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Tricarbonylrhenium(I) Bromide Complexes With Diimine Ligands: Structural, Electrochemical, and Spectroscopic Studies

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Tricarbonylrhenium(I) Bromide Complexes With Diimine Ligands: Structural, Electrochemical, and Spectroscopic Studies

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Four rhenium(I) complexes, $[Re(CO)_3Br(L^n)]$ (n = 1-4), $[L^n = (4-fluorophenyl)pyridin-2-ylmethyleneamine (L¹), (4-chlorophenyl)pyridin-2-ylmethyleneamine (L²), (4-bromophenyl)pyridin-2-ylmethyleneamine (L⁴)] have been synthesized and characterized by CHN analyses, ¹H, ¹³C-NMR, IR, and UV-vis spectroscopy. The molecular structure of <math>[Re(CO)_3Br(L^1)]$ is a distorted octahedron around rhenium with one Br, facial arrangement of three COs, and one diimine. UV-vis absorption and emission properties of the complexes have been studied at room temperature and the redox potentials are approximately insensitive to the substituent on the phenyl ring of ligands.

Keywords bidentate diimine ligand, electrochemistry, emission, rhenium complex, X-ray crystallography

INTRODUCTION

Tricarbonylrhenium(I) complexes of the type fac-[Re $(diimine)(CO)_3L$ (L = auxiliary monodentate ligand) have very interesting properties such as relatively high thermal and photochemical stabilities, high redox potentials, and luminescence in the visible region, which have led to their applications as light switches,^[1] ion sensors,^[2] intercalating agents for nucleic acids,^[3] probes for biological molecules,^[4] and models in fundamental studies of energy and electron-transfer reactions relevant to solar energy conversion. Tuning the physicochemical properties of these complexes by changing the nature of the diimine offers a high degree of versatility for the design of new systems, which may perform useful, specific functions.^[5] The majority of research in this field has focused on the use of polypyridine derivatives such as 2,2'-bipyridine and 1,10-phenanthroline as ligands.^[6–13] However, there are little data on complexes with unsymmetrical diimine ligands containing iminopyridine.[14-21]

According to this view, we herein describe the synthesis, properties, and structural characterization of Re(I) complexes of the type [$Re(CO)_3BrL$] in which L is an unsymmetrical bidentate iminopyridine ligand (Scheme 1).



EXPERIMENTAL

General

All chemicals were of reagent grade and used as received. Solvents were purified by literature methods.^[22] Synthesis and molecular structures of 2 and 3 have previously been reported.^[23,24] The ligands were prepared according to reported procedures.^[25] Elemental analyses were performed using a Heraeus CHN-O RAPID elemental analyzer (Alzahra University, Iran). IR spectra were recorded on a Bruker Tensor 27 spectrophotometer (Alzahra University, Iran). Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer (Alzahra University, Iran); λ_{max} (log ε). NMR spectra were obtained on a BRUKER (250 MHz) spectrometer (Tarbiat Modares University, Iran). Proton chemical shifts are reported in parts per million (ppm) relative to an internal standard of Me_4Si . All voltammograms were recorded with a three-electrode system consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and Au as a working electrode. A Metrohm multipurpose instrument model 693 VA processor with 694A VA stand was used (Alzahra University, Iran). Cyclic

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voltammograms were obtained in chloroform with 0.1M tetrabutylammonium perchlorate (TBAClO₄) as the supporting electrolyte. In all electrochemical experiments the test solution was purged with argon for at least 5 min. Emission spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer at room temperature (Alzahra University, Iran).

Syntheses of the Complexes

Synthesis of $Re(L^1)(CO)_3Br(1)$

A mixture of [Re(CO)₅Br] (406 mg, 1 mmol) and L¹ (200 mg, 1 mmol) in dry, degassed toluene (30 cm³) was heated at reflux for 4 h under N₂ to give a bright red solution. The solvent was removed at reduced pressure and the crude material recrystallized from CH₂Cl₂/hexane to give Re(L¹)(CO)₃Br as pure orange crystals. Yield: 89%. IR (cm⁻¹, KBr): 2021, 1910, 1893 (C=O, vs); 1584 (C=N, s). ¹H-NMR (250 MHz, DMSO-d₆): 9.35 (s, 1H, H₅), 9.13 (d, 1H, J_{HH} = 5.50 Hz, H₁), 8.38 (m, 2H, H₂, H₄), 7.88 (m, 1H, H₃), 7.62–7.74 (m, 4H, aromatic ring). ¹³C-{¹H} NMR (250 MHz, DMSO-d₆)(: 196.3, 195.9, 185.5, 170.0, 154.8, 153.2, 140.4, 130.5, 129.7, 124.4, 124.2, 116.5, 116.1. For C₁₅H₉FBrN₂O₃Re, Anal. Calcd. (%): C, 32.73; H, 1.65; N, 5.09; Found (%): C, 32.74; H, 1.67; N, 4.99.

