, however, is great on the molecular geometry (Supplemental Fig. S1) and also on the crystal packing.

Weak intermolecular interactions influence the crystal packing in the reported crystal structures. Along with the van der Waals and C–H··· π interactions, hydrogen bonds of the type C–H···O and C–H···Cl are observed. Details of these hydrogen bonding interactions are presented in Table 4. Surprisingly, the π ··· π stacking interactions exist only in the crystal structure of 1; viz. between the two parallel and centro-symmetrically (2 - x, 2 - y, 2 - z) related aryl C(11)–C(16) rings [the corresponding interplanar spacing is 3.5002(11) Å, giving the centroid–centroid separation of 3.6229(16) Å and the ring offset of ca. 0.94 Å].

 Table 4
 Parameters of hydrogen bonding interactions in complexes

 1-4
 -4

	D–H…A	H…A (Å)	D…A (Å)	D–H…A (°)
Complex 1	C(12)–H(12)····Cl(1)	2.71	3.590(3)	157
	$C(17)-H(17)\cdots Cl(1)^{a}$	2.71	3.594(2)	160
	$C(19)-H(19B)\cdots O(4)^{b}$	2.56	3.363(4)	142
Complex 2	$C(18B)-H(18C)\cdots O(2)^{c}$	2.45	3.597(8)	164
Complex 3	C(16)-H(16)Cl(1A)	2.75	3.625(6)	157
Complex 4	C(22)-H(22)···Cl(1)	2.70	3.587(4)	161
	$C(27)-H(27)\cdots Cl(1)^{a}$	2.63	3.546(5)	167

Symmetry codes: (a) 1 + x, y, z (b) 2 - x, 3 - y, 2 - z (c) 1/2 + x, y, 3/2 - z

Conclusion

In this work, we report the synthesis, characterization and crystal structures of four Re(I)-tricarbonyl diimine complexes with the N,N'-bis(substituted benzylidene)ethane-1,2-diamine Schiff bases. All four complexes have been fully characterized by FTIR, ¹H NMR, UV–Vis spectros-copy and X-ray diffraction analysis. Electrochemical behavior of the investigated complexes has been studied using cyclic voltammetry. Due to the chelating effect of the diimine ligands, the coordination geometries of Re in the prepared complexes are distorted octahedral.

Supplementary materials

The on-line electronic supplementary material contains Fig. S1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 738421–738424. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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