Synthesis of $Re(L^2)(CO)_3Br(2)$

This complex was prepared by a procedure similar to **1** using 216 mg (1 mmol) of L².^[26] Orange crystals were collected by filtration and dried *in vacuo*. Yield: 91%. IR (cm⁻¹, KBr): 2023, 1912, 1888 (C=O, vs); 1583 (C=N, s). ¹H-NMR (250 MHz, DMSO-d₆)(: 9.33 (s, 1H, H₅), 9.09 (d, 1H, J_{HH} = 5.25 Hz, H₁), 8.36 (m, 2H, H₂, H₄), 7.84 (m, 1H, H₃), 7.30–7.61 (s, 4H, aromatic ring). ¹³C-{¹H} NMR (250 MHz, DMSO-d₆) (: 196.9, 196.4, 186.2, 170.5, 154.8, 153.2, 149.3, 140.4, 133.4, 130.6, 129.8, 129.4, 124.0. For C₁₅H₉ClBrN₂O₃Re, Anal. Calcd. (%): C 31.79, H 1.59, N 4.94. Found (%): C 31.89, H 1.50, N 4.99.

Synthesis of $Re(L^3)(CO)_3Br(3)$

This complex was prepared by a procedure similar to **1** using 261 mg (1 mmol) of L³.^[27] Orange crystals were collected by filtration and dried *in vacuo*. Yield: 87%. IR (cm⁻¹, KBr): 2025, 1914, 1886 (C=O, vs); 1588 (C=N, s). ¹H-NMR (250 MHz, DMSO-d₆) (: 9.32 (s, 1H, H₅), 9.09 (d, 1H, J_{HH} = 5.25 Hz, H₁), 8.36 (m, 2H, H₂, H₄), 7.85 (m, 1H, H₃), 7.37–7.68 (m, 4H, aromatic ring). ¹³C-{¹H} NMR (250 MHz, DMSO-d₆) (: 197.3, 196.6, 186.4, 170.5, 154.8, 153.2, 149.7, 140.4, 132.4, 130.5, 129.8, 124.3, 121.9. For C₁₅H₉Br₂N₂O₃Re Anal. Calcd. (%): C, 29.47; H, 1.48; N, 4.58. Found (%): C, 29.46; H, 1.46; N, 4.57.

Synthesis of $Re(L^4)(CO)_3Br(4)$

This complex was prepared by a procedure similar to **1** using 308 mg (1 mmol) of L⁴. Orange crystals were collected by filtration and dried *in vacuo*. Yield: 88%. IR (cm⁻¹, KBr): 2021, 1896 (C=O, vs); 1581 (C=N, s). ¹H-NMR (250 MHz, DMSO-d₆)(: 9.32 (s, 1H, H₅), 9.08 (d, 1H, J_{HH} = 5.20 Hz, H₁), 8.35 (m, 2H, H₂, H₄), 7.85 (m, 1H, H₃), 7.31–7.65 (m, 4H, aromatic

ring). ${}^{13}C-{}^{1}H$ NMR (250 MHz, DMSO-d₆)(: 197.9, 196.8, 186.7, 170.2, 154.9, 153.2, 150.1, 140.4, 138.2, 130.6, 129.8, 124.3, 96.1. For C₁₅H₉BrIN₂O₃Re, Anal Calcd. (%): C, 27.37; H, 1.37; N, 4.26. Found (%): C, 27.30; H, 1.42; N, 4.20.

Crystal Structure Determination

Data were collected on a Bruker-Nonius Kappa-CCD diffractometer (University of Toronto, Canada) using monochromated MoK α radiation and measured using a combination of φ scans and ω scans with κ offsets to fill the Ewald sphere. The data were processed using the Denzo-SMN package.^[26] Absorption corrections were carried out using SORTAV.^[27] The structures were solved and refined using SHELXTL V6.1 for full-matrix leastsquares refinement based on F^2 .^[28] All H-atoms were included in calculated positions and allowed to refine in a riding-motion approximation with U_{iso} tied to the carrier atom.

RESULTS AND DISCUSSION

Synthesis

 $[\text{Re}(\text{CO})_3\text{Br}(\text{L}^n)]$ (n = 1-4) was prepared by the reaction of the appropriate ligand with $[\text{Re}(\text{CO})_5\text{Br}]$ in toluene and precipitated in analytically pure form. All complexes are soluble in THF, dichloromethane, and chloroform solvents and insoluble in ether and hexane. These complexes are stable in air in the solid state for three weeks.

Structure of $[Re(CO)_3Br(L^1)]$, 1

A view of **1** along with the atom-numbering scheme is shown in Figure 1. The crystallographic data are summarized in Table 1



FIG. 1. Structure of **1** in the crystal, showing the atom-labeling scheme. Thermal ellipsoids with 50% probability.

 TABLE 1

 Crystal data and structure refinement for 1

 TABLE 2

 Selected bond lengths (Å) and bond angles (°) for 1

Emprical formula	$C_{15}H_9BrFN_2O_3Re$
Formula weight	550.35
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 21/c
a	8.9326(2) Å
b	25.5742(5) Å
С	6.9479(3) Å
β	108.9170(14)°
Volume	1501.48(8) Å ³
Z	4
Density (calculated)	2.435 Mg/m^{3}
Absorption coefficient	10.780 mm^{-1}
F(000)	1024
Crystal size	$0.08 \times 0.05 \times 0.02 \text{ mm}^3$
Theta range for data collection	2.89 to 27.48°.
Index ranges	$-8 \le h \le 11, -32 \le k \le 30,$ $-9 \le l \le 9$
Reflections collected	10161
Independent reflections	3402 [R(int) = 0.0473]
Completeness to theta = 25.00°	99.8%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.805 and 0.614
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	3402/3/213
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	$R_1 = 0.0376, wR_2 = 0.0843$
R indices (all data)	$R_1 = 0.0522, wR_2 = 0.0912$
Largest diff. peak and hole	2.747 and $-1.979 \text{ e.}\text{\AA}^{-3}$

and selected bond distances and angles are given in Table 2. Compound 1 crystallizes in the monoclinic space group P21/c. The geometry of rhenium atom can be best described as distorted octahedral defined by one bromide, three facial carbonyls, and the diimine ligand (L¹). The steric requirements of the bidentate ligand causes distortion of the octahedral coordination, clearly seen by bite angles [N1–Re1–N2, 74.59(18)°] (Table 2). Trans angles at Re^I are in the 170.9(2)–178.7(2)° range, also showing a deviation from an ideal octahedral arrangement. The axially disposed bromo and carbonyl ligands are disordered over two positions with the refined site occupancy factors of about 0.92 and 0.08. The coordinated bromide is slightly tilted toward the diimine ligand, causing a narrowing of the N–Re–Br angles [84.97(13)° for N1-Re1-Br1, 86.31(13)° for N2-Re1-Br1]. The Re–N bond lengths are similar and within the range expected

Re1-C2	1.916(5)	Re1-Br1	2.6113(7)
Re1-C1	1.920 (7)	O1-C1	1.143(6)
Re1-C3	1.925 (6)	O-C2	1.148 (5)
Re1-N1	2.172 (5)	O3-C3	1.147 (6)
Re1-N2	2.186 (5)		
C2-Re1-C1	88.0 (3)	C3-Re1-N2	101.0 (2)
C2-Re1-C3	88.1 (3)	N1-Re1-N2	74.59 (18)
C1-Re1-C3	88.8 (3)	C2-Re1-Br1	93.25 (19)
C2-Re1-N1	96.4 (2)	C1-Re1-Br1	178.7 (2)
C1-Re1-N1	95.3 (3)	C3-Re1-Br1	90.82 (19)
C3-Re1-N1	174.0 (2)	N1-Re1-Br1	84.97 (13)
C2-Re1-N2	170.9 (2)	N2-Re1-Br1	86.31 (13)
C1-Re1-N2	92.6 (3)		· · · ·

for such complexes.^[15,29] The rhenium–carbonyl bond lengths do not show any significant differences [1.916(5) and 1.925(6) Å] and are consistent with those observed in similar complexes.^[15,16,30]

Despite the fact that the donor nitrogens are sp²-hybridized, the chelate ring is significantly puckered in this complex and some strain in the chelate ring is suggested by the deviation from 120° angle about the nitrogen, C4-N1-Re1 [126.0(4)°], C8-N1-Re1 [116.4(4)°], C4-N1-C8 [117.7(5)°]. The crystal packing in the unit cell is shown in Figure 2. As shown in Figure 2, the phenyl rings of the ligands are on one side and are approximately parallel to each other. Therefore, there is partial overlapping between these moieties with a nearest distance of 3.53 Å between the parallel the planes. Structure of complex 1 is similar to complexes 2 and 4, as reported previously.^[23,24] No significant changes are observed in the bond length, bond angles, and dihedral angles in these complexes (Table 3), which is consistent of with absorption, emission, and redox properties.

TABLE 3

Comparison of bond lengths and dihedral angles of the pyridine, chelate, and benzene ring in compounds 1, 2, and 4

	1	2 ^a	4 ^a
Re-N _{ave} [Å]	2.179	2.176	2.183
Re-C _{ave} [Å]	1.920	1.941	1.924
Re-Br [Å]	2.611	2.616	2.614
Dihedral angle (°) between planes	1.456	1.248	1.638
of pyridine ring and chelate ring			
Dihedral angle (°) between planes	41.200	45.092	42.884
of chelate ring and benzene ring			
Dihedral angle (°) between planes	40.433	46.193	42.615
of pyridine ring and benzene ring			
Torsion angle (°) N-C-C-N	1.378	-2.852	-1.338

^aData from Otwinowski and Minor^[26] and Blessing.^[27]



FIG. 2. Crystal packing in the unit cell for 1.

IR Spectra

The IR spectra of complexes recorded in KBr pellets displayed three metal carbonyl bands in the 2025-1886 cm⁻¹ region (Table 4). This is consistent with C_s symmetry for the compounds with two $\alpha 1$ bands and an αn band. Under the conditions of the measurement, the latter bands are clearly separated in 1, 2, and 3, but the two bands were overlapped in complex 4. This complex shows two peaks in this region.^[29] The wavenumbers of the CO stretches are very sensitive to the d_{π} electron density (oxidation state) of the rhenium center. The constancy of the wave numbers among the complexes, as observed in Experimental section, indicates that the ligands induce an equivalent perturbation on the metal center. The IR spectra of complexes also show strong bands in the 1588–1581 cm⁻¹ region corresponding to the azomethine (C=N). These bands shift to lower wavenumbers relative to ligands (1629–1631 cm^{-1} for the ligands). The observed shift in C=N stretch after complexation confirms the coordination of the azomethine $(C=N).^{[25,31]}$

¹H, ¹³C-NMR Spectra

The peak assignments for the ¹H NMR spectra are presented in the Experimental section for each complex. These peaks are assigned based on the splitting of the resonance signals, spin coupling constants, literature data and in accordance with the molecular structure determined by the X-ray crystal structure analysis. The ¹H resonances of the coordinated ligands are observed in complexes **1–4**. Aside from the aromatic H-atoms, which appear at 7.24–9.13 ppm, the imine protons appear as a singlet at 9.32–9.35 ppm. The downfield shift of the imine protons relative to the free ligands can be attributed to the deshield-ing effect resulting from the coordination of the metal by the ligands.^{[32–34] 13}C NMR spectra show that carbon atoms of the complexes **1–4** appear at 116–197 ppm. For the complexes, the signals due to the diimine ligands appear at 116–170 ppm and in keeping with the *fac* arrangement of the CO ligands, the ¹³C {¹H} NMR spectra show three low-field signals assignable to the CO groups.

Absorption and Emission Properties

The electronic spectra of the complexes were recorded in the 700–200 nm range. The spectral data are presented in Table 4. The uncoordinated ligands are completely transparent above 335 nm.^[24] The absorption spectra of all the complexes exhibit a broad band close to 451 nm. This lowest energy feature in each

Absorption, florescence, and electrochemical properties of $BrRe(CO)_3L$ complexes						
Complex	Cyclic voltammetry $E_p(V)^a$	$\begin{array}{c} Emission^a\\ \lambda_{max}(nm) \end{array}$	Absorption UV-Vis $\lambda_{max}(nm)$ (log $\varepsilon/M^{-1}cm^{-1}$) (solvent = CHCl ₃)	IR IR (cm ⁻¹ , KBr)		
1	1.51	643	452 (3.39), 332 (3.78), 242 (4.19)	2021, 1910, 1893 (C=O); 1584 (C=N)		
2	1.53	649	451 (3.59), 331 (4.04), 242 (4.39)	2023, 1912, 1888 (C=O); 1583 (C=N)		
3	1.52	639	451 (3.62), 337 (4.06), 242 (4.38)	2025, 1914, 1886 (C=O); 1588 (C=N)		
4	1.49	637	451 (3.41), 351 (3.85), 242 (4.32)	2021, 1896 (C=O); 1581 (C=N)		

 TABLE 4

 Absorption, florescence, and electrochemical properties of BrRe(CO)₃L complexes

^aRecorded in aerated CHCl₃ at 298 K. Excited at 452 nm (1), 451 nm (2), 451 nm (3), and 451 nm (4).

Solvent dependence of MLCTaAbsorption at 289 K UV-vis λ_{max} (nm) (log $\varepsilon/M^{-1}cm^{-1}$) Complex Solvent 1 408 (3.47) DMSO 1 422 (3.65) CH₃CN 1 437 (3.31) CH_2Cl_2 1 452 (3.38) CHCl₃ 2 DMSO 414 (3.58) 2 424 (3.21) CH₃CN 2 444 (4.06) CH_2Cl_2 2 451 (3.58) CHCl₃ 3 406 (3.62) DMSO 3 CH₃CN 415 (3.07) 3 443 (3.28) CH_2Cl_2 3 CHCl₃ 451 (3.62) 4 410 (3.70) DMSO 4 415 (3.35) CH₃CN 4 443 (3.55) CH_2Cl_2 4 451 (3.41) CHCl₃

TABLE 5

case is the metal-to-ligand [Re($d\pi$)-ligand(π^*) ¹MLCT transition] charge transfer transition.^[14,35–39] Other higher energy bands are observed, which are due to intraligand transitions. However, position of the low-energy MLCT absorption band, is approximately insensitive to the substituent on the phenyl ring of ligands but this band, for complexes (1-4), is quite sensitive to solvent. The absorption maximum blue-shifts with increased solvent polarity (Table 5). Similar effects have been reported for MLCT absorptions of bipyridine and phenanthroline complexes of rhenium.^[14-21,33,34]



FIG. 4. Cyclic voltammograms of 1 in CHCl₃ at 50 and $c = 3 \times 10^{-3}$, (a) 100, (b) 200, (c) 300, (d) 400, (e) 500 mVs^{-1} .

Excitation of the complexes at 451-452 nm leads to the observation of the emission bands at 637-649 nm (Table 4, Figure 3). With reference to previous spectroscopic studies on other similar rhenium(I) complexes,^[40-44] the emission was assigned as derived from excited states of a ³MLCT origin. Consistent with the UV-vis absorption spectra, the emission bands are approximately insensitive to the substituent on the phenyl ring of ligands in the complexes 1–4.

Electrochemistry

The electrochemical behavior of the complexes was examined by means of cyclic voltammetry in CHCl₃ and is presented in Table 4. The Four ligands are electroinactive in the working potential region. A typical cyclic voltammogram of 1 is shown in Figure 4. An irreversible oxidation is observed in the anodic region for complexes 1-4 at about 1.50 V versus SCE, which can be assigned to $\text{Re}^+ \rightarrow \text{Re}^{2+,[14-16,45]}$ The corresponding cathodic peak was not observed, however, even under fast-scanrate conditions (Figure 4). No significant changes are observed with variation of the ligands in the oxidation wave of the complexes.

CONCLUSION

Four rhenium complexes, $[Re(CO)_3Br(L^n)]$ $[L^n = (4-fluoro$ phenyl)pyridin-2-ylmethyleneamine (1), (4-chlorophenyl) pyridin-2-ylmethyleneamine (2), (4-bromophenyl)pyridin-2ylmethyleneamine (3), (4-iodophenyl)pyridin-2-ylmethylenea mine (4)] have been synthesized. The crystal structure of 1 revealed that the coordination geometry of the rhenium atom could be best described as distorted octahedral geometry defined by one bromide, facial arrangement of three-coordinated carbonyls, and the diimine ligand (L). All of these complexes exhibit low-energy absorption bands at about 451 nm, corresponding to a MLCT transition. Excitation of the complexes at 451–452 nm leads to the observation of the emission bands at 637-649 nm. An irreversible oxidation is observed in the anodic region for complexes 1-4 at about 1.50 V. However, the potentials and absorption bands are insensitive to the substituent on the phenyl ring of the iminopyridine ligands.





FIG. 3. Emission spectrum of 2 in CHCl₃ at 25°C.

SUPPLEMENTARY MATERIALS

Crystallographic data for compound **1** are given in Table 1. The crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 798904. The copies of these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033).

